## NOVEL GLYCEROL DRY REFORMING CATALYSTS WITH MONOMETALLIC AND BIMETALLIC ACTIVE SITES

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## MASTER OF SCIENCE

IN

## CHEMISTRY

by SALİM CAN AKYÜREK SEPTEMBER 2021

To My Lovely Sister, Elif I certify that I have read this thesis and, in my opinion, it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Prof. Dr. Emrah ÖZENSOY (Supervisor)

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Prof. Dr. Ömer Dağ

I certify that I have read this thesis and in my opinion it is fully adequate, in scope and quality, as a thesis of the degree of Master of Science

Prof. Dr. Ahmet Kerim Avcı

Approved for the Graduate School of Engineering and Sciences

Prof. Dr. Ezhan Karaşan Director of the Graduate School of Engineering and Sciences

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## ABSTRACT

## Novel Glycerol Dry Reforming Catalysts with Monometallic and Bimetallic Active Sites

### SALİM CAN AKYÜREK

M.S. in Chemistry Advisor: Prof. Dr. Emrah ÖZENSOY September 2021

Novel glycerol dry reforming catalysts with monometallic (Ru) and bimetallic (Ru and Ni or Ru and Co) active sites which are supported on a custom-design ternary mixed oxide support material (i.e., Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-ZrO<sub>2</sub>, AZT) with varying compositions were examined. Characterization of the synthesized catalytic system was carried out with XRD, Raman, BET, XPS, ICP-MS, SEM, and EDX techniques. Structure of the Ru active sites as a function of Ru loading was also investigated with in-situ FTIR spectroscopy via CO adsorption. Catalytic reactivity results revealed that 1 wt.% Ru/AZT70 catalyst can outperform the 1 wt.% Ru/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst in GDR reaction, where the latter catalyst is known to be the best catalyst in the literature for GDR reaction. 0.5wt.% Ru/AZT70 catalyst showed close activity compared to 1wt.% Ru/AZT70 catalyst. Furthermore, catalytic promotional effect of Ni for low Ru loadings in GDR reaction was also demonstrated.

## ÖZET

## Monometalik ve Bimetalik Aktif Bölgelere Sahip Yeni Gliserol Kuru Reform Katalizörleri

## SALİM CAN AKYÜREK

Kimya Bölümü Yüksek Lisans Tezi Tez Danışmanı: Prof. Emrah ÖZENSOY Eylül 2021

Bu çalışmada, özel tasarım, üçlü karışık oksit destek malzemesi (yani, Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-ZrO<sub>2</sub>, AZT) üzerine, farklı miktarlarda konuşlandırılmış, tek metalli (Ru) ve çift metalli (Ru ve Ni veya Ru ve Co) aktif bölgeleri olan, yeni gliserol kuru reformlama katalizörlerini incelendi. Sentezlenen katalitik sistemin karakterizasyonu, XRD, Raman, BET, XPS, ICP-MS, SEM ve EDX teknikleri ile gerçekleştirildi. Ru yüklemesinin bir fonksiyonu olarak, Ru aktif bölgelerinin yapısı, ayrıca CO adsorpsiyonu yoluyla in-situ FTIR spektorskopisi ile araştırıldı. Katalitik reaktivite sonuçları, ağırlıkça %1 Ru/AZT70 katalizörünün, GDR reaksiyonunda, ağırlıkça %1 Ru/La<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> katalizöründen (yani literatürde GDR reaksiyonu için bilinen en iyi katalizörden) daha iyi performans gösterebileceğini ortaya koydu. Ağırlıkça %0.5 Ru/AZT70 katalizörü, ağırlıkça %1 Ru/AZT70 katalizörüne kıyasla yakın aktivite gösterdi. Ayrıca, RuNi bimetalik katalizöründeki Ni stelerinin, düşük miktarlarda kullanılan Ru sitelerini, GDR tepkimesindeki, iyileştirici etkisi gösterildi.

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## **Chapter 1**

## Introduction

### 1.1 What is Syngas?

Syngas or in other words synthesis gas, is the common word that is used to describe a ubiquitously utilized gas mixture in the chemical industry. This gas mixture is composed of mostly H<sub>2</sub>, CO and occasionally some CO<sub>2</sub>. The acronym is used because the mixture is used as an intermediate in the process of creating synthetic natural gas.<sup>[1]</sup> Synthetic natural gas is used as a fuel and mostly composed of methane, CH<sub>4</sub>. Syngas is flammable; thus, can be used in internal combustion engines.<sup>[2][3]</sup>

Furthermore, synthesis gas, is also used as a raw material in many large-scale chemical processes such as Fischer-Tropsch Synthesis, synthesis of CH<sub>3</sub>OH, C<sub>2</sub>H<sub>6</sub>O and/or NH<sub>3</sub>. The last three chemicals, methanol, dimethyl ether and ammonia, are consumed by the chemical industry in very large volumes.<sup>[4]</sup>

### **1.2 Fossil Fuels and Biodiesel**

The global energy consumption is dominated by the usage of fossil fuels.<sup>[5]</sup> Fossil fuel usage comes with its own problems such as production complexity, high production costs, and environmental pollution. These problems called attention to alternative and renewable options. Accordingly, biodiesel is one of the promising alternatives as it is a renewable fuel that can be mixed with the refinery diesel and can be used in existing diesel

engines in the absence of any other modifications. As a result of this interest in biodiesel, the biodiesel market grew from 5.4 million tons in 2006 to 35.8 million tons in 2017 where Germany is the leading country in biodiesel the production (3.1 million tons/year).<sup>[6]</sup>

The synthesis protocol for the biodiesel typically involves the trans-esterification of animal-based or vegetable oils with methanol and/or ethanol. The reaction products also include glycerol. Glycerol is a major side product constituting almost 10% by mass of the biodiesel product mixture.<sup>[7,8]</sup> In 2020, the global glycerol supply is estimated to be 6 times greater than that of the global glycerol demand.<sup>[7]</sup> This also creates an increase in the biodiesel prices since the by-product of the reaction is causing huge amounts of waste. If this waste can be used in alternative ways, the price for the biodiesel production can be lowered. In order to valorize this surplus chemical, catalytic transformation of glycerol to syngas (CO + H<sub>2</sub>) can be used.

### 1.3 Hydrogen as an Energy Vector

H<sub>2</sub> is a clean energy carrier. The usage of hydrogen is expected to grow further in the future because the hydrogen fuel cell industry continues to expand globally via technological developments. Figure 1 shows the primary sources of global hydrogen production in 2005<sup>[9]</sup>:



Figure 1: Primary sources of global hydrogen production in 2005<sup>[9]</sup>.

Global hydrogen demand is also in an increasing trend. From 1990 to 2018, global demand for hydrogen has increased from 35 million ton to 70 million ton.<sup>[10]</sup> As one can see from Figure 1, most of the hydrogen is produced via Steam Reforming of Methane (SRM).

### 1.3.1. Steam Reforming for Hydrogen Production

In the SR process, methane reacts with water at high temperature (973 K – 1273 K) to produce carbon monoxide and hydrogen.<sup>[14]</sup> Based on the reaction the stoichiometry, it can be seen that for every mole of methane, one can produce 3 moles of hydrogen. At the end of the SR process, produced carbon monoxide can be reacted with water again to produce more hydrogen<sup>[15]</sup>. Latter reaction is called the water-gas shift (WGS) reaction.

One can also use glycerol in the steam reforming reaction where glycerol reacts with water to produce hydrogen and carbon dioxide.<sup>[15]</sup> Some advantages of glycerol steam

reforming to methane steam reforming are, 7 moles of hydrogen can be produced instead of 3 moles, for an equivalent amount of reactant and the reactant type is not a fuel but a biomass-related chemical.

SR processes also have various drawbacks and challenges. One of these challenges is that these reactions have some side reactions which yield methane from the reaction of carbon dioxide, carbon monoxide or glycerol with hydrogen as shown below in reactions (1-3):

 $CO + 3 H_2 \rightleftharpoons CH_4 + H_2O \tag{1}$ 

 $CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2O$  (2)

$$C_{3}H_{8}O_{3} + 2 H_{2} \rightleftharpoons 2 CH_{4} + 2 H_{2}O + CO \qquad (3)$$

Another challenge is that, H<sub>2</sub> production was typically observed to be lower than the aforementioned theoretical limit, the theoretical value.<sup>[16-18]</sup> Also, the coke formation is an important issue when it comes to the steam reforming reactions. The formation and deposition of coke on the catalytic active sites decrease the catalyst performance and lifetime significantly.<sup>[19-20]</sup>

In the SR process, typically H<sub>2</sub>/CO ratios of >2 are obtained. This value is good for hydrogen production purposes. In contrast, in order to synthesize/produce long-chain hydrocarbons, one would need a hydrogen to carbon monoxide ratio around  $1.^{[21]},^{[22]}$ 

#### **1.3.2.** Glycerol Dry Reforming for Hydrogen Production

Glycerol dry reforming (GDR) is a catalytic process to convert glycerol into syngas through a carbon negative path, where  $CO_2$  (a greenhouse gas) and glycerol are used as the reactants. Overall GDR reaction can be described as below:

$$C_{3}H_{8}O_{3} + CO_{2} \rightarrow 4 CO + 3 H_{2} + H_{2}O, \Delta H^{0} = 292 \text{ kJ/mol}$$
 (4)

