A PRELIMINARY WORK ON DESIGN AND DEVELOPMENT OF SOUR WATER GAS SHIFT CATALYSTS FOR SYNTHETIC NATURAL GAS PROCESS

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to my family…

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ABSTRACT

A PRELIMINARY WORK ON DESIGN AND DEVELOPMENT OF SOUR WATER GAS SHIFT CATALYSTS FOR SYNTHETIC NATURAL GAS PROCESS

The main goal of this study is to design and develop a model sour water gas shift catalyst showing high performance in terms of activity, stability & selectivity and conducting performance screening by mimicking the syngas composition of the potential coal gasifier under ideal, sulfur-free conditions. According to the literature, dry powder entrained-bed type gasifier seems potential gasifier for the Synthetic Natural Gas (SNG) production processes, and it contains low steam/CO ratio, below 0.8. On the other hand, classical sour water gas shift (SWGS) catalysts work under high steam/CO ratio, specifically, above 2 or 3. In this context, from literature, one of the potential SWGS catalysts which is suitable for dry-powder syngas composition was chosen as a reference. Activated carbon supported KCoRe as the model SWGS catalysts were developed and these catalysts were tested under ideal, sulfur-free syngas composition. The effect of reaction conditions (i.e., reaction temperature and steam to carbon monoxide ratio) and catalyst preparation & support pre-treatment methods (i.e., impregnation method, air & nitric acid pre-treatment on the Activated Carbon support) were investigated on the prepared catalyst. Activity and selectivity were determined in terms of conversions of CO and H_2, respectively. Experimental results showed that reaction conditions are very important parameters on the performance of the catalysts. At low steam/CO ratios, it is necessary to increase the temperature in order to get high activity. The effect of the impregnation method may vary from support to support since impregnation depends on the surface chemistry of the support material. Co-impregnation method may not be suitable for air oxidized AC supported catalysts. Both air and nitric acid treatments are helpful to increase the performance of the catalysts by increasing the oxygen bearing surface groups on the AC support.

ÖZET

SENTETİK DOĞAL GAZ PROSESLERİ İÇİN EKŞİ SU GAZI KAYDIRMA KATALİZÖRÜ TASARIMI VE GELİŞTİRME ÜZERİNE ÖN HAZIRLIK ÇALIŞMASI

Bu çalışmanın temel amacı aktivite, kararlılık ve seçicilik bakımından yüksek performans gösteren bir model ekşi su-gazı kaydırma katalizörü tasarlamak ve geliştirmek ve ideal, sülfür içermeyen koşullar altında potansiyel kömür gazlaştırıcısının sentetik gaz kompozisyonunu taklit ederek performans izlenimi yürütmektir. Literatüre göre, kuru toz sürüklemeli yatak tipi gazlaştırıcı sentetik doğal gaz üretimi süreçleri için potansiyel gazlaştırıcı görünmektedir ve düşük buhar/karbon monoksit oranı içermektedir, 0.8'in altında. Diğer yandan, klasik ekşi su gazı kaydırma katalizörleri yüksek buhar/karbon monoksit oranında, spesifik olarak 2 veya 3'ün üzerinde, çalışmaktadır. Bu kapsamda, literatürden kuru toz sentetik gaz kompozisyonu için uygun olan potansiyel ekşi su gazı kaydırma katalizörlerinden biri referans olarak seçilmiştir. Model su gazı kaydırma katalizörleri geliştirilmiştir ve bu katalizörler ideal, sülfür içermeyen sentez gazı kompozisyonu altında test edilmiştir. Hazırlanan katalizörler üzerinde reaksiyon koşulları (reaksiyon sıcaklığı ve buhar/karbon monoksit oranı) ve katalizör hazırlama & destek ön iyileştirme yöntemleri (emdirme yöntemi, aktif karbon desteği üzerinde hava ve nitrik asit ön iyileştirmesi) etkileri incelenmiştir. Aktivite ve seçicilik sırasıyla karbon monoksit ve hidrojen gazı dönüşümlerine göre belirlenmiştir. Deneysel sonuçlar, reaksiyon koşullarının katalizör performansı üzerinde çok önemli parametreler olduğunu göstermiştir. Düşük buhar/karbon monoksit oranlarında, yüksek aktivite elde etmek için sıcaklığı artırmak gereklidir. Emdirme destek materyalinin yüzey kimyasına bağlı olduğu için emdirme yöntemi etkisi destekten desteğe değişiklik gösterebilir. Birlikte emdirme yöntemi AC2 destekli katalizörler için uygun olmayabilir. Hem hava hem de nitrik asit iyileştirmeleri aktif karbon desteği üzerinde oksijen taşıyıcı yüzey gruplarını artırarak katalizör performansını artırmaya yardımcıdır.

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ΔH	Enthalpy Change
AC	Activated Carbon
BOS	Birlesik Oksijen Sanayi
CCP	Carbon Capturing Processes
CGU	Coal Gasification Unit
CI	Co-Impregnation
GHG	Greenhouse Gas
HTS	High Temperature Shift
IWI	Incipient Wetness Impregnation
LTS	Low Temperature Shift
SNG	Synthetic Natural Gas
SWGS	Sour Water-Gas Shift
WGS	Water Gas-Shift

1. INTRODUCTION

Energy dependence is an undeniable fact in our modern world. Moreover, energy deficiency has been increasing in parallel with the growing population (Liu et al., 2015) all around the world. Hence, improving energy production processes have been gaining great interest more and more. Besides responding to the energy demand, these processes should also have other features such as being sustainable, environmentally friendly, feasible, and secure, also having low investment cost, and less toxic emissions.

In fact, most of the energy production processes have still depended on fossil sources (Liu et al., 2015) and they have a huge negative impact on the surroundings. For example, greenhouse gas (GHG) emission and herewith global warming are two of the biggest problems nowadays. Therefore, on the behalf of protecting our today and future; sustainable, secure, and harmless to the environment energy sources must be provided to reduce pollution and toxic emissions (Osa et al., 2011).

Natural gas is the most abundant, clean and easy-to-transfer energy source with respect to other consumable energy sources (Wang et al., 2019; Yuan et al., 2016). On the other hand, its reserves are not as much as fossil reserves (Yuan et al., 2016). At this point, it can be concluded that despite being polluted to the environment, fossil energy sources cannot be abandoned since their reserves are tremendous, they are still dominant energy sources, and they are easily adoptable to the already existing energy production processes in industrial scale. Because of that reason, the existing processes driven by fossil sources, especially coal-derived plants, should be improved to produce cleaner energy without abandoning fossil sources.

Herein novel coal to synthetic natural gas (SNG) technologies have been gaining great interest with carbon capturing processes (CCP) or sequestration of CO_2 (Hla et al., 2010) to produce cleaner natural gas by utilizing coal reserves. There are two main motivations to develop SNG technology to produce energy. One of them is that natural gas is a clean and primary energy source and the other one is that GHG emission could be reduced by using this technology.

SNG technology consists of coal gasification unit (CGU), WGS unit, CO_2 capturing, and methanation unit (Hla et al., 2010). There are mainly three types of gasification reactors that are used in coal gasification. These are fixed-bed, fluidized-bed, and entrained-bed type reactors (Wang et al., 2019). According to the reactor selected, syngas could be producible in a broad range of composition depending on where it is further used such as generation of power or heat, synthesizing chemicals, and producing hydrogen as a fuel (Hla et al., 2010).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{1.1}$$

Coal gasification technologies seem very useful to produce syngas for SNG technology (Hla et al., 2010). However, CO content in the syngas composition via coal gasification is very high. To adjust syngas (CO/H_2) composition to a desired ratio, the gasification process is followed by a WGS reaction. WGS is a settled-down and well-known reaction, (see Eq. 1.1), for many decades in industry (Hla et al., 2010).

For example, H_2/CO ratio should be three for classical methanation reactions. However, as it mentioned before, CO content is very high when the syngas comes from coal gasification and this ratio is less than three normally. Therefore, WGS reaction plays a critical role here.

Syngas compositions change depending on the type of the sources. Syngas can be produced by partial oxidation of any carbon containing feedstock such as oil, natural gas or biomass (Hla et al., 2010). On the other hand, syngas could also come from CGU and this syngas has been using in the SNG production plant since the main goal is converting coal into more valuable products.

Coal-derived syngas contain much more CO to compare with oil-derived or natural gas-derived syngas. Moreover, natural gas-derived syngas is free from the impurities whereas coal-derived syngas contains contaminants. (Hla et al., 2009). These contaminants could be sulfur or nitrogen compounds and undesired particles, and they may have deleterious effects on the process. When syngas which is used in the WGS unit contains high amounts of sulfur, the process is called sour WGS (SWGS).

Traditional, commercial WGS reaction catalysts which work under sulfur free conditions can be divided into two main groups: iron-based oxide, Fe-Cr_2O_3, and copper-based oxide catalysts, Cu-ZnO (Hla et al., 2010). The first group works at high temperatures (500°C) and the second group works at low temperatures (200°C). There is no catalyst for moderate temperatures for WGS reaction. Therefore, classical WGS reaction is carried out in two stages: in the first stage, reaction occurs at high temperature with Fe-based catalyst and then the second stage is used to run the reaction at low temperature with Cu-based catalysts (Silva et al., 2018).

Despite having a high performance and being used industrially for many years, traditional WGS catalysts are not suitable for sour conditions since they are poisoned under the presence of sulfur (Silva et al., 2018). Hence, sulfur tolerant WGS catalysts should be needed to carry on WGS reactions in sour conditions.

In this context, molybdenum is the well-known element which has sulfur tolerance (Silva et al., 2018). Molybdenum also has great coherence with cobalt and nickel. For this reason, Mo, Co, and Ni are the most common elements which are used in classical SWGS catalysts to utilize them in the WGS reactor where syngas comes from CGU. As a support, usually alumina (Al_2O_3) which is the well-known support for many catalysts is chosen. Therefore, CoMo/Al_2O_3 or NiMo/Al_2O_3 are the most preferred catalysts for SWGS reaction in industry so far (Antoniak-Jurak et al., 2016).

Moreover, as can be seen from the WGS equation, (see Eq. 1.1), steam is one of the reactants. Therefore, the ratio of steam to carbon monoxide becomes very important to carry out the reaction. Commercial sulfur tolerant catalysts work under high steam to CO ratio, specifically 2 or above 2. However, this ratio can be very low, less than 0.8, when raw syngas comes from some type of coal gasifier such as entrained bed type gasifier to the WGS unit (Liu et al., 2015).

To solve all these problems, the catalyst which is sulfur tolerant and able to work under both broad temperature range and low steam to carbon monoxide ratio should be required to sustain the reaction under the SWGS reaction conditions. There have been ongoing studies to improve the catalyst for WGS reaction that can be performed well in sour conditions.

In this context, academic research is done to have an idea about the whole SNG production process, coal gasification, the importance of the WGS unit in this process, and the range of process parameters for the WGS unit depending on the gasification reactor.

The aim of this study is design and development of model SWGS catalyst which is novel and robust. Inspired from previous works in the literature, trimetallic KCoRe/Al_2O_3 catalyst seems an alternative for classical SWGS catalyst because of its high performance. On the other hand, Activated Carbon (AC) has been used as a support for many catalysts since it has many advantages such as highly porous structure and tailorable surface structure. Therefore, in the current work a series of powder form trimetallic (potassium, cobalt, and rhenium) catalysts were prepared over pre-treated Activated Carbon (AC) supports through using both sequential and co-impregnation methods. Performance screening of the prepared catalysts was made in a series of experiments under the ideal feed (sulfur-free) conditions. Reaction temperature, steam/CO ratio, catalyst preparation method and support pretreatment method were the parameters of the experimental design.

2. LITERATURE SURVEY

2.1. Coal to Synthetic Natural Gas (SNG) Processes

The energy demand has been increasing in parallel with growing population all around the world and energy deficiency has become larger day by day. Since current and settled energy production processes are mostly dependent on fossil-based energy sources (Liu et al., 2015) which has a huge negative impact on the environment, one of the most important problems nowadays is to meet this energy requirement in a clean way. Because of that reason, producing energy by utilizing green technologies is very important for our future.

Recent research showed that reserves of natural gas are scarce when compared with the other energy sources, especially fossil reserves. According to the studies that have been done on this topic, the oil reserves sustain for 55 years more whereas, coal reserves can sustain nearly twice that of natural gas reserves, 109 years (Yuan et al., 2016).

Coal has been used in many industrial applications to produce heat and power for many years because of its huge reserves. It is possible to produce energy by direct combustion of coal (Liu et al., 2015). However, this process is very harmful to the environment. Large amount of CO_2 emits to the atmosphere while coal combustion processes. CO_2 is a well-known gas with its greenhouse effect, and it creates a threat for global warming which is the most important problem of the modern world.

On the other hand, among all the energy sources natural gas has many advantages as a primary energy source such as being clean (less waste), easily transferable, and flexible (Wang et al., 2019; Yuan et al., 2016). Furthermore, the combustion process of natural gas, which has less waste residue and dust content is cleaner than that of coal. Natural gas combustion emits 40% less CO_2 to the environment than that of coal combustion (Wang et al., 2019). Therefore, natural gas is known as one of the cleanest energy sources.

Although natural gas is a more efficient energy source compared with fossil fuels, the existing and well-established fossil fuel-based technologies are not directly abandoned. In this context, utilizing coal reserves in a clean way is a challenge that humanity is facing (Liu et al., 2015). Herein, SNG production from fossil-based feedstock, especially coal, becomes a very effective process. The SNG production plant mainly contains four parts: Coal gasification unit (CGU), water gas shift (WGS) unit, CO_2 capture unit, and finally methanation unit. As a final product, methane which is the clean natural gas is produced from coal in the coal to SNG plant. SNG production plants can be considered as potential future low emission technologies (Hla et al., 2010).

2.2. Coal Gasification Processes in the World and in Turkey

Coal gasification is a well-established process, and it has been used for many years in industry. Developing new and clean coal gasification processes become a very important issue day by day to produce natural gas which is less toxic for the environment by utilizing coal reserves. Hence, some of these processes are at the improvement stage and pilot scale utilization is on the way (Koytsoumpa et al., 2015). The others are settled in industrial scale especially in the countries that have huge coal reserves but are heavily importer of natural gas such as China.

Coal gasification is the first part of the SNG production process. Gasification of coal is an alternative and cleaner way to use coal reserves instead of direct combustion of coal. Gasification which is the front-runner technology seems a very useful process to convert coal into the more valuable products. It is based on converting carbon-containing feedstock into the synthesis gas which is CO and H_2 mixed gas and it is also known as syngas (Liu et al., 2015).

Improving coal gasification technologies and then adopting these novel technologies into the coal to synthetic natural gas (SNG) production processes has been gaining great interest. Basically, there are two main motivations to develop these technologies (Wang et al., 2019;): coal utilization in a clean manner and decreasing greenhouse gas (GHG) emission which is the main source of global warming.

Coal gasification is an important step in coal to SNG processes because its design parameters such as coal type, gasification temperature, gasification reactor type etc., affects the efficiency of the process, the composition of the syngas and conversion degree of coal to syngas (Yuan et al., 2016). It is a thermochemical process, and, in this step, chemical reaction occurs between coal and oxygen (Wang et al., 2019;) and syngas is produced.

It is known that syngas production by utilizing coal gasification technology is very efficient (Hla et al., 2010). Carbon containing sources could be converted into methane which is then could be used in many processes such as heat or power production systems (Yuan et al., 2016).

The common gasification processes used in many industrial applications are shown in Figure 2.1. The Lurgi type of gasifier is the oldest technology, but it has still been widely used to process coal. British Gas Lurgi (BGL) gasifier is another fixed-bed type of the gasifiers, and it is basically a slugging version of the Lurgi gasifier. The Winkler gasifier is the first commercialized gasifier for fluidized-bed technology (Bell et al., 2011)

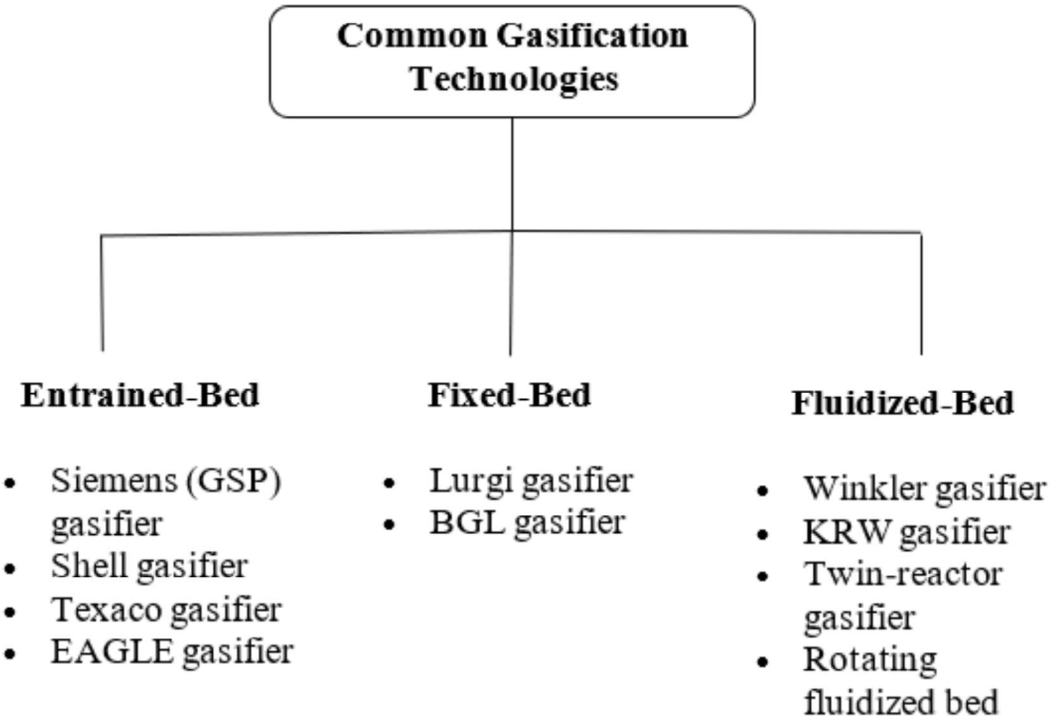


Figure 2.1. Common gasification technologies in the world.

The United States (U.S.), European Union (E.U.) and Japan are the first countries to develop and commercialize clean coal technologies (Melikoglu, 2018). The limited resources of oil and natural gas in Europe brought the requirement to use fossil-based energy sources in a clean way in order to produce energy. Coal to SNG production plants have been gaining greatest interest in this strategy. Moreover, large scale methanation processes have been used for many years in Europe and especially in the U.S. (Koytsoumpa et al., 2015).

Most of the existing coal-to-SNG processes are based on Lurgi gasification. The British Gas Company cooperates with Lurgi in order to improve novel technology which is called British Gas/Lurgi gasifier for SNG process. When compared with classical Lurgi gasifiers, the novel BGL gasifier has lower investment cost (Yang et al., 2017).

In some countries such as U.S., China, Ukraine and Korea these clean coal technologies are constructed and operate industrially. The large commercial lignite based SNG production plant was established by the Dakota company in the U.S. by using the Lurgi gasifier technology. On the other hand, many other countries such as Indonesia, Pakistan, Peru, India, Canada, Japan and Australia; they are at feasibility research stage (Koytsoumpa et al., 2015).

Clean coal technologies (CCT) are strongly needed especially in countries where their coal reserves are abundant, and they are importers of other energy sources such as natural gas. In this perspective, China has the highest demand to convert coal into clean energies (Melikoglu, 2018).

Since China has larger coal reserves (Yang et al., 2017), its investments on these technologies have been increasing and starting to catch up with other countries (Melikoglu, 2018). Therefore, CCTs are very important for China, and they are irreplaceable. The British Gas/Lurgi Gasifier (BGL) and Lurgi fixed-bed gasifier are the most common gasifiers in the coal gasification process of the coal-to-SNG plant in China since it is more suitable for China's coal and they are also more useful for the sake of investment and economic benefits (Yang et al., 2017). For example, the Lurgi fixed-bed gasifier which is the most common gasifier in China needs a large amount of steam (Huang et al., 2017 and Yang et al., 2017).

South Africa is also abundant in coal reserves. Therefore, there is a need to improve and adopt CCTs into the energy production plants. In this context, Sasol company, the biggest customer of Lurgi fixed-bed gasifier, (Yang et al., 2017) uses Lurgi fixed-bed coal gasification in the coal to SNG production plant largely since the Lurgi process is more suitable for the coal of South Africa (Dyk et al., 2006).

Korea imports coal from other countries such as Australia, China, U.S., Indonesia and Russia. For Korea, improving CCTs is extra important since it should utilize the suitable process according to where it imports the coal. Since the entrained-bed type gasifier can apply any type of coal, they worked with this type of gasifier (Yun et al., 2007).

In Turkey, in parallel with growth in population, Turkey's greenhouse gas emissions have been increasing linearly. Moreover, if the energy policy goes like that in Turkey, even in 2023, the main energy source will be fossil-based despite the Turkish government having a renewable energy target at that year. (Melikoglu, 2013)

On the other hand, it is expected to increase Turkey's natural gas demand by 2.6% until 2030 (Melikoglu, 2013). Furthermore, lignite reserves in Turkey are at medium levels (Melikoglu, 2017). Having a technology to convert these lignite resources into clean natural gas would be a perfect move for Turkey.

In this concept, it is planned to increase the amount of power produced from 10.000 MW to 30.000 MW by using lignite-based coal to SNG processes until 2023 according to the energy policy of the Turkish government. However, these processes are at an early stage in Turkey. Moreover, research and development studies on the CCTs were at a stagnation point between 1990-2000 because of natural gas booming (Melikoglu, 2018).

In order to promote this energy strategy of Turkey, Unlu et al. studied five different types of Turkish lignite; Saray, Can, Orhaneli, Tuncbilek, and Soma. They tested their suitability for the entrained-bed type gasifier since it has more tolerance for all types of coal. They found that Tuncbilek and Soma are the most appropriate lignite for this type of gasifier (Unlu et al., 2017).

