Chemical Engineering Journal 118 (2006) 11–15

Chemical Engineering Journal

www.elsevier.com/locate/cej

Methane steam reforming and ethanol steam reforming using a Ni(II)-Al(III) catalyst prepared from lamellar double hydroxides

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Received 11 November 2005; received in revised form 9 January 2006; accepted 10 January 2006

Abstract

In this work the methane steam reforming (MSR) and the ethanol steam reforming (ESR) on Ni(II)-Al(III) catalyst prepared from lamellar double hydroxides (LDHs) as precursor are studied. A comprehensive analysis of the kinetics results obtained at different water/methane and water/ethanol feed ratio and its correlation with the structural characteristic and redox behavior of the catalyst is carried out.

The results show evidence that the catalyst behavior is related with the presence of only one type of active site in the Ni/Al_2O_3 catalyst. The competition for the active sites between reactants is verified for MSR. This behavior is also observed in ethanol steam reforming since methane steam reforming determines the products distribution in the exit stream. There would be an optimum inlet water concentration that gives a maximum performance in terms of H_2 and CO_2 selectivity and, simultaneously, a minimum CO selectivity. This is a promissory result taking into account that the hydrogen flow entering a PEM fuel-cell requires a CO concentration lower than 20 ppm.

Keywords: Steam reforming; Methane; Ethanol; Hydrogen production; Ni(II)-Al(III) LDH

1. Introduction

In the last decade considerable efforts have been made to develop renewable energy technologies. They can contribute to solve the problems of energy supply, environment protection and regional development. In recent years, fuel cells have drawn the attention because they represent an alternative technology for power generation through the direct conversion of the chemical energy of the fuels in electrical energy. The hydrogen may become an important fuel in the future as an energy carrier for electrical vehicles and electric power plants. The bioethanol produced by biomass fermentation is an attractive source of hydrogen because of its high hydrogen content, non-toxicity and safe storage. Among the various processes and primary fuels that have been proposed for hydrogen production, steam reforming of ethanol becomes an interesting technology. Then, a promissory strategy consists of developing efficient catalysts for ethanol steam reforming (ESR).

Different research groups have examined several solids as probable catalysts for this process [2–16].

In previous work [1,17] we have investigated the steam reforming of ethanol (ESR) based on Ni/Al_2O_3 catalyst obtained from lamellar double hydroxides (LDHs) as precursors. We have proposed the following reactions scheme at 773 K, without impairing reactions responsible for carbon formation:

$$C_2H_5OH + H_2O \rightarrow CO_2 + 2H_2 + CH_4 \quad \text{(a)}$$

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad \text{(b)}$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \quad \text{(c)}$$

where reaction (a) proceeds up to completion and reactions (b) and (c) are considered as being close to equilibrium. The catalyst was stable for water/ethanol molar feed ratio higher than 3.3. At 773 K the H_2 yield obtained for water/ethanol molar feed ratio about 6 was 5.2 (being 6 the theoretical maximum). In order to optimize the Ni/Al catalyst behavior, the role of the

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doi:10.1016/j.cej.2006.01.003

active species must be investigated. However, few studies have been published on this topic applied to Ni as steam reforming catalyst.

