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Cu/Zn-based catalysts for H_2 production via steam reforming of methanol

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ABSTRACT

The performances of different *x*Cu10Al, *x*Zn10Al ($x = 1, 3$, and 5), 5%Zn5Cu10Al and 5%Cu5Zn10Al catalysts prepared by impregnation method then pelletised, were investigated in the steam reforming of methanol (SRM) at 350 °C under a gas hourly space vilosity of 15,500 h^{-1} with steamed water and methanol mixture ($H_2O/CH_3OH = 2$). The impregnation of copper over alumina supports shows better results than that of zinc. Concerning copper based catalysts, the gas selectivity was found to be strongly dependent on the reduction state of the copper and its dispersion over the support. The presence of zinc over Alumina seems to favor the reverse water gas shift reaction. Among all the tested series, the 5%Cu5Zn10Al shows the highest performance due to the presence of $ZnAl_2O_4$ spinal form that stabilises the Cu^+, which is the most active specie in the SRM.

1. Introduction

The dependence on the renewable energy has become a must because of the decreasing reserve of fossil fuels. Meanwhile, fossil fuel use continues to impose massive environmental and economic costs. Moreover, the costs in our current energy path became continuously steep and impose the technology of hydrogen PEM fuel cells as a promising alternative to internal combustion engines. Somehow, the application of this technology needs solving the problem of H_2 supply. Therefore, having a hydrogen source in liquid form that can supply H_2 when needed is preferable. One method of great interest in recent years is hydrogen production from methanol via steam reforming over copper based catalysts (1).

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad (1)$$

Knowing that the presence of the minor amount of CO can poison the platinum anode of the PEM fuel cells, catalysts showing good activities must be developed. Copper oxide supported on alumina system is one of the most important catalysts widely used in the environmental catalysis area [1]. For carbon monoxide oxidation, CuO/Al_2O_3 catalysts may substitute the noble metals catalysts because of their high catalytic activity [2]. Moreover, the role of ZnO as a promoter of Cu based catalysts is well known, and is explained by different mechanisms [3]. Alumina is considered as a support material that increases the surface area and the thermal stability of reduced copper. However, alumina could also play a direct role in the catalysts through the adsorption and the activation of methanol [4]. The present work focuses on a comparative investigation of copper and/or zinc containing pelletised catalysts supported on alumina in SRM.

2. Experimental

2.1. Catalyst preparation

Alumina (Al_2O_3) was prepared by sol–gel method, mentionned in a previous paper [5]. The deposition of copper was performed by the impregnation onto the calcined Al_2O_3 of an aqueous solution containing given amounts of $Cu(NO_3)_2$ or $Zn(NO_3)_2$ seperately, to obtain catalysts *x*Cu10Al and *x*Zn10Al with different molar ratios (with $x/10$: molar ratio and $x = 1$, 3 and 5). After drying at 100 °C for 20 h, solids were calcined under air at 600 °C for 4 h. An aqueous solution containing a given amount of $Cu(NO_3)_2$ was impregnated over the calcined 5Zn10Al to obtain 5%Cu5Zn10Al (5 wt.% of CuO). And a given amount of $Zn(NO_3)_2$ was impregnated over 5Cu10Al catatlysts in order to obtain 5%Zn5Cu10Al (5 wt.% of ZnO). Then the mixture was dried overnight, calcined at 600 °C under air flow for 4 h. These solids were pelletised and sieved to obtain catalysts with defined particle size, in the range of $0.35 < d_p < 0.80$ mm in order to eliminate mass transport limitation of the reaction rate.

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Table 1
Methanol conversion and product composition for methanol steam reforming over Al_2O_3, *x*Cu10Al, *x*Zn10Al, 5%Zn5Cu10Al and 5%Cu5Zn10Al catalysts.