2.2.1. Gasifier Types

Most of the studies have focused on the plant configuration and feedstock of the gasifiers although gasifier types play an important role in syngas composition. The literature is very poor about how the gasification reactor affects the whole process. Basically, there are three main gasifier types based on gas-solid interacting mode (Basu, 2010) and they have been recently used in gasification processes of coal. These are fixed-bed gasifier, fluidized-bed gasifier, and entrained-bed gasifier. (Wang et al., 2019) All of them have solid based feedstock and they have specific properties which are listed in Table 2.1 (Basu, 2010) and they can find a place in different plants.

Table 2.1. Gasifier Types and Their Properties.

Parameters	**Fixed/Moving Bed**	**Fluidized Bed**	**Entrained Bed**
Tolerance for fines	Limited	Good	Excellent
Tolerance for coarse	Very good	Good	Poor
Gas exit temperature (°C)	450-650	800-1000	1260
Feedstock tolerance	Low-rank coal	Low-rank coal and biomass	Any coal
Oxidant requirements	Low	Moderate	High
Reaction zone temperature (°C)	1090	800-1000	1990
Steam requirements	High	Moderate	Low
Nature of ash produced	Dry	Dry	Slagging
Cold gas efficiency	80%	89%	80%
Application	Small capacities	Medium capacities	Large capacities

The entrained flow type gasifier has a fast residence time, and it can be operated under high pressure. The fluidized type of reactor is suitable for low rank coal and wastes which contain impurities. The fixed type of reactor is more reliable than the others. On the other hand, it cannot be used for single large-scale operations, and it has relatively low efficiency (Liu et al., 2015).

Among all gasifier types, the entrained-bed type gasifier seems to be the most advantageous one (Yuan et al., 2016). Firstly, it can be adoptable for different types of feedstocks. Secondly, it is more environmentally friendly since its products are free from contaminants (Yuan et al., 2016 and Qin et al., 2018). Moreover, tar formation is the technical challenge of the gasification process. Therefore, an entrained-bed type gasifier seems more efficient than that of other gasifiers (Dutta et al., 2011). High carbon consumption occurs in this type of reactor because of its high reaction rate. Last but not least it has high coal processing capacity (Qin et al., 2018).

Furthermore, for entrained-bed gasifiers, there are two types of feeding options: slurry-feed and dry-powder feed (Qin et al., 2018). Slurry feed type has high steam to carbon monoxide ratio whereas dry powder gasifier contains low steam to carbon ratio.

Zheng et al. (2005), studied four different types of gasifiers; Shell, Texaco, BGL and KRW in order to analyze the gasification reactors. Those are dry-powder entrained-bed, slurry feed entrained-bed, fixed-bed, fluidized-bed type of gasifiers, respectively. For the sake of capital cost, BGL and KRW are the most suitable gasifiers. On the other hand, entrained type gasifiers have more benefits such as environmentally friendly and feedstock flexibility.

2.2.2. Syngas Compositions

Syngas is produced mostly by partial oxidation of oil or natural gas (Hla et al., 2010). Even heavy oil residues from petroleum production plants can be used as a syngas source for refinery margin (Silva et al., 2018). However, oxidation of fossil feedstock especially coal oxidation is the most preferred one these days since coal reserves are high and it is the best and the cleanest way of utilizing coal reserves instead of direct combustion process.

There is one point that should be taken into consideration when applying the coal derived SNG process into the industrial plants. As predictable, the carbon content of the coal is tremendous (Hla et al., 2010) when compared with the natural gas-based syngas production process. Whilst the CO content of the natural gas-derived syngas is about 5-10%, it is about 40-60% for the coal-derived syngas (Hla et al., 2009). Therefore, as logical, carbon oxides (CO or CO_2) to hydrogen ratio will be high in coal-derived syngas.

The composition of typical syngas which comes from coal gasification is 60% CO, 30% H_2, and 10% CO_2 (Hla et al., 2010). When the coal-derived syngas comes from the dry-feed gasifier, its CO content is high, whereas when it comes from the slurry-feed gasifier, its H_2 content is high (Hla et al., 2011).

The composition of syngas can change depending on the gasification process. Among the range of syngas content, the most suitable composition is then further utilized in the specific applications such as power or heat generation, hydrogen fuel, and chemicals as reductants (Hla et al., 2010).

Slurry feedstock of the entrained type of gasifier contains more steam and less carbon content. Therefore, the steam to CO ratio is high. Commercial SWGS catalysts can work under this condition. On the other hand, dry-powder feedstock contains less steam and more carbon content (nearly 70% CO on the syngas composition). Commercial SWGS catalysts cannot work under this condition. Both feedstocks can be used according to the specific applications. Hence, the huge amount of steam is needed to use dry powder feedstock (Liu et al., 2015).

Hla et al., (2010) studied the effect of CO, H_2O and H_2 content by mimicking the dry-feed coal gasifier composition (65% CO, 30% H_2, 2% CO_2 and 3% N_2) for two different types of high temperature WGS catalysts and for one sulfur-tolerant WGS catalyst. The steam to carbon monoxide ratio was selected in this study as 3:1 and reaction temperature was 450°C. The results showed that the sour WGS catalyst used in the study, CoMo/Mg-Al_2O_3, is more suitable for the syngas which contains less amount of CO.

Table 2.2. The examples of raw syngas compositions for different types of gasifiers (Hla et al., 2010).

Bed Type	**Fixed**	**Fixed**	**Entrained**	**Entrained**	**Entrained**	**Entrained**
Feed Form	Dry	Dry	Dry	Slurry	Slurry	Slurry
Coal	Illinois #6	Illinois #6	Illinois #5	SUFCO Low Sulfur	Illinois #6	Pittsburgh#8
CO, vol%	45.8	29.5	63.1	41.8	44.0	42.7
H_2, vol%	26.4	52.2	26.7	37.6	37.3	37.9
CO_2, vol%	2.9	5.6	1.5	19.8	16.9	17.3
Ar, vol%	NR	NR	NR	0.08	0.08	0.07
H_2O, vol%	16.3	5.1	2	NR	NR	NR

Table 2.3. Raw syngas composition for some of the entrained-bed type of gasifiers (Qin et al., 2018).

Gasifier	**Source**	**T (°C)**	**P (MPa)**	**Compositions (mol %)**			
				CO	H_2	CO_2	H_2O
GSP	Literature	1560	4	63.7	26.2	3.6	5.7

Table 2.3. Raw syngas composition for some of the entrained-bed type of gasifiers (Qin et al., 2018). (cont.)

GSP	Literature	1554	3.8	67.36	23.89	7.37	NR
	Industrial	1350-1750	3.8	66.92	23.85	7.8	NR
Shell	Literature	1500	4	60.3	23.5	6.3	8.9
	Literature	1505.5	4.38	65.29	21.21	5.01	5.92
	Literature	981.5	4	60.3	23.5	6.3	8.9
	Literature	984	4.38	62.21	20.42	5.5	9.43
	Literature	163.1	4	55.5	22	5.5	16.4
	Literature	164.9	4.11	55.57	18.27	5.75	18.24
Texaco	Literature	254	6.4	21.8	14	7.2	56.6
	Literature	241	6.4	21.37	14.01	6.15	57.31

Table 2.4. Raw syngas compositions for two feedstocks of the entrained-bed type gasifier (Hla et al., 2011).

Conditions	**CO (%)**	**H_2 (%)**	**CO_2 (%)**	**N_2 (%)**
Dry-feed coal-derived syngas	65	30	2	3
Slurry-feed coal-derived syngas	44	37	16	3

Furthermore, Yun et al., (2007) studied with the inert free syngas composition of 62-68% CO, 19-27% H_2, 6-15% CO_2. Sasaki et al., (2014) studied with the syngas composition of 60% CO, 5% CO_2, 20% H_2, 13.5 N_2.

2.3. Water Gas Shift and Sour Water Gas Shift

Since syngas is produced from gasification of carbon-containing materials such as natural gas and coal, carbon monoxide content in the syngas is high. Classical WGS reaction is used to adjust syngas (CO and H_2) ratio before it is sent to the other reactors for further applications such as methanation.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2.1}$$

Water gas shift is the mature and one of the well-known reactions, (see Eq. 2.1), which is used industrially for many decades (Hla et al., 2010). In the commercial WGS units, there are two main stages: the high temperature stage is followed by the low temperature stage. These stages are well-adapted to the raw syngas which contain relatively low CO content and less impurities.

On the other hand, the CO content of the syngas which comes from coal gasification is much higher than that of natural gas-derived gasification (Hla et al., 2009). The higher shift is required. Therefore, a suitable catalytic WGS unit should be incorporated into the SNG production plant when the syngas comes from coal-derived gasification to the WGS unit (Hla et al., 2010). Moreover, coal-derived syngas contains much more impurities, especially sulfur compounds compared to natural gas-derived syngas. The syngas that has high sulfur content are called sour gas.

It can be concluded that there are two main differences between the WGS and SWGS processes. The first one is that sour gas contains high sulfur compounds and the second one is that sour gas has high CO content.

There are two main types of catalysts used in the WGS unit for each stage. These catalysts are called high temperature shift (HTS) and low temperature shift (LTS) and they are effective when the syngas is sulfur-free. It should be needed to improve another type of catalyst that works under sulfur contamination. In this concept, $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts were developed and they are commercially used in SWGS reactions.

Classical WGS catalysts are poisoned by sulfur whereas sour gas shift catalysts cannot work well without sulfur. Hla et al., (2010) investigated the effect of sulfur content on the activity of CoMo catalysts. According to the results, the sour WGS catalyst performs low activity when the sulfur content is lower than 500 ppm. However, it shows better activity than that of HTS catalyst when the sulfur content is higher than 1000 ppm (Silva et al., 2018). The catalysts for both reactions will be examined in detail in the following parts.

2.4. Catalysts Used for WGS Reaction

In every chemical reaction, the bonds in the reactant(s) molecules are broken and new bonds are formed in order to create new chemical product(s). The minimum energy needed to break the bonds is called activation energy.

In the presence of a catalyst, the reaction pathway changes to decrease the activation energy and some intermediate product(s) are formed as can be seen from Figure 2.2.

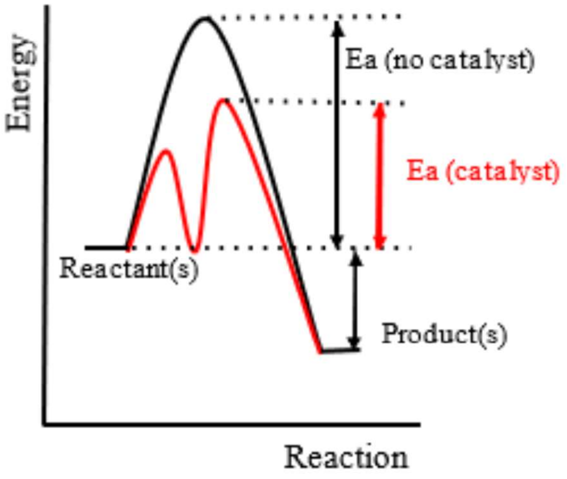


Figure 2. 2. An illustrative example of the effect of catalyst on the reaction pathway so as to activation energy.

Catalyst structure has basically two parts: the active phase and the support. The selected metal(s) which is called active phase is impregnated into the support surface to prepare the catalyst. Mainly there are two types of catalysts: homogeneous and heterogeneous. When the catalyst is in the same phase with both reactants and products is called homogeneous and when it is not, it is called heterogeneous.

Seyitoglu et al., (2015) used two stages of the WGS reactor to achieve higher performance. The first one works at a high temperature range, 300-450°C, the second one operates at a low temperature range, 120-300°C (Zaeer et al., 2017).

Industrial WGS reaction occurs in two stages, the high temperature stage is followed by low temperature stage, to optimize the CO conversion and to keep the reaction temperature under control (Silva et al., 2018). Therefore, commercially there are two types most common catalysts which are mainly used in classical WGS reactions:

- Iron-based HTS catalysts.
- Copper-based LTS catalysts.

High temperature catalysts were first developed by the Badische Anilin & Soda-Fabrik (BASF) company in the 19th century. They contain 80-95% Fe_2O_3, 5-15% Cr_2O_3, 1-5% CuO. These catalysts work at 250-400°C (Hla et al., 2010).

Low temperature catalysts contain 51% Cu and 31% ZnO and they can operate at the temperature at 190-275°C (Hla et al., 2010).

HTS catalysts are poisoned by the sulfur. However, they can be recovered after removing the sulfur compounds. Unlike HTS catalysts, LTS catalysts are irreversibly poisoned by sulfur. Therefore, there is a need to design another type of catalyst which can work under sour conditions. Sour gas shift catalysts will be discussed in detail in the following part.

2.5. Catalysts Used for SWGS Reaction

The WGS reaction (see Eq. 2.1) is exothermic. Therefore, it is difficult to control the reaction temperature when the syngas comes from a dry powder gasifier where the CO (one of the reactants of the WGS reaction) is high. In industrial applications, in order to solve this problem more steam (the other reactant of the WGS reaction) is added into the raw syngas before the WGS unit. On the other hand, from a thermodynamic point of view it is possible to limit the CO conversion by increasing the temperature, but it requires another cooling stage in the process. In order to make the process simpler, sulfur-tolerant and state of the art catalysts which can work under lean steam conditions (steam to carbon ratios is less than 0.5) are needed (Liu et al., 2015).

As it mentioned before, when syngas comes from gasification of coal, it contains high amounts of CO and some other impurities such as nitrogen or sulfur containing compounds and undesired particles compared with that of other sources of gasification. Even if pretreatments for desulfurization are done before the WGS unit, still there might be H_2S in the syngas composition because of incomplete sulfur removal process (Silva et al., 2018).

Then the syngas is called sour gas. Since classical WGS catalysts suffer from sulfur poisoning (Silva et al., 2018) they cannot be used in sour conditions. Therefore, the novel, sulfur-tolerant and state of the art catalysts should be required to perform WGS reaction in sour conditions as a part of the SNG production plant.

The activity of the SWGS catalysts mostly depends on the sulfur content in the feed of the WGS reactor to stay active. There are many ongoing studies about how H_2S content affects the activity of the SWGS catalysts. Hla et al., (2010) investigated the effect of H_2S content on the commercial SWGS catalyst which is $CoMo/Al_2O_3$. The results showed that when the sulfur content is low at a certain level, the sour shift catalyst loses its activity (Silva et al., 2018).

Sulfur-tolerant catalysts also known as sour-shift catalysts normally work at 230-450°C (Hla et al., 2010). Commercial sour $CoMo/Al_2O_3$ catalyst is resistant to sulfur and it works under the temperature range of 160-450°C (Yang et al., 2017). In fact, the catalyst would be perfect if it remains active both in sour conditions and sulfur-free conditions.

2.5.1. Commercial SWGS Catalysts

Commercial high temperature WGS catalysts lose their activity in the presence of sulfur compounds, but they can be recovered by removing sulfur. Whereas low temperature catalysts are irreversibly poisoned by sulfur species (Nikolova et al., 2020). Therefore, sour shift catalysts are highly desired.

To the best of our knowledge, molybdenum is the best element to use in the WGS catalyst that works under sour conditions. Sulfidation of the molybdenum species makes the sulfidation activation energy lower and great dispersion of the MoS_2 on the catalyst surface is achieved by increasing the active sites (Silva et al., 2018). Since molybdenum has a high sulfur tolerance, it is the most common metal of SWGS catalysts. So many studies have been conducted to find the second or third metal as a promoter that has a synergy with molybdenum, and they should have the ability to increase the catalytic activity when combining with molybdenum.

Electronegative metals are the best to consider as a promoter in the Mo-based catalysts since they can remove electron(s) from the oxygen side of the MoO species and MoS_2 which is an active site for sulfur-tolerant catalysts can easily be formed (Sasaki et al., 2014).

In this concept, cobalt and nickel are the best candidates to be promoters for the Mo-based sulfur-tolerant catalysts. Additionally, since alumina (Al_2O_3) is the well-known support for many industrial applications, $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ are the most common catalysts in industry for the SWGS processes. Alkali-promoted, usually potassium derivatives, classical CoMo catalysts are very effective for the coal gasification processes (Antoniak-Jurak et al., 2016).

2.5.2. Metals Used for SWGS Catalysts

As far as we know, molybdenum is the best sulfur-resistant element. Hence, it has an undeniable place when designing suitable catalysts for WGS reaction in sour conditions. Additionally, it is found that cobalt and nickel have a great synergy with molybdenum as a promoter metal. Therefore, CoMo and NiMo are two of the most known catalysts which are used in SWGS reactions. However, there are many ongoing studies in order to discover other metal(s) which have high performance in sour conditions.

Silva et al., (2018) investigated the effect of metal types on the activity of the Nb_2O_5 supported SWGS catalysts. They prepared Pt/Nb_2O_5, Au/Nb_2O_5, and Cu/Nb_2O_5 and tested their efficiency by mimicking the industrial conditions with and without sulfur (H_2S) in the feed. Results showed that Cu/Nb_2O_5 does not work even under clean conditions, Au/Nb_2O_5 can stay active under sour conditions but inactive without sulfur, Pt/Nb_2O_5 seems the most suitable catalyst since it can work under both conditions. In the spent catalysts of Pt/Nb_2O_5, there is no trace for niobium sulfide. It means that Pt/Nb_2O_5 is sulfur tolerant.

Although noble metals such as Pt, Pd, Ru, Rh, Os, and Ir show high performance, they are very expensive (Zhang et al., 2012). Rather than noble metals there is a limited number of other metals that can be used in the catalysts of WGS reactions such as Fe, Cr, Co, Ni, Re, Ti as well as Mo and W (Li et al., 1999; Hla et al., 2010 and Mi et al., 2017).

2.5.3. Promoters Used for SWGS Catalysts

Sasaki et al., (2014) investigated the effect of the promoter by adding different types of metals such as Ca, Mg, Zn, Zr, Ti, Co and Ni as a promoter by taking monometallic Mo/Al_2O_3 catalyst as a standard. The catalytic activity of the corresponding catalysts decreases in the following order: Ni > Co > standard = Ti > Zr > Zn Mg > Ca.

The noble metals such as Pt, Rh, Au and Pd can be used in WGS catalysts because of their high activity. However, they are rare and expensive. Therefore, current studies have been focused on utilizing cheap and more abundant transition metals such as Cu, Ni, Co, Fe, Mn, Mo into the WGS catalysts. Among these metals, Ni is the most attractive one and it has been used for many catalysts as a promoter.

Andreev et al., (1999) prepared monometallic Ni and Mo catalysts, bimetallic NiMo catalyst and their potassium-promoted versions in order to observe the effect of the promoter on the activity of the WGS catalyst. It is found that potassium addition increases the activity for monometallic Ni and bimetallic NiMo catalysts whereas the activity of monometallic Mo catalyst is higher than that of without potassium.

On the other hand, there is one important problem when using nickel metal in the catalyst: sintering between the metal particles and the support materials. The addition of the second metal can both solve this problem and increase the catalytic activity. In this context, Ni-Cu; Ni-Au, Ni-Rh; Ni-Pt have been studied so far. Moreover, the addition of rhenium has gained interest as a second metal in order to prepare WGS catalysts (Chayakul et al., 2011).

Rhenium is used for many industrial applications as a promoter or main metals in catalysts. For example, one of the bimetallic catalysts, Pt-Re, is used in the hydrogen production industry, Ni-Re catalysts for steam reforming, and Re-Co catalysts are used for Fischer-Tropsch reaction. Moreover, rhenium sulfide catalyst is used for hydroprocessing of petroleum products, and it performs higher activity than that of molybdenum sulfides (Nikolova et al., 2020).

Recently, Iida et al., (2006) considered using rhenium in preparation of WGS catalysts since both Pt-Re/TiO_2 and Pd-Re/TiO_2 showed good catalytic activity for the WGS reactions. It is also found that Pt-Re/TiO_2 (rutile) and Pt-Re/ZrO_2 catalysts showed high activity for low temperature WGS reactions.

The effect of addition of rhenium into the Co/CeO_2 and Ni/CeO_2 WGS catalysts is also investigated. It can be concluded from this study that the addition of rhenium into the Ni/CeO_2 and Co/CeO_2 monometallic catalysts induced the activity for the WGS catalysts. This higher activity by adding rhenium may be attributed to better redox process on the surface of the ceria support and better CO adsorption by increasing the dispersion metal active sites (Nikolova et al., 2020; Chayakul et al., 2011 and Chayakul et al., 2011).

Mi et al., (2017) used niobium as a promoter for classical CoMo catalyst but modifying the alumina support with magnesium. Then according to the results, the niobium doped CoMo/$MgAl_2O_3$ catalyst showed better performance than that of the niobium free one. Therefore, it can be concluded that niobium may be helpful to improve classical SWGS catalysts (Silva et al., 2018).

Sulfided Mo and NiMo catalysts and their potassium-promoted types performed the highest activity for the WGS reaction. Potassium leads to increase the reducibility of the molybdenum species hence it increases the catalytic activity (Andreev et al., 1999).

Liu et al., (2015) prepared a series of potassium modified CoMo catalysts over the $MgAl_2O_4$ modified alumina support. The addition of potassium as a promoter increases the activity of the catalyst by better dispersion of the MoO_3 active sites and increasing the surface area.

Potassium is not reductive when it is used itself in monometallic catalysts. However, it becomes reductive by using it together with other metals in the catalysts (Lian et al., 2011). Cerium and potassium have a synergistic effect when used together as a promoter (Zhang et al., 2012).

Tungsten metal was used as a promoter for potassium promoted CoMo/Al_2O_3 catalyst and it showed better activity than that of tungsten free version (Wang et al., 2009).