This reaction can be taken into account as a combination of two consecutive reactions:

$$C_{3}H_{8}O_{3} \rightarrow 3CO + 4H_{2}, \Delta H^{0} = 251 \text{ kJ/mol}$$
(5)

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H^0 = 41 \text{ kJ/mol}$$
 (6)

Here, glycerol first decomposes into syngas followed by the reverse WGS reaction (RWGS). GDR reaction typically requires high temperatures (i.e., above 773 K).<sup>[23-24]</sup> This is simply because, glycerol molecule needs high temperatures to thermally decompose. Decomposition of glycerol occurs through dehydrogenation and dehydration routes yielding various hydrocarbons or oxygenates.<sup>[25]</sup>

Valliyappan et al. studied the effects of the carrier gas flow rate, temperature, particle diameter and packing material during the pyrolysis of glycerol. When they changed the carrier gas flow rate ( $N_2$ ) from 30 to 70 mL/min, the yield of gas decreased and at the same time, an increase in the liquid yield was observed. Products were mostly consisted of hydrogen and carbon monoxide, whereas a small amount of carbon dioxide, methane and ethylene was still detectable. Also, higher flow rates favored carbon monoxide and hydrocarbon production rather than increasing hydrogen yield, which suggests that carbon monoxide and hydrocarbons are the main pyrolysis products. Next step was to fix the flow

rate to 50 mL/min and change the temperature in order to observe the influence of temperature on the glycerol pyrolysis. When the temperature was increased from 923 K to 1073 K, relative yield of gaseous products increased while liquid yield of prooducts decreased. Also, as the temperature increased, the hydrogen yield increased significantly whereas carbon monoxide yield decreased. The hydrocarbon yields were constant up to 1023 K and they decreased significantly at 1073 K. For temperatures less than 1023 K, syngas yield increased slightly with increasing temperature, but at 1073 K, a sharp increase in the hydrogen yield was observed, which was attributed to the decomposition of the hydrocarbons to the coke and hydrogen. When they examined the different reaction pathways during the pyrolysis of glycerol, they observed multiple dehydrogenation and dehydration steps which result in hydrogen, carbon monoxide, carbon dioxide, ethylene, methane, acetic acid, acetaldehyde, acetone, ethanol, water, methanol, acrolein, and char.<sup>[26]</sup>

Wang et al.<sup>[24]</sup> examined the thermodynamic conditions for the glycerol dry reforming process. Experiments on the influence of the gas feed pressure revealed that as the feed pressure increased, the amount of hydrogen and syngas decreased significantly. Carbon dioxide to glycerol ratio is another important factor in the GDR reaction. When this particular ratio is below 1, increase in temperature results in increase in the yield of hydrogen, which is in agreement with the work of Valliyappan et al.<sup>[25]</sup> Although, when the carbon dioxide to glycerol ratio (CO<sub>2</sub>/G) is above 1, with increasing temperature, the increase in the hydrogen yield reaches a maximum around 950 K and starts to decrease for higher temperatures. Thus, for  $0 < CO_2/G < 1$  and T > 950 K, the amount of hydrogen that can be produced converges to the theoretical limit of 4 moles per mole of glycerol. Furthermore, high CO<sub>2</sub>/G and high temperature favor the carbon monoxide production.<sup>[25]</sup>

Since different ratios of H<sub>2</sub>/CO is needed for different applications, this information can be used to control the syngas ratio in the GDR reaction. In this work<sup>[25]</sup>, coke formation was investigated for 7 different CO<sub>2</sub>/G ratios (i.e., 0, 0.5, 1, 2, 3, 4, 5) and at 17 different temperatures (between 600 and 1000 K with an increment of 25 K). Results were as follows; lower CO<sub>2</sub>/G ratios favored the coke formation while increasing the temperature decreased the amount of coke produced. Also, they noted that GDR caused higher amount of coke when compared to the glycerol steam reforming.<sup>[27,28,29]</sup>

### **1.4 GDR Catalysts in Literature**

### 1.4.1. Ni Based Catalysts

In the literature, there are many papers investigating the GDR process on different types of catalysts and supports. One of them was published by Siew et al.<sup>[30]</sup> In their work, La promoted 3 wt.% Ni catalyst on Al<sub>2</sub>O<sub>3</sub> support was used. Temperature range was 923 K to 1123 K and the CO<sub>2</sub>/G ratio was changed from 0 to 5. They reported that the La promotion increased the Brunauer-Emmett-*Teller* (BET) surface area of the catalyst by 13% and also caused better metal dispersion and finer crystallite size. They found out that the optimum conditions for the GDR reaction on this catalyst were T = 1023 K, CO<sub>2</sub>/G = 1.67 and P = 1 atm which gave the highest syngas yield. The yield for glycerol conversion at the 1023 K was ca. 90%.

Arif et al. studied the effect of support type on Ni based catalysts in GDR applications.<sup>[33]</sup> They synthesized 15 wt.% Ni catalysts on 3 different supports, namely: CaO, ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>. Catalytic activity tests were done at 973 K, under atmospheric pressure and at CO<sub>2</sub>/G = 1. 15 wt.% Ni on CaO showed the highest glycerol conversion (~26%) and

hydrogen yield (~21%). When the effect of temperature examined, 1073 K was found out to be the optimum temperature for the reaction.

In another study, Narazimah et al.<sup>[31]</sup> examined Ag promoted Ni catalysts on SiO<sub>2</sub>. As the loading of the silver increased from 0 wt.% to 5 wt.%, at 973 K and CO<sub>2</sub>/G ratio of 1, the hydrogen yield and glycerol conversion values reached their maximum values of 27% and 33% respectively. When they changed the support material to  $Al_2O_3^{[32]}$ , values for hydrogen yield and glycerol conversion increased to 32% and 40.7% at 1073 K, CO<sub>2</sub>/G = 0.5 and 3 wt.% Ag promotion, respectively. This high activity, however, came with a higher instability of the catalyst. The 72 h stability tests gave good results only if the catalysts were additionally reduced at the 10<sup>th</sup> hour. Also, observation of some whisker-type carbon species was another problem that caused the deactivation of the catalyst. In all these experiments, Ni loading was kept constant at 15%.

Tavanarad et al. studied mesoporous Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>[34]</sup> They changed the Ni composition in the catalyst and tried the GDR reaction at 873 - 1023 K, CO<sub>2</sub>/G = 1, atmospheric pressure. As the Ni composition increased from 0 wt.% to 20 wt.%, surface area decreased from 188 m<sup>2</sup>/g to 143 m<sup>2</sup>/g and Ni crystalline size increased almost 4 times (from 5.1 nm to 18.9 nm). From the GDR catalytic activity tests, it was shown that 15 wt.% Ni on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the greatest glycerol conversion and the highest hydrogen yield among the 4 different catalysts. Also, when the temperature was increased above 973 K, H<sub>2</sub>/CO ratio converged to 1. The stability of the 15wt.% Ni on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, however, decreased significantly after 3 h, due to whisker-type carbon formation.

In another study, Roslan et al. investigated the rhenium promotion effect on Ni based catalysts.<sup>[35]</sup> 15 wt.% Ni and 3 wt.% Re promoted 15 wt.% Ni catalysts were synthesized on the SBA-15 support. BET Surface area decreased by almost 25% when the catalyst was promoted with Re. For the GDR catalytic activity tests, the catalysts were tested at 973, 1073,1173 K and at 3 different CO<sub>2</sub>/G ratios (0.5, 1, 3). Optimum reaction condition was found to be at 973 K, CO<sub>2</sub>/G ratio of 1, and 1 atm pressure. 3 wt.% Re promoted catalyst showed higher hydrogen yield and glycerol conversion (55% and 57% respectively) than non-promoted 15 wt.% Ni catalyst (18% and 20% respectively). The oxidation of carbonaceous species and the reduction of carbon deposition that is caused by the presence of Re was reported to be the possible reasons for this increase in the activity.

### **1.4.2.** Noble Metal Catalysts

Tavanarad et al. used platinum, palladium, rhodium, ruthenium and iridium as catalytic active sites in GDR reaction.<sup>[36]</sup> Support for the catalysts were chosen to be magnesium aluminate (MgAl<sub>2</sub>O<sub>4</sub>). When the BET surface areas of the catalysts were tested, Pd, Rh, and Ru catalysts showed higher surface areas than Ir, and Pt catalysts, while Pd catalyst had the highest specific surface area (SSA). However, the crystallite size was the highest in the Pt catalysts which was almost three times greater than that of Pd and Rh catalysts. Activities of the catalysts were tested at 873 - 1023 K with 1 wt.% active site loading for each metal. Among the 5 different noble metal catalysts, Rh showed the highest glycerol conversion at 1023 K and CO<sub>2</sub>/G = 1. They also noted that increasing the temperature decreased H<sub>2</sub>/CO ratio. In the stability tests, Rh catalyst showed the greater stability against other four catalysts in 5 h stability test. In 20 h stability test, Rh catalyst lost almost 35% of its activity in terms of glycerol conversion. Overall, they claimed the catalytic

activity of these five metals could be ranked as follows: Rh > Ru > Ir > Pd > Pt in the GDR reaction.