From Ross's research up to date, different methods of preparation and activation of Ni/Al LDH precursor as catalyst have been reported [18–23]. Ross et al. [18] have studied the activity of co-precipitated and impregnated Ni/Al_2O_3 catalysts during methane steam reforming (MSR). They suggest that the activity varies markedly with catalyst preparation. The unreduced catalysts contained a surface nickel aluminate phase which, under reduction, gives dispersed nickel atoms closely associated with alumina sites, apart from metallic crystallites arising from the reduction of nickel oxide. The results prompt us to suggest that the disperse nickel atoms probably participate in CH_4 reforming on supported catalyst while metallic nickel sites are responsible for the activity in the co-precipitated catalyst. Later, the same authors [19], using kinetics measurements, verified on the co-precipitated catalyst a competition between CH_4 and water by the nickel sites. Xu and Froment [20] have reported the kinetic expression for methane steam reforming on commercial Ni/Al_2O_3 catalyst. The rate equation shows a non-monotonic dependence upon steam partial pressure. Considering that this behavior is related with a reaction competition of both reactive, which means that water and methane are adsorbed on the same active site. Marquevich et al. [21] have proposed a process to produce hydrogen from steam reforming of vegetable oil (sunflower) over co-precipitated Ni/Al_2O_3 catalyst. They investigated the effect of temperature and steam/carbon feed ratio over hydrogen production and concluded that organic oil and steam molecules compete by the same metal site. This competition does not affect the reaction rate until very high steam/carbon ratio. This is due to the higher metal area of the catalyst used. Methane steam reforming and oxy-steam reforming over supported Ni/Ce-ZrO_2 catalyst is reported by Sheng Dong et al. [22]. They affirm that two kinds of active sites, one for methane activation and the other for the activation of oxygen-containing reactants (steam or oxygen), are well balanced in the catalyst. Methane dissociation occurs on metallic nickel sites meanwhile steam can be adsorbed dissociatively on nickel surface and also on Ce/ZrO_2 support. The authors claim that the support plays a key role in providing active sites to adsorb H_2O. Recently, Fatsikostas and Verykios [23] have studied ethanol steam reforming over Ni-based catalyst. The catalyst was prepared by wet impregnation method of the carriers La_2O_3, γ-Al_2O_3 and La_2O_3/γ-Al_2O_3. Ethanol steam reforming was investigated by temperature-programmed surface reaction of preadsorbed ethanol or water. The authors propose that the presence of steam seems to promote desorption of adsorbed ethanol and suggest that both molecules compete for the same active sites.

Taking into account that MSR determines the products distribution in ethanol steam reforming [1], we have studied the methane steam reforming (MSR) on Ni(II)-Al(III) catalyst. The kinetics measurements obtained at different water/methane feed ratio are discussed and correlated with the structural characteristic and redox behavior of the catalyst. Previously a comprehensive analysis of published ESR kinetic results [1] obtained from experiments performed at different water/ethanol feed ratio using the same catalyst is carried out.

2. Experimental

2.1. Catalyst preparation and characterization

A precursor of Ni/Al_2O_3 catalyst developed and provided by Royal Military College of Canada was used. The sample was characterized by sorptometry in order to determine the BET specific area. The experiments were performed with nitrogen at 77 K in a Micromeritics Gemoni 2360 equipment. Also, X-ray diffraction (XRD) spectra of fresh precursor and reduced sample were recorded for 2θ values between 5 and 70° in a Siemens D 5000 equipment using Cu Kα radiation, Ni filter and 40 kV. Temperature programmed reduction (TPR) experiments were performed with a thermal conductivity detector, on samples of 30 mg in a 98% (molar) nitrogen and 2% (molar) hydrogen gas mixture, using a gas flow rate of 100 ml/min and a temperature range of 293–1173 K with a temperature ramp rate of 5°/min. The experimental parameters were carefully selected to follow Monty and Baiker's recommendations [24]. Ni content was determined by atomic absorption in a Varian-Techtron AA 5 equipment.

2.2. Kinetics experiments

Kinetics experiments were carried out in a conventional fixed bed reactor operated isothermally at atmospheric pressure. The flow system was equipped with a set of mass-flow controllers for methane and nitrogen and with a HPLC pump and a vaporizer for feeding water. The gas mixture (methane, water and nitrogen) is fed to the reactor through heated conducts to avoid water condensation. The methane steam reforming was performed under the following conditions: *T*, 773 K; atmospheric pressure; catalytic mass, 0.012–0.020 g; methane wet molar fraction, 0.1; dry feed rate, 200 ml/min; water/methane molar ratio, 2–6; nitrogen balance. Methane conversion was defined

$$X_{\text{methane}} = \frac{F_{\text{methane in}} - F_{\text{methane out}}}{F_{\text{methane in}}} \tag{1}$$

where F is the molar flow rate; in the input stream and out the output stream.

