Performances of Al_2O_3 Supported Catalyst for Steam Reforming Process

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The aim of this study is to assess the influence of metallic component for two catalysts (Pt/Al_2O_3 and Co/Al_2O_3) in the ethanol steam reforming process. Both catalysts were prepared by the pore volume impregnation method and they were characterized by X-ray diffraction, UV-visible spectroscopy, IR infrared spectroscopy and TGA thermal analysis. The reaction tests were carried out in a fixed bed reactor coupled online with a gas chromatograph. The experimental results show that Platinum catalyst has a better selectivity for hydrogen production during ethanol steam reforming.

Keywords: alumina, catalyst, hydrogen, steam reforming, catalytic test

The bioenergy may be realized either by burning biomass directly or upgrading it into useful and more valuable materials such as fuel gas, fuel oil and materials for chemical industries [1]. The ethanol produced by fermentation of starch and sugar with lower cost is a very attractive option for hydrogen production. Thus the steam reforming of ethanol (SRE) is preferable alternative because ethanol is a renewable raw material, which can easily be derived from biomass, and the carbon dioxide from this process can be consumed in biomass growth, completing a nearly closed carbon cycle [2].

Haga et al. [1] studied the catalytic proprieties of supported cobalt catalysts for steam reforming of ethanol at a reaction temperature of 673 K and W/F 0.45 $(g \cdot s)/cm^3$ and concluded that among four catalyst studied, the conversion of ethanol on Co catalyst is greatly influenced by the support. The catalyst Co/Al_2O_3 exhibited high selectivity for the steam reforming of ethanol by reason of restraint of the methanation of carbon monoxide and the decomposition of ethanol.

Batista et al. [3] studied the efficiency of steam reforming process over Co/Al_2O_3 and Co/SiO_2 catalyst. Both catalysts have shown average conversion, higher than 70% for SRE at 400^0C. The increasing of ethanol conversion and reduction of liquid products were observed when the cobalt content was higher. Ethylene formation occurred only on the Co/Al_2O_3 catalyst with small Co contents. The Co/Al_2O_3 showed higher efficiency for CO removal.

Sahoo et al. [4] studied the kinetic modeling of steam reforming of ethanol for the production of hydrogen over Co/Al_2O_3 catalyst. The Co/Al_2O_3 catalyst prepared by wet impregnation technique was found to be the most effective for the production of hydrogen. They concluded that the optimum operating conditions in order to achieve hydrogen rich product stream with minimum CO and CH_4 are temperature of 773 K, S/E molar ratio=3-5 and W/F 15-17 kg cat/(mol/s).

Noble metals and transitions metals such as Pt and Co were found to have high catalytic activity for the reforming reaction. However from a practical point of view, noble metals are expensive and less available. In this way, supported Pt or Co catalysts are better alternatives. Although, Co-containing catalysts have been less studied than Pt or Ni, it has been revealed that Co/Al_2O_3 shows considerable activity for the CH_4/CO_2 reaction [5,6], the Fischer-Tropsch reaction [7-9] and the steam reforming of ethanol [3,10-12].

Platinum based catalysts were studied in several articles. The $Pt\text{-}Ni/Al_2O_3$ catalyst [13] was used for ethanol steam reforming for a temperature range of 673-727 K and the authors concluded that the catalyst is resistant to coke deposition and the temperature of 773 K was considered the optimum reaction temperature.

Navarro et al. [14] studied the oxidative reforming of ethanol over Pt catalysts supported on Al_2O_3 modified with Ce and La. Based on the results obtained by these authors, the catalytic behaviour of supported Pt catalysts is strongly promoted by the presence of Cerium atoms in the support.

Although the ethanol steam reforming process has received more attention in the recent years, the present study assess the behaviour of Co/Al_2O_3 and Pt/Al_2O_3 catalysts in the SRE process in order to observe the influence of the metallic phase on the catalytic activity for hydrogen production.

Experimental part

Catalyst synthesis

The catalysts used in this study were prepared by pore volume impregnation method. The Al_2O_3 support was treated in air flow at 773 K for 3 h prior to impregnation in order to eliminate surface impurities. The support was impregnated with $H_2PtCl_6 \cdot 2H_2O$ (Aldrich) and $Co(NO_3)_2 \cdot 6H_2O$ (98% Aldrich)dried at 373 K and then calcined in air flow at 823 K for 6 h.