In another work, Bulutoglu et al. prepared and investigated 1 wt.% Rh on CeO2 and 1 wt.% Rh on ZrO<sub>2</sub> catalysts in the glycerol dry reforming reaction. Carbon monoxide molecule was used as a probe molecule to investigate the properties of the two catalysts via in-situ FTIR spectroscopy. It was shown that both Rh and Rh<sup>+</sup> features coexisted on the surface of the supports. Different infrared peaks may correspond to different bonding types of the carbon monoxide to the Rh sites, such as bridge-bonded CO or linearly bonded (atop) CO. Catalytic activity tests were carried out at 873 - 1023 K and CO<sub>2</sub>/G ratios between 1 and 4. Rh on ZrO<sub>2</sub> showed greater GDR activity when compared to Rh/CeO<sub>2</sub>. The highest activity was reached at the temperature of 1023 K. When the CO<sub>2</sub>/G ratio increased, glycerol conversion was decreased for both catalysts, but the same parameter had a different effect on the carbon dioxide conversion.  $CO_2$  conversion stayed almost constant for  $CO_2/G = 2-4$ . Glycerol conversion increased to a maximum value of 76% and 72% (for RhZr and RhCe, respectively) when the temperature was kept constant at 1023 K. The increase in the temperature also helped to decrease the coke formation and obtaining a H<sub>2</sub>/CO ratio of almost 1. At 1023 K and CO<sub>2</sub>/G ratio of 4 Rh on CeO<sub>2</sub> was much more stable than Rh on ZrO<sub>2</sub>. Carbon dioxide conversion was decreased by almost 40% for the ZrO<sub>2</sub> supported Rh catalyst, whereas other catalyst's performance on the CO<sub>2</sub> conversion was decreased by only 23%. Also, tracking of methane in the products was another way to check for the stability of the catalysts since it can be linked to the catalyst deactivation. Rh/CeO<sub>2</sub> catalyst reaction showed less amount of methane produced, which supported the idea that it is more stable than the ZrO<sub>2</sub> supported Rh catalyst. This work is an important study in the literature since

it shows the carbon dioxide conversion for the first time for the glycerol dry reforming reaction.

So far in the literature, different metal precursors were tested on different support materials in the glycerol dry reforming reaction. Change in the support material effects the catalytic activity in a great extent. In an attempt to find a better support material, in the current work, a new, custom made ternary oxide support material was investigated.

### 1.5 AZT: A Ternary Oxide Support

In 2007, Imagawa et al.<sup>[39]</sup> synthesized a new support with increased thermal stability to be used in NO<sub>x</sub> storage-reduction (NSR) applications. The two main problems of NSR catalysts, namely thermal deterioration and sulfur poisoning, were tried to be resolved by synthesizing new support materials. For the sulfur poisoning problem, Matsumoto et al.'s work on NSR catalysts' support choices were taken into account.<sup>[38]</sup> TiO<sub>2</sub>, due to its high acidity, has found to be bringing high durability against sulfur poisoning in the support material. Then, in order to eliminate the problem of thermal deterioration caused by the solid phase reaction, ZrO<sub>2</sub> was mixed with the TiO<sub>2</sub>.<sup>[40]</sup> Last but not least, Al<sub>2</sub>O<sub>3</sub> was chosen to be the third oxide material, in order to increase the thermal stability of the support. This choice is originated from the work of Kanazawa et al.<sup>[41]</sup> Their work included a ternary oxide mix of Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> and the observation was that; Al<sub>2</sub>O<sub>3</sub> performs as a diffusion barrier for the other two oxide particles, preventing thermal aging and sintering of the support material.

In a later work<sup>[41]</sup>, different batches of AZT samples were prepared with the following ratios: %50/%35/15 (corresponding to relative masses of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub>,

respectively) at different temperatures. When the support material was calcined at 773 K, SSA had the highest value of 277 m<sup>2</sup>/g. Upon increasing the calcination temperature, SSA decreased to a great extent, to 80 m<sup>2</sup>/g at 1173 K. Furthermore, AZT material that was calcined at 1073 K showed the highest NO<sub>x</sub> storage ability.

Say et al.<sup>[43]</sup>, also worked on an AZT support material for NO<sub>x</sub> storage and reduction application. In this work, AZT material showed no XRD peaks and stayed amorphous upo to a calcination temperature of 1173 K. In the Raman spectra, tetragonal ZrO<sub>2</sub> peaks were observable at 973 K and 1173 K calcination temperatures. SSA values were in a good agreement with the Imagawa et al.'s work on AZT, with a value of 264 m<sup>2</sup>/g for the for the AZT sample that was calcined at 973 K.

In the current study, three different support materials and five different catalysts were chosen for investigation. Various AZT support materials with different compositions were synthesized . Namely, AZT70 (50%/35%/15%), AZT50 (50%/25%/25%), and AZT30 (50%/15%/35%), where the number next to the AZT represents the relative ratio of ZrO<sub>2</sub> over TiO<sub>2</sub>.

After support synthesis, 5 different catalyst samples were prepared on the support AZT70; 1wt.% Ru on AZT70, 0.5wt.% Ru on AZT70, 0.1wt.% Ru on AZT70, 0.1wt.% Ru + 0.4wt.% Ni on AZT70, 0.1wt.% Ru + 0.4wt.% Co on AZT70.

Catalyst choices were made in order to synthesize a catalyst with low cost and high efficiency. From the previous works in the literature, it was clear that Rh is the most active metal when it comes to GDR. On the other hand, Rh is an expensive metal with a cost over 1000\$ per gram.<sup>[44]</sup> In order to replace Rh, Ru is proposed in this project as a much cheaper

(17\$ per gram)<sup>[44]</sup> alternative that can yield similar activity and stability. Accordingly, in an attempt to decrease the cost without losing efficiency, Ru-Ni and Ru-Co bimetallic catalysts were proposed. Ni is also known for its activity in GDR. If the activity and stability of Rh or Ru based catalysts can be achieved with the combination of Ru-Ni or Ru-Co, this would help the synthesis of cost-efficient catalysts for glycerol dry reforming.

## **Chapter 2**

## **Experimental:**

### 2.1 Sample Preparation

#### 2.1.1. AZT30

Sol – gel method was applied for the synthesis of the AZT support materials. Firstly, 8.023 mL of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma-Aldrich, 97%) was mixed with 30 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub> (Sigma-Aldrich,  $\geq$ 99.5%, ACS grade). Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. In a separate beaker, 3.274 mL of Zr[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma Aldrich, 99.9%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. Th a separate beaker, 3.274 mL of Zr[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma Aldrich, 99.9%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. The Zr solution was added to the Ti solution and the stirring continued for another 10 min. In a third beaker, 14.943 g of Al(OCH[CH<sub>3</sub>]C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (Sigma Aldrich, 97%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. The Al solution was added to the first beaker and the final solution was covered with a parafilm and stirred for 30 min at 550 rpm. After 30 min, the stirring speed was changed to 390 rpm and approximately 3.5 mL of 0.5 M HNO<sub>3</sub> was added very slowly, until the gel formation was obtained. Then, the solution was kept under the fume hood at room temperature for 48 h for drying. Then, the support material was calcined at 1023 K for 2 h in air in a muffle furnace.

### 2.1.2. AZT50

Sol – gel method was applied for the synthesis. Firstly, 5.731 mL of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma-Aldrich, 97%) was mixed with 30 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub> (Sigma-Aldrich,  $\geq$ 99.5%, ACS grade). Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. In a separate beaker, 5.455 mL of Zr[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma Aldrich, 99.9%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. The Zr solution was added to the Ti solution and the stirring continued for another 10 min. In a third beaker, 14.943 g of Al(OCH[CH<sub>3</sub>]C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (Sigma Aldrich, 97%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for another 10 min. In a third beaker, 14.943 g of Al(OCH[CH<sub>3</sub>]C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (Sigma Aldrich, 97%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. The Al solution was added to the first beaker and the final solution was covered with a parafilm and stirred for 30 min at 550 rpm. After 30 min, the stirring speed was changed to the 390 rpm and approximately 3.5 mL of 0.5 M HNO<sub>3</sub> was added very slowly, until the gel formation was obtained. Then, the solution was kept under the fume hood at room temperature for 48 h for drying. Finally, the support material was calcined at 1023 K for 2 h in air in a muffle furnace.

#### 2.1.3. AZT70

Sol – gel method was applied for the synthesis. Firstly, 3.438 mL of Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma-Aldrich, 97%) was mixed with 30 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub> (Sigma-Aldrich,  $\geq$ 99.5%, ACS grade). Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. In a separate beaker, 7.639 mL of Zr[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Sigma Aldrich, 99.9%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. The Zr solution was added to the Ti solution and the stirring continued

for another 10 min. In a third beaker, 14.943 g of Al(OCH[CH<sub>3</sub>]C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (Sigma Aldrich, 97%) was mixed with 40 mL of CH<sub>3</sub>CH(OH)CH<sub>3</sub>. Resulting mixture was covered with a parafilm and stirred for 10 min at 550 rpm. The Al solution was added to the first beaker and the final solution was covered with a parafilm and stirred for 30 min at 550 rpm. After 30 min, the stirring speed was changed to 390 rpm and approximately 3.5 mL of 0.5 M HNO<sub>3</sub> was added very slowly, until the gel formation was obtained. Then, the solution was kept under the fume hood at room temperature for 48 h for drying. Next, the support material was calcined at 1023 K for 2 h in air in a muffle furnace.