2.5.4. Supports Used for SWGS Catalysts

It is an undeniable fact that alumina is suitable for the WGS reaction. However, alternative supports such as carbon, silica, zeolites, titania and zirconia have been tested so far. For example, Laniecki et al., (2000) prepared a series of NiMo catalysts over three different types of supports: gamma alumina (as a standard), titania and zirconia. According to the result, titania showed better activity than that of alumina whereas zirconia performed less activity than that of standard catalysts. The high activity of the titania supported catalyst may be attributed to its better homogeneous support surface.

Sasaki et al., (2014) investigated the effect of the supports by using different types of supports such as silica, titania and zirconia by taking monometallic Mo/Al_2O_3 catalyst as standard. CO conversion rate in the presence of the catalysts decreases in the following order: Mo/TiO_2 = Mo/ZrO_2 > Mo/Al_2O_3 > Mo/SiO_2.

Sasaki et al., (2014) compared two sour shift catalysts, NiMo/TiO_2 and commercial CoMo over MgO modified Al_2O_3. It can be concluded that ⅕ of the NiMo/TiO_2 has the same conversion with the CoMo/MgO-Al_2O_3 (Silva et al., 2018).

Mixed oxide supports show different surface properties rather than using them alone. Laniecki et al., (2006) studied the activity of the commercial NiMo catalysts over TiO_2-ZrO_2 mixed oxide support. It is observed that the mixed oxide supported catalysts performed higher activity than that of NiMo/TiO_2 and NiMo/ZrO_2. This situation can be attributable to relatively high support surface area, better acidic-basic properties of the mixed oxide support and better metal dispersion on the support.

Cerium oxide also known as ceria is widely used as a support for many industrial applications. Many studies showed that addition of appropriate metals into the ceria support enhances the activity of the desired catalyst (Chayakul et al., 2011).

Analyzing the studies done on the subject about improving catalytic activity for the sour shift catalysts by changing the metal(s), it is considered the most effective way is making modifications on the support. In this concept, Mi et al., (2017) studied with classical CoMo catalyst supported on the niobium modified MgO-Al_2O_3 mixed oxide. Niobium addition increased the catalytic activity by having similar effects with the other high-performance catalysts, such as decreasing the sulfidation activation energy of the molybdenum species and increasing the dispersion of molybdenum species.

The activity of PtRe, PtCo, PtMo, PtSn, PtCu over zirconia doped ceria catalysts were examined. PtRe and PtCo showed better activity when compared with monometallic platinum catalysts over the same support. The rest of them performed worse than the standard monometallic platinum catalyst. Moreover, PtRe is more stable than PtCo catalyst. Rhenium addition increases the platinum dispersion on the supports (Choung et al., 2005).

Activated carbon (AC) support has been used in the catalyst preparation process a lot since it has many advantages as a support besides carrying essential support properties. First of all, it can be stable in both acidic and basic media. Moreover, it has a large specific surface area, the support can be easily recovered from the metals and the support can be tailored for better surface chemical properties. (Aksoylu et al., 2001; Antoniak-Jurak et al., 2016; Lian et al., 2011 and Naji et al., 2022).

Although AC has many advantages compared with other supports, there is limited study on commercial CoMo catalysts over AC support in the literature. Antoniak-Jurak et al., (2016) investigated the difference between alumina supported, potassium promoted CoMo catalyst, and its AC supported version. AC supported catalysts showed better activity than the other.

Surface chemistry of the support material is very important on the activity of the catalysts since it affects the interaction between the support and the metals loaded on the support and the reducibility of the metal species (Aksoylu et al., 2000).

Surface oxygen bearing groups create an acidic or basic media on the support and it helps to redox processes on the support (Aksoylu et al., 2000). There are two main oxygen bearing surface groups (see Table 2.5) in the AC supports: the acidic (CO_2 releasing) groups and less acidic (CO releasing) groups. The first group makes the surface accessible for the precursor solutions of the metals by decreasing hydrophobicity. The second group increases the interaction between the support surface and the metals (Aksoylu et al., 2001).

Table 2.5. Some acidic and basic oxygen bearing surface groups on the AC surface.

Surface Groups	**Releasing Group**	**Reference Temperature**
Carboxylic	CO_2	523K 373-673K 473-523K
Lactone	CO_2	900K 623-673K 463-923K

Table 2.5. Some acidic and basic oxygen bearing surface groups on the AC surface. (cont.)

Phenol	CO	873-973K
Carbonyl	CO	973-1253K 1073-1173K
Anhydride	$CO+CO_2$	873K 900K 623-673K
Ether	CO	973K
Quinone	CO	973-1253K 1073-1173K

Carboxylic, lactone, phenol, carbonyl, anhydride, ether and quinone are the main surface groups on the AC support.

Since raw carbon materials contain high amounts of impurities and unfavorable pore structure, they are not suitable to be directly used as a catalyst support. They should be treated first. High micropore content in the raw carbon materials leads to the diffusion resistance, blocking and active surface limitations (Antoniak-Jurak et al., 2016). Therefore, by oxidizing treatments it is aimed to destruct the pores and to create medium or large size pores into the catalyst surface.

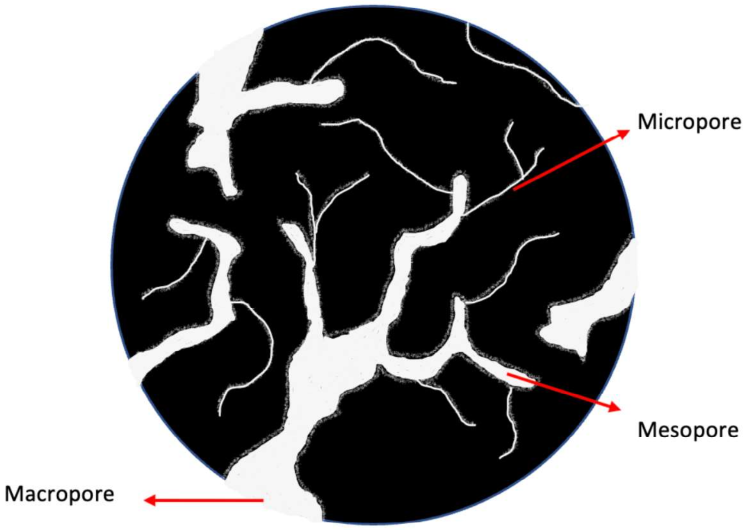


Figure 2.3. A schematic representation of activated carbon pore structures and pore size.

The thermal or chemical treatment methods help to change the nature and the concentration of the surface groups of the AC support. It is possible to create micro, meso or macropore structures at different proportions (Figueiredo et al., 1999). For example, thermal treatment on the AC support increases the meso and macropores while decreasing micropores. The research on this field is very scarce but thermal treatment can be considered for possible future application of the AC support in the WGS catalysts (Antoniak-Jurak et al., 2015).

(Aksoylu et al., 2000) studied the effects of the two pre-treatment methods on the two different types of AC supports, Hydraffin and Norit. Liquid phase oxidation (HNO_3) and gas phase oxidation (O_2) were applied for two types of AC, and with their non-treated derivatives six different supports were prepared in total. The results showed that both oxidation treatments increase the oxygen bearing surface groups which can be either acidic or basic and they determine the support's activity by forming anchoring sites for metals.

Air (O_2) oxidation treatment has a large effect on increasing the CO releasing groups but unlikely its effect is limited on increasing the CO_2 releasing groups. On the other hand, nitric acid treatment increases both CO and CO_2 releasing groups. While knowing that CO_2

releasing groups have much more acidity than that of CO releasing groups, it can be said that nitric acid treatment gives higher acidity to the carbon support surface (Ozkara et al., 2003).

Gas phase (air) oxidation increases the amount of hydroxyl and carbonyl surface groups and liquid phase (nitric acid) oxidation increases the carboxylic acid surface groups (Figueiredo et al., 1999).

Besides having more oxygen surface groups on the AC support, it is also aimed to increase the hydrophilicity of the support surface by applying treatment methods. Hence, the support surface becomes available to give better interaction with the metal precursor(s) that are impregnated into it (Aksoylu et al., 2000).

2.5.5. Effect of Experimental Conditions

Nikolova et al., (2020) prepared monometallic Re over γ-alumina catalyst and its bimetallic and trimetallic combinations by utilizing Ni, Co and K as a promoter by the sequential incipient wetness impregnation method. The fixed-bed reactor was used in this study in order to carry out the performance tests. The reaction temperature was in the range of 180-400°C and steam to carbon monoxide ratio was selected as 0.3 which is in accordance with dry-powder gasifier syngas requirements. It is concluded that KCoRe trimetallic catalyst performed the best activity when compared with others since these three metals have a great synergy when they are used together. Therefore, KCoRe/γAl_2O_3 can be considered as a promising WGS catalyst candidate for further applications.

Liu et al., (2015) studied the effect of K_2O addition on the performance of the CoMo/Mg-Al_2O_3 catalyst with a steam to carbon ratio of 0.3 and for the raw syngas containing 64.9% CO, 8.1 CO_2, 25.1 H_2, 1.9 N_2. It is shown that addition of K_2O increases the catalytic activity. Moreover, even if thermodynamically unfavorable it is concluded that the catalyst performed better conversion at higher temperatures. This means that the WGS reaction is controlled kinetically, not thermodynamically. Therefore, the reaction conditions and catalyst characteristics are very important parameters on the performance of the WGS reaction.

2.5.6. Effect of Steam/Carbon Monoxide Ratio

Presence of the steam in the sulfided WGS reaction promotes the hydrolysis of the sulfide phase, and it helps to increase the catalytic activity (Andreev et al., 1999).

$$2CO \leftrightarrow CO_2 + C \tag{2.2}$$

$$nCO + 2nH_2 \overset{\Delta}{\rightarrow} n(CH_2 -) + nH_2O \tag{2.3}$$

High temperature iron based WGS catalysts tend to produce carbon by Boudouard reaction, (see Eq. 2.2) (Basu et al., 2010). Since carbon monoxide is one of the reactants of the WGS reaction, it blocks the occurrence of the WGS reaction when the steam (the other reactant of WGS) content is very low. Additionally, they can promote the formation of the hydrocarbons by the Fischer-Tropsch reaction (see Eq. 2.3) above (Qin et al., 2018).

Steam to carbon monoxide ratio becomes very important when considering different types of syngas composition. Generally, commercial SWGS catalysts work when the steam to carbon monoxide ratio is above 2 or 3 in order to depress carbon formation and to boost the catalyst performance (Liu et al., 2015).

Most of the studies have focused on developing the sulfur-tolerant catalysts for the slurry type syngas which has a high steam to carbon monoxide ratio. Therefore, Liu et al., (2015) studied with the KCoMo/Al_2O_3 catalyst. It showed high performance when CO content is high in the syngas.

Dry powder coal gasification process seems very efficient. However, when the syngas is produced by this method, it requires low steam content (the steam to carbon monoxide ratio is usually less than 0.8) and high temperature. Additionally, it has a high CO content. This syngas is called lean steam raw syngas. Because of these reasons it is difficult to adopt dry powder gasifiers into the SNG plant (Liu et al., 2015).

Liu et al., (2015) investigated the effect of steam to carbon monoxide ratio on the activity of the potassium modified commercial CoMo catalysts over magnesium modified alumina support, $MgAl_2O_4$. The outlet CO content was screened by changing the steam to carbon monoxide ratio. Low CO content in the products means high activity from the kinetic point of view of the WGS reaction. As it is understandable from the WGS equation (see Eq. 2.1) when the steam to carbon ratio monoxide is increased, the outlet CO so as the activity is decreased.

Liu et al., (2015) also studied the effect of K_2O content on the activity of the potassium modified commercial CoMo catalysts over $MgAl_2O_4$ modified alumina support at different steam to carbon monoxide ratios. The results showed that for all the steam to carbon monoxide ratios, addition of the K_2O caused an increase in the catalytic activity. Moreover, the addition of extra steam affects the activity of the catalysts more prominently when the steam to carbon monoxide ratio is low rather than that of high steam to carbon monoxide ratio.

When the content of the side products such as methane is increased, the reaction temperature may become uncontrollable. This situation can be prevented by increasing the steam to carbon monoxide ratio (Liu et al., 2015).

3. EXPERIMENTAL WORK

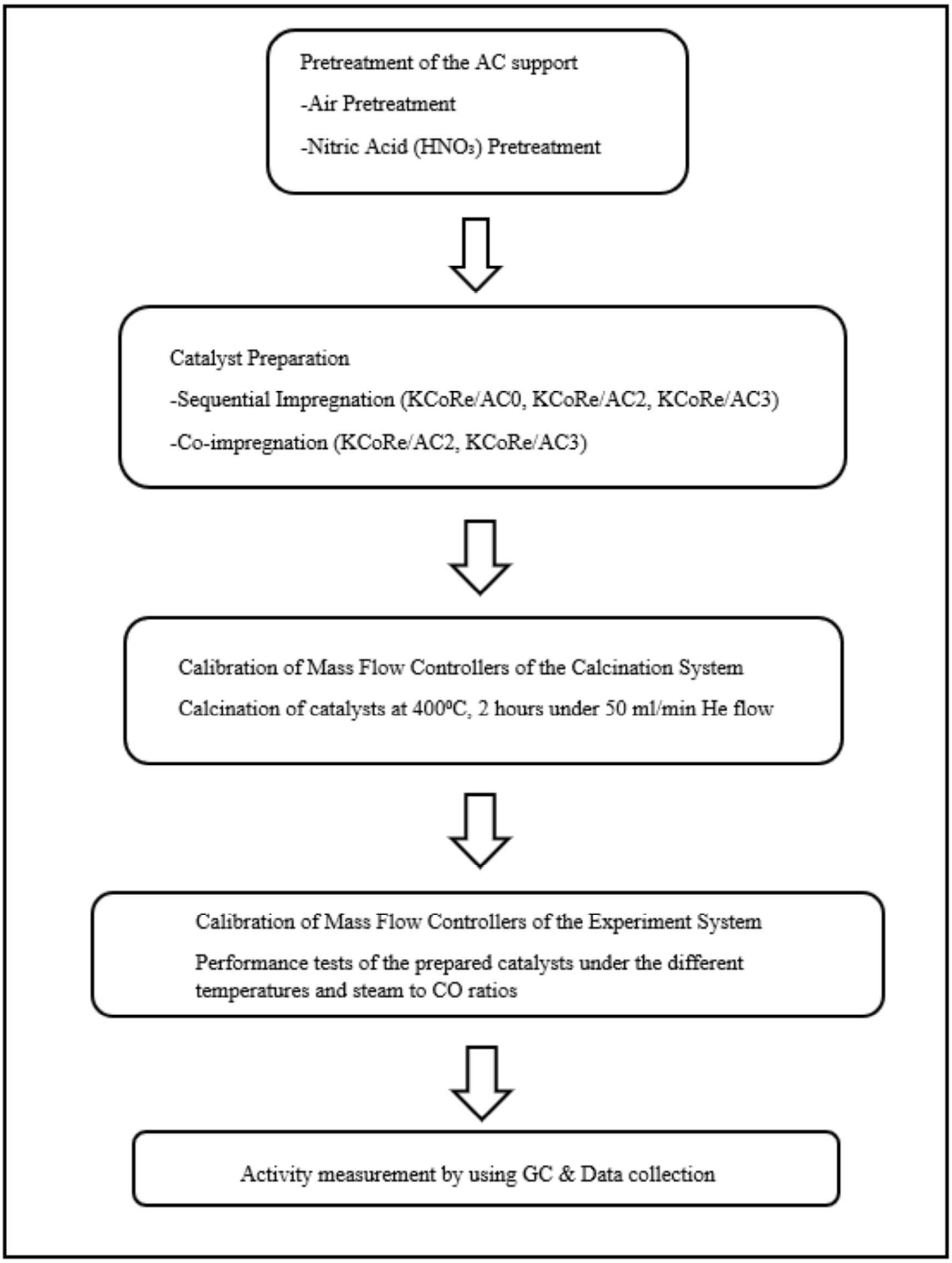


Figure 3.1. A schematic representation of the experimental work done in this study.

3.1. Materials

3.1.1. Chemicals

The chemicals used for support preparation are listed in Table 3.1 and the metals used for impregnation are listed in Table 3.2.

Table 3.1. Chemicals used in support (AC0, AC2, and AC3) preparation.

Chemicals	**Formula**	**Grade**	**Source**	**Molecular Weight (g/mole)**
Activated Carbon (AC)	C	ROW	Norit 0.8	12.0
Hydrochloric Acid	HCl	Research	Merck	63.0
Nitric Acid	HNO_3	Research	Merck	36.5

Table 3.2. Metals used in catalyst preparation.

Metals	**Precursors**	**Formula**	**Grade**	**Source**	**Molecular Weight of precursor (g/mole)**
Cobalt (Co)	Cobalt (II) nitrate hexahydrate	$Co(NO_3)_2{\cdot}6H_2O$	Research	Roth	291.03
Rhenium (Re)	Ammonium perrhenate	NH_4ReO_4	Research	Alfa Aesar	268.24
Potassium (K)	Potassium Carbonate	K_2CO_3	Research	Sigma Aldrich	138.20

3.1.2. Gasses and Liquids

The gasses which are used in this study were supplied from BOS (Birleşik Oksijen Sanayii) Company, Istanbul, Turkey. Specifications of the gasses and liquids are listed in Table 3.3 and Table 3.4.

Table 3.3. Specifications and applications of the gasses used in this study.

Gas	**Specification**	**Application**
Carbon monoxide	99.99% BOS	Reactant, GC calibration
Carbon dioxide	99.99% BOS	Reactant, GC calibration
Hydrogen	99.99% BOS	Reactant, GC calibration
Argon	99.99% BOS	GC calibration, inert
Dry Air	78.4% N2 + 21.5% O2 (BOS)	GC
Argon	99.99% BOS	GC carrier gas
Helium	99.99% BOS	Calcination system
Oxygen	99.99% BOS	Calcination system
Nitrogen	99.99% BOS	Calcination system

Table 3.4. Specifications and applications of the liquids used in this study.

Liquid	Specification	Application
Water	Deionized	Reactant, Vaporizer

3.2. The Experimental Set-Up

The experimental part of this study can be divided into four subsystems:

i. The AC system was used to prepare AC supports for catalysts by applying different pre-treatment methods for raw Norit ROW 0.8 AC samples.

ii. Catalyst preparation system includes the impregnation system which was used to impregnate the precursors of the selected metals into the different types of AC support.

iii. Reaction test system was basically used to perform the desired WGS reaction on the prepared catalysts in ideal conditions.

iv. Product analysis system consists of a GC analyzer which is used to analyze the amount of products obtained and to calculate the efficiency of the reaction.

3.2.1. AC Support Preparation System

To observe the effect of the support on the activity of sour WGS catalyst, AC was treated by using different methods. The name of the supports and the corresponding treatment methods are summarized below.

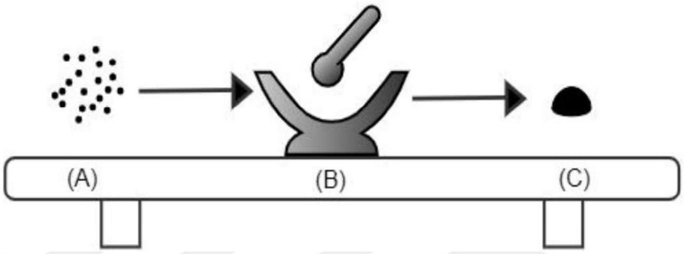
Table 3.5. The names and treatment methods of AC samples.

Name	**Treatment**
AC0	Raw Norit 0.8 ROW
AC1	HCl washed NORIT 0.8 ROW
AC2	HCl washed and air oxidized NORIT 0.8 ROW
AC3	HCl washed and HNO_3 oxidized NORIT 0.8 ROW

Different systems are required for each method and all of them will be explained in the following paragraphs.

3.2.1.1. AC0 Preparation System.

AC0 preparation system is used to convert granular form of the AC into powder form. This is the first step, and it is required before further treatment of the AC.



A. Granular form of the AC, B. Mortar and Pestle, C. Powder form of the AC

Figure 3.2. AC0 Preparation System.

The system includes only mortar and pestle to press AC samples and its schematic representation is shown in Figure 3.2.

3.2.1.2. AC1 Preparation System.

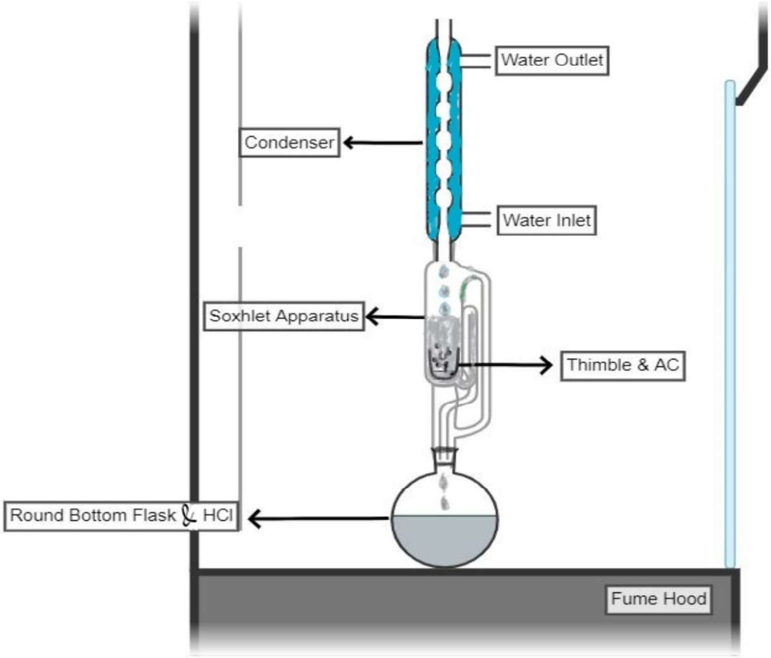


Figure 3.3. AC1 Preparation System.

AC1 preparation system is used to wash AC0 samples with hydrochloric acid. The system consists of basically round bottom flask, soxhlet apparatus, thimble, and condenser. Heater is connected to the system to adjust the temperature of the system. Glass wool wrapped with aluminum foil is also used as an insulator and rounded around the bottom flask. The process should be carried in the fume hood. Dimensions of the thimble should be selected according to the amount of AC0 treated. In this study for a 20g AC0 sample, a 33mmx90mm thimble was used. The schematic representation is shown in Figure 3.3.