Catalysts Characterization

The catalysts were characterized by X-ray diffraction, UV-visible spectroscopy, infrared spectroscopy (FTIR) and thermal analysis (TGA).

The X-ray diffraction analysis was performed on a Bruker Advance D8 diffractometer with CuKα radiation (40 mA, 40 kV) with a scanning speed of 2 s/step; the diffractograms were collected for 2θ values ranging from 10^0-70^0.

Ultraviolet-visible spectroscopic measurements were performed in the range of 200-800 nm using a JASCO 540V spectrophotometer. Magnesium oxide was the reference material.

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TGA measurements were carried out in flow air at a temperature rate of 10^0/min using a SETRAM LABSYS EVO thermal analyzer. Sample loading was typically 100 mg using a 400 μL alumina crucible.

The FT-IR measurements were performed with a Tensor 27 FT-IR SpectrometerBruker, employing KBr pellet technique.

Catalytic tests

The ethanol steam reforming was performed in a fixed bed reactor. The reaction temperature was measured by a thermocouple placed close to the catalytic bed. The catalyst was previously reduced in situ with hydrogen at 823 K for 6 h. Ethanol aqueous solution (10 vol%) was fed by a Varian pump with a V_{cat}/F ratio of 3.33 ml·s/mL. The gaseous product compositions in the reactor effluent were analyzed by on line gas chromatograph (Varian, model 3800) with two thermal conductivity detectors using a 13x molecular sieve packed column (for H_2 analysis) and a Porapack-N column (for CO_2, CH_4 and CO analysis). The concentrations of the outlet products were calculated by excluding water, that is, dry-based gas composition.

Results and discussions

Catalysts Characterization

XRD data (fig. 1) for Co/Al_2O_3 catalyst show the formation of mainly Co_3O_4 and $CoAl_2O_4$ in the calcined catalyst. The absence of a separate CoO phase from XRD analysis indicates the complete consumption of all the initial Co (II) oxide. The formation of Co_3O_4 and $CoAl_2O_4$ was recognized through strong peak intensities shown at $2\theta=31^0$ and 37^0 respectively as literature mentioned [15].

On the other hand in the case of Pt/Al_2O_3 catalyst (fig. 2) the XRD spectrum presents the characteristic peaks of γ Al_2O_3 which highlight the crystalline character of pore walls. Thus peaks at $2\theta=25.6^0$, 39.62^0, 45.52^0 and 67.01^0 are attributed to γ Al_2O_3. Pt particles seem to be fairly small and hidden in the main peaks of alumina structure. It is worth mentioned that in many case the characteristic peak position of Pt is overlapped with that of γ Al_2O_3so the observed peak for Pt is rather difficult. In our Pt/Al_2O_3 catalyst it was observed a small peak at 39^0 which underline the presence of Pt [16].