### 2.1.4. 1 wt.% Ru on AZT70 Catalyst

Incipient wetness impregnation method was used for introducing Ru onto the support materials. 0.62 mL of the precursor  $Ru(NO)(NO_3)_x(OH)_y$  in dilute nitric acid solution (Sigma Aldrich, 1.5% Ru (w/w)) was added to the 1 g of AZT70 support carefully in order to get 1wt.% Ru loading (0.01 g). Synthesized catalyst was reduced under H<sub>2</sub> (5% H<sub>2</sub> in Ar, 100 mL/min) at 773 K for 2 h.

### 2.1.5. 0.5 wt.% Ru on AZT70 Catalyst

Incipient wetness impregnation method was used for introducing Ru onto the support materials. 0.31 mL of the precursor  $Ru(NO)(NO_3)_x(OH)_y$  in dilute nitric acid solution was added to the 1 g of AZT70 support carefully in order to get 0.5wt.% Ru loading (0.005 g). Synthesized catalyst was reduced under H<sub>2</sub> (5% H<sub>2</sub> in Ar, 100 mL/min) at 773 K for 2 h.

### 2.1.6. 0.1 wt.% Ru on AZT70 Catalyst

Incipient wetness impregnation method was used for introducing Ru onto the support materials. 0.062 mL of the precursor  $Ru(NO)(NO_3)_x(OH)_y$  in dilute nitric acid solution was added to the 1 g of AZT70 support carefully in order to get 0.1wt.% Ru loading (0.001 g). Synthesized catalyst was reduced under H<sub>2</sub> (5% H<sub>2</sub> in Ar, 100 mL/min) at 773 K for 2 h.

### 2.1.7 0.1 wt.% Ru + 0.4 wt.% Ni on AZT70 Catalyst

Incipient wetness impregnation method was used for introducing Ru onto the support materials.  $0.062 \text{ mL of } Ru(NO)(NO_3)_x(OH)_y$  in dilute nitric acid solution and 21.1 mg of the precursor Ni(NO\_3)\_2 · 6H\_2O (Sigma Aldrich,  $\geq$ 97%, 19.57% Ni (w/w)) were added to the 1 g of AZT70 support carefully in order to get 0.1wt.% Ru (0.001 g) and 0.4wt.% Ni (0.004 g) loadings. Synthesized catalyst was reduced under H<sub>2</sub> (5% H<sub>2</sub> in Ar, 100 mL/min) at 773 K for 2 h.

### 2.1.8 0.1 wt.% Ru + 0.4 wt.% Co on AZT70 Catalyst

Incipient wetness impregnation method was used for introducing Ru onto the support materials.  $0.062 \text{ mL of } Ru(NO)(NO_3)_x(OH)_y$  in dilute nitric acid solution and 20.6 mg of  $Co(NO_3)_2 \cdot 6H_2O$  (Sigma Aldrich,  $\geq 98\%$ , ACS Reagent) precursor were added to the 1 g of AZT70 support carefully in order to get 0.1wt.% Ru (0.001 g) and 0.4wt.% Co (0.004 g) loadings. Synthesized catalyst was reduced under H<sub>2</sub> (5% H<sub>2</sub> in Ar, 100 mL/min) at 773 K for 2 h.

### **2.2 Experimental Analysis Techniques**

### 2.2.1. X-Ray Diffraction (XRD)

The XRD analysis was carried out by working on a Pananalytical Multipurpose X-Ray Diffractometer (XRD-MPD) which is coupled with Cu K $\alpha$  (1.5405 Å) source of X-Ray at 45 kV/40 mA. The samples were crushed into fine powder by using a mortar, then put on top of a silicon single crystal. This crystal was placed into the diffractometer. All the samples were scanned over 80 degrees (between 10° and 90°). Offset value was 0. Step size was 0.01 and time per step was 30 s.

### 2.2.2. Raman Spectroscopy

Raman spectra were acquired using a HORIBA Jobin Yvon LabRam HR800 Raman spectrometer. A Raman BX41 microscope, spectrograph (that has 800 mm focal length) and a detector was also supplied to the instrument. The laser that was also supplied with the instrument was a Nd: YAG laser that has a wavelength of 532.1 nm. During the experiments, laser output power was set to 20 mW. The equipment was calibrated by using the 520.7 cm<sup>-1</sup> peak of the reference Si wafer. Raman spectra was recorded between 100 - 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

### 2.2.3. BET

Micromeritics Tristar 3000 analyzer was used for the BET SSA analysis. The analysis was carried out by using a low-temperature isothermal adsorption/desorption of nitrogen gas. Measured samples (finely ground powders with a mass of ca. 0.15 g) were placed inside the BET tubes and heated to 673 K for 4 h in order to get rid of H<sub>2</sub>O, CO<sub>2</sub> and other possible impurities prior to measurements.

### 2.2.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

An Agilent 7700x ICP-MS (Agilent Technologies Inc., Tokyo, Japan) equipped with an octopole reaction system and a helium collision cell for spectral interference removal was used to determine Ru, Ni, and Co concentrations at the ppm level. MicroMist glass concentric nebulizer, quartz Scott-type spray chamber (both from Agilent Technologies, Inc.) and Ni sampler/skimmer cones were used for the operation of ICP-MS. 1  $\mu$ g/L tuning solution was used for short term stability to perform daily instrumental optimization. External calibration solutions were prepared by using SPEX CertiPrep CLMS-2AN and Ru containing Merck Millipore multi element ICP-MS standards. The calibration curve was drawn with eight different concentrated standards which were diluted serially from 10 ppm to 0.15625 ppm and included 2 %v/v HNO<sub>3</sub>(aq) as a blank solution. MassHunter software was used for the analysis. Operating parameters can be summarized as follows: the number of points per peak = 1, replicates = 5, sweeps per replicate = 100, integration time per mass = 0.30 s, the plasma gas flow (argon) = 15 L/min, the helium gas flow (collision cell) = 4.3 ml/min, the carrier gas flow (argon) = 1 L/min and the plasma forward power = 1550 W.

### 2.2.5 Scanning Electron Microscope (SEM)

SEM experiments were performed using a FEI Quanta 200 FEG system. Acceleration voltage was set to be 10 kV during the analysis.

#### 2.2.6 Energy Dispersive X-Ray Spectroscopy (EDX)

EDX measurements were done by using a FEI Quanta 200 FEG system. Acceleration voltage was set to 15 kV during the analysis. Analysis was carried out by using the "Edax Genesis" program.

### 2.2.7 X-Ray Photoelectron Spectroscopy (XPS)

A SPECS XPS spectrometer was used in the XPS analysis. A monochromatic Al, K $\alpha$ , X-Ray irradiation with hv = 1486.74 eV, 400 W and PHOIBOS-MCD energy analyzer was equipped with this spectrometer. A conducting copper sticky tape was used to mount the samples for measurement. In order to avoid surface charging, an electron flood gun was used.

### 2.2.8 Fourier-Transform Infrared Spectroscopy (FTIR)

In-situ FTIR measurements were done, by using an FTIR (Bruker Tenson 27) spectrometer connected to a custom-design catalytic reactor. A Hg-Cd-Te (MCT) IR detector was used to collect the infrared data. Liquid nitrogen was used in order to cool the detector. The spectra were collected by taking the average of 64 scans with a 4 cm<sup>-1</sup> resolution. Catalyst samples were first ground into powder inside a mortar, then, finely grounded samples were pressed onto a lithographically etched tungsten grid (P/N PW10379-003) which has a high conductance. A tantalum foil was welded on top of this tungsten grid in order to keep track of the temperature. Then, sample was connected to the copper holder legs assembled to a ceramic vacuum feedthrough and a K-type thermocouple (chromel and alumel with 0.015" radius from Omega Engineering, Inc) was welded to the tantalum foil. A DC power supply and PID electronics which were controlled by a computer was used in order to adjust the sample temperature. Amount of catalyst powder that was put into the grid was around 20-25 mg. The sample was placed inside the batch reactor. After that, the outgassing procedure was initiated at room temperature for 30 min. Then, the sample was heated to 773 K (with a heating rate of 12 K/min). By heating the sample, we aimed to get rid of the possible contaminations on the sample surface. After reaching 773 K, temperature was kept constant for 30 min and then the sample was cooled down to 323 K. At 323 K, background infrared spectrum was taken, followed by CO dosage of 20 Torr for 10 min. During this dosage, gasphase infrared spectrum was taken. After 10 min, the system was pumped out and CO adsorption infrared spectrum was taken for the sample at 1 min, 5 min and 10 min. Since there was no significant changes with time after the first 5 min, 5 min spectra was used for each sample. Below is a representation of the custom-design in Situ-FTIR catalytic analysis system:



Figure 2: Representation of the in-situ FTIR System.

## 2.3 Catalytic Activity Experiments

All catalytic activity tests were carried out by Prof. Ahmet Kerim Avcı research group located at Boğaziçi University, Chemical Engineering Department. In order to perform catalytic activity experiments, a reactor system that consists of three parts was used (Figures 3-5). These parts can be named as inlet, reaction and product analysis sections.

### 2.3.1 Inlet Section

In this section, a precise pump of Shimadzu LC-20AT HPLC is used in order to dose the glycerol inside the reactor system. The gases that were dosed other than the glycerol were dosed in to the reactor from their cylinders. Bronkhorst EL-FLOW Select mass controllers (MFC) were used in this dosing process. Connections for these processes were done by using Swagelok tubes, unions and t-joints that have sizes changing between 1/16" to 1/4".