Sample	Methanol conversion (%)	Surface specific area ($m^2\,g^{-1}$)	Activity ($\mu mol\,m^{-2}\,h^{-1}$)					Carbon assessment
				H_2	CO_2	CO	CH_4	
Al_2O_3	76	362	151	92.9	5.1	2.0	0.0	0.26
1Cu10Al	91	249	242	74.9	24.9	0.1	0.1	0.82
3Cu10Al	92	175	339	75.0	24.9	0.1	0.0	0.99
5Cu10Al	97	160	354	75.0	24.9	0.1	0.0	0.99
5%Zn5Cu10Al	96	188	302	74.4	24.8	0.8	0.0	0.89
1Zn10Al	79	235	194	75.4	24.0	0.4	0.2	0.63
3Zn10Al	78	204	192	73.7	25.0	0.3	0.9	0.54
5Zn10Al	81	157	303	72.3	24.4	0.2	3.1	0.44
5%Cu5Zn10Al	98	164	366	75.1	24.9	0.0	0.0	0.99

2.2. Experimental conditions

Steam reforming of methanol was carried out in a quartz tubular fixed bed reactor with an inner diameter value of 8 mm at atmospheric pressure and reaction temperature of 350 °C. All runs were performed using 0.2 cm^3 of catalyst under an argon flow rate of 26 $cm^3\,min^{-1}$ (GHSV = 15,500 h^{-1}). The catalysts were pretreated under an argon flow at 350 °C for 12 h before test. The composition of the liquid feed to the reactor was 0.8 $cm^3\,h^{-1}$ of water + methanol mixture ($H_2O/CH_3OH = 2$) evaporated at 150 °C before its introduction into the reactor. The product stream was passed through a chilled condenser to trap any unreacted water and methanol and possible condensable by-products. The mixture of dry gases effluent was analysed on-line by a gas chromatograph (GC-Varian 3800) equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). After the test, both catalysts and liquid fraction were placed seperately in vials heated at 80 °C then injected via head space method (Varian GENESIS Head-Space) and analysed by a gas chromatograph (GC-Varian STAR 3400) equipped with mass spectroscopy (HS–GC–MS). This allows us to identify the by-product condensed in the liquid fraction and adsorbed over the catalysts. The results reported are based on reactant conversions and selectivity to carbon-containing products for each catalyst. The carbon assessment in Table 1 presents a calculation form of the ratio between the quantities of carbon presented in the products issued from the SRM reaction as gases (CO, CO_2 and CH_4) and as liquid fraction (non reacted part of methanol and carbonated by-products) and the carbon used as a reactant to feed the SRM reaction (initially introduced methanol). The ratio must be equal to 1 and the difference represents the adsorbed carbonate and the by-products and the coke formed over the catalysts during the test.

2.3. Catalysts characterization

The IR absorption spectra was recorded for all the catalysts after the SRM test, by an IR spectrophotometer type Bruker Equinox 55, in a conventional fixed bed micro-reactor and studied between 25 and 400 °C (5 °C min^{-1}) with “operando” Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy and accumulating 64 scans in the range of wave number 4000–400 cm^{-1}.

The Electron Paramagnetic Resonance (EPR) measurements are performed at room temperature on an EMX BRUKER spectrometer with a cavity operating at a frequency of −9.5 GHz (X band). The magnetic field was modulated at 100 kHz and the power supply was sufficiently small to avoid saturation effect. Modulation amplitudes from 0.5 to 10 G were used. The *g*-values were determined using the relation: $h\nu = g\beta H$ where h is the Planck constant, β is the Bohr magneton, H the magnetic field and ν the microwave frequency measured with high precision using a frequency-meter. All the thermal treatments of the samples are carried out in a microflow reactor, which is assembled with a quartz EPR tube to allow the introduction of the sample into the resonance cavity.

The structures of the solids were analyzed by powder XRD technique at room temperature with a Bruker diffractometer using Cu Kα as radiation scanning (1.5406 Å) and 2θ angles ranging from 10° to 80° with a step size of 0.02° and a count time of 2 s.

Temperature Programmed Reduction (TPR) was carried out with a flow type reactor and using a Zeton Altamira apparatus. Hydrogen (5 vol.% in Ar) was passed through a reaction tube containing the calcined catalyst under atmospheric pressure at 30 $cm^3\,min^{-1}$. The tube was heated with an electric furnace at 5 °C min^{-1}, and the amount of H_2 consumed was monitored by a thermal conductivity detector.