Products yield is defined as the relation between product molar flow rate and methane molar flow rate in the feed.

In this work the results obtained during the steam reforming of methane (MSR) were compared with those reported previously for ethanol steam reforming [1]. The experiments using ethanol and water as reactants were performed under the following conditions: catalytic mass, 0.840 g; temperature, 773 K; total feed rate, 210 ml/min; ethanol molar fraction, 0.017; water/ethanol molar ratio, 1–6; nitrogen balance. The reaction tests were carried out in a packed bed reactor described in previous paper [1]. Ethanol conversion denoted X_{ethanol} and products selectivity's denoted S_{i} were evaluated according to Eqs. (2)–(4):

$$X_{\text{ethanol}} = \frac{F_{\text{ethanol in}} - F_{\text{ethanol out}}}{F_{\text{ethanol in}}} \tag{2}$$

$$S_{H_2} = \frac{F_{H_2\text{produced}}}{3(F_{\text{ethanol in}} - F_{\text{ethanol out}}) + (F_{\text{water in}} - F_{\text{water out}})} \quad (3)$$

$$S_{\text{i carbon-containing product}} = \frac{F_{\text{carbon-containing product}}}{(F_{\text{ethanol in}} - F_{\text{ethanol out}})n} \quad (4)$$

where F is the molar flow rate and n the calculated as number of C atoms in the ethanol/number of C atoms in the product.

Taking into account that the total selectivity to compounds containing carbon ($S_{\text{i carbon-containing product}}$) must be equal or lower than 1, the fraction of reactant converted, which was not detected in the reactor outlet, was assigned to the formation of carbonaceous deposits adsorbed on the catalyst surface as coke deposit. Therefore, coke selectivity is calculated by Eq. (5).

$$S_c = 1 - \sum S_{\text{i carbon-containing product}} \quad (5)$$

For all runs (MSR and ESR), prior to catalytic tests, the catalyst was reduced "in situ" under flowing of hydrogen (10 ml/min) and nitrogen (90 ml/min) at 823 K for 1 h and under flowing of hydrogen (10 ml/min) for 0.5 h. After reduction the catalyst was cooled down to reaction temperature.

2.2.1. *Preliminary tests*

Previous to formal experiments, preliminary tests were carried out in order to avoid any limitations to diffusion. To guarantee that the experiments were carried out within a region of intrinsic kinetics, the effect of intraparticle and external film diffusion on MSR and ESR was examined by using different average sizes of catalyst particles and different total flow rates. These results indicate that both the intraparticle diffusion limitation and the film resistance are negligible for particles diameters below 0.177 or 0.450 mm, for ESR and MSR, respectively, and total gas flow equal or greater than 150 ml/min. The catalyst bed was diluted with glass particles in order to avoid adverse thermal effects.

3. Results and discussion

3.1. *Catalyst characterization*

The fresh precursor has a specific area of 15 m^2/g and a Ni content of 35% (w/w). XRD pattern of the fresh sample shows the characteristic reflections of (0 0 3), (0 0 6), (0 1 2), (0 1 5) and (0 1 8) planes of a crystallized lamellar double hydroxide (Fig. 1a (◆) symbol). In the zone close to $2\theta = 60$–$62°$, the typical doublet of d (1 1 0)–d (1 1 3) planes of LDH was also observed. It must be noted that no excess of crystalline phase was present.

The TPR profile (Fig. 2) shows a broad peak with a maximum at 710 K which can be attributed to the reduction of Ni(II) contained in the oxidic forms derived from Ni–Al LDH compounds as it was reported by Jitianu et al. [25]. It must be pointed out that the amount of H_2 consumed reveals that the Ni contained in the sample was completely reduced between 573 and 973 K.

