LOW-TEMPERATURE WATER-GAS SHIFT REACTION WITH Ru/TiO₂ AND Ru/Al₂O₃ CATALYSTS

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ABSTRACT

This study investigates the catalytic performance of Ru/TiO₂ and Ru/Al₂O₃ in the water-gas shift reaction (WGS) at low temperatures. The catalysts were prepared and characterized, and their properties were related to their performances. The catalytic activity was determined with the WGS reaction, using the feed gas with 11% CO, 22.72% H₂O, and 66.28% argon at 453–573 K. In presence of the Ru/Al₂O₃ catalyst, it was found that the water feeding content led to beneficial effects on the catalytic activity. An 82% CO conversion was achieved in the WGS processing with the Ru/TiO₂ catalyst, under steady state, at 573 K.

KEYWORDS

water-gas shift reaction; catalysts; low temperatures

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1. INTRODUCTION

The water-gas shift reaction (WGS) is used traditionally for the production of hydrogen and syngas, which are applied in the synthesis of several industrial intermediates (i.e. ammonia and methanol). In addition, there is a growing demand for the use of hydrogen to be consumed in Fischer-Tropsch synthesis and fuel cells (Byron Smith et al., 2010).

Equation (1) represents the process WGS as an exothermic reaction ($\Delta H_{298K}^{\circ} = -41.1 \text{ kJmol}^{-1}$), operating relatively slowly and reversibly. The reaction thermodynamics predicts limited equilibrium conversions at elevated temperatures, while it can reach high conversions at lower temperatures, although with the disadvantage of slow kinetics (Pérez et al., 2016).

Two catalysts are used to promote the WGS reaction. Oxides of iron and chromium are the high temperature catalysts, used in operations at the range of 673–773 K. These systems have two main disadvantages: low activity and thermodynamic limitations leading to rapid sintering. The low temperature catalysts based on copper, zinc oxide, and alumina, have been used traditionally in operations at the range of 473–673 K (Luengnaruemitchai et al., 2003; Jeong et al., 2014). The copper catalysts have disadvantages such as being susceptible to sulfur poisoning, having pyrophoric properties, and needing preconditioning under intermittent operations (Ruettinger et al., 2003).

According to Pazmiño et al. (2012), noble metal catalysts are attractive materials to process WGS at low temperatures. They offer higher stability during start and closing cycles (start up and shutdown) than the conventional catalysts. Furthermore, these catalysts are stable to air and have tolerance to impurities such as sulfur (Liu et al., 2012).

In the search of a catalyst active and stable at a low temperature, precious metals such as Au and platinum group metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum) have been studied, using the supports CeO_2 , ZrO_2 , Al_2O_3 ,

and TiO_2 . This paper reports the results of activity studies at low temperature for WGS reaction. The catalysts Ru/TiO_2 and $\text{Ru/Al}_2\text{O}_3$, prepared and characterized, were evaluated.

2. MATERIAL AND METHODS

2.1 Catalyst preparation

The ruthenium catalysts (2 wt% Ru/TiO_2 and 2 wt% $\text{Ru/Al}_2\text{O}_3$) were prepared using the wet incipient impregnation method. The materials used for the preparation of the catalyst were titanium dioxide (Evonik, Brazil) and alumina (Oxiteno, Brazil) as supports, and the precursor salt of the active phase was $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich, Germany). First, the metal salt was dissolved in water and, then, the support (TiO_2 or Al_2O_3) was added and completed for 0.50 L. The impregnation process was performed under continuous stirring, for 48h. The solid material was then dried at 60 °C for 24h. After drying, the catalyst was reduced in presence of an equimolar gas mixture (H_2 , N_2 , 0.025 Lmin^{-1}) at 400 °C, for 3 hrs.

2.2 Catalyst characterization

Structural and textural characteristics were investigated using the BET (BELSORP II / BEL) method for specific surface area and pore volume, DRX (XRD-6000 Shimadzu Equipment) for identification of solid phases, SEM/EDX (SEM, FEI brand, Quanta 200 FEG, 200-30 kV) morphology, and FTIR (FTIR Bruker VERTEX 70 FT-IR) for surface chemical groups characteristic of the supports. All samples were used to characterize the material prepared originated after the final reduction procedure.

2.3 Kinetic measurements

The kinetic data were obtained using an experimental unit equipped with a tubular stainless steel reactor of internal diameter of 0.006 m and a height of 0.150 m. The operations were conducted for three hours under atmospheric pressure and temperatures of 453, 493, 533, and 573 K, respectively. Water flow rate of 0.0015 h^{-1} was maintained using a syringe pump, while a CO flow rate of $1.50 \times 10^{-5} \text{ m}^3 \text{ h}^{-1}$ was introduced using a gas mixture consisting of 15 % CO in argon. The feed

Table 1. Textural characteristics of Ru/TiO₂ and Ru/Al₂O₃ catalysts.