3.2.1.3. AC2 Preparation System.

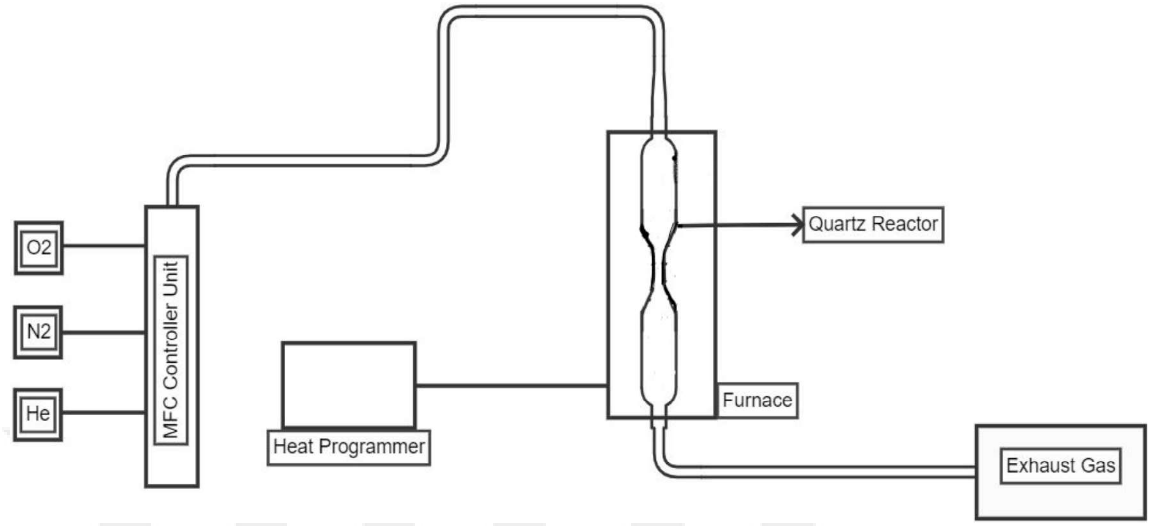


Figure 3.4. AC2 Preparation (Calcination) System.

AC2 preparation system is used for calcination of the AC1 sample. The system basically includes O_2, N_2, and He gas regulators and their mass flow controllers, quartz glass reactor, furnace, and heat programmer to keep the reactor temperature at desired level for calcination. The schematic representation is shown in Figure 3.4.

3.2.1.4. AC3 Preparation System.

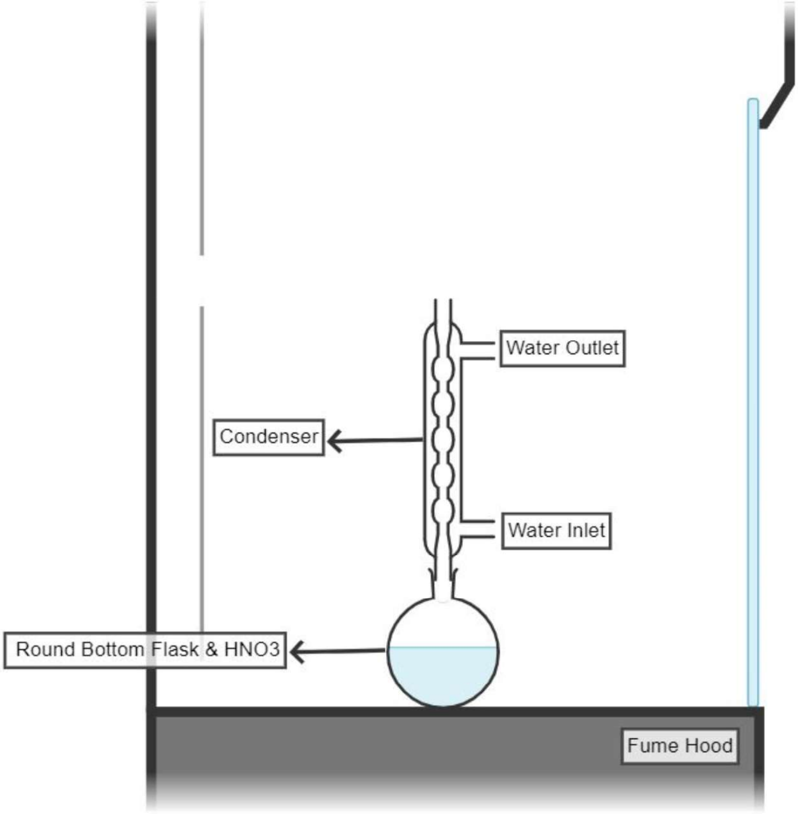
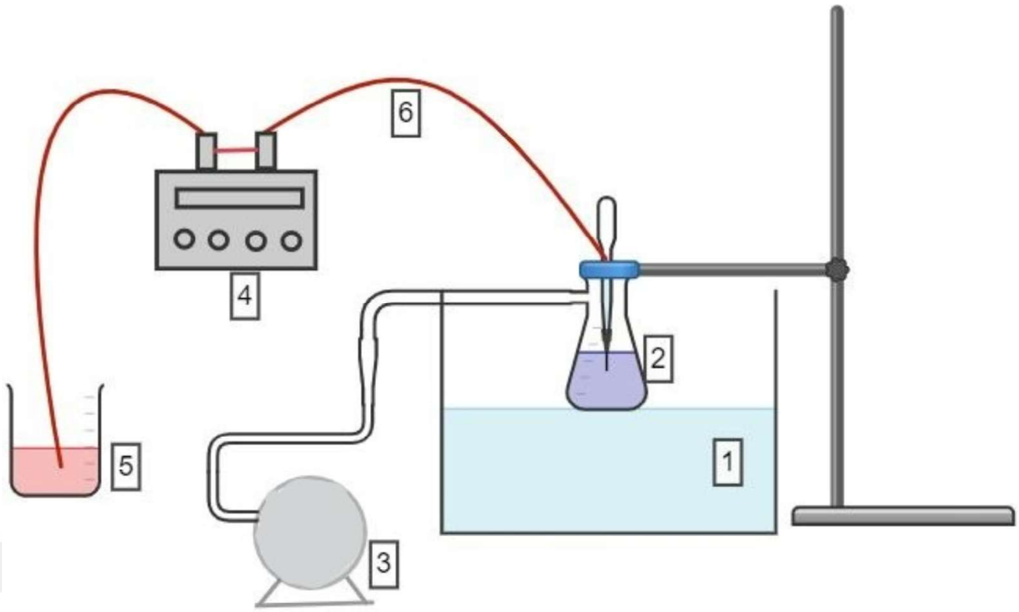


Figure 3.5. AC3 Preparation System.

The AC3 preparation system is used to wash the AC1 sample with nitric acid. The system consists of a round bottom flask and condenser. Heater is connected to the system to adjust the temperature of the system. Glass wool wrapped with aluminum foil is also used as an insulator and rounded around the bottom flask. The process should be carried in the fume hood. The schematic representation is shown in Figure 3.5.

3.2.2. Catalyst Preparation System

The catalyst preparation system is used to impregnate the metals over the support. Since the metals cannot directly be adsorbed on the surface of the support, their precursor solutions which were listed in the materials section of this chapter are prepared. The system consists of ultrasonic mixer, Buchner erlen, vacuum pump, peristaltic pump, reactant storage tank, and silicone tubing. Buchner erlen is also clamped to the system by using a retort stand.



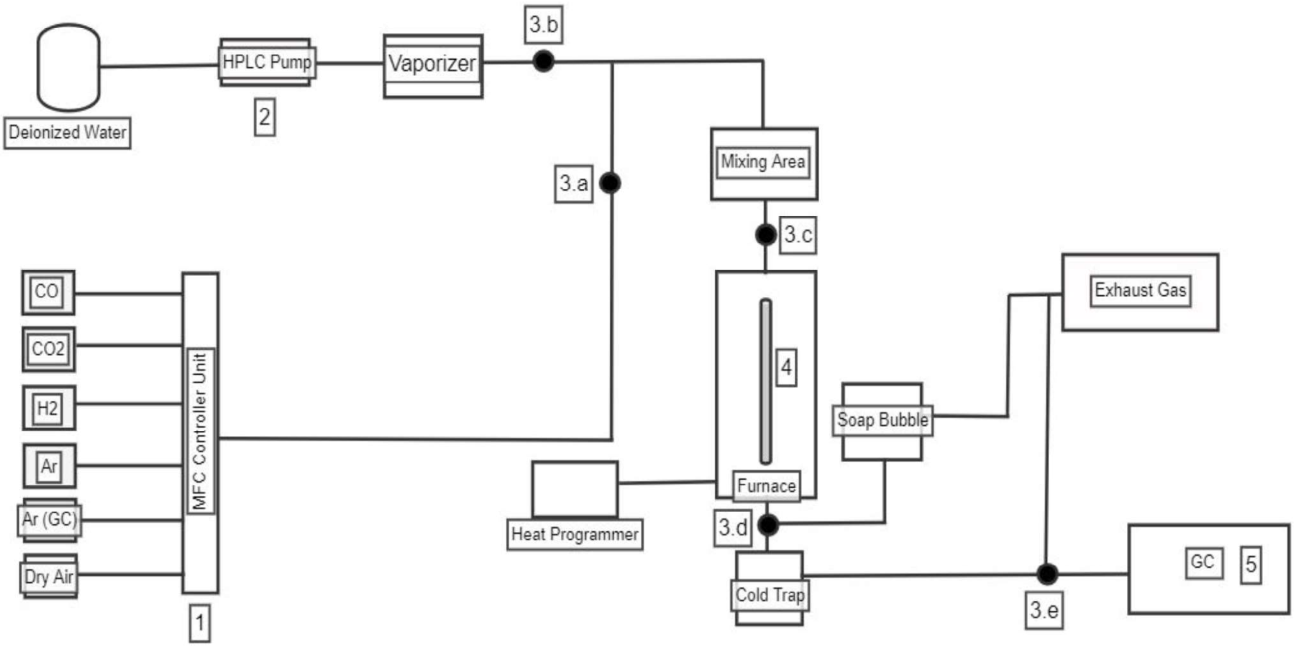
1.Ultrasonic Mixer, 2. Buchner erlen, 3. Vacuum Pump, 4. Peristaltic Pump, 5. Reactant Storage Tank, 6. Silicone Tubing

Figure 3.6. The impregnation system used to prepare catalysts.

The schematic representation of the system is shown in Figure 3.6.

3.2.3. Catalyst Performance Testing System

The performance testing system which was constructed at Bogazici University Chemical Engineering Department was used throughout the study. The system basically consists of the furnace, the metal reactor placed into the furnace, programmable temperature controller to keep the reactor temperature under control, MFCs of the reactants, HPLC to pump the deionized water to the vaporizer, vaporizer to convert the liquid water into steam, mixing box to let the reactants mixed before sending to the reactor, cold trap to keep the liquid water if there is any inside the products, soap bubble to calculate the flow rate of the reactants, and GC analyzer to obtain CO conversion data. Additionally, the flow of the reactants and products inside the system is controlled via the three-way valves which are placed on the system. Also, glass wool wrapped with aluminum foil is used as an insulator around the suitable place in the system in order to prevent heat loss. The schematic representation of the process diagram is shown below.



1.Mass Flow Controllers (MFCs), 2.HPLC Pump, 3.Three-way Valves, 4.Reactor (Stainless Steel), 5.GC Analyzer.

Figure 3.7. A schematic representation of the performance testing system.

3.2.4. Product Analysis System

Product steam was analyzed by using Gas Chromatography (GC). CO concentration data was obtained from Agilent Technologies 6850 Series II Gas Chromatograph. GC specifications are listed in Table 3.6.

Table 3.6. GC Specifications.

Type	**GC 6850**
Carrier Gas	Argon
Pressure of the carrier gas	5 bars
Front detector temperature	150°C

3.3. Catalyst Preparation

The catalyst preparation system consists of support preparation and impregnation system. The activated carbon supported catalysts were prepared by incipient to wetness impregnation method. KCoRe/AC0 was prepared by sequential impregnation. KCoRe/AC2 and KCoRe/AC3 were prepared by both sequential and co-impregnation. The metal loadings were 5.8%Re, 2.4%Co, and 2.2%K for all the catalysts that are prepared in this study.

3.3.1. Pretreatment of the AC Support

Four different processes were applied to the AC samples. Firstly, granular forms of the Norit ROW 0.8 AC samples were crushed to obtain powder form by using mortar and pestle. Then, it was sieved as its mesh size 45-60 which corresponds to 300-200 µm. This step was actually not a treatment process, but it is necessary for further treatment processes of the AC samples. Therefore, the obtained sample is called AC0. The following procedures were then applied to AC0 material.

In order to obtain AC1 from AC0, the system was set-up as shown in Figure 3.2. The process basically includes washing AC0 with hydrochloric acid solution to remove ash and sulfur content. The whole process was done in the fume hood. Firstly, 200 mL, 2N HCl solution was added into the round bottom flask. Approximately 20g AC0 sample was put into the thimble. A 33mmx90mm thimble was used for 20g AC0. Then, the thimble was placed into the soxhlet apparatus carefully. The thermocouple end of the heating coil was placed under the bottom of the flask and all the parts were connected to each other. In order to prevent heat loss, the round bottom flask was surrounded with aluminum foil-wrapped glass wool. The heater was set up to 200°C and the tap water was opened. The 12 hours washing procedure was started after seeing the first condensation at the junction point of the condenser and soxhlet apparatus. The first siphon was observed. At the end of the 12 hours, the last siphon waited, and the equipment was disconnected. The slurry was rinsed with distilled water and the same procedure was repeated for 6 hours with deionized water instead of HCl solution at 150°C to get rid of HCl from the AC sample. Finally, the slurry was dried at 110°C overnight. AC1 was not directly used in this study, it was an intermediate material, and it was needed to prepare AC2 and AC3 supports.

AC1 support was then treated with air (O_2) to obtain AC2. For this process, the calcination system represented in Figure 3.3 is used. Approximately 10 g of AC1 support was placed inside the quartz glass down flow reactor and the reactor was placed into the furnace. The AC1 was heated until the temperature was up to 450°C from room temperature under the flow of 150 ml/min N_2. AC1 was calcined at this temperature under the flow of 190 ml/min N_2 - 10 ml/min O_2 (95% N_2 - 5% O_2) for 10 hours. Then, the sample was left to cool down under the flow of 150 ml/min N_2 only. It was sheltered under inert.

The system which is represented in Figure 3.4 is used to prepare AC3 support. The whole process was carried out in the fume hood. 350 ml, 5N HNO_3 solution was added into the round bottom flask which contains approximately 20 g AC1. There was no need to use the soxhlet apparatus during this process. The condenser was directly connected to the flask. The heater was set up to 175°C and the tap water was opened. After observing yellowish brown steam, the washing process was started for 3 hours. The AC3 sample was let to precipitate overnight. The solution was transferred to the 2L beher. The liquid level was completed with deionized water to 1.5L. The solution was stirred at 250 rpm at 250°C until it lost 300 ml of water. It was let to settle down then the liquid part was transferred into another beher. The liquid level was completed again to 1.5 L. The procedure was repeated 3 times. After purifying the support from nitric acid by washing with water, it was filtered by using a vacuum filter and it was dried in the etuv at 110°C overnight. It was sheltered under inert.

3.3.2. Impregnation

All the catalysts used in this study were prepared by using incipient wetness impregnation (IWI) in either sequential or co-impregnation of the metals.

Classically, the impregnation method had been carried out by ejecting an excess amount of precursor solutions of the metals into the supports. The interaction between the metals and the catalyst surface was determining the metal loadings and it was not clear how much metal is loaded. In the incipient wetness impregnation method, the minimum amount of precursor ejects to the support and by applying vacuum all the metals are absorbed from the pores of the catalyst support. Therefore, similar metal loading can be achievable (Aksoylu et al., 2001).

The impregnation system which is shown in Figure 3.2 was used in order to perform the IWI method for the catalysts. Mainly 5 different types of catalysts were prepared over 3 different types of AC supports. The metals and their precursors were listed in Table 3.2. The pretreatment methods of the AC as a support were listed in Table 3.5. The catalysts that are studied in this work are summarized in the following table.

Table 3.7. The prepared catalysts in order to use in the experiments in this study.

Catalyst	**Metal Loadings**	**Support Type**	**Impregnation Type**
KCoRe/AC0	K, Co and Re	AC0	Sequential
KCoRe/AC2	K, Co and Re	AC2	Sequential
KCoRe/AC3	K, Co and Re	AC3	Sequential

Table 3.7. The prepared catalysts in order to use in the experiments in this study.(cont.)

KCoRe/AC2	K, Co and Re	AC2	Co-Impregnation
KCoRe/AC3	K, Co and Re	AC3	Co-Impregnation

Some of the catalysts were prepared by using both sequential and co-impregnation methods in order to observe the effect of the impregnation type. Moreover, AC support was used in three different forms in order to observe the effect of the treatment methods. AC support without treatment is called AC0, by air treatment it is called AC2 and by nitric acid treatment it is called AC3.

In order to prepare the catalysts by sequential impregnation, approximately 2g of AC support was weighed and put into the Buchner erlen. The bottom of the erlen was kept on the surface of the water inside the ultrasonic mixer with a clamp (see Figure 3.6). High vacuum was applied in order to purify the pores of the AC support from the air inside it. The support was left to mix in these conditions for 30 minutes. On the other hand, an appropriate amount of rhenium precursor was prepared. The precursor solution was translated from the beaker to the Buchner Erlen via silicon tube. The injector was connected to the end of the silicon tube and the precursor was dropped from this injector over the support surface. The peristaltic pump was used to transfer the precursor solution at a flow rate of 5 mL/s. After impregnation was completed, the vacuum and the pump were closed. The catalyst in the erlen was left on the ultrasonic mixer for 1.5 hours to get a more homogeneous catalyst. After that the catalyst was put in the etuv overnight at 110°C.

The following day, the calcination procedure was applied to the catalyst. This process was carried out in the calcination system which is shown in Figure 3.4. The catalyst was calcined in three stages, and these are shown below in table. After calcination, the rhenium loaded was completed.

Firstly, the catalyst sample was put into the glass quartz reactor and the reactor was placed into the calcination system (see Figure 3.4). The helium gas was sent to the reactor at a flow rate of 25 mL/min. The temperature inside the furnace was increased from the room temperature to 125°C and it was left at this temperature for 20 minutes. Then the temperature was raised from 125°C to 300°C and the system was left at this temperature for 20 minutes.

Finally, the temperature was raised from 300°C to 400°C and the system was left at this temperature for 2 hours. Herewith, the calcination procedure was completed.

Table 3.8. Temperature raising steps in calcination process.

Segments	**Starting and End Temperatures**	**Duration**	**Segment Gas**
First	Heating from 25°C to 125°C	20 min	25 ml/min Helium
Second	Heating from 125°C to 300°C	20 min	25 ml/min Helium
Third	Heating from 300°C to 400°C	2 h	25 ml/min Helium

The same impregnation procedure was repeated with cobalt precursor on the Re/AC sample. Then, the same calcination procedure was applied to the sample. For the last metal (potassium) loading, the same impregnation procedure was applied on the CoRe/AC sample. However, the calcination procedure was not applied for this time. The last calcination was done before the catalyst performance testing in the experiment system. This will explain in detail in the catalyst pretreatment section of the following part.

In order to prepare the catalysts by co-impregnation, the impregnation system was used again. The same impregnation technique was applied but this time only one solution which contains all precursors of three metals was prepared and impregnated to the catalyst support (AC) surface. As in the last metal loading in the sequential impregnation, the calcination procedure was not applied. The catalyst was calcined before the reaction in the experiment system.

3.4. Performance Screening

After preparation of the model SWGS catalysts, performance tests of these catalysts were done under ideal conditions, in order words by mimicking sour conditions without sulfur content. The experiments were carried out with two different steam to carbon ratios: 0.3 and 0.8 and at two different temperatures: 350°C and 400°C. Five different types of catalysts were used during the experiments: KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 prepared by sequential impregnation and KCoRe/AC2, KCoRe/AC3 prepared by co-impregnation.

3.4.1. Catalyst Pretreatment

As it mentioned before, the last calcination for the sequential impregnation and the only calcination for the co-impregnation was not performed during the catalyst preparation. The day before the experiment is carried out, the calcination and the reduction process of the catalyst were done in the experiment system.

The day before the experiment was carried out, 75 mg of the catalyst was weighed. The catalyst bed is created in the middle of the metal steel reactor by using glass wool and the weighted catalyst placed on the catalyst bed. The thermocouple was placed in the middle of the reactor to measure the reaction temperature. Then the reactor was placed inside the furnace of the experiment system.

After making all the connections, the catalyst was calcined at 400°C for 4 hours under the flow of argon at a flow rate of 50 ml/min. Then, the catalyst was reduced at 400°C for 4 hours under the flow of hydrogen at a flow rate of 50 ml/min. After completing both the calcination and reduction process in the system, the furnace was shut down and it was let to cool down overnight to start the experiment the following day.

3.4.2. Performance Tests

Reaction parameters that are used in the experiments in this study are summarized below.

Table 3.9. Reaction Parameters.

Parameter	**Value**
Catalyst Particle Size (mesh)	45-60 (344-255μm)

Table 3.9. Reaction Parameters. (cont.)

Catalyst Amount (mg)	75
Calcination Temperature (°C)	400
Reduction Temperature (°C)	400
Reaction Temperature (°C)	350 and 400
Steam to carbon monoxide	0.3 and 0.8
Reaction Flow Rate (ml/min)	100 mL/min

YÖK

As it mentioned in the previous section, the two days experiment starts with calcination and reduction of the catalyst inside the testing system. Since the catalyst had already been inside the reactor from the previous day, only gas flow rates and reaction conditions (temperature and steam to carbon monoxide ratio) were set up before the experiment.