The fresh precursor was directly reduced before reaction without a previous calcination treatment, as it was detailed in experimental section. In spite of the fact that the TPR results indicate the complete reduction of Ni(II) species, XRD pattern of the reduced sample shows the characteristic lines of Ni metallic with a very low intensity (Fig. 1b (□) symbol). The mean size of Ni crystallites calculated by Scherrer equations was 6 ± 1 nm. These results suggest that a larger fraction of the metallic Ni cannot be detected by the XRD technique because the Ni metal particles are highly disperse in a structure of aluminium oxide [26].

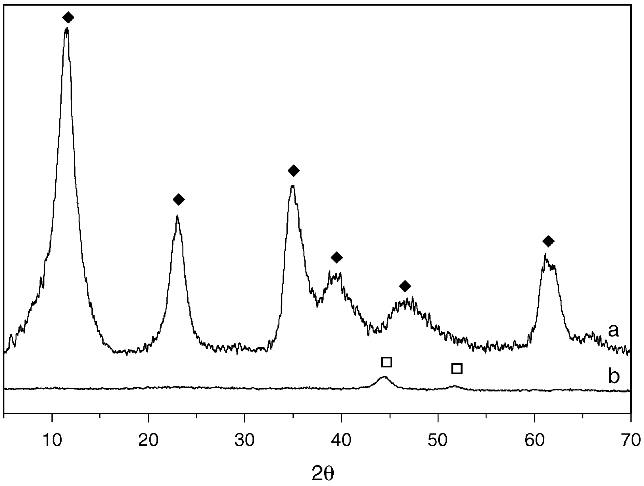

Fig. 1. DRX patterns of the Ni(II)–Al(III) LDH precursor, (a) fresh sample and (b) reduced sample.

3.2. *Kinetics experiments*

3.2.1. *Ethanol steam reforming*

In Fig. 3, the effect of the water/ethanol molar feed ratio (R) on ethanol conversion and products selectivity is shown. It can be seen that ethanol is completely converted for all R values and no intermediate products (acetaldehyde and ethylene) were detected. S_{H_2} increases with R, S_C decreases when R increases from 1 to 3.3 and remains constant for $R > 3.3$.

At $R = 3$, S_{CO} and S_{CO_2} increase and S_C decreases with respect to $R = 1$ and, in addition $S_{CO_2} > S_{CH_4}$. These results suggest that the extent of reaction (a) increases with respect to $R = 1$ since carbon formation decreases.

$$C_2H_5OH + H_2O \rightarrow CO_2 + 2H_2 + CH_4 \quad (a)$$

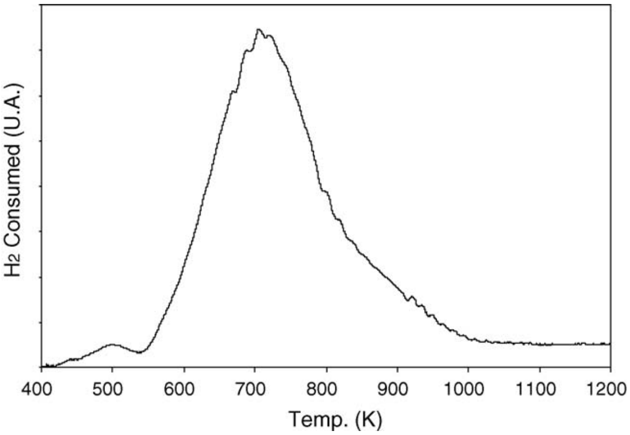

Fig. 2. TPR profile of Ni(II)–Al(III) fresh sample.