Hydrogen, carbon dioxide and nitrogen gas pressures were reduced to 3 bar before the dosing procedures via MFCs. Single-stage gas regulators were used to adjust the pressure. All the MFCs were calibrated before the experiments. In order to prevent the gases from flowing back, on-off valves were connected after the MFCs.

A 0.1 L graduated cylinder and the pump of HPLC were used in order to feed the glycerol into the system. Due to the high viscosity of the chemical, the 1/16" pipe that was used in the system was wrapped around with a heating line. This line was also sealed by using a glass wool and aluminum foil in order to minimize the heat loss. In order to keep this line's temperature constant at 100  $^{\circ}$ C and have a better glycerol flow, a PID controller from TETRA was used.

The gaseous feed and the dosed glycerol were united by a t-joint before entering the reactor. The injected gaseous mixture was heated to 400  $^{0}$ C by the help of a 3-zone furnace that is shown in Figure 5. This heating helps the mixture to become homogeneous and keeps the CO<sub>2</sub>/Glycerol ratio constant.



Figure 3: Schematic representation of the catalytic reaction system.<sup>[67]</sup>



Figure 4: Catalytic reaction system that is used in this work.<sup>[67]</sup>



Figure 5: Illustration of the reactor inlet and injector.<sup>[67]</sup>

### 2.3.2 Reaction Section

The reaction part of the experimental system has a packed bed quartz reactor. This reactor was inside of a three-zone furnace (PROTHERM PZF 12/50/500) in order to perform the heating process. Two cold traps inside of Dewar flasks were the other parts of this section.

The quartz reactor's middle part was aligned with the furnace's middle part to heat the reactor with a good efficiency. Other parts of the 3-zone furnace were at 310 <sup>o</sup>C constantly. This was a counter-measurement for the condensation of glycerol.

Two cold traps (components labeled as 7a and 7b in the Figure 3) were used to condense water and any hydrocarbons that may be formed due to the side reactions. After the traps, the connection passes through soap bubble meter. This is a flow meter that is used

in order to measure the actual flow rate of any specific gaseous stream. Also, leak check and MFC calibrations were done by using the same soap bubble meter as well.

### 2.3.3 Product Analysis Section

In order to analyze the products, two gas chromatographs (GCs) were used in order to find out the composition of gaseous product stream.

One of the gas chromatographs was a Shimadzu GC-2014. This chromatograph also had a thermal conductivity detector (TCD) and a permanent gas column. Other gas chromatograph was a Shimadzu GC-8A. A TCD was also equipped with this chromatograph, although, instead of a permanent gas column, there was a Porapak Q column. Specifications of the two chromatographs are listed below in Table 1:

	Shimadzu GC-2014	Shimadzu 8-A
	(GC-1)	(GC-2)
Carrier gas	Argon	Helium
Carrier gas flow rate (NmL	25	30
min <sup>-1</sup> )		
Material of the Column	Stainless Steel	Stainless Steel
Material of the Column	Molecular Sieve 5A	Porapak Q
Packing		
Width of the Column	2.1 mm	2.1 mm
Length of the Column	4.6 m	3 m
Temperature of the Column	50 °C	90 °C
Type of the Detector	Thermal Conductivity	Thermal Conductivity

Temperature of the Detector	150 °C	150 °C
Current of the Detector	50 mA	120 mA
Temperature of the Injector	80 °C	90 °C
Loop Volume of the Sample	1.3 mL	1.3 mL

Table 1: Specifications of the two chromatographs
# **Chapter 3**

# **Results and Discussion**

### **3.1 Catalytic Activity**

Reaction conditions for the catalytic activity experiments were as follows:

- Temperature = 1023 K,
- Pressure = 1 atm,
- CO<sub>2</sub>/G = 3 (Nml/min / Nml/min),
- Weight of the catalyst = 10 mg, r
- Reaction time = 5 h.
- The catalysts were reduced for 2 h in 40 Nml/min in pure H<sub>2</sub> before the reaction.

1 wt.% Ru/LZ catalyst was used as a benchmark catalyst. Additional control experiments were also carried out using the AZT70 support material (i.e., without active metal centers) and using a blank reactor. Figure 6 summarizes the corresponding H<sub>2</sub>, CO and H<sub>2</sub>/CO product yields, while Figure 7 illustrates the CO<sub>2</sub> and glycerol (i.e., reactant) percent conversion values. distribution of hydrocarbon-based products such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> are also shown in Figure 8. In addition, relative performance of the investigated catalysts for 10 mg catalyst weight in the 5 h stability tests are also depicted in Figure 9. Furthermore, the influence of catalyst mass on the reactant conversions and non-hydrocarbon products

(H<sub>2</sub>, CO and H<sub>2</sub>/CO) are presented in Figure 10, and Figure 11, respectively. Effect of the catalyst weight on the stability tests are also shown in Figure 12.

Figures 6 and 7 clearly indicate that neither the pure AZT 70 support material (which lacks any active metal center) nor the blank reactor has any significant CO<sub>2</sub> or glycerol conversion, suggesting that the process is mostly catalytic.



Figure 6: H<sub>2</sub> and CO product yields for the investigated catalysts (10 mg), support material (AZT70) without an active metal center, blank reactor and, theoretical equilibrium conversion values.



Figure 7: CO<sub>2</sub> and glycerol conversion results for the investigated catalysts (10 mg), support material (AZT70) without an active metal center, blank reactor and, theoretical equilibrium conversion values.



Figure 8: Hydrocarbon product yields for the investigated catalysts (10 mg), support material (AZT70) without an active metal center, blank reactor and, theoretical equilibrium conversion values.



Figure 9: Stability experiments for the investigated catalysts (10 mg) (in terms of CO<sub>2</sub> conversion).



Figure 10: Reactant conversion results for the 0.1wt.% Ru/AZT70, RuNi/AZT70 and RuCo/AZT70 catalysts with two different catalyst amounts (10 mg and 20 mg).



Figure 11: Product yields for the the 0.1wt.% Ru/AZT70, RuNi/AZT70 and RuCo/AZT70 catalysts with two different catalyst amounts (10 mg and 20 mg).



Figure 12: Stability experiments for the catalysts 0.1wt.% Ru/AZT70, 0.1wt.%Ru + 0.4wt.%Ni/AZT70, 0.1wt.%Ru + 0.4wt.%Co/AZT70 and equilibrium in terms of CO<sub>2</sub> Conversions

The benchmark catalyst 1 wt.% Ru on LZ was the most successful catalyst so far in the literature, with 15% CO<sub>2</sub> conversion<sup>[64]</sup>. However, as can be seen from Figure 7, 1 wt.% Ru on AZT70 catalyst gave excellent results with a CO<sub>2</sub> conversion of 19%, exceeding the earlier success of the benchmark catalyst. Furthermore, the 0.5 wt.% Ru/AZT70 catalyst gave interesting results as well. Metal loading has decreased to half when going from 1 wt.% Ru to 0.5 wt.% Ru, but the activity decreased only by a factor of ca. 0.22. As the catalyst activity increased, product selectivity shifted towards to the products with less hydrogen (H<sub>2</sub>, CO) and water, which can be seen in Figures 6 and 7. When only the monometallic catalysts were compared, as expected, decreasing metal loading decreases the reactant conversion values and product yields (Figures 6 and 7). Accordingly, 0.1 wt.% Ru/AZT70 had a CO<sub>2</sub>

conversion value of 4 %. Interestingly, conversion values of the 0.5 wt.% Ru/AZT70 catalyst were much closer to the 1 wt.% Ru catalyst than it is to 0.1 wt.% Ru catalyst.

As Ru metal loading increased, syngas production increased (Figure 6), whereas the hydrocarbon production decreased (Figure 8). Also, the comparison between 1 wt.% Ru/AZT70 and the benchmark catalyst (1 wt.% Ru/LZ) suggested that 1 wt.% Ru/AZT70 catalyst showed greater CO<sub>2</sub> and glycerol conversions (Figure 7) with a slightly larger methane conversion (Figure 8). In contrast, ethane production was greater for the 1 wt.% Ru/LZ benchmark catalyst (Figure 8). Syngas production for the 1 wt.% Ru/LZ and 1 wt.% Ru/AZT70 catalysts was very close to each other, with a slightly larger values for 1 wt.% Ru on AZT70 catalyst (Figure 6).

When it comes to the bimetallic catalysts, the results were slightly unexpected. From the previous studies, it was known that Ru and Ni were both active metals in GDR reactions, while Co was less active.<sup>[30-36]</sup> 0.1 wt.% Ru + 0.4 wt.% Ni/AZT70 bimetallic catalyst resulted in H<sub>2</sub> product yield almost as high as the 0.5 wt.% Ru/AZT70 catalyst (Figure 6). This bimetallic Ni catalyst also resulted in the largest H<sub>2</sub>/CO value among the currently investigated catalysts (Figure 6). This may be related to the total active metal amount on the <sup>1</sup> 0.1 wt.% Ru + 0.4 wt.% Ni/AZT70 bimetallic catalyst.