Gas flow rates that should be set up before the experiments for different steam to carbon monoxide ratios are listed below.

Table 3.10. Gas flow rates for different steam to CO ratios.

Gas	**Flow Rate (Steam/CO=0.3)**	**Flow Rate (Steam/CO=0.8)**	**Flow Rate (Steam/CO=3.0)**
CO	15	15	15
CO_2	2.5	2.5	2.5
H_2	7.5	7.5	7.5

Table 3.10. Gas flow rates for different steam to CO ratios. (cont.)

Ar	70.5	65	30
Steam	4.5	12	45

The reaction gasses and the liquid water were sent to the system. The steam and gasses were mixed at the mixing area for 1.5 hours before being sent to the reactor. After that, the reaction occurred inside the reactor and the data were taken from Gas Chromatograph (GC) for each half an hour for 6 hours. Then the system was closed and let to cool down.

The performance tests were done for five types of the catalysts at two different temperatures and at two different steam to carbon monoxide ratios (the ratio 3.0, was only used for the determination of the optimum temperature). All the experiments that are used in this study are summarized below.

Table 3.11. The experiments which their results were used in this study.

Exp. Number	**Catalysts**	**Support**	**Steam/CO ratio**	**Reaction Temperature (^{0}C)**	**Impregnation Method**
18	KCoRe/AC	AC3	3.0	300	Sequential
5	KCoRe/AC	AC3	3.0	350	Sequential
3	KCoRe/AC	AC3	3.0	400	Sequential
2	KCoRe/AC	AC3	3.0	450	Sequential
55	KCoRe/AC	AC0	0.3	350	Sequential
61	KCoRe/AC	AC0	0.3	400	Sequential

Table 3.11. The experiments which their results were used in this study. (cont.)

54	KCoRe/AC	AC0	0.8	350	Sequential
60	KCoRe/AC	AC0	0.8	400	Sequential
53	KCoRe/AC	AC2	0.3	350	Sequential
59	KCoRe/AC	AC2	0.3	400	Sequential
52	KCoRe/AC	AC2	0.8	350	Sequential
58	KCoRe/AC	AC2	0.8	400	Sequential
45	KCoRe/AC	AC2	0.3	350	Co-Impregnation
43	KCoRe/AC	AC2	0.3	400	Co-Impregnation
46	KCoRe/AC	AC2	0.8	350	Co-Impregnation
47	KCoRe/AC	AC2	0.8	400	Co-Impregnation
51	KCoRe/AC	AC3	0.3	350	Sequential
57	KCoRe/AC	AC3	0.3	400	Sequential
49	KCoRe/AC	AC3	0.8	350	Sequential
56	KCoRe/AC	AC3	0.8	400	Sequential
32	KCoRe/AC	AC3	0.3	350	Co-Impregnation
38	KCoRe/AC	AC3	0.3	400	Co-Impregnation

Table 3.11. The experiments which their results were used in this study. (cont.)

37	KCoRe/AC	AC3	0.8	350	Co-Impregnation
40	KCoRe/AC	AC3	0.8	400	Co-Impregnation

4. RESULTS AND DISCUSSION

WGS reaction plays a significant role in the SNG production plant. For classical WGS reactions, there are two types of catalysts which are used industrially, high temperature shift (HTS) and low temperature shift (LTS) catalysts. For WGS reaction in sour conditions, two types of sulfur tolerant WGS catalysts are also available, and they are well-adopted into the industrial applications. These are $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$. However, as it mentioned in the literature survey part, when the syngas comes from the coal gasification, it might have low steam to carbon monoxide ratio and studies on developing a suitable catalyst for this condition is scarce.

Therefore, the main goal of this study was basically to prepare a model sour WGS catalyst and investigate the performance of this catalyst under ideal reaction conditions. In this context, a series of trimetallic (rhenium, cobalt, and potassium) catalysts were prepared over the AC supports which were treated by using different pretreatment methods such as air (O_2) and HNO_3 treatment. Then, these catalysts were tested under ideal reaction conditions which is syngas composition without sulfur content.

Presence of heterogeneous catalysts make the process competitive. In the catalytic reaction, the most important factor in order to decide the catalyst performance is catalyst activity. However, this is not the only criteria since it cannot make us sure that we obtain fully the desired product by looking at the activity of the catalyst. Therefore, the selectivity becomes a very important parameter on the catalyst performance either. Moreover, the catalysts should be stable during the reaction period. This term is called stability. Hence, activity, selectivity, and stability are the most important criteria on the performance of the catalysts.

In this study, it is aimed to synthesize a model, granular SWGS catalyst which is able to show high performance in terms of activity, stability and selectivity under the ideal flow having H_2/CO ratios mimicking sulfur-free composition of a potential (entrained type) coal gasifier and low steam/CO ratio.

Actually, it is better to point out before discussing the results that the catalysts prepared in this study were model sour water gas shift catalysts. According to the literature, $KCoRe/Al_2O_3$ catalyst was found potential future SWGS catalyst because of its high performance for the dry powder syngas composition which has very low steam/CO ratio. Therefore, it was chosen as a reference catalyst. However, it should be noted that the reference catalyst was tested under realistic conditions which have sulfur content and it showed high activity under the temperature range which is chosen in this study. On the other hand, although the catalysts prepared in this study for the SWGS unit, they are tested under sulfur-free conditions.

4.1. Effects of the Catalyst Preparation and Reaction Conditions

Since catalyst properties and the reaction conditions are the most important parameters in order to determine the catalyst performance; metal impregnation method, support treatment method, reaction temperature and steam/CO ratio were the main parameters considered during this study.

Support-metal interaction is one of the most important parameters on the catalyst performance. By impregnating metal precursors into the support surface, the active sites where the desired reaction takes place are created. Sequential and co-impregnation methods were used during catalyst preparation in this study.

Support treatment methods also affect the catalyst performance by changing the distribution and types of the surface groups on the support. There are two types of catalyst treatment methods used in this study: air treatment and nitric acid treatment.

Reaction conditions such as pressure, temperature, flow rates of the reactant(s) also affect the performance of the catalysts. Depending on the desired process, one or more parameters could be used to test the performance of the catalyst. WGS is an exothermic reaction and temperature is a significant factor for this reaction.

Therefore, first experiments on this study were performed at high steam to carbon monoxide ratio in order to test the catalyst and to have an idea about the optimum reaction temperature for this catalyst. The experiments were done at four different temperatures.

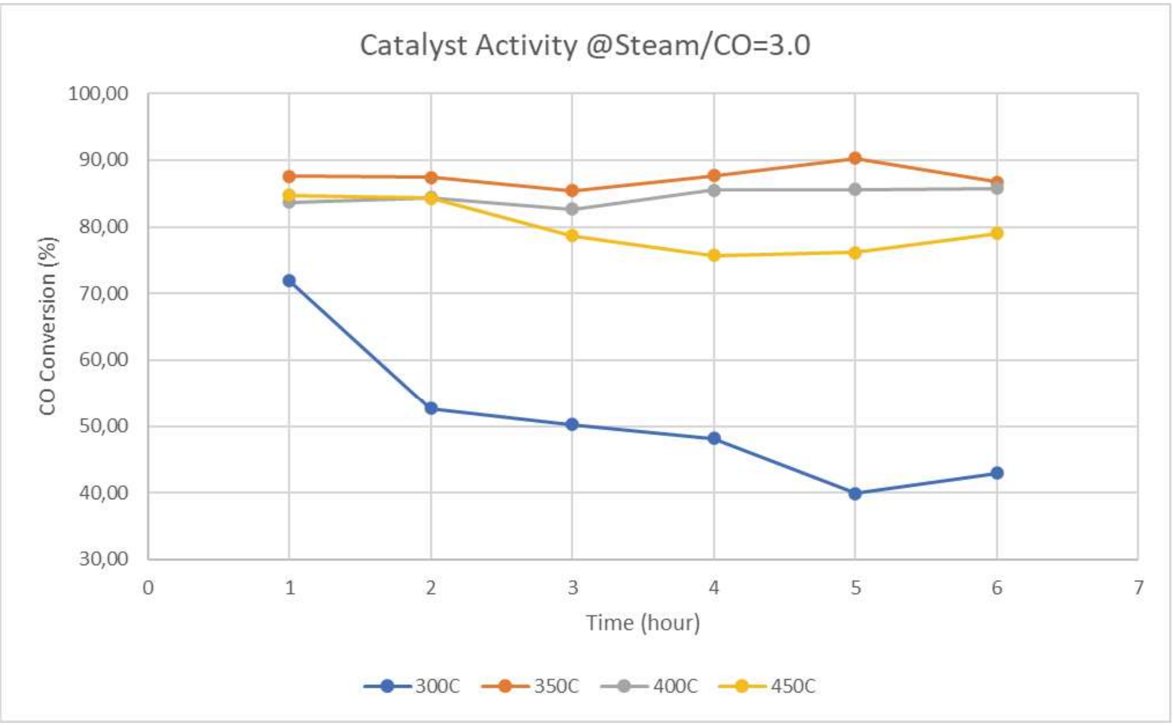


Figure 4.1. The effect of reaction temperature on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at steam/CO=3 and calcined at 400°C)

As it can be seen from Figure 4.1, when the steam/CO ratio is equal to three, the catalyst showed high performance which means that the catalyst prepared in this study can work as much as classical WGS catalysts. The optimum temperature was found as 350°C in these conditions. When the temperature was increased from 350°C to 400°C, the performance of the catalyst started to decrease. However, there is no drastic decrease between the performance at 350°C and that of 400°C. On the other hand, if the reaction temperature rises from 400°C to 450°C, the activity decreases too much. Therefore, two temperatures (350°C and 400°C) were chosen in this study in order to compare the temperature effect on the catalysts.

To the best of our knowledge, there are plenty of SWGS catalysts which work when the syngas comes to the WGS unit at high steam to carbon monoxide ratio. To be more specific, commercial sour WGS catalysts such as CoMo/ Al_2O_3 and NiMo/ Al_2O_3 work when the steam/CO ratio is higher than 2 or 3 also known as slurry conditions. Because of the kinetics of the WGS reaction, the addition of excess steam makes the reaction occur in the forward direction. Therefore, high conversion of CO could be obtained.

However, literature survey showed that when syngas comes from dry powder entrained bed gasification its steam/CO ratio is generally 0.3 and it is desired to develop industrial sour WGS catalyst which is able to work when the steam/CO is below 0.8. Therefore, it is required to develop a brand-new catalyst which is suitable for dry powder conditions, low steam/CO ratio. In this study, two steam to carbon monoxide ratios were chosen, 0.3 and 0.8.

To sum up, the effects of the catalyst preparation method, support treatment method, temperature and steam to carbon monoxide ratio on the catalyst performance were analyzed and the results will be discussed in the following parts.

4.2. Effects of the Reaction Conditions

4.2.1. Effects of the Reaction Temperature

A set of experiments were done to observe the effect of the temperature that the reaction occurred on the catalyst activity. In the first set, the steam to carbon monoxide ratio was kept as 0.3 and the experiments were conducted for all five types of catalysts at 350°C and at 400°C. In the second set, the steam to carbon monoxide ratio was kept as 0.8 and the experiments were conducted for all five types of catalysts at 350°C and at 400°C. The results will be shown in the following figures.

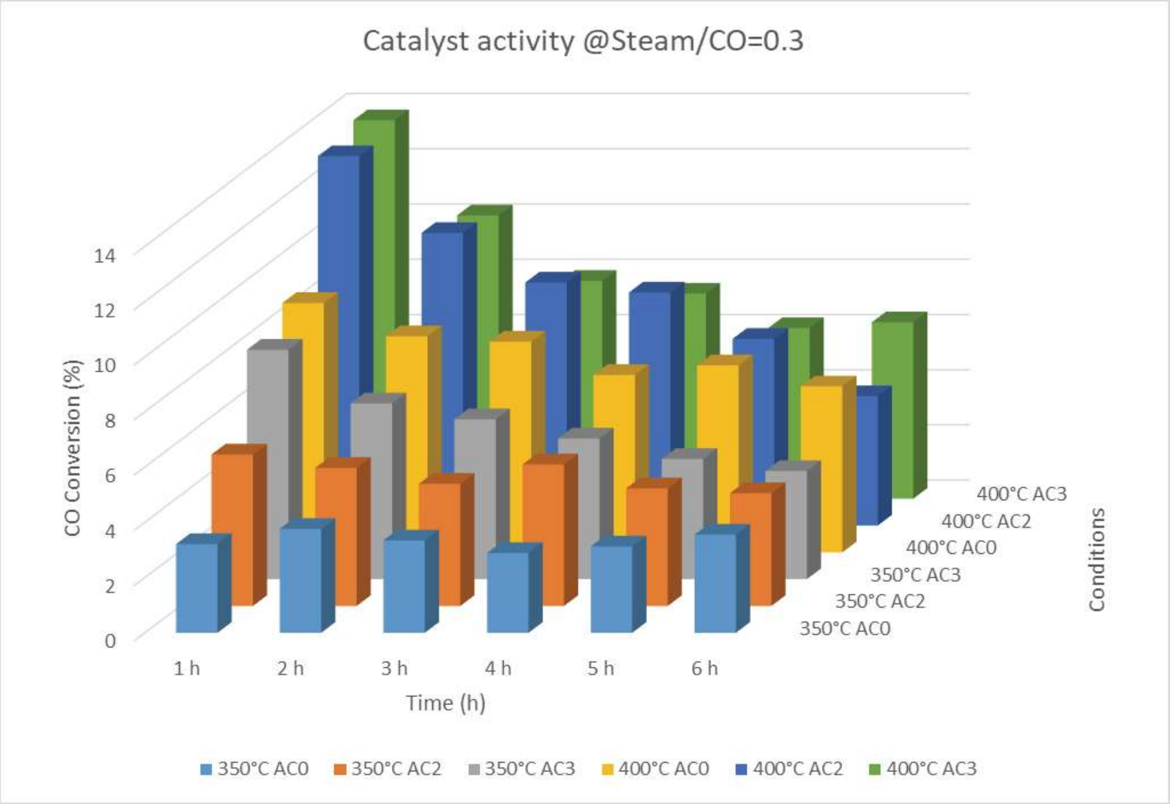


Figure 4.2. The effect of reaction temperature on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at steam/CO=0.3 and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

The water gas shift equation is shown below.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{4.1}$$

WGS (see Eq. 4.1) is an exothermic reaction, having ΔH value of -41.1 kJ/mol. As it can be seen from Figure 4.1, when the steam/CO ratio is very high, the optimum temperature was found as 350°C and if the temperature raised to 400°C, the catalytic activity started to decrease. However, according to the results (see Figure 4.2), it seems that all the catalysts showed better performance at 400°C when the steam/CO ratio is quite low, in this case, 0.3.

This situation may be explained with rather low conversion values, far away from thermodynamic equilibrium, obtained. However, in the presence of excess amounts of steam, the WGS reaction may take place properly in the forward direction.

The other point here is that at 400°C, the catalytic activities for both AC2 and AC3 supported catalysts were very close to each other. Whereas, at 350°C, AC3 supported catalysts have a slightly higher activity. This may happen because the AC3 supported catalyst reached its maximum performance at 400°C in these conditions and it may not show better activity than that of AC2 supported one anymore.

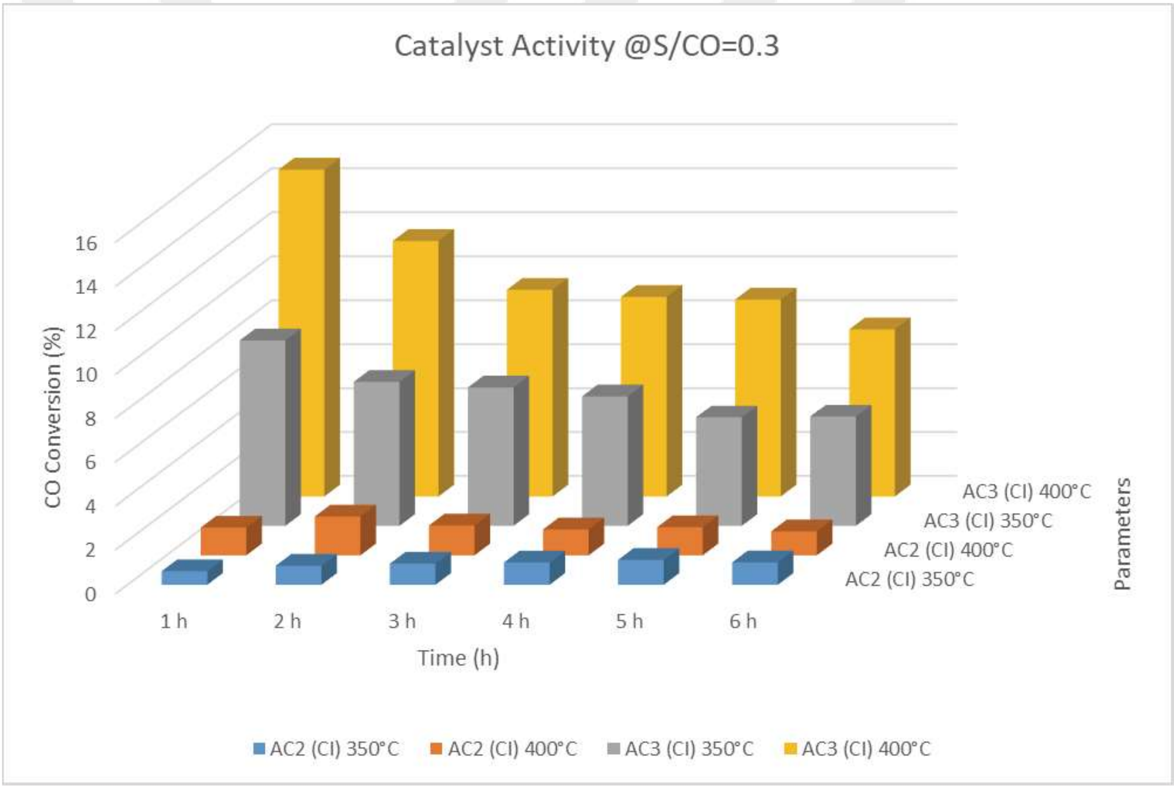


Figure 4.3. The effect of reaction temperature on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at steam/CO=0.3 and calcined at 400°C. The catalysts were prepared by co-impregnation method)

It can be concluded that the catalysts prepared by co-impregnation also showed better activity at 400°C rather than that of 350°C when the steam/CO ratio is equal to 0.3.

On the other hand, there is one big difference between the performance of the catalysts prepared by sequential impregnation (see Figure 4.2) and the performance of the catalysts prepared by co-impregnation (see Figure 4.3). As it can be seen from Figure 4.2, the catalytic activity for both AC2 and AC3 supported catalysts seems almost the same at 400°C. However, this is not valid when AC2 and AC3 catalysts were prepared by co-impregnation method.

There are two possible explanations here. One of them could be the surface chemistry of the catalysts. Since surface chemistry of the support material affects the support-precursor interaction and the metal dispersion, AC3 supported catalyst may have more suitable chemistry for co-impregnation method compared with AC2 supported one. The effect of treatment methods on the catalyst support surface will be discussed at the following parts. However, to have an idea, nitric acid treatment decreases the micropore structures in the AC3 support and makes the support surface more available for the precursor solution. The second explanation may be that the AC3 supported catalyst prepared by sequential impregnation (see Figure 4.2) would reach its maximum performance at 400°C as already mentioned.

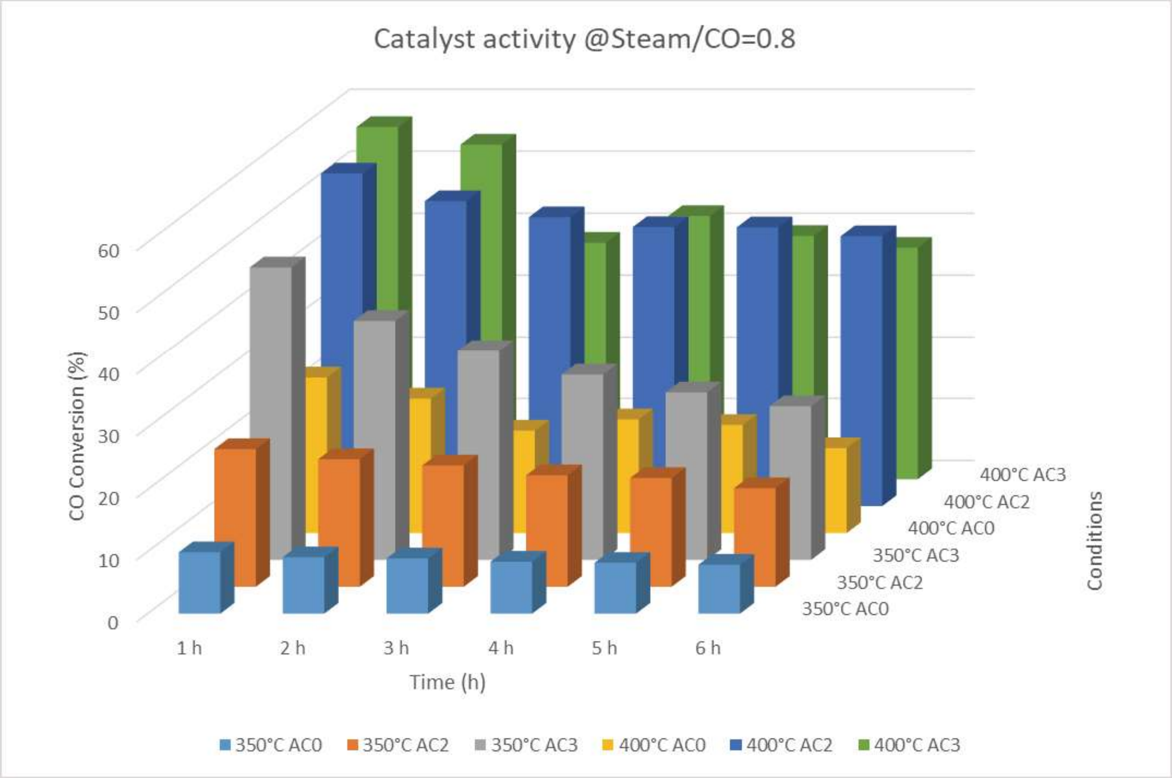


Figure 4.4. The effect of reaction temperature on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at steam/CO=0.8 and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

Steam/CO ratio effects on the catalytic activity will be investigated in the following part. However, the first noticeable point here, as expected, raising the steam/CO ratio from 0.3 (see Figure 4.2) to 0.8 (see Figure 4.4) boosts the activity for all types of the catalysts. Because at high steam/CO ratio, high steam content may allow the WGS reaction to take place properly.