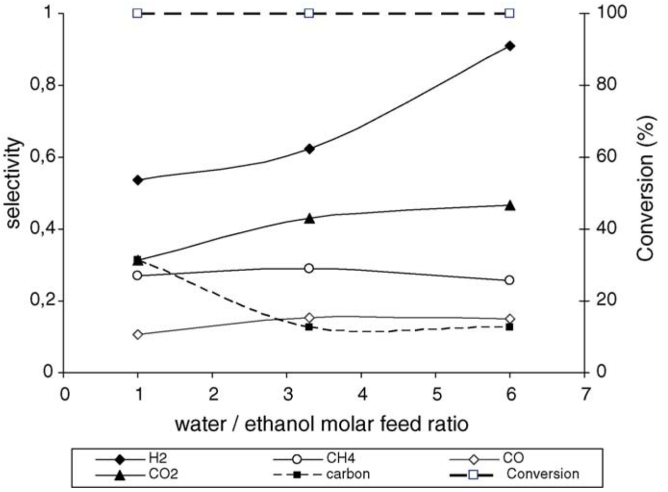

Fig. 3. Ethanol steam reforming. Effect of the water/ethanol molar feed ratio (R) on ethanol conversion and products selectivity. T: 773 K, mass of catalyst: 0.840 g; total feed rate: 210 ml/min; ethanol molar fraction: 0.017; water/ethanol molar ratio: 1–6. Results published in reference [16].

The increase of S_{CO} and S_{CO_2} can be explained by the methane steam reforming reactions:

$$CH_4 + H_2O = CO + 3H_2 \quad \text{(b)}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \quad \text{(c)}$$

At $R = 6$, products selectivity remains practically constant with respect to $R = 3$, except S_{H_2} which increases significantly. Since products selectivity is a function of R, it could be suggested that there is a competition between the reactants for the same active sites. The same behavior was obtained by Xu and Froment [20] for steam reforming of methane using a Ni/Al_2O_3 catalyst. Later Elnashaie et al. [27] carried out a simulation of methane steam reforming using Xu and Froment's kinetics [20]. They found that methane conversion showed a non-monotonic dependence on water partial pressure.

3.2.2. *Methane steam reforming*

Methane steam reforming was carried out at different H_2O/CH_4 feed ratio and different catalyst mass in order to analyze the effect of water during methane steam reforming. In all the experiments inlet methane concentration, temperature, and volumetric flow were constant and their values were chosen in order to assess that the products distribution obtained could not be affected by the equilibrium. In Fig. 4 experimental CH_4 conversion versus H_2O/CH_4 feed ratio (R) for different catalyst mass is shown. In the same figure equilibrium CH4 conversion is also shown. Although equilibrium CH_4 conversion always increases with R, the kinetic behavior is quite different. It can be seen that CH_4 conversion presents a maximum or continuously decreases when water feed concentration increases. This means that water has an opposite behavior on methane conversion depending on water partial pressure. Positive and negative order dependence on the reaction rate upon steam partial pressure can be observed depending of water/methane molar ratio and catalyst mass. This behavior suggests that both reactants, CH_4 and H_2O, compete for a same active site.

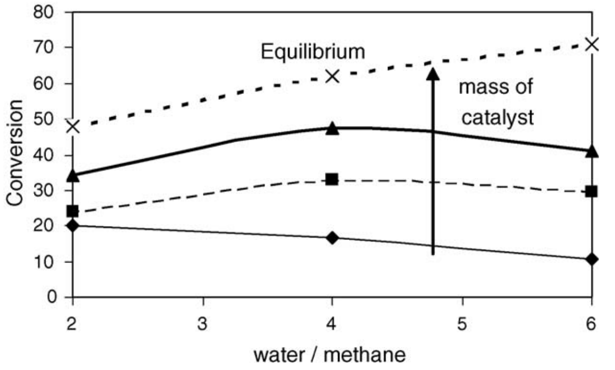

Fig. 4. Methane steam reforming. Methane conversion vs. water/methane molar feed ratio. Mass of catalyst: 12 mg, 16 mg, 20 mg; T: 773 K; atmospheric pressure; methane wet molar fraction: 0.1; dry feed rate: 200 ml/min.