Catalyst	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Mean Pore Size (Å)
Ru/TiO ₂	82.06	0.37	183.37
Ru/Al ₂ O ₃	260.16	0.53	81.70

ratio H₂O/CO was 2:1 molar. The concentrations of the reagents (CO, H₂O) and those of the reactor effluent (H₂, CO₂, CO, H₂O) were determined using a gas chromatograph equipped with a Porapak Q column and a thermal conductivity detector, operating with argon as carrier gas.

3. RESULTS AND DISCUSSIONS

3.1 Catalyst characterization

The orders of magnitude superficial specific area, pore volume, and average pore size of the catalyst Ru/TiO₂ and Ru/Al₂O₃ measured by nitrogen adsorption at 77 K are shown in Table 1. In general, the catalysts are prepared with supports having large surface areas, as an indication of

better dispersion of the active phase. The larger surface area of the catalyst Ru / Al₂O₃ is due to a greater number of small pores contained in a pore volume greater. Comparing the two catalysts, Ru/Al₂O₃ showed pore volume 40% larger than that of the catalyst Ru/TiO₂.

Figure 1 shows the XRD analyses of the catalysts. The XRD of the Ru/TiO₂ shows the presence of the solid phases anatase (JCPDS number 84-1286) and rutile (JCPDS number 01-1292). The brookite crystalline phase, another polymorph of TiO₂, was not identified. The main TiO₂ peaks are observed at 2θ = 25.31°, 37.67°, 47.95°, ascribed to the anatase phase (A), and peaks corresponding the rutile phase (R) are observed at 2θ = 27.48°, 36.10°, 56.57°. The peaks observed were compared with literature data and indicated that the materials were polycrystallines.

Figure 1. XRD pattern of Ru/TiO₂ and Ru/Al₂O₃ catalysts.

Figure 2. SEM images of Ru/TiO₂ catalyst a) magnified $\times 2500$; b) magnified $\times 5000$ and SEM image of Ru/Al₂O₃; c) magnified $\times 2500$; and d) magnified $\times 5000$.

The ruthenium particles, which were produced from the decomposition of RuCl₃·3H₂O, should be observed in the sample Ru/TiO₂ catalyst. As can be seen in Figure 1, TiO₂ is a mixture of anatase and rutile, and most of the Ru peaks are overlapped with rutile TiO₂. This makes it difficult to identify Ru from the TiO₂ support with XRD. The XRD pattern of the catalyst Ru/Al₂O₃ shows characteristic peaks of the support and the presence of metal with an intensity of 639.52, 726.61, and 763.84, which can be considered low. The peak corresponding to ruthenium in the metallic form centred on the Bragg angles 2θ were of 37.15°, 45.95°, and 66.89°, respectively.

The morphology of Ru/TiO₂ and Ru/Al₂O₃ were examined using the SEM. Figure 2 shows the SEM images magnified $\times 2500$ and $\times 5000$ for Ru/TiO₂ (2a, 2b) and Ru/Al₂O₃ (2c, 2d), respectively. It was not possible to identify Ru metal particles in the catalysts, only being possible to show the morphology of supports TiO₂ and Al₂O₃. In Figure 3 (a) and (b) are shown a semi-quantitative assessment of the elements present in the catalytic

system, being verified the presence of the supports and metal.

Figure 4 shows the FTIR spectrum of Ru/TiO₂ and Ru/Al₂O₃ catalysts in the wave length region 4000–500 cm⁻¹. Hydrogen bridges and crystallization water (3405 cm⁻¹) were observed in all stages in the preparation of both catalysts.

The band at 3465 cm⁻¹ is attributed to the O-H stretching, comprising contributions from (1) non-dissociated O-H species and (2) O-H species (dissociated from H₂O), both adsorbed. The vibration at 1620 cm⁻¹ represents the deformation (bending) of the OH stretch observed at 3405 cm⁻¹ (Delmastro et al., 1992; Marcos et al., 2006; Pereira et al., 2002; Phillipi et al., 1971; Rosário, 2012). The presence of this type of group on the surface of the material is seen as important for such groups have a major effect on the coordination of atoms on the surface, leading to different properties and energy states. These affect directly the stability of the crystalline form, as they depend on the energy balance between the surface

Figure 3. EDX spectra of the ruthenium catalyst a) Ru/TiO₂ and b) Ru/Al₂O₃.

Figure 4. IR spectrum of Ru/TiO₂ and Ru/Al₂O₃ catalysts.

and volume of the material, as previously shown (Castro, 2005; Marcos, 2006; Rosário, 2012).

The broad band at 1500–700 cm⁻¹ arises from Ti–OH and Ti–O for the Ru/TiO₂ catalyst, and Al–O–H and Al–O for the Ru/Al₂O₃ catalyst. 1300 cm⁻¹ corresponds to the OH groups present on the surface, and the region below 1000 cm⁻¹ is noted

as characteristic of metal–oxygen bonds (Boumaza et al., 2009; Brito, 2009; Rosário, 2012).