Bimetallic 0.1 wt.% Ru + 0.4 wt.% Co/AZT70 catalyst showed greater stability in the 5 h stability tests (Figure 9) and gave greater CO<sub>2</sub> conversion when compared to the 0.1 wt.% Ru + 0.4 wt.% Ni/AZT70 bimetallic catalyst. From Figure 9, it can be seen that the CO<sub>2</sub> conversion was much more stable for 1 wt.% Ru on AZT70, 0.5 wt.% Ru on AZT70, and 0.1 wt.% Ru + 0.4 wt.% Co on AZT70 catalysts as compared to 0.1 wt.% Ru + 0.4 wt.% Ni/AZT70 bimetallic catalyst and 0.1 wt.% Ru/AZT70 monometallic catalyst. 0.1 wt.% Ru + 0.4 wt.% Ni on AZT70 seemed to be slightly exceeding te corresponding thermodynamic limits for the glycerol conversion (Figure 9). This was probably an experimental error caused by the low metal loading of the catalysts. Due to the sudden increase in the hydrocarbon yields, glycerol conversion calculation method gives a result that is above the thermodynamic limits.

The activities, product yields and reactant conversions of the 0.1 wt% Ru/AZT70, 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 and 0.1 wt.% Ru + 0.4 wt.% Co/AZT70 catalysts were further investigated in order to understand the bimetallic promotional effects.

When the reactant conversions for the 0.1 wt% Ru/AZT70, 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 and 0.1 wt.% Ru + 0.4 wt.% Co/AZT70 catalysts were investigated as a function of catalyst weight (Figure 10), it is seen that 0.1 wt.% Ru/AZT70, showed an almost linear increase in CO<sub>2</sub> with the increasing catalyst amount (i.e., from 4% to 9%). 0.1 wt.% Ru + 0.4 wt.% Co/AZT70 bimetallic catalyst also showed a similar trend. In stark contrast, 0.1 wt% Ru/AZT70, 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 bimetallic catalyst revealed an increased conversion of a factor of ca. 5 upon doubling catalyst mass..

It can be realized in Figure 11 that in the 10 mg measurements, 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 bimetallic catalyst containing significantly lower Ru loading and the 0.5 wt.% Ru/AZT70 catalyst containing significantly more Ru active sites had almost the same amount of H<sub>2</sub> production. Figure 10 indicates that although, the CO<sub>2</sub> conversion of the 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 bimetallic catalyst for 10 mg was well below expectations (i.e., 2%). When the catalyst amount increased to 20 mg, CO<sub>2</sub> conversion increased to 11.50%, i.e., almost by a factor of 5 (Figure 10). This latter conversion value was

significantly higher than that of the 0.5 wt.% Ru/AZT70 catalyst (Figure 6). When the costs of the two catalysts are compared, 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 bimetallic catalyst production cost was almost 1/5 of the 0.5 wt.% Ru/AZT70 catalyst.

The stability experiments also showed that all three catalysts, especially 0.1 wt% Ru + 0.4 wt.% Ni /AZT70 bimetallic one, had good stability when the catalyst amount was increased to 20 mg (Figure 12).

#### **3.2 Characterization of the Support Material**

#### **3.2.1 Raman Experiments**

Vibrational structure of the synthesized support materials were investigated via Raman spectroscopy. Raman signals corresponding to various AZT support materials (Figure 13) are assigned as follows: the broad shoulder 146 cm<sup>-1</sup> peak can be attributed to multiple structures such as rutile TiO<sub>2</sub>, anatase TiO<sub>2</sub>, tetragonal ZrO<sub>2</sub>, and less likely to rutile TiO<sub>2</sub>, 270 cm<sup>-1</sup> and 458 cm<sup>-1</sup> are assigned to tetragonal ZrO<sub>2</sub>. 335 cm<sup>-1</sup> and 559 cm<sup>-1</sup> peaks that are much more evident in the lowest ZrO<sub>2</sub> composition support, i.e., AZT30, are related to the monoclinic ZrO<sub>2</sub> whereas 458 cm<sup>-1</sup> and 851 cm<sup>-1</sup> peaks can be identified as rutile TiO<sub>2</sub> peaks. The peak at 784 cm<sup>-1</sup> is also visible in the AZT30 case and belongs to anatase TiO<sub>2</sub>. <sup>[43,45,46]</sup>

When the pure  $TiO_2$  is considered, the phase of the material changes from anatase to rutile when the temperature is increased between 873 K and 973 K.<sup>[65]</sup> Rutile phase is the

thermodynamically stable one and anatase phase is a metastable phase. Once the phase is transformed into rutile by the elevated temperatures, this transformation is irreversible.<sup>[65]</sup>

The phase changes in ZrO<sub>2</sub> required much higher temperatures. Cubic ZrO<sub>2</sub> to Tetragonal ZrO<sub>2</sub> transition occurs around 2573 K. Also, Tetragonal ZrO<sub>2</sub> transforms to monoclinic ZrO<sub>2</sub> around 1273 K.<sup>[66]</sup>

In the case of AZT50 and AZT70 support materials, Figure 13 shows that rutile TiO<sub>2</sub> and tetragonal ZrO<sub>2</sub> are the prominent phases. These results are in good agreement with the literature values for AZT70.<sup>[43]</sup> Figure 13 indicates that decreasing Zr content of the AZT support material (note that Zr content decreases in the following order AZT70 > AZT50 > AZT30), monoclinic ZrO<sub>2</sub> and anatase TiO<sub>2</sub> features strengthen while rutile TiO<sub>2</sub> peaks diminish. The 1093 cm<sup>-1</sup> peak that is slightly there for AZT50 and fully grown in AZT30 is yet to be determined, still under investigation.



Figure 13: Raman Spectra of Different AZT Support Materials



Figure 14: Raman spectra of cubic, monoclinic, and tetragonal  $ZrO_2$  <sup>[45]</sup>



Figure 15: Raman Spectra of Bulk TiO<sub>2</sub> and Ti/Al Mixture at different temperatures<sup>[46]</sup>

#### **3.2.2 XRD Experiments**

XRD analysis of the prepared AZT30, AZT50, and AZT70 support materials given in Figure 8 showed us that we have a mostly disordered crystal structure . This is also consistent wit the former studies in the literature, as AZT materials showed amorphous behavior up to a calcination temperature of 1073 K.<sup>[42,43]</sup>



Figure 16: XRD patterns of various AZT support materials.

#### **3.2.3 BET Experiments**

From the BET analysis that is shown in Figure 17, it was observed that as the  $ZrO_2$  content of the support materials increases, SSA values also increase. These SSA values are in good agreement with the literature values.<sup>[47]</sup>



Figure 17: BET specific surface area analysis of different AZT support materials.

#### **3.2.4 XPS Experiments**

O1s XPS spectra of the AZT support materials reveal two main signals at 530.0 eV and 532.2 eV as can be seen in Figure 18.

Fun et al., Kumar et al. and Lackner et al. reported O1s signals in XPS for the M-O interactions in TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>, support materials located at 530.0-531.0 eV.<sup>[48-50]</sup> In these reports, M-OH interactions for the same materials were also reported to be between 532.0-533.0 eV.

Thus, in Figure 18, the peak at 530.0 eV is probably an overlapping signal due to Al-O, Ti-O and Zr-O features consistent with the presence of a disordered mixed oxide structure evident in the current XRD data (Figure 16). The other peak, at 532.2 eV due to surface hydroxyl functionalities is not present in the AZT70 case, and starts to grow when the Zr concentration decreases, or, as the Ti concentration increases. Thus, it apparent that surface hydroxyls are more expressed for lower Zr or higher Ti loadings. This argument is also in agreement with the Zr3d XPS spectra that will be shown in the forthcoming sections.



Figure 18: O1s XPS spectra of the different AZT support materials.

In the C1s XPS spectra of the different AZT support materials given in Figure 19, we can identify three distinct features, which are located at 284.2, 285.7, and 287.5 eV. These peaks correspond to C=C, C-OH, and C=O surface functionalities, respectively.<sup>[51,52]</sup> Not that these different surface carbon functionalities may originate from synthetic residues of the support precursors; Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Zr[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> and Al(OCH[CH<sub>3</sub>]C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>.



Figure 19: C1s XPS spectra of the different AZT support materials.

Al2p XPS spectra of the different AZT support materials reveal two peaks at 72.4 eV and 75.5 eV which can be seen in Figure 20. These peaks should not be mistaken with the spin-orbit splitting peaks of Al2p, since the spin orbit splitting of Al2p is very small (~0.4 eV) and cannot be resolved with the current XPS system. Thus, one can argue that, these peaks are due to two different Al<sup>3+</sup> species with different coordinations and chemical environments.<sup>[49]</sup>



Figure 20: Al2p XPS spectra of the different AZT support materials.

For the Ti2p spectra of the different AZT support materials that can be seen in Figure 21, the literature values for spin-orbit splitting of Ti2p are ca. 5.6 - 6.0 eV. In our case, the splitting values are consistent with the literature values. Peaks 457.7 eV and 463.3 eV correspond to spin-orbit splitting of Ti<sup>3+</sup>. 457.7 eV is Ti<sup>3+</sup>2p<sub>3/2</sub> and 463.3 eV is Ti<sup>3+</sup>2p<sub>1/2</sub> with a splitting of 5.6 eV. Peaks 460.9 eV and 466.3 eV correspond to spin-orbit splitting of Ti<sup>4+</sup>. 460.9 eV is Ti<sup>4+</sup>2p<sub>3/2</sub> and 466.3 eV is Ti<sup>4+</sup>2p<sub>1/2</sub> with a splitting of 5.4 eV.<sup>[53]</sup> From the Ti 2p XPS spectra, we can see that the highest Ti<sup>3+</sup> content is in the AZT70 and highest Ti<sup>4+</sup> content is in the AZT50 support. In AZT30, however, the Ti<sup>3+</sup> is comparable to Ti<sup>4+</sup>. Variation in

surface composition of different AZT support materials is expected to influence GDR reactivity.