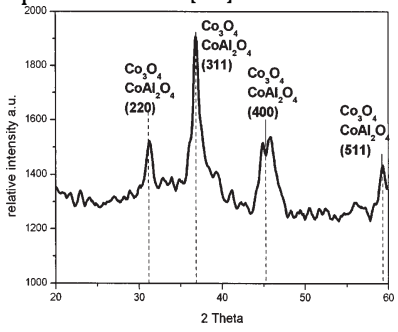

Fig. 1. XRD patterns of Co/Al_2O_3 catalyst

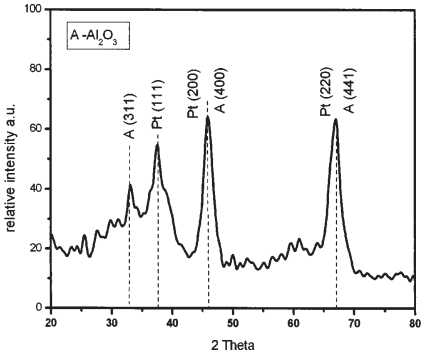

Fig.2. XRD patterns of Pt/Al_2O_3 catalyst

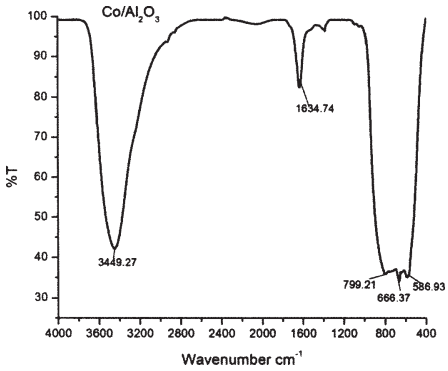

Fig.3. FTIR spectra of Co/Al_2O_3 catalyst

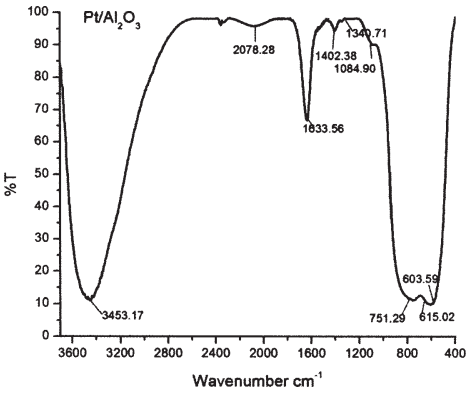

Fig.4. FTIR spectra of Pt/Al_2O_3 catalyst

Observing the FTIR spectra of Co/Al_2O_3 catalyst (figure 3) we notice the presence of a band at 3449.27 cm^{-1} which can be assigned to the stretching vibration of hydroxyl groups O-H. Within the region of 800-500 cm^{-1}, strong doublet peaks at 666.37 and 586.93 cm^{-1} are typical metal-oxygen vibration in the cubic spinel oxide of Co_3O_4 as reported in literature [17]. The water bending mode is observed in sample at 1634.74 cm^{-1} while O-H and metal-oxygen stretching bands toward higher wavenumber region.

The FT-IR spectra of Pt/Al_2O_3 catalyst is shown in figure 4. The characteristic FT-IR peaks in the 500-650 cm^{-1} i.e. 603.59 cm^{-1} and 615.02 cm^{-1} are assigned to the vibration of AlO_6 present in boehmite [18] and the 751.29 cm^{-1} peak due to the presence of γ Al_2O_3. All these peaks are combined characteristic of γ Al_2O_3 and boehmite. The 1084.90 cm^{-1} peak is due to the presence of δ(OH) in boehmite.

UV-VIS spectra were obtained in order to identify different Co species formed after the preparation process. The result obtained for Co/Al_2O_3 catalyst is shown in figure 5 where the absorbance functions of the corresponding bands are plotted as a function of the wavelength.

The relatively high intensity of the broad absorption bands at about 491.5 nm and 747 nm in the sample spectra shows the presence of Co phases with large amounts of the cobalt atoms in octahedral and tetrahedral symmetries [19]. It is known that the high temperature treatment leads to the dispersion of Co_3O_4 particles and the formation of an inactive $CoAl_2O_4$ phase, where the Co^{2+} ions are both tetrahedrally and octahedrally coordinated [20].

The presence of $CoAl_2O_4$ species is highly undesirable due to a low reducibility of cobalt on aluminates compounds leading to less inactive catalysts.

UV-VIS spectra for Pt/Al_2O_3 catalyst is presented in figure 6. The spectrum shows four charge transfer bands in the UV region, located at 208, 253, 293 and 344 nm. The band at 293 nm is assigned to the charge transfer between alumina and the surrounding ligands, whereas the band at 208 nm is atributed to electronic transitions.