3. Results and discussion

3.1. Test results

Table 1 shows the steam reforming of methanol results for Al_2O_3, *x*Cu10Al, *x*Zn10Al, 5%Cu5Zn10Al and 5%Zn5Cu10Al prepared catalysts tested under the experimental conditions discribed in Section 2.2. All the catalysts were tested at a fixed temperature of 350 °C. Test results have shown that a high CO formation was revealed in the presence of alumina test alone. The H_2 formation was artificially high due to the major quantity of carbon species adsorbed over the alumina proved by the low CO_2 formation. The formaldehyde and methyl formate species were detected via HS–GC–MS as carbon species highly adsorbed over the alumina causing a low carbon assessment. Moreover, infra red spectroscopy has shown that carbonate species are adsorbed over the alumina test alone and coke formation was revealed by EPR (Electron Paramagnetic Resonance) spectroscopy and thermal analysis.

By adding copper to alumina, the H_2 formation was kept high (~75%) and 0.1% of CO was detected over all the tested catalysts. An amount of 0.1% of CH_4 was detected over 1Cu10Al and disappears while increasing the copper content (3Cu10Al and 5Cu10Al). This is related to the reaction between CO and H_2 (2).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{2}$$

Moreover, the conversion rate was increased by increasing the copper loading and shows a maximum value for the 5Cu10Al (97%). The 1Cu10Al catalyst has shown a carbon assessment value of 0.82, which is lower than that of 3Cu10Al and 5Cu10Al (0.99). This is related to the traces of oxygenated carbon species as carbonate that were adsorbed over the catalysts and detected by infra-red spectroscopy and to the formaldehyde (CH_2O) and methyl formate ($C_2H_4O_2$) species, presented as traces over the catalyst and detected by HS–GC–MS.

The *x*Zn10Al catalysts have shown a hydrogen selectivity that decreases with the zinc content. Meanwhile, by increasing the zinc load over the alumina support, the amount of CO decreases and induces the increase of CH_4. Moreover, the carbon assessment has shown decreasing values with the zinc load which is explained by the presence of formaldehyde and methyl formate species adsorbed over the catalysts and detected via HS–GC–MS. Hence, the presence of intermediate species during the steam reforming reaction can be desorbed as gaseous formaldehyde or if retained on the catalytic surface, further dehydrogenated giving rise to CO (3) [6].

$$CH_2O \rightarrow CO + H_2 \tag{3}$$

The low carbon assessment was also explained by the coke formation over the zinc based catalysts detected by EPR spectroscopy. Data presented in Table 1, have shown that by adding zinc to alumina, the methanol conversion lightly increases compared to the alumina tested alone and the 5Zn10Al catalyst has shown the highest conversion (81%) among all the zinc based catalysts. The role of ZnO as a promoter of Cu based catalysts is well known, and is explained by different mechanisms [7]. But in our case, it is worthy to notice that by adding 5% of ZnO over 5Cu10Al the CO emission was relatively increased. Moreover, the H_2 formation and the carbon assessment were decreased. Thus, in our case the ZnO impregnated over the copper based catalyst covers partially the surface of the copper catalysts and can enhances the decomposition of the methanol or the by-products formed during the reaction (4).

$$CH_3OH \rightarrow CO + 2H_2 \tag{4}$$

In addition, the activity results shown in Table 1 reveal that by adding 5% of ZnO over the 5Cu10Al the activity decreases and the surface specific area increases compared to 5Cu10Al. Somehow, we did not notice a major effect of the surface specific area on the catalytic activity, as it was the case of Agarwal et al. [8].