On the other hand, the catalytic activities of the catalysts follow the same trend as in the previous set of experiments at steam/CO ratio is equal to 0.3. The catalysts still showed better activity at 400°C.

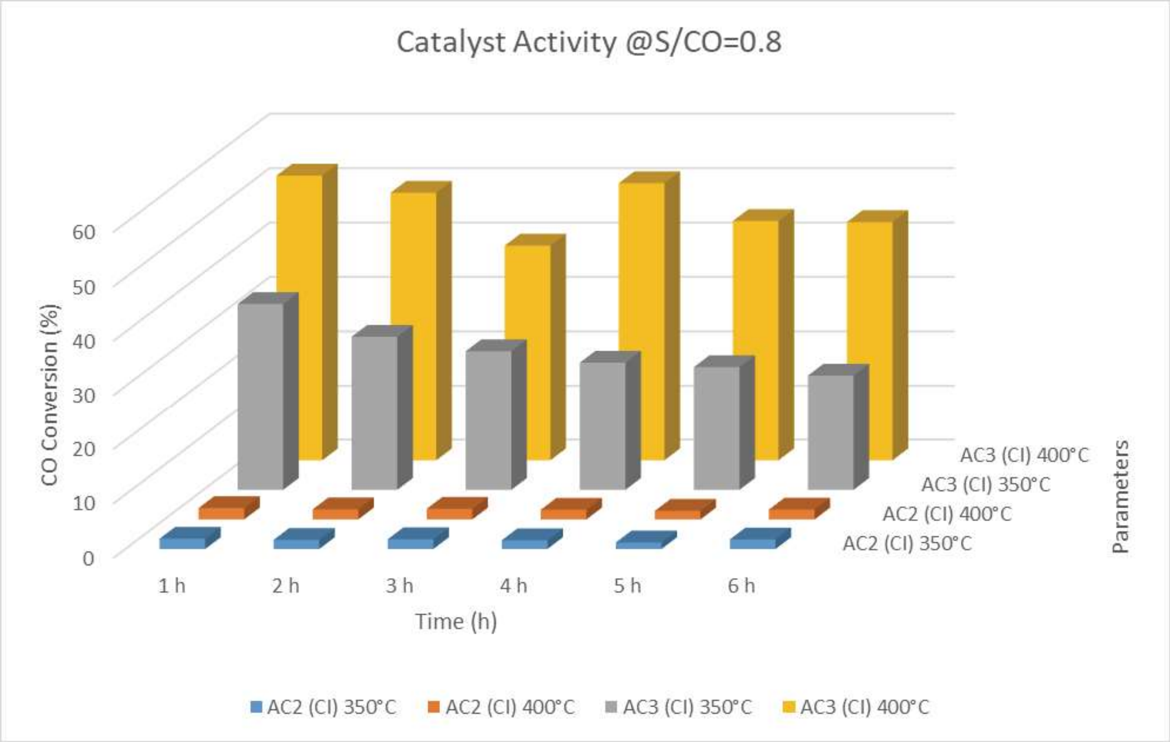


Figure 4.5. The effect of reaction temperature on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at steam/CO=0.8 and calcined at 400°C. The catalysts were prepared by co-impregnation method)

These results (see Figure 4.5) also in accordance with the previous experiments for the catalysts which are prepared by the co-impregnation method but tested at steam/CO ratio is equal to 0.3 (see Figure 4.3). The AC3 supported catalyst showed better activity again and its activity almost 5 times higher than that of AC3 supported catalyst prepared by sequential impregnation at 350°C.

When comparing the results in Figure 4.5 with the results in Figure 4.3, it can be seen that the steam/CO ratio does not have a significant effect on the catalytic activity of the AC2 supported catalyst. Although it will be discussed in the pre-treatment effect on the catalyst support, still it is better to point it here that AC2 support may not be suitable for the co-impregnation method since it contains more micropore structures and it has a more hydrophobic surface compared with AC3 support. This may explain the lower activity of the AC2 supported catalyst when they are prepared by co-impregnation method.

4.2.2. Effects of the Steam to CO ratio

A set of experiments were done to observe the effect of the steam/CO ratio on the catalyst activity. In the first set, the reaction temperature was kept at 350°C and the experiments were conducted for all five types of catalysts for steam/CO ratio 0.3 and 0.8. In the second set, the reaction temperature was kept at 400°C and the experiments were conducted for all five types of catalysts for steam/CO ratio 0.3 and 0.8. The results will be shown in the following figures.

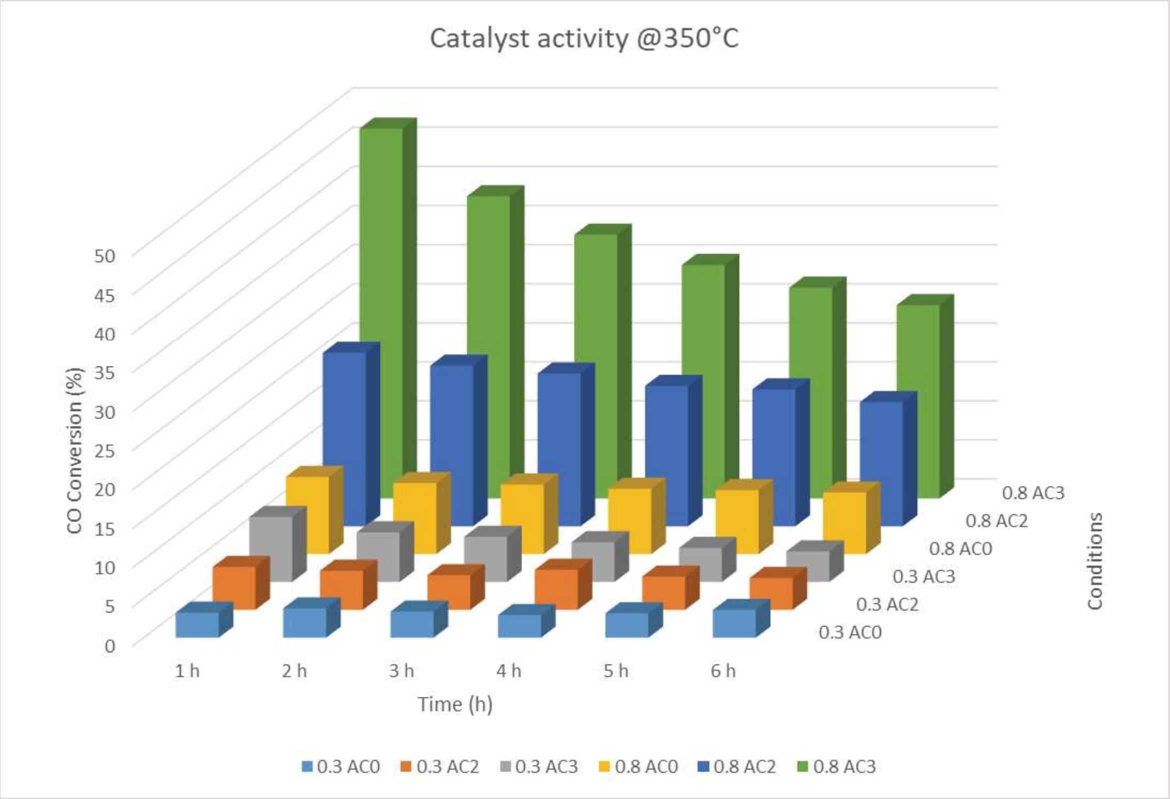


Figure 4.6. The effect of steam/CO ratio on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 350°C and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

First of all, it was already expected that increasing steam content helps to increase the catalytic activity by raising the conversion of carbon monoxide from the kinetic point of view of the WGS reaction. It is known from literature that most of the SWGS catalysts work under high steam to carbon monoxide ratio, especially above 2 or 3. Similarly, as it can be seen from Figure 4.1, the catalysts prepared in this study showed very high activity when the steam/CO ratio is equal to 3. Because high steam content helps to reduce the possibility of the occurrence of the side reactions where CO is mostly the reactant. At low steam/CO ratio, the effect of side reactions is not as much as when WGS reaction occur properly. Therefore, from Figure 4.6 it seems that increasing the steam to carbon monoxide ratio from 0.3 to 0.8 is beneficial for the activity of all types of catalysts.

The main goal of this study was to develop a model SWGS catalyst which can work at low steam/CO ratio. According to the results, the catalysts prepared in this study showed low activity especially at very low steam/CO ratio which is 0.3. However, it should be remembered that the catalysts were tested under ideal, sulfur-free conditions although they are SWGS catalysts. It is not known how they will react under the realistic conditions.

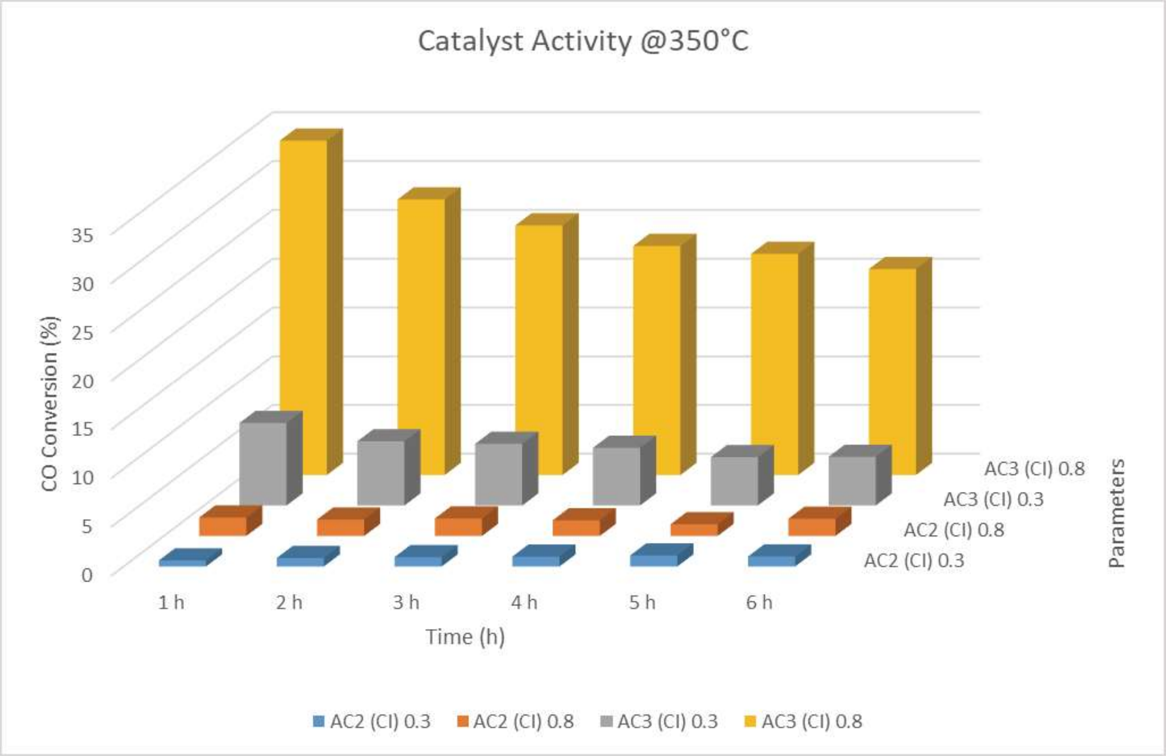


Figure 4.7. The effect of steam/CO ratio on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 350°C and calcined at 400°C. The catalysts were prepared by co-impregnation method)

Similarly, increasing the steam/CO ratio seems helpful to increase the catalytic activity of the catalysts prepared by co-impregnation method even if this effect is not observed clearly for the AC2 supported catalyst.

As in the previous set of experiments the amount of increment in the activity is not the same for all types of the catalysts. For example, steam/CO ratio seems much more effective on the AC3 supported catalyst rather than that of AC0 and AC2 in Figure 4.6. Likely, as it can be seen from Figure 4.7, for AC3 supported catalysts, the catalytic activity drastically increases by increasing the steam to carbon monoxide ratio compared with the AC2 supported one.

This situation may be explained with the better surface chemistry of the AC3 supported catalysts rather than that of AC2. It is known that AC3 support has much more acidic surface groups than the others since it is prepared by the nitric acid treatment. Acidic groups are responsible for the more hydrophilic support surface area. It means that the support becomes more available for the metal precursor solutions.

The surface chemistry of the AC3 may be allowed to create the active sites on the support surface and let metals show their effects more on the catalyst property. In this context, rhenium impregnation enhances the activity of the catalyst by breaking the bonds in the reactant molecules and forming new bonds to obtain the product molecules. Cobalt has a synergetic effect as in the commercial CoMo/Al_2O_3 SWGS catalyst. Potassium increases the stability for most of the well-known catalysts.

The better dispersion of the metals on the more acidic surface of the AC3 support may be the reason that the AC3 supported catalyst showed relatively higher activity than that of other supported catalysts for the WGS reaction.

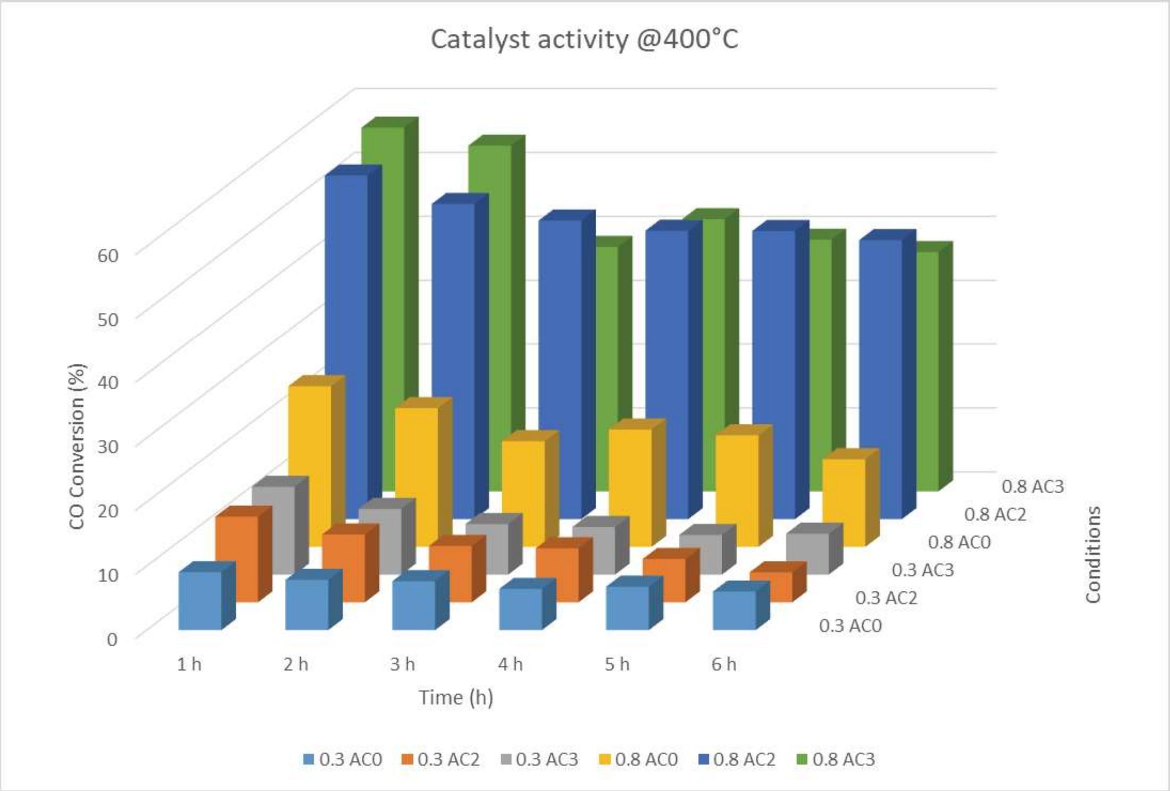


Figure 4.8. The effect of steam/CO ratio on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 400°C and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

When the temperature was raised to 400°C from 350°C, the activities of all types of catalysts increased slightly. At this temperature the activities of both AC2 and AC3 supported catalysts are very close to each other. There is no significant difference as in the case for 350°C.

This situation may be explained by the fact that AC3 supported catalysts reached their maximum conversion degree at this temperature. Therefore, it did not show better activity than that of AC2 supported catalysts.

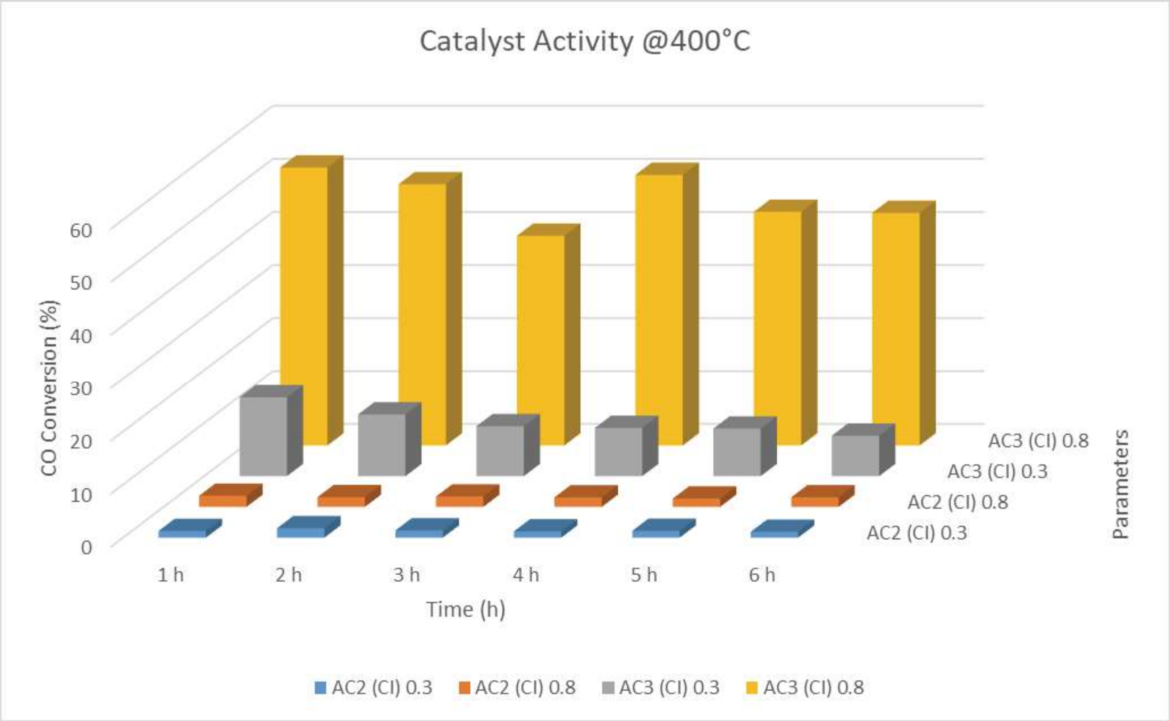


Figure 4.9. The effect of steam/CO ratio on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 400°C and calcined at 400°C. The catalysts were prepared by co-impregnation method)

As in the previous set of experiments for the catalysts prepared by co-impregnation method and tested at 350°C, AC3 supported catalysts showed better activity especially at high steam/CO ratio at 400°C. Increasing steam/CO ratio from 0.3 to 0.8 boosts the catalytic activity for the catalyst prepared by co-impregnation method. Moreover, the activity of the catalysts almost doubled when compared to the result in Figure 4.7. It can be said that again AC3 supported catalyst may be more suitable for the co-impregnation method rather than that of AC2 supported one.

4.3. Effects of the Catalyst Preparation

4.3.1. Effects of Impregnation Method

For the sake of comparison of the effect of the impregnation method, a set of experiments were done at two different reaction temperatures and two different steam/CO ratios for the AC2 supported catalysts prepared by sequential impregnation method. Then, the same experimental set was repeated for the AC2 supported catalysts prepared by co-impregnation method.