For the lowest catalytic mass the negative order of water is always observed, even for water/methane molar ratio as low as 2. This negative effect of the water is due to the relative small number of active sites present in the lower catalyst load used. On the other hand, for the other two catalyst loads the negative and positive dependence is verified in the range of R analyzed. Therefore, the behavior obtained for different water/ethanol molar ratio during the ESR experiments (Fig. 3), could be a consequence of the competitive mechanism.

The H_2, CO and CO_2 yield versus H_2O/CH_4 feed molar ratio (R) obtained from the methane steam reforming using the same catalyst is presented in Fig. 5. It can be seen that H_2 and CO_2 production increases with R while CO production decreases. These results agree with that reported by Elnashaie et al. [27] and explain the strong increase in H_2 selectivity at $R = 6$ verified in the ethanol steam reforming (Fig. 3). The authors showed that the reaction rate corresponding to the Eq. (b) has a non-monotonic dependence on water partial pressure while the dependence of the reaction rate of Eq. (c) on water partial pressure is a monotonic function. This means that there would be an optimum inlet water concentration that gives a maximum performance in terms of hydrogen and CO_2 selectivity and, simultaneously, a minimum CO selectivity.

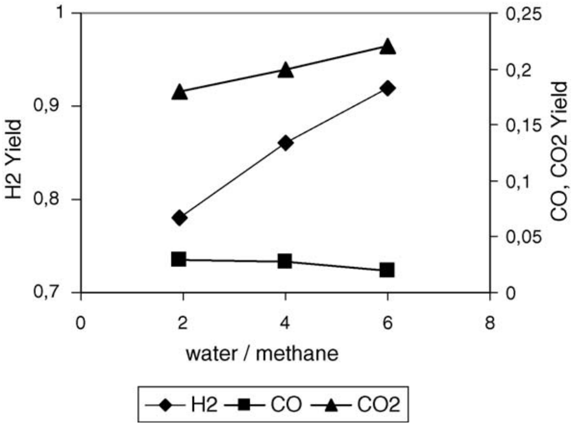

Fig. 5. Methane steam reforming. H_2, CO and CO_2 yield vs. water/methane molar feed ratio. T: 773 K; atmospheric pressure; mass of catalyst: 16 mg, 20 mg; methane wet molar fraction: 0.1; dry feed rate: 200 ml/min.

The efforts must be addressed to obtain a catalyst from Ni(II)-Al(III) LDH precursor with a single and highly disperse Ni/Al phase reducible at low temperature. In our laboratory we synthesized a LDH precursor of NiAl catalyst using the homogeneous precipitation method by urea hydrolysis. The samples were characterized after different thermal treatments and evaluated in the steam reforming reaction [28]. Under the same operative conditions, catalytic mass of 20 mg and $R = 2.2$, the methane conversion was 43% and the hydrogen yield reached 1.5. With the catalyst used in this work the methane conversion and the hydrogen yield were 40 and 0.85%, respectively. These results indicate that the hydrogen selectivity is largely improved probably due to a higher dispersion of nickel metal particles.

4. Conclusions

The competition for the active sites between reactants is verified for methane steam reforming. This behavior is also observed during ESR since methane steam reforming determines the concentration of products in the exit stream. The competition for the same active site leads to a maximum in H_2 and CO_2 production and a minimum in CO formation as a function of water/methane molar feed ratio in the methane steam reforming.

In addition, using optimization methods the water/ethanol molar feed ratio that minimize CO production and maximize H_2 production can be found. This is a promissory result, taking into account that the hydrogen flow entering to a PEM fuel-cell requires a CO concentration lower than 20 ppm.

Ni(II)–Al(III) LDH compounds present, after reduction treatment, Ni metal particles highly dispersed in an aluminum structure which act as the unique active site for water and methane adsorption. This active site is able to carry out the steam reforming at mild temperatures.

Acknowledgments

To Mr. Roberto Tejeda for TPR measurements. To University of Buenos Aires, CONICET and ANPCYT for the financial support.

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