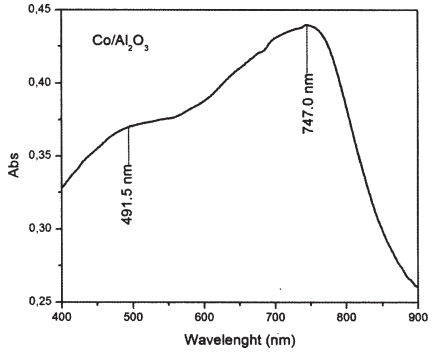

Fig.5. UV-VIS spectra of Co/Al_2O_3 catalyst

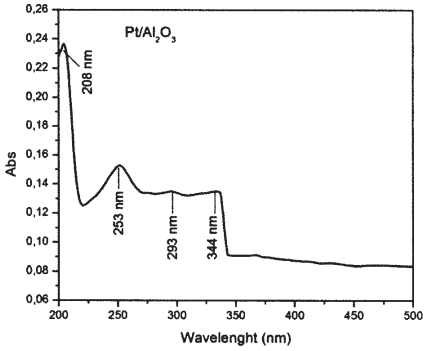

Fig.6. UV-VIS spectra of Pt/Al_2O_3 catalyst

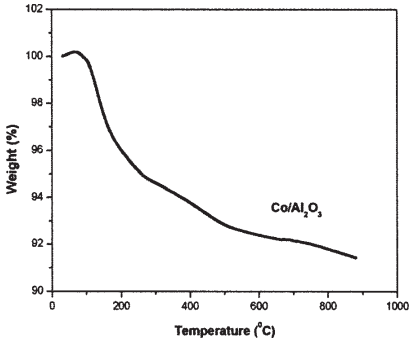

Fig.7. TGA profile of Co/Al_2O_3 catalyst

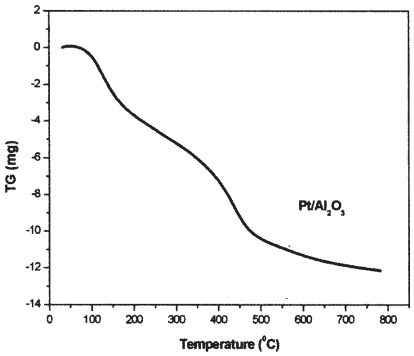

Fig.8. TGA profile of Pt/Al_2O_3 catalyst

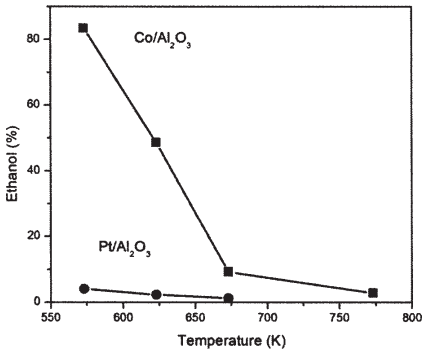

Fig.9. Effect of reaction temperature on the concentration of ethanol in the outlet stream over Pt/Al_2O_3 and Co/Al_2O_3 catalysts. Experimental conditions: 573-773 K, V_{cat}/F=3.33 ml·s/ml, ethanol 10%.

The TGA profile for Co/Al_2O_3 catalyst show that the weight loss curves exhibited several small inflections at 50-200^{0}C, due to the endothermic loss of water molecules in the cobalt hydrate shell and subsequent decomposition of the nitrate anions. Thus the nitrate decomposition may be written as:

$$Co(NO_3)_2 \rightarrow CoO + N_2O_5 \quad (1)$$

followed by air oxidation:

$$3CoO + 1/2\, O_2 \rightarrow Co_3O_4 \quad (2)$$

In addition a small peak was formed around 250^{0}C representing the formation of $CoAl_2O_4$ phase:

$$CoO + Al_2O_3 \rightarrow CoAl_2O_4 \quad (3)$$

Beyond these decomposition temperatures, the oxide catalyst remained practically stable up to 900^{0}C. The formation of oxide species from TGA analysis is consistent with the XRD results [15].

For Pt/Al_2O_3 catalyst the curve obtained from TGA analysis (fig. 8) shows that the total mass loss occurs at different temperature regions. The first region occurs at room temperature until 83^{0}C and corresponds to the removal of the entire organic solvent and physisorbed water.