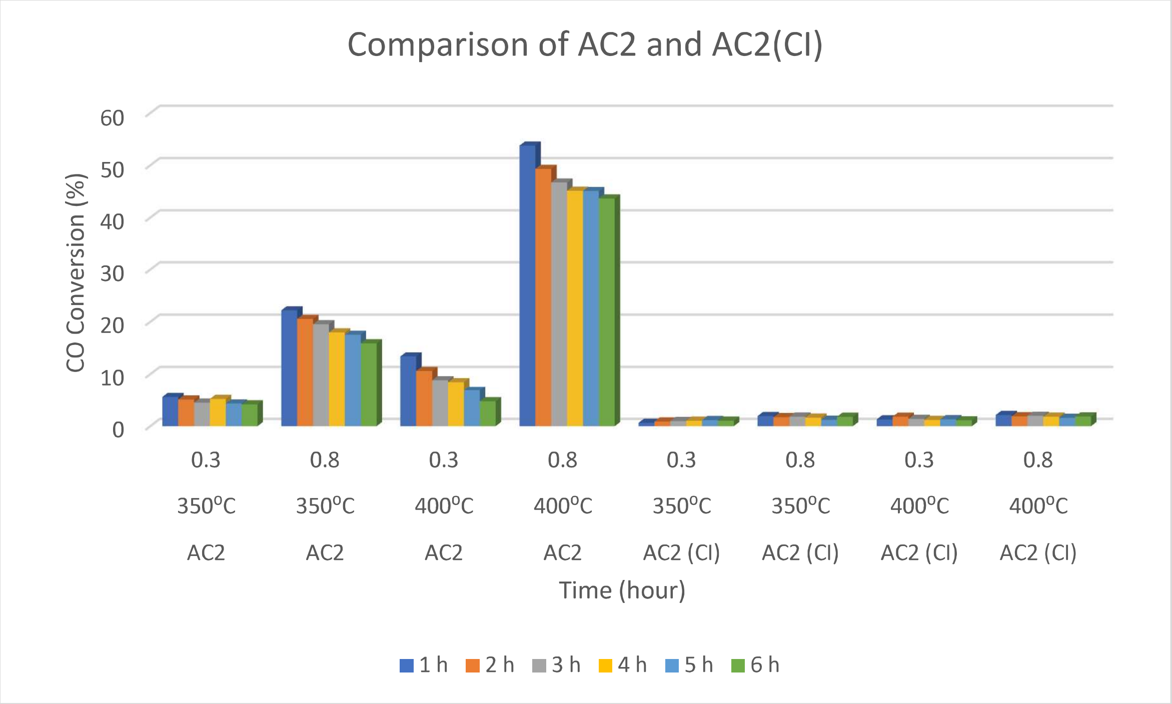


Figure 4.10. The effect of impregnation method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC2 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, and calcined at 400°C. The catalysts were prepared by both sequential and co-impregnation method)

The first noticeable spot from the Figure 4.10, when the KCoRe/AC2 catalyst is prepared by the co-impregnation method, the catalytic activity was very low for all conditions. Therefore, the co-impregnation method may not be suitable for the AC2 supported catalyst.

AC2 support is prepared by air (O_2) treatment of the AC0 (untreated) sample. Air oxidation increases both acidic and less acidic oxygen bearing surface groups on the support. While the acidic groups are responsible for the hydrophilicity of the surface of the support, the less acidic groups are responsible for the interaction between the metals loaded and the support surface.

The acidic groups on the surface of the AC2 support are not much like in the nitric acid treated AC support (AC3). Therefore, the surface of the AC2 seems less hydrophilic compared with AC3 support. Because of that reason, the AC2 support surface may not interact well with the precursor solution when all the metals are loaded at the same time by the co-impregnation method. This may explain the low activity of the AC2 supported catalysts prepared by co-impregnation method.

Moreover, in the co-impregnation method, because metals are loaded at the same time into the catalyst surface, they may block each other's dispersion. The metal dispersion on the AC2 may be much better by sequential impregnation. Therefore, low activity of the KCoRe over AC2 support prepared by co-impregnation may be explained by the less support-metal interactions.

In the sequential impregnation method, the metals were loaded in the following orders into the support surface: rhenium, cobalt and potassium. Potassium is an alkali metal, and it may interact with the acidic surface groups of the support. Potassium is actually used to stabilize the surface because of its alkali properties. Therefore, it is better to impregnate potassium precursor (K_2CO_3) into the support surface lastly in the sequential impregnation method.

On the other hand, when the catalysts were prepared by co-impregnation method, potassium may interact with the acidic groups on the surface first before the other metals showed their effect on the support. This could be the reason that the catalysts performed low activity when prepared by co-impregnation method.

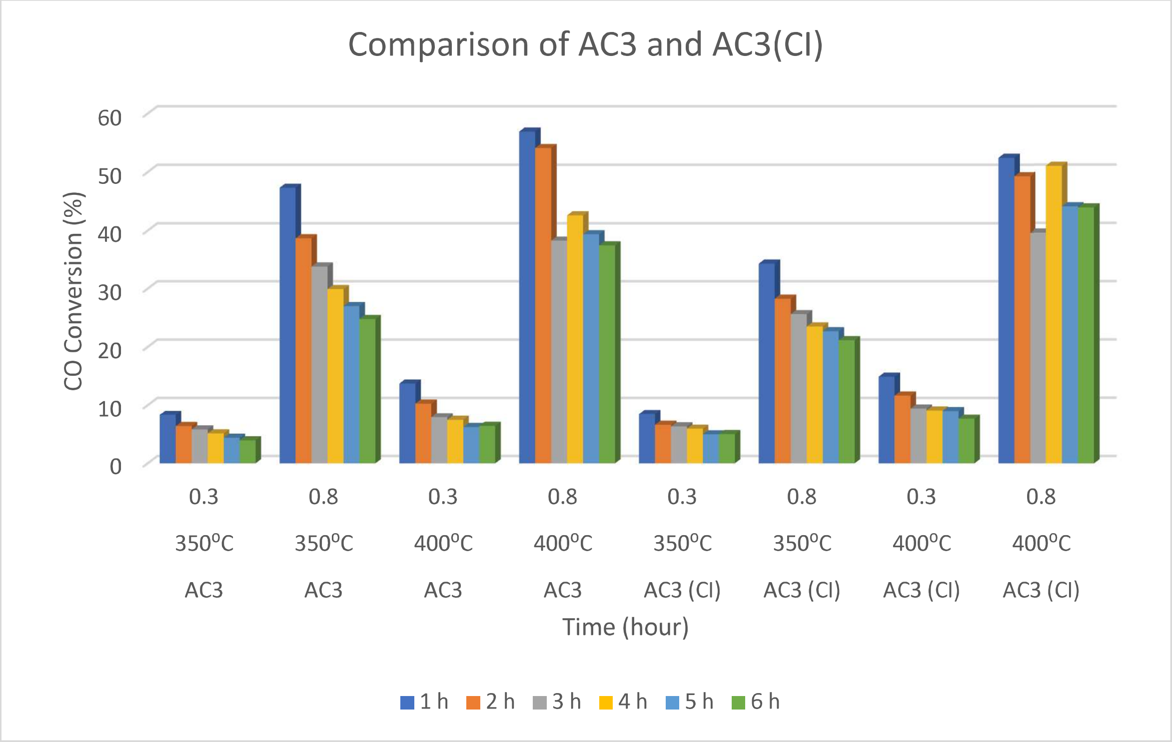


Figure 4.11. The effect of impregnation method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, and calcined at 400°C. The catalysts were prepared by both sequential and co-impregnation method)

It can be concluded from Figure 4.11, the catalytic activity for the KCoRe/AC3 catalyst prepared by sequential impregnation is slightly differ than that of prepared by co-impregnation method. The impregnation method does not have the effect on the AC3 supported catalyst as much as on the AC2 supported catalyst.

This situation may be attributed to the surface chemistry of the AC3 support. Nitric acid treatment increases the acidic oxygen bearing surface groups and because of its corrosive effect it makes the micropores collapse in order to create meso or macrostructures. Therefore, AC3 support has a highly acidic surface, and it contains more macropores and mesopores compared with AC2 support.

By nitric acid treatment, the more acidic oxygen bearing surface groups are formed and these groups make the support surface more available for the precursor solutions.

Therefore, even the precursor solution which contains all of the metals at the same time may interact with the support easily. Therefore, there is no big difference in the catalytic activity between AC3 supported catalysts prepared by both sequential and co-impregnation methods.

Moreover, in the co-impregnation method, even if potassium interacts with the acidic surface groups, there may still be enough acidic groups for other metals to interact to create the active sites.

Micropores may cause the sintering of the metal atoms and blockage of the micropores could occur easily. Therefore, mesopores are a better place for the reaction. AC3 has much more mesopores compared with AC2 support. Micropores may be blocked by impregnating all the metals at the same time into the AC2 support by co-impregnation. On the other hand, this blockage may be prevented in the AC3 support which has less micropores.

4.3.2. Effects of the Pre-treatment Method of the AC Support

Surface chemistry of the support material has many effects on the catalytic activity. One of the most important properties of the AC is that its surface can be tailored by the treatment methods. This makes the AC well-known as a support of the catalysts for many industrial applications.

Treatment of AC support modifies the amount and types of the oxygen bearing surface groups. These groups determine the redox properties of the support, and they will interact with the metal precursors, hence they affect the catalyst performance.

In this study, two types of treatment methods were used: air (O_2) treatment in a gas phase and nitric acid treatment in a liquid phase in order to observe the effect of the treatment method on the catalyst activity.

For the sake of comparison of the catalysts which are supported by AC material treated by different methods. Firstly, three experiments were picked up among the set of experiments done to see the effect clearly. The reaction temperature was at 350°C and steam/CO ratio was 0.3 for the three different catalysts: KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3.

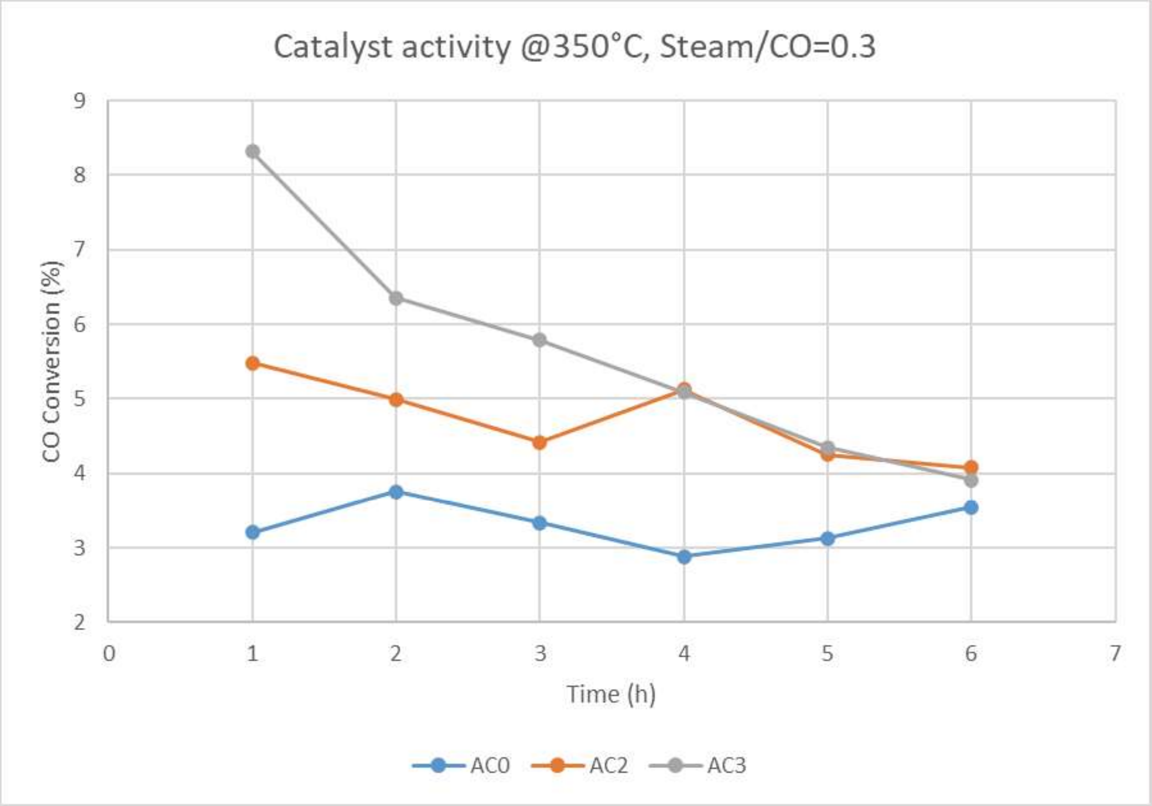


Figure 4.12. The effect of pre-treatment method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 350°C, steam/CO=0.3 and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

In the conditions that are declared above, the catalyst activity for all types of catalysts is low. On the other hand, among those catalysts, AC3 supported one started with the highest conversion value for carbon monoxide. However, it cannot protect its stability during the experiment carried out (6 hours).

Their low activity may be attributed to the low steam/CO ratio. Among them, AC3 supported catalysts showed better activity since it has better surface chemistry than the others. Nitric acid treatment makes the AC3 support more available for the precursor solution. Therefore, metal dispersion is better on the AC3 support. On the other hand, air treatment is also beneficial for the catalyst since it increases both the acidic and less acidic oxygen bearing surface groups. These groups may have some contributions on the catalytic activity and metal dispersion but not as much as on the AC3 support.

The other important point is that the stability of the AC3 supported catalyst dramatically decreased in these conditions during the experiment (6 hours). Since it is known from Figure 4.1 that AC3 supported catalysts showed better activity at very high steam/CO ratio, this low stability may be attributed to both low steam/CO ratio and relatively low reaction temperature.

It can be also concluded that AC2 supported catalysts showed better stability than that of AC3 supported one. Surface properties of the support material may lead to this situation. Potassium is an alkali metal and impregnation of potassium may stabilize the relatively less acidic surface of the AC2 support material more than AC3 support. It may lead to better metal dispersion on the AC2 support, and these metals create an active site for the desired reaction. Hence, it may explain the better stability of AC2 supported catalysts during performance tests performed.

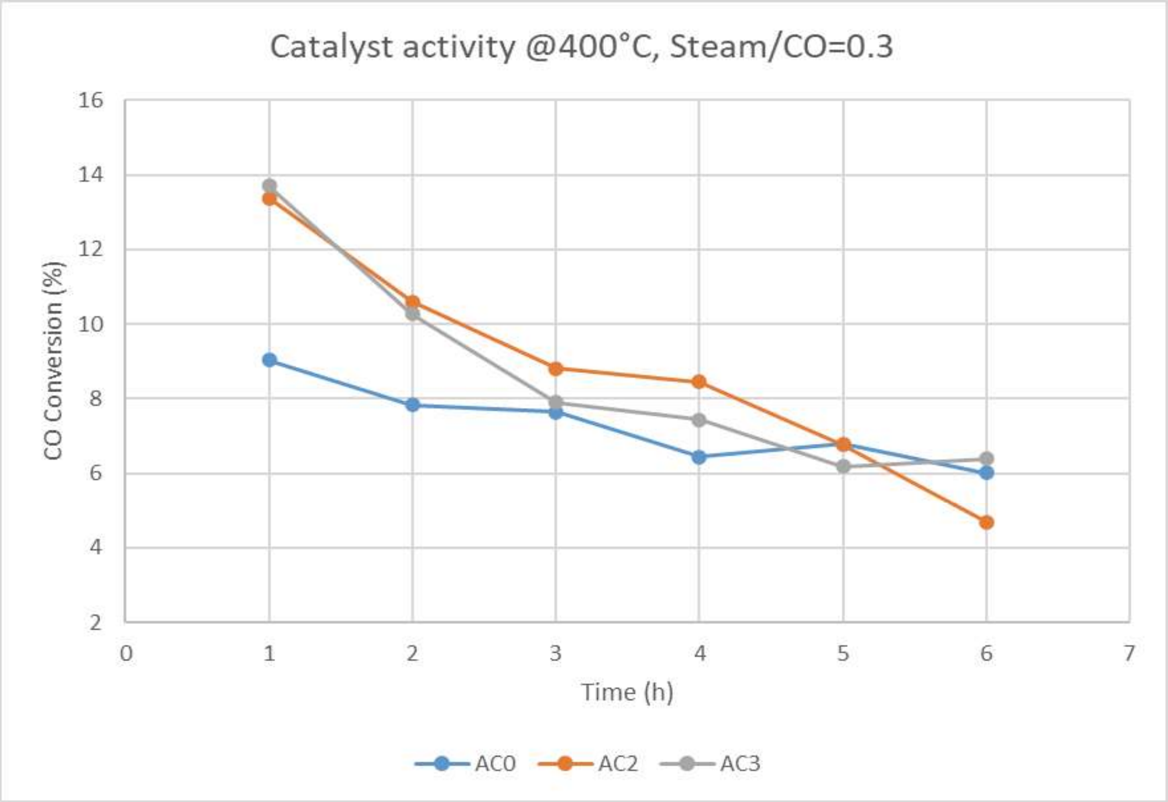


Figure 4.13. The effect of pre-treatment method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 400°C, steam/CO=0.3 and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

Since the steam/CO ratio is still low, the catalytic activities are also low but not as much as at 350°C. On the other hand, the catalytic activity of the AC2 supported catalyst was very close to the AC3 supported one at 400°C. It may have happened because the AC3 supported one reached its maximum performance and it is not better from AC2 supported one after this temperature.

From Figure 4.12, it can be seen that the AC3 supported catalyst has very low stability at 350°C and when steam/CO ratio is equal to 0.3. Whereas corresponding AC2 supported catalysts had relatively better stability. From Figure 4.13, it is observed that the stability of both AC2 and AC3 supported catalysts decreased at 400°C. This may be attributed to the fact that the support surface-metal interactions affect the metal dispersion differently by changing the temperature hence the catalytic activity.

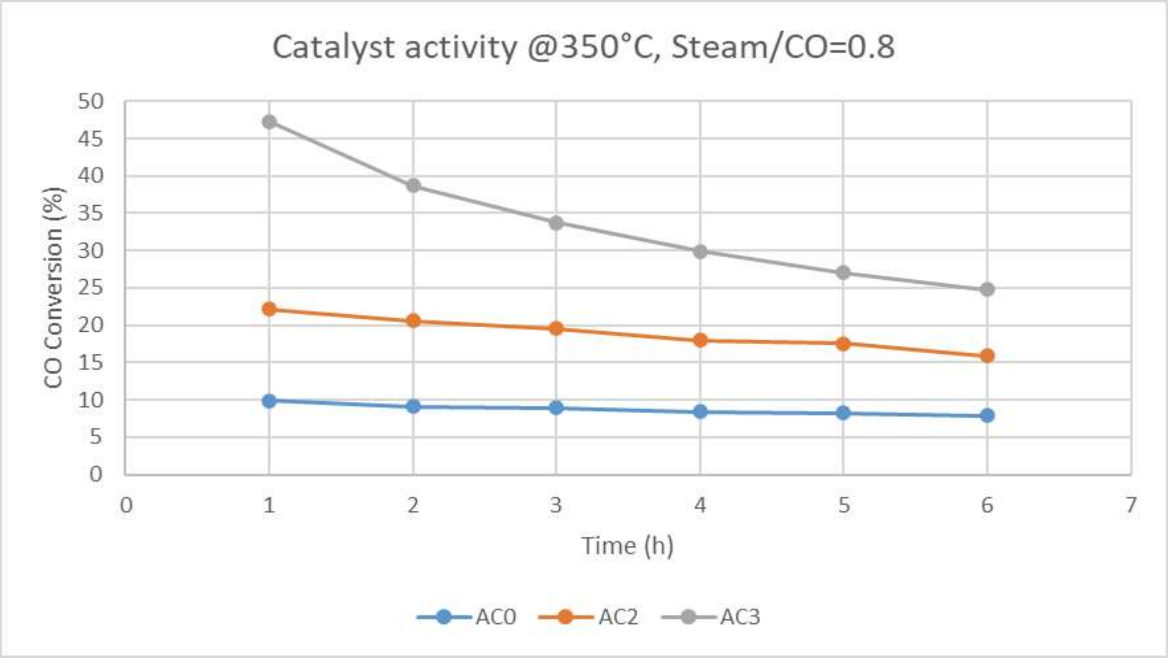


Figure 4.14. The effect of pre-treatment method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 350°C, steam/CO=0.8 and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

Compared with the previous set of experiments at 350°C and the steam/CO ratio is equal to 0.3, it is observed that the catalytic activity increased when increasing the steam/CO ratio as expected. Still, AC3 supported catalysts showed better activity in these conditions.

From Figure 4.14, it can be concluded that the stability of the AC2 supported catalyst is much better than that of a low steam/CO ratio. From Figure 4.1, it was found that at a very high steam/CO ratio our catalysts work with a high catalytic activity and the optimum temperature was found as 350°C. Because of that reason, the stability for AC2 supported catalysts could be increased at 350°C when increasing the steam/CO ratio to 0.8.

However, the stability of AC3 supported catalysts is still low. This may be attributed to the surface chemistry of the catalyst support. Since it is known that AC3 support is more acidic than that of AC2 supported one. AC2 support has a relatively neutral surface. It may have an effect on the stability of the catalysts.

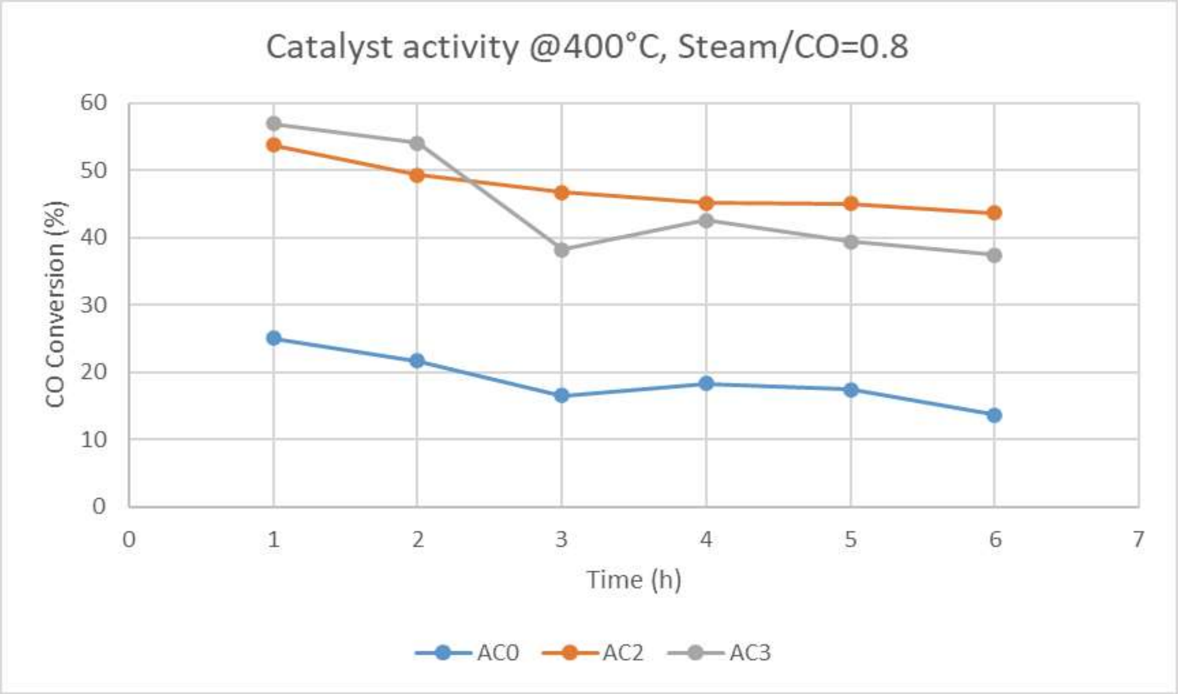


Figure 4.15. The effect of pre-treatment method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 400°C, steam/CO=0.8 and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

From Figure 4.15, it can be seen that the catalytic activity of both AC2 and AC3 supported catalysts was nearly the same level. This may be explained again because AC3 supported catalyst reached its maximum activity and it cannot show better activity than that of AC2 supported one anymore. However, from all these results, the catalyst showed their best activity in these conditions i.e., high temperature and high steam/CO ratio, as expected.