Figure 21: Ti2p XPS spectra of the different AZT support materials.

In Zr3d XPS spectra of the different AZT support materials, there are three major peaks that can be seen in Figure 22 at 180.7, 182.3, and 183.4 eV. The literature values for the Zr3d<sub>5/2</sub> features are typically found at; ZrO<sub>x</sub> ~ 181.0 eV, ZrO<sub>2</sub> ~ 182.0 eV and Zr(OH) ~ 183.0 eV.<sup>[54]</sup> Hence, the 182.3 eV peak that can be seen in the spectra of AZT70, corresponds to Zr<sup>4+</sup>3d<sub>5/2</sub>. The peak at 183.4 eV is related to to Zr-OH and the 180.7 eV peak may be associated to Zr<sup>3+</sup>3d<sub>5/2</sub>. Thus, higher Zr concentration results in enhancement of Zr<sup>4+</sup> species while weakening the Zr-OH functionalities (as in the AZT70 spectra). As the Zr content of

AZT system decreases (e.g., AZT50 and AZT30),  $Zr^{3+}$  and Zr-OH functionalities increase (e.g., AZT50 and AZT30). The observation regarding the relationship between Zr content of the AZT system and the surface hydroxyls is also in good agreement with the O1s XPS data that was shown earlier.



Figure 22: Zr3d XPS spectra of the different AZT support materials.

# **3.3 Characterization of the Active Sites**

### **3.3.1 SEM - EDX Experiments**

From the SEM image of 1wt.% Ru on AZT70 in Figure 23, it is clear that this sample has no definite morphology and reveals an amorphous topography. Lack of well-define ordered crystallites are also in good agreement with the corresponding XRD data which is shown in the forthcoming sections (Figure 33).



Figure 23: SEM Image of 1wt. % Ru on AZT70.

EDX analysis of the 1wt. % Ru on AZT70 enabled the determination of the relative amounts and existence of Al, Zr, Ti, and Ru species (Figure 24).



Atomic % by Eleme <del>nt</del>							
Filename	СК	οк	AIK	ZrL	RuL	TiK	
genspc.spc	58.86	32.52	6.25	1.46	0.04	0.87	

Figure 24: EDX analysis of 1 wt.% Ru on AZT70.

SEM images of 0.5 wt.% Ru on AZT70 given in Figure 25 showed similar features to that of 1 wt.% Ru on AZT70 which are in good agreement with the XRD data for 0.5 wt.% Ru on AZT70 that will be shown in section 3.3.2 in Figure 33.



Figure 25: SEM Image of 0.5 wt% Ru on AZT70 Sample

EDX analysis of the 0.5 wt% Ru on AZT70 sample (Figure 26) verified the existence of Al, Zr and Ti species, however, Ru was close to the detection limit of the instrument.



Figure 26: EDX Analysis of 0.5 wt% Ru on AZT70.

SEM image of 0.1 wt.% Ru on AZT70 that is shown in Figure 27 indicates a sample that has no definite morphology, in line with the corresponding XRD data for this sample that will be shown in section 3.3.2 in Figure 33.



Figure 27: SEM Image of 0.1 wt% Ru on AZT70.

EDX analysis of the 0.1 wt% Ru on AZT70 sample justified the presence of Al, Zr and Ti species, however, Ru was below the detection limit of the instrument (Figure 28).



Figure 28: EDX Analysis of 0.1 wt% Ru on AZT70 Sample.

SEM image of 0.1wt.% Ru + 0.4wt.% Ni on AZT70 shown in Figure 29 also reveals no definite morphology, consistent with the corresponding XRD data shown in section 3.3.2 in Figure 33.



Figure 29: SEM Image of 0.1 wt% Ru + 0.4 wt% Ni on AZT70.

EDX analysis of the 0.1 wt% Ru + 0.4 wt% Ni on AZT70 sample showed the presence of of Al, Zr and Ti species. However, Ru was below and Ni was close to the detection limit of the instrument (Figure 30).



Figure 30: EDX Analysis of 0.1 wt% Ru + 0.4 wt% Ni on AZT70.

SEM image of 0.1 wt.% Ru + 0.4 wt.% Co on AZT70 shown in Figure 31 indicates, no definite morphology in line with the corresponding XRD data shown in section 3.3.2 in Figure 33.



Figure 31: SEM Image of 0.1 wt% Ru + 0.4 wt% Co on AZT70.

EDX analysis of the 0.1 wt% Ru + 0.4 wt% Co on AZT70 sample revealed signals due to Al, Zr and Ti species. However, Ru was below and Co was close to the detection limit of the instrument (Figure 32).



Figure 32: EDX Analysis of 0.1 wt% Ru + 0.4 wt% Co on AZT70.

## 3.3.2 XRD Experiments

In the literature, XRD lines for the Ru particles may be observed at 2-theta values of 28, 35 and 54°.<sup>[59]</sup> On the other hand, as shown in the XRD patterns of the catalysts given in Figure 26, no well-defined diffraction line is detected on any of the catalysts suggesting

an amorphous and a disordered crystal structure. Lack of Ru, Ni, and Co XRD lines implies a high dispersion and small average particle sizes for the active sites.



Figure 33: XRD patterns of full catalyst formulations containing different active sites.

#### 3.3.3 Raman Experiments

Mar et al. reported 3 different  $RuO_x$  related peaks in their Raman spectroscopic studies.<sup>[60]</sup> First of these peaks was located at around 520 cm<sup>-1</sup> and belonged to a sharp and intense  $E_g$  mode. The second peak was located at around 640 cm<sup>-1</sup> and corresponded to an

 $A_{1g}$  mode with a much lower intensity than that of the  $E_g$  mode. The third and final peak was due to  $B_{2g}$  mode observed around 710 cm<sup>-1</sup> with an extremely tiny intensity In our Raman spectra in Figure 34, these relatively less prominent Ru related peaks between 500-700 cm<sup>-1</sup> overlap with the strong M-O signals of the AZT support material. Accordingly, peaks at 163, 248, 426 and 824 cm<sup>-1</sup> can be assigned to the AZT support material as discussed in the earlier chapter.



Figure 34: Raman spectra of monometallic active sites on the AZT70 support.

Hou et al. investigated the Raman signatures of Ni-Co-O containing materials. They identified two Raman active peaks for the  $NiO_x$  species within 500-800 cm<sup>-1</sup>. One of them was around 530 cm<sup>-1</sup> and the other one was located at 680 cm<sup>-1</sup>. For the CoO<sub>x</sub> material, three different Raman peaks were observed at 455, 513, and 660 cm<sup>-1</sup>.

In the Raman spectra of bimetallic active sites in Figure 28, Raman peaks that may be related to Ru, Ni and Co are in the region between 450-750 cm<sup>-1</sup>.<sup>[60-61]</sup> The peaks are highly convoluted and overlapping. The rise of the intensity of 400-900 cm<sup>-1</sup> region may be due to the NiO<sub>x</sub> / CoO<sub>x</sub> peaks but there is no clear evidence because of the low Ni/Co loading. Peaks at 163, 248, 426 and 824 cm<sup>-1</sup> are related to the support material and discussed in the earlier chapter.



Figure 35: Raman spectra of bimetallic active sites on AZT70 support.

#### **3.3.4 ICP-MS Experiments**

We also determined the bulk elemental compositions of the synthesized catalysts via ICP-MS analyses. As can be seen in Figure 29, bulk elemental compositions of the synthesized materials obtained by ICP-MS were consistent with the nominal synthetic metal-loadings. Standard deviations for the 5 replicate ICP-MS measurements for each sample were as follows:  $\pm 0.03$  % for Ru measurements,  $\pm 0.01$  % for Ni measurements and  $\pm 0.01$  % for Co measurements.



Figure 36: ICP-MS analysis for the quantification of the active metal sites of the synthesized catalysts.
## 3.3.5 In-Situ FTIR CO Adsorption Experiments

CO adsorption via in-situ FTIR spectroscopy was utilized to obtained detailed insight regarding the oxidation state and the relative particle size of the active metal centers of the currently synthesized GDR catalysts. The probe molecule, CO, can bind onto the Ru sites in many different ways. Examples of some of these adsorption configurations are shown below in Figure 30:



Figure 37: Various types of CO adsorption configurations on Ru.