The loss of mass for the second region begins at 188.71^{0}C up to 533.6^{0}C. This loss was attributed to the removal of the water present in the structure of the support as follows [21]:

$$Al(OH)\, n\, H_2O \rightarrow AlO(OH) + n\, H_2O \quad (4)$$

$$2AlO(OH) \rightarrow Al_2O_3 + H_2O \quad (5)$$

SRE tests

The desired product from steam reforming of ethanol is hydrogen in order to be used for different applications. However, due to a complex reaction network, several by-products can be formed on the metal and support: CH_4, CO, C_2H_4, and CH_3CHO. C_2H_4 is a highly undesired product since it is a precursor to coke and it will lead to fast catalyst deactivation. CH_4 production lowers the selectivity to hydrogen and a downstream CH_4 reformer would be required to increase the H_2 production but will increase the costs also. Minimization of by-product formation is essential in achieving high H_2 selectivity, increasing catalyst stability and lowering the downstream processing for H_2 purification [22].

Figures 9, 10 and 11 show the concentration of products obtained in the effluents of ethanol steam reforming over Pt/Al_2O_3 and Co/Al_2O_3 catalysts as a function of reaction temperature. Normally the conversion of ethanol increased when reaction temperature increases and the complete conversion of ethanol into CH_4, CO CO_2 and H_2 was achieved at 723 K for Pt/Al_2O_3. For Co/Al_2O_3 catalyst a higher temperature of 773 K was required for the conversion of ethanol or other byproducts e.g. acetaldehyde into C_1 products.

The produced CO by ethanol reforming was converted into CO_2 through the water gas shift reaction. Over the Co/Al_2O_3 catalyst the less amount of methane at low temperatures indicated that Co shown a weaker capability

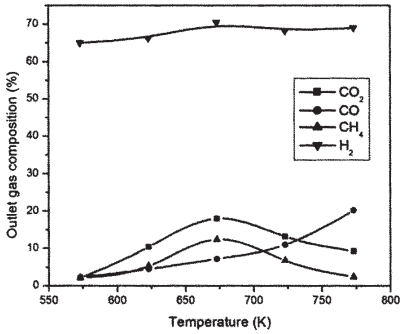

Fig.10. Effect of reaction temperature on the distribution of the outlet gas product in ESR over Co/Al_2O_3 catalyst. Experimental conditions are the same as in figure 9

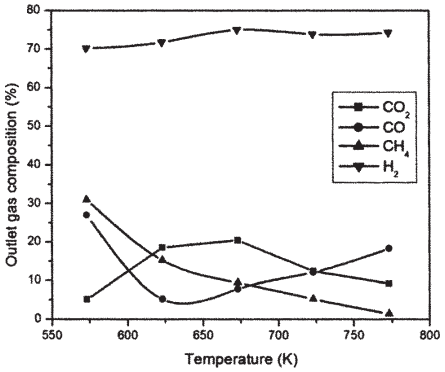

Fig.11. Effect of reaction temperature on the distribution of the outlet gas product in ESR over Pt/Al_2O_3 catalyst. Experimental conditions are the same as in figure 9

of breaking the C-C bond in ethanol molecule [23]. On the other hand Pt/Al_2O_3 catalyst seems to be more effective for ethanol decomposition to methane and carbon monoxide, thus breaking C-C bond in ethanol molecule. We can assume that the reaction pathways of ethanol steam reforming at these lower temperature dependents on the capacity of the metallic phase of the catalyst to break the C-C bond in ethanol molecule.

At higher temperatures, the increasing of CO concentration together with the decreasing of the CH_4 and CO_2 concentrations specify that the reforming of methane with water and the water gas shift reaction occurred as main reaction in the mechanism of SRE process. The remaining methane was completely reformed into hydrogen and carbon monoxide and the water gas shift reaction also approached the equilibrium at 773 K.

Conclusions

In this study, cobalt and platinum on Al_2O_3 catalysts have been investigated for hydrogen production by the steam reforming of ethanol.

The UV-VIS spectra indicated that large amounts of the Co species are located in octahedral and tetrahedral symmetries, and no peaks assigned to cobalt aluminate species were found.

Experimental tests showed that the two catalysts used produced a hydrogen-rich gas mixture during the ethanol steam reforming at lower temperature. After ethanol and the intermediate compounds like acetaldehyde was completely converted into hydrogen, carbon oxides and methane, steam reforming of methane and reverse water gas shift were the major reactions which decide the outlet gas composition.

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