3.2 Catalytic activity

The Ru/Al₂O₃ and Ru/TiO₂ catalysts demonstrated a high activity for the water gas-shift reaction without methane production at

Figure 5. Catalytic activity of the Ru/TiO₂ and Ru/Al₂O₃ catalysts in the water-gas shift process in a fixed bed reactor. Conditions: catalyst mass 0.25 g, 101 325 Pa, 453–573 K, H₂O/CO = 2:1.

temperatures above 540 K. Figure 5 shows that at 573 K, the conversion (82%) obtained with the Ru/TiO₂ catalyst was close to that of the equilibrium curve predicted by thermodynamics, while at 453–493 K, conversions were below 30% for both catalysts. According [Basińska et al. \(1999\)](#), the average particle size of metallic ruthenium influence on the catalytic activity of the WGS reaction and the activity of the catalysts is related clearly to the kind of support used. Catalysts with TiO₂ support produce more H₂ than those with Al₂O₃ support. [Panagiotopoulou and Kondarides \(2004\)](#) investigated noble metals supported on TiO₂ in the WGS reaction, and showed that systems, including TiO₂ support for noble metals, possess greater activity at temperatures below 623 K. The researchers concluded that morphological and structural features appropriate for the support (high metal dispersion and small crystallite size of TiO₂) may be considered promising for processing the WGS reaction.

3.2.1 Effect of feed water vapour concentration

The WGS reaction thermodynamics shows unfavourable equilibrium at high temperatures.

Thus, to achieve higher conversions of CO under the conditions practiced, the water flow in the reactor feed was increased. To evaluate this effect, two feed streams were used: 11.36 % CO, 22.72 % H₂O, and 11.36 % CO, 45.45 % H₂O, with molar ratios of CO: H₂O/1:2 and 1:4.

Figure 6 shows the effect of the feed water vapour on CO conversion in presence of Ru/Al₂O₃ catalyst. The performance of the WGS process was improved when the molar ratio CO:H₂O was changed from 1:2 to 1:4. The CO maximum conversion increased from 75% to 85%, at 573 K, reaching the value predicted by the thermodynamics equilibrium. A linear relation between the conversion of CO and temperature was observed for each amount of fed water.

According to [Lund \(2002\)](#), the excess water vapour in the reactor feed, which operates the WGS, has two main effects: increased equilibrium conversion and coke formation. Since the reaction is mildly exothermic and typically occurs under adiabatic conditions by increasing the water in the reactant feed at a lower temperature, a higher catalyst bed is required ([Oliveira, 2012](#)).

Figure 6. Catalytic activity of the Ru/Al₂O₃ catalyst in the water-gas shift process in a fixed bed reactor. Effects of feed vapour water concentration. Conditions: catalyst mass 0.25 g, 101 325 Pa, 453–573 K.

Figure 7. Stability tests for Ru/TiO₂ catalyst in processing the WGS reaction in a fixed bed reactor. Conditions: catalyst mass 0.25 g, 101 325 Pa, 453 – 573 K, H₂O/CO = 2:1.

Luengnaruemitchai et al. (2003) evaluated the effect of CO and H₂O concentrations in the water-gas shift reaction with Pt/CeO₂ in the range 473–533 K. The authors found that the water vapour content increases significantly the catalytic performance, causing an increase in the maximum CO conversion of 18% to 85%, at 533 K. Nevertheless, for some catalysts, such as Au/CeO₂ and Au/Fe₂O₃, water has a lesser effect on the

catalytic activity. For both catalysts, conversions have increased from 8% to 15% and from 33% to 53%, respectively.

3.3 Catalyst stability

The maintenance of catalyst activity in processing the WGS reaction can be a measure of their stability for the production of hydrogen.

Figure 8. Stability tests for Ru/Al₂O₃ catalyst in processing the WGS reaction in a fixed bed reactor. Conditions: catalyst mass 0.25 g, 101 325 Pa, 453 – 573 K, H₂O/CO = 2:1.

Stability tests with the Ru/TiO₂ and Ru/Al₂O₃ catalyst were carried out for 3 hours at 453, 493, 533, and 573 K using a feed gas with 11.36% CO, 22.72% H₂O, and 66.8% of argon. The results shown in Figure 7 indicate that the CO concentration decreased initially and, then, stabilized reaching a steady state after two hours of operation in the four operating temperatures. One can see that no significant loss of activity was detected during the experiment, over three hours. This stability of activity must be directly related to its greater resistance to coke formation, as a result of metal-support interactions. The catalyst Ru/Al₂O₃ was also tested and showed activity for CO conversion via WGS, similar to that of the catalyst Ru/TiO₂, and is presented in the Figure 8.

activity of catalysts containing ruthenium were maintained at about 85 % of CO conversion until three hours of reaction, at 573 K. Investigations on catalytic systems based on ruthenium clearly showed that TiO₂ and Al₂O₃ supports are suitable for the WGS reaction.

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4. CONCLUSIONS

The activities of the ruthenium catalysts, Ru/Al₂O₃, and Ru/TiO₂, were investigated to promote the WGS reaction. As a result, the catalysts were deemed suitable for the WGS reaction at mild operating conditions. It was observed that the water as a reactant had a positive effect on the WGS process carried out with Ru/Al₂O₃ catalyst. Processing tests showed that the

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