Chin et al. performed <sup>[62]</sup> FTIR studies on CO adsorption on Ru catalysts and a total of 11 different CO adsorption configurations were deduced from the FTIR spectra. Support materials were Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Some of these features were attributed to metallic Ru sites whereas there were also oxidized Ru particles/clusters that bound to the probe molecule. Upon increasing the temperature (from 323 K to 573 K), some of the linearly adsorbed and tricarbonyl bonding sites were observed to be lost.<sup>[62]</sup>

Mcquire et al. also reported an experimental FTIR study on CO adsorption on Ru catalysts supported on TiO<sub>2</sub>.<sup>[63]</sup> Temperature was 553 K and the results gave only two peaks related to CO adsorption. There was no evidence related to bridged metal carbonyls in the spectra. This raised the question of different bonding patterns and intensities of CO on different supports.<sup>[63]</sup>

In our current studies, prior to in-situ FTIR analysis (Figure 38), catalysts were reduced at 873 K under 10 Torr of H<sub>2</sub> for 1 h and then surface of the catalysts were cleaned at 873 K under vacuum for 30 min. Then, 20 Torr of CO was dosed at 323 K. Gas phase and in vacuum sample spectra were collected. In vacuum, sample spectra were collected after 1 min, 5 min and 10 min of the introduction of CO. There were 6 different peaks in the spectra related to the probe molecule, CO (Figure 38). Identifications of these peaks were done using the literature studies <sup>[63,68-70]</sup>. Two peaks at 1994 and 2064 cm<sup>-1</sup> are due to the dicarbonyl CO species on Ru<sup>0</sup> (Figure 38). At 2023 cm<sup>-1</sup> there is a peak that can be identified as linearly adsorbed CO on Ru<sup>0</sup> (Figure 38). At 2119 and 2173 cm<sup>-1</sup> there was a peak related to the linearly adsorbed CO on Ru<sup>n+</sup> and at 2131 cm<sup>-1</sup> the peak corresponds to the tricarbonyl CO species on Ru<sup>n+</sup> (Figure 38).

Furthermore, Figure 38 shows that 2023, 2119 and 2173 cm<sup>-1</sup> peaks that are related to linearly adsorbed CO on Ru<sup>0</sup> and Ru<sup>n+</sup> are well resolved for the 1 wt.% Ru on AZT70 catalyst and starts to disappear once the metal loading decreases. Also, the close similarity between 0.5 wt.% Ru on AZT70 and 0.1 wt.% Ru + 0.4wt.% Ni on AZT70 data is another observation that can be further investigated. These two in-situ FTIR spectra are almost identical to each other.

From Figure 38, it can be seen clearly that the shapes and FWHM of the peaks are changing as the metal loading changes. For the higher Ru loadings, we have broad futures around dicarbonyl and linearly adsorbed peaks. This observation is consistent with the presence of large Ru/RuO<sub>x</sub> nanoparticles. Large Ru/RuO<sub>x</sub> nanoparticles reveal high-coordination sites for CO adsorption and broader IR futures.

When we decrease the Ru loading, we start to observe smaller Ru clusters on the support. CO binds to these clusters very similarly (Figure 38). This similarity decreases the FWHM of the peaks, resulting in sharper peaks, as can be seen at 2065 cm<sup>-1</sup> and 1994 cm<sup>-1</sup>. Thus, higher Ru loadings lead to broad features whereas low Ru loadings lead to well defined features in the FTIR spectra. For high Ru loadings, majority of the particles are nanoparticles and there is a minority of clusters. In low Ru loadings, majority of the Ru/RuO<sub>x</sub> species are in the form of small (possibly sub-nanometer size) clusters and and bigger (> 1 nm) nanoparticles exist as minority species. Furthermore, Figure 31 indicates that there exist more than one oxidation state for Ru species (i.e., Ru<sup>x+</sup> and Ru<sup>0</sup>) on the surface of Ru/AZT catalysts.



Figure 38: In-situ FTIR CO adsorption measurements for the active sites

## **Chapter 4**

## Conclusion

In the current study, three different ternary oxide support materials, Ru monometallic catalysts with various metal loadings and Ru-Ni and Ru-Co bimetallic catalysts were synthesized, structurally characterized and tested in "Glycerol Dry Reforming" catalytic performance tests.

Three different ternary oxide (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>) support materials with different compositions were synthesized by sol-gel method and calcined at 1023 K under air. In all of the three supports, Al<sub>2</sub>O<sub>3</sub> mole percent was kept constant as 50% and ZrO<sub>2</sub> over TiO<sub>2</sub> relative ratio was changed from 70% to 50% and 30%. Raman spectroscopic analysis showed that as the Zr content of the AZT system decreased, monoclinic-ZrO<sub>2</sub> and anatase-TiO<sub>2</sub> phase became more dominant, while for the higher ZrO<sub>2</sub> loadings, tetragonal-ZrO<sub>2</sub> and rutile-TiO<sub>2</sub> were the prominent phases. XRD analysis suggested that, all three supports exhibited amorphous and disordered crystal structures. BET specific surface are values for the AZT30, AZT50 and AZT70 supports were measured to be 170, 181, and 197 m<sup>2</sup>/g, respectively. Thus, increasing ZrO<sub>2</sub> composition resulted in an increase in the specific surface are of the samples.

XPS O1s analysis of the AZT support materials indicated that as the Zr content of the AZT system decreased, M-OH features grew in intensity. Thus, surface hydroxyls were more expressed on the AZT system for lower ZrO<sub>2</sub> or higher TiO<sub>2</sub> loadings. Al2p XPS data revealed that there were two different  $Al^{3+}$  species with different coordination on the AZT surface. Similarly, at least two different Ti species were detected in Ti2p XPS measurements on the AZT support surfaces (namely; Ti<sup>4+</sup> and Ti<sup>3+</sup>) AZT70 had the highest Ti<sup>3+</sup> content whereas AZT50 had the highest Ti<sup>4+</sup> content. For high Zr content, Zr<sup>4+</sup> species dominated the surface with a minuscule contribution from Zr-OH species. In contrast, lower Zr content lead to the prominence of Zr<sup>3+</sup> surface species and surface M-OH functionalities.

Before the characterization experiments, synthesized catalyst samples were reduced at 773 K under H<sub>2</sub> for 2 h followed by a second reduction step at 1073 K under H<sub>2</sub> for 2 h.

SEM images for the catalyst samples revealed that the materials as having disordered morphology with no well-defined crystallites. Presence of Al, Zr, Ti, O, Ni, Co in the catalyst composition was verified via EDX analysis. Ru was also detectable for 1 wt% Ru loading but was close to/below the detection limit for lower Ru loadings.

XRD analysis of the catalyst samples with Ru, Ru+Ni, and Ru+Co active sites revealed an amorphous structure with no ordered crystalline phases. Lack of Ru/RuO<sub>x</sub> related XRD signals were consistent with small Ru particle size and good Ru dispersion on the AZT support materials. Amount of active sites on the catalyst surfaces were also quantitatively verified via ICP-MS analysis. Bulk elemental compositions obtained by ICP-MS were consistent with nominal synthetic metal-loadings with standard deviations of  $\pm 0.03$ for Ru,  $\pm 0.01$  for Ni and  $\pm 0.01$  for Co.

CO Adsorption via in-situ FTIR provided insight on the Ru active sites. It was observed that as the active metal loading increased, Ru particle size increased leading to broader, convoluted IR peaks. Likewise, as the metal loading decreases, Ru/RuO<sub>x</sub> species existed in the form of sub-nanometer size clusters rather than nanoparticles, which resulted in sharper, narrower IR peaks for the adsorbed CO. Also, more than one Ru oxidation state were detected for Ru sites (i.e., Ru<sup>n+</sup> and Ru<sup>0</sup>). In-situ FTIR spectra of RuNi bimetallic catalyst and 0.5 wt.% Ru monometallic catalyst showed a similarity, which can be correlated with the similar activities of these two catalysts.

GDR catalytic performance tests were carried out under the following typical conditions: T = 1023 K, P = 1 atm,  $CO_2/G = 3$  (Nml/min / Nml/min), weight of the catalyst = 10 or 20 mg, reaction time = 5 h. The catalysts were reduced for 2 h in pure H<sub>2</sub> flow (40 Nml/min) before the reaction.

Catalytic activity tests revealed that:

- 1 wt.% Ru/AZT70 catalyst is the most active catalyst in the literature, with a CO<sub>2</sub> conversion of 19%. This value outperforms the CO<sub>2</sub> conversion of the former best catalyst in the literature (1 wt.% Ru/LZ) by ca. 3%.
- 0.5 wt.% Ru/AZT70 catalyst, despite of its lower metal loading with respect to 1 wt.% Ru/AZT70, had a CO<sub>2</sub> conversion of 15%.
- Both 0.1 wt.% Ru/AZT70 and 0.1 wt.% Ru + 0.4 wt.% Co catalysts revealed 4% and 9% CO<sub>2</sub> conversions for 10 mg and 20 mg catalyst weight, respectively.
- 0.1 wt.% Ru + 0.4 wt.% Ni /AZT70 catalyst, exhibited a six-fold increase in activity (from 2% to 12%) when the catalyst amount was changed from 10 mg to 20 mg.
- All the catalysts had good stability in the 5 h stability tests, except for the 0.1 wt.% Ru + 0.4wt.% Ni /AZT70 catalyst in the 10 mg experiment, which showed a sudden decrease in the activity after the first 1 h.

- Unexpectedly, 0.1 wt.% Ru + 0.4 wt.% Co / AZT70 catalyst showed notable stability in 5 h stability tests..
- 0.1 wt.% Ru + 0.4 wt.% Ni / AZT70 catalyst's H<sub>2</sub> production yield and CO<sub>2</sub> conversion were comparable to that of 0.5 wt.% Ru / AZT70, despite the fact that Ru metal loading was decreased by 80% in the former catalyst. This observation, together with the very similar in-situ FTIR CO Adsorption spectra of the two catalysts, suggest that, RuNi bimetallic catalysts can be used in the GDR process as active and cost-efficient catalysts.

In the future, different types of RuNi bimetallic and 0.5 wt.% Ru monometallic catalysts will be examined in order to have an insight on the bimetallic cost-efficient catalysts. Also, AZT30 and AZT50 supports will be used to synthesize analogous catalysts and will be tested in the GDR catalytic activity tests.

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