4.3.2.1. Oxygen (Air) Pre-treatment.

In order to look in detail how the pretreatment methods affect the activity of the catalysts, first oxygen (air) pretreatment supported (AC2) catalyst activity was compared with the untreated supported catalyst activity.

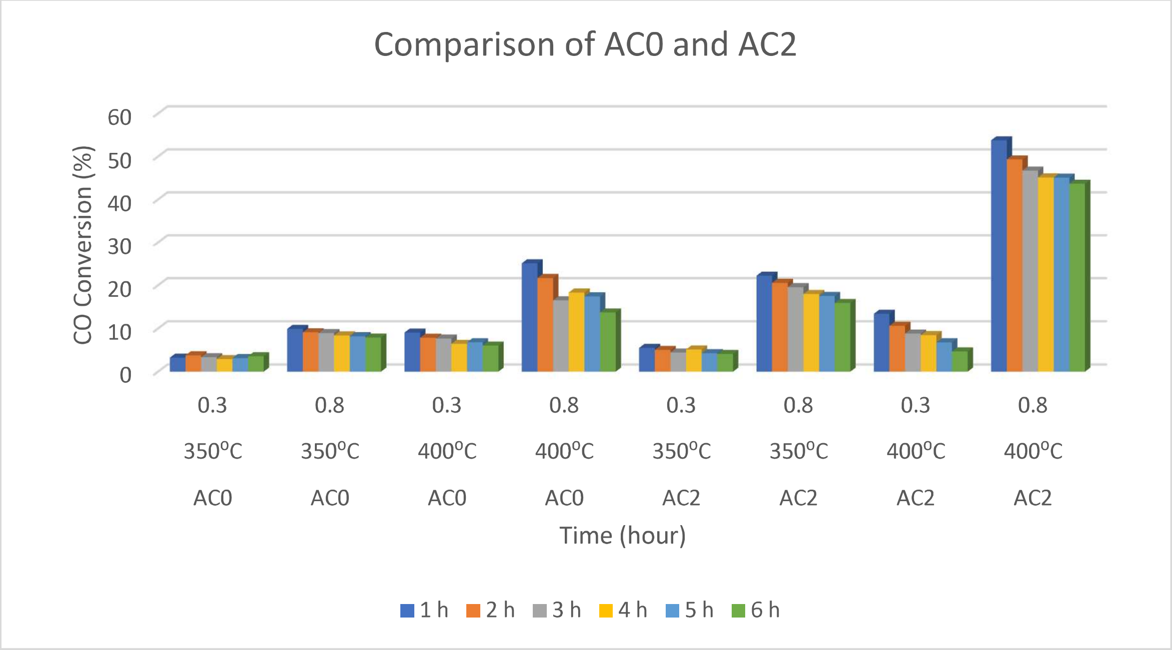


Figure 4.16. The effect of oxygen pre-treatment method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0 and KCoRe/AC2 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, calcined at 400°C. The catalysts were prepared by sequential impregnation method)

AC2 catalysts are prepared by applying air treatment on the non-treated AC0 catalysts. Air (O_2) treatment helps to increase both acidic and less acidic oxygen bearing surface groups on the activated carbon support. These groups are responsible for support-metal interaction and metal dispersion on the catalyst support as it mentioned before. Therefore, it is expected an increment in the activity when the AC support material is treated with air (O_2).

From Figure 4.16, even a small increment for the catalysts activity in all the conditions can be observed. On the other hand, the catalytic activity was affected the most dramatically at high temperature and high steam/CO ratio. It is reasonable since the activity was better under these conditions.

It can be also observed that when the steam/CO ratio is low, the air pretreatment of the support material does not have a dramatic effect on the catalyst activity. On the other hand, the catalyst activity boosted when the steam/CO ratio was relatively high. It may be because the WGS reaction could take place better in these conditions on the catalyst surface by knowing that increasing the steam/CO ratio has a positive effect on the catalytic activity.

4.3.2.2. HNO$_3$ Pre-treatment.

As far as we know, the best way of creating acidic surface functional groups on the AC support is nitric acid treatment. In order to observe the effect of the liquid phase, nitric acid treatment of the AC support on the catalytic activity, the same experiments were repeated for the catalysts supported untreated AC0 and for the catalysts supported nitric acid treated AC3.

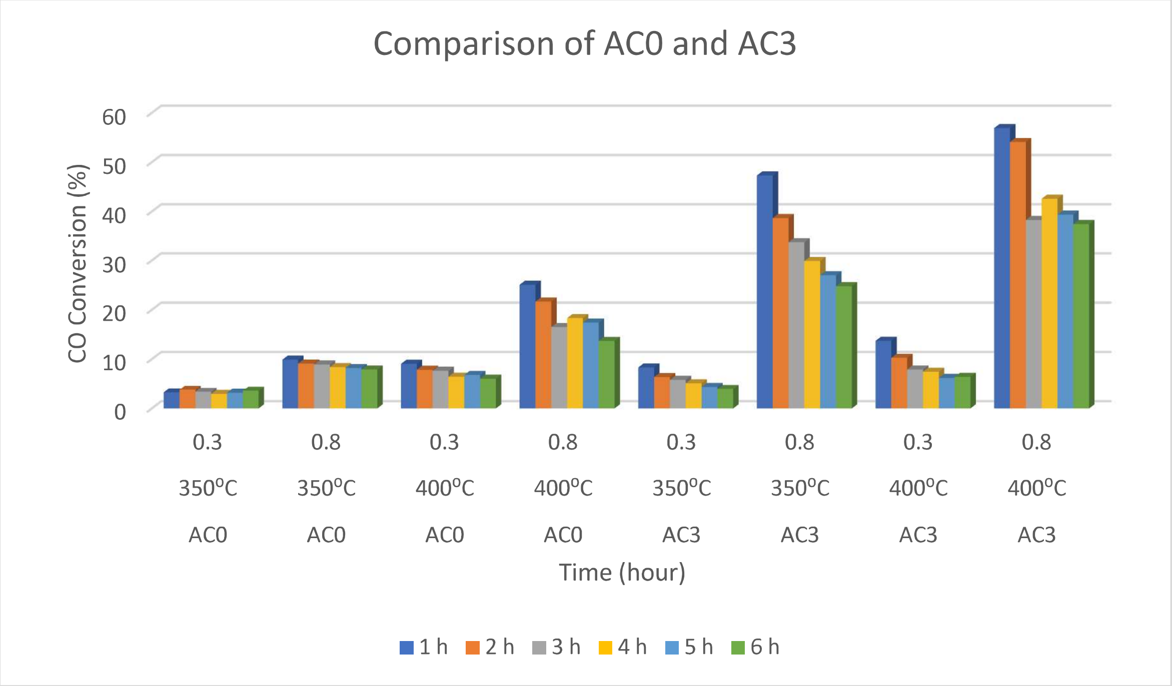


Figure 4.17. The effect of nitric acid pre-treatment method on the catalyst activity. (All experiments were conducted for 6 hours on KCoRe/AC0 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, calcined at 400°C. The catalysts were prepared by sequential impregnation method)

The noticeable spot at first sight in the Figure 4.17, CO conversion hence the activity for the nitric acid treated AC3 supported catalysts were higher for all the experimental conditions. Therefore, nitric acid treatment may be beneficial for the sake of catalytic activity.

It can be seen from Figure 4.17; nitric acid treatment has no sharp increasing effect on the activity when the temperature is relatively low and the steam to carbon monoxide ratio is also low. This is logical when considering our previous results and the literature survey that most of the SWGS catalysts are much more active at high temperature and high steam to carbon ratio.

Nitric acid treatment increases the oxygen bearing surface groups which gives more acidity. Therefore, the more acidic AC support is obtained with this treatment. The more acidic groups on the support surface the more hydrophilic surface. It means that during the impregnation of the metals into the support surface, the metal precursor solution is more absorbed by the hydrophilic surface of the AC support.

Due to the corrosion caused by nitric acid, some of the micropores in the AC surface become bigger, hence meso or macropores are formed. Since in general, mesopores are the active sites for the desired reaction, this may cause an increment in the catalytic activity.

When comparing air treatment and nitric acid treatment effects on the catalyst activity, it is observed that both treatment methods were beneficial for the sake of activity of the catalyst. On the other hand, from Figure 4.16 and 4.17, it is also concluded that nitric acid treatment was more efficient at 350°C to compare with air treatment. Whereas the catalytic activities of both AC2 and AC3 supported catalysts seem almost the same at 400°C. This may be because the AC3 supported catalyst reached its maximum performance at 400°C.

4.4. H_2 Selectivity

Until this point, the activity and stability of the catalysts that were produced were analyzed in this study. In chemistry, activity is about the conversion of one of the reactants into product(s). Stability is about how long the catalyst performs the same activity under the reaction conditions. As it mentioned before, even if it is provided a high activity and high stability from the catalyst that is produced, it does not guarantee that the desired product is obtained. Therefore, we have to look at the selectivity of the desired product. Selectivity means that in what percentage the desired product we have in the total amount of products.

In the WGS reaction, there are two products: H_2 and CO_2. Since it is mentioned in the literature survey part, CO_2 causes greenhouse gas emissions, hence it is very toxic to the environment. Therefore, H_2 is the desired product in the WGS reaction.

In order to have an idea about the selectivity, H_2 selectivity was calculated at 350°C and 400°C for all types of catalysts under both 0.3 and 0.8 steam to carbon monoxide ratio. The selectivity values will be shown in the following figures. The selectivity values were calculated by taking 2 hour's data as a basis to make sure that the reaction settled down.

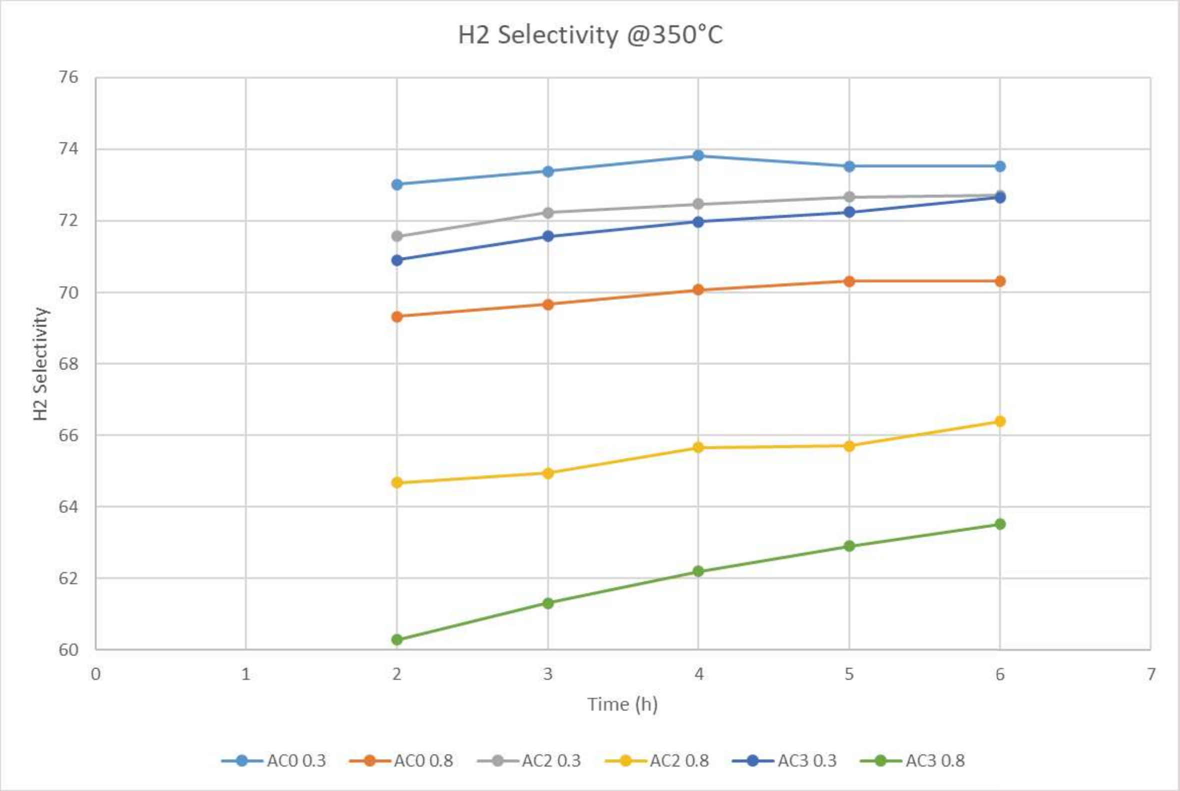


Figure 4.18. H_2 selectivities for different types of catalysts. The calculations were done based on 2 hours data after the system settled down. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 350°C and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

Since it is known that activity of the catalysts produced in this study was better at 400°C and steam/CO ratio is equal to 0.8, H_2 selectivity would be better at steam/CO ratio is equal to 0.8 rather than that of 0.3. However, the results showed that the opposite situation is true. The H_2 selectivity was better when steam/CO ratio was equal to 0.3.

Normally, when steam to carbon monoxide ratio is low, the WGS reaction does not occur in the forward direction. In accordance with that it was observed low activity at low steam/CO ratio during this study. This may be the reason for the high H_2 selectivity at low steam/CO ratio for all types of catalysts. Because the H_2 content in the feed stream was higher (6 times higher than CO_2 content) and the WGS reaction could not take place properly, it may be observed high H_2 selectivity at low steam/CO ratio.

The other important point here is that it was observed that the activity of the catalyst for almost all the reaction conditions that were analyzed increased in the following order: KCoRe/AC0, KCoRe/AC2, and KCoRe/AC3, respectively. On the other hand, for the sake of selectivity, this is not valid. AC0 supported catalysts showed better selectivity than that of others. This situation supports that high activity does not guarantee that the desired product is obtained. It may be attributed to the support chemistry of the catalysts supported over treated AC0.

Since AC0 is untreated support, there are no oxygen bearing surface groups on this support material as much as other treated supports (AC2 and AC3). Therefore, the precursor-support interactions were different for all types of catalysts. Hence, the reduction of some of the groups may occur on the catalysts supporting both AC2 and AC3 at this temperature. It may lead to low H_2 selectivity.

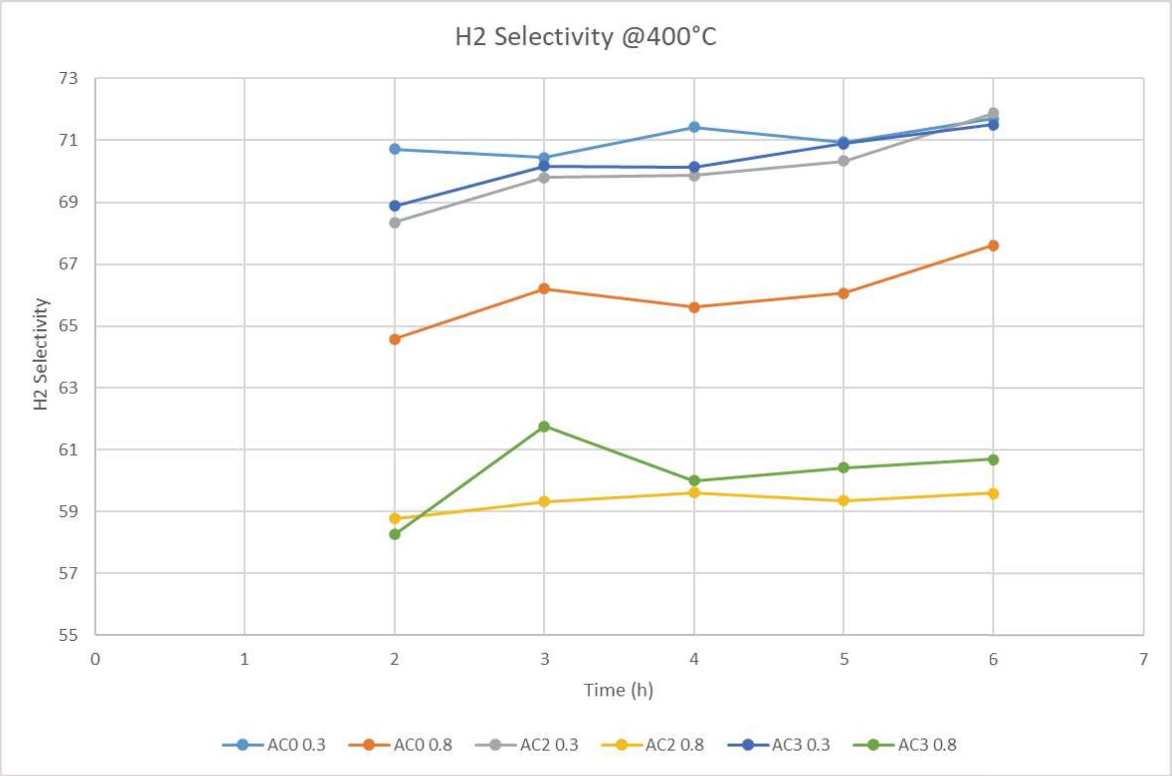


Figure 4.19. H_2 selectivities for different types of catalysts. The calculations were done based on 2 hours data after the system settled down. (All experiments were conducted for 6 hours on KCoRe/AC0, KCoRe/AC2 and KCoRe/AC3 catalysts with metal loadings: 5.8%Re, 2.4%Co, 2.2%K, at 400°C and calcined at 400°C. The catalysts were prepared by sequential impregnation method)

It can be observed from Figure 4.18 and Figure 4.19 that the H_2 selectivity was not affected dramatically with changing the temperature. It may be because temperature has a little effect on the converting reactants into products in these temperature ranges. The WGS reaction might be mostly controlled kinetically, not thermodynamically. Therefore, the steam/CO ratio was more effective on the selectivity.

It is also observed that when the temperature is raised to 400°C from 350°C, the H_2 selectivity becomes better when the reaction occurs on the AC3 supported catalyst at both steam/CO ratio selected compared with AC2 supported catalyst. By taking into account that temperature has a little effect on the selectivity, this situation may be related with the surface chemistry of the supports again.

Since the selectivity at both steam/CO ratio followed the same trend at the same temperature, it can be concluded that the reduction on the AC2 supported catalyst may have occurred more than that of AC3 supported catalyst. It may lead to low selectivity when the AC2 supported catalyst is used rather than AC3 supported one at 400°C.

5. CONCLUSIONS & RECOMMENDATIONS

Before starting to summarize results, it should be noted that the catalysts prepared in this study were model SWGS catalysts. They were prepared by taking one of the potential SWGS catalysts as a reference catalyst. Because the reference catalyst, $KCoRe/Al_2O_3$, is found suitable for the dry powder entrained-bed type syngas composition which contains sulfur compounds in recent study. However, the catalysts prepared in this study were tested under ideal, sulfur-free conditions.

The results of the experiments which are done in this study are as follows:

Firstly, the AC3 supported catalyst was tested under the high steam/CO ratio in order to prove that it is as good as industrial catalysts. The optimum reaction temperature was found as 350°C. However, 400°C is also considerable under this condition. The aim of the study was to develop catalysts which can work under lean, in other words, low steam/CO ratios especially below 0.8. Therefore, reaction temperature effect was investigated for the catalysts at low steam/CO ratios. The results showed that 400°C is much better at low steam/CO ratios. This may be explained with rather low conversion values, far away from thermodynamic equilibrium, obtained. On the other hand, reaction temperature does not have much effect on the H_2 selectivity, but the stability of the catalysts tends to decrease at 400°C rather than that of 350°C.

Secondly, the steam/CO ratio effect was investigated, and the results were in accordance with the literature. Increasing steam/CO ratio from 0.3 to 0.8 helped to increase CO conversion since it contains more steam and pushes the WGS reaction in the forward direction.

AC2 and AC3 supported catalysts were prepared by both sequential and co-impregnation methods in this study in order to see the effect of the impregnation technique. It is found that the impregnation method does not really have much effect on the AC3 supported catalysts. On the other hand, there is a huge difference between AC2 supported catalysts prepared by either sequential or co-impregnation method. AC2 supported catalysts showed better performance when they were prepared by sequential impregnation.

Lastly, the support pre-treatment method on the catalyst performance was investigated. AC2 support prepared by air treatment and AC3 support prepared by nitric acid treatment. The untreated support is called AC0. The results showed that any of the treatment methods was helpful to increase the catalyst activity by increasing the oxygen bearing surface groups on the support surface. Although there is no huge difference between the activities on the AC2 and AC3 supported catalysts when they are prepared by sequential impregnation, AC3 supported catalyst is still better at 350°C.

It is recommended that especially AC2 and AC3 catalysts can be tested under sulfur-containing feed composition for further studies. Although AC3 seems to have relatively higher catalytic activity, in terms of stability, AC2 showed better performance. Different metal loading can be tested for the AC2 and AC3 catalysts. It is obvious that the reaction temperature should be increased to have better performance at low steam/CO ratios. Therefore, in order to determine the optimum reaction conditions, the temperatures which are higher than 400°C can also be tested under lean steam/CO ratio.

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