By impregnating 5% of CuO over 5Zn10Al, the catalyst behavior becomes similar to 3Cu10Al and 5Cu10Al without any CO formation. The highest activity observed with the 5%Cu5Zn10Al catalyst seems to be related to the presence of Cu_2O species that were only detected in this case among all the tested catalysts. These results correlate with Oguchi et al. [9]; they have reported Cu_2O as active species in the SRM over CuO/ZrO_2 catalysts. Thus, the presence of the CuO over the Zn based catalysts makes the copper species more exposed to the surface which favors the promoting effect of the zinc on the reducibility of CuO over alumina [10]. The carbon assessment of 5%Cu5Zn10Al has shown a higher value than that of 5Zn10Al. This could be explained by the fact that in the presence of copper over 5Zn10Al, the carbon oxygenated species tend to be more desorbed from the catalyst surface by interacting with the different oxidative states of the copper during the test. Modeling and simulation studies done by Faungnawakij et al. [11] over $Cu/ZnO/Al_2O_3$ have shown that at S/C = 2 the conversion reached almost 100% even at 100 °C. They have also shown that at S/C = 2 and a temperature range between 100 and 400 °C, the H_2 yield approaches the 100%. This is related to the enhancement of the MeOH conversion and to suppression of the reverse water gas shift reaction [11]. Somehow the 5Cu10Al catalyst has also shown a high activity in the SRM reaction with 75% of H_2 and 25% of CO_2 production, but compared to the 5%Cu5Zn10Al catalyst 0.1% of CO were detected. In the presence of the 5%Cu5Zn10Al catalysts the SRM reaction is enhanced allowing to reach ideal conditions by the formation of 3 mol of H_2 for 1 mol of CO_2 with a methanol conversion of 98% and a value of carbon assessment equal to 0.99. In order to understand the behavior of these catalysts, physical characterizations were done before and after test.

3.2. Catalysts characterization

XRD patterns of the Al_2O_3, 5Cu10Al, 5%Zn5Cu10Al, 1Zn10Al, 5Zn10Al and 5%Cu5Zn10Al catalysts before and after test are shown in Fig. 1A. The 5Cu10Al pattern before test has shown the presence of CuO (JCPDS: 00-045-0937) and $CuAl_2O_4$ (JCPDS: 00-033-0448) species. Patel and Pant [12] have concluded that the presence of alumina enhances the dispersion of CuO species by the stabilization of isolated Cu^{2+} ions in their matrix, and moderately by the formation of spinel like $CuAl_2O_4$. However after test, CuO species disappeared and Cu^0 (JCPDS: 00-004-0836) became visible. According to our data, the performance of 5Cu10Al catalysts in the SRM reaction is related to the presence of Cu^0 species. After adding 5% of ZnO over 5Cu10Al, peaks assigned to the $CuAl_2O_4$ species became more visible and the CuO species were also revealed but, the ZnO form was not detected. According to the literature [13–15], both the $CuAl_2O_4$ and $ZnAl_2O_4$ have nearly identical diffraction patterns. This explains the absence of zinc as ZnO species in the patterns and indicates their presence as $ZnAl_2O_4$ spinel species. XRD patterns for 1Zn10Al and 5Zn10Al catalyst have reviled the presence of $ZnAl_2O_4$ (JCPDS: 01-082-1043) spinel species before and after test (Fig. 1A). Thus, our assignment of $ZnAl_2O_4$ phase agrees with the assignment made by Turco et al. [4] in a related study. Furthermore, the particle size of the $ZnAl_2O_4$ species in the 1Zn10Al (2.7 nm) before test are much lower than that for the 5Zn10Al catalyst (4.4 nm). Thus, the increasing selectivity of the CH_4 could be related to the particle size of the $ZnAl_2O_4$ species that can trap the H_2 on their surface and favours its reaction with the CO (2). By adding 5% of CuO over 5Zn10Al, the presence of $ZnAl_2O_4$ covers the CuO peaks so they are not shown before test. But after test, some weak broad peaks were shown and are assigned to the Cu_2O (JCPDS: 03-065-3288) species. Some authors [16], have reported that Cu_2O (Cu^+) phase was formed as a transient species in the reduction of Cu^{2+} to Cu^0 although no activity was attributed to it. But others [9] have reported Cu_2O as active species in the SRM over CuO/ZrO_2 catalysts. According to our results, the presence of copper impregnated onto the zinc species retard the copper reduction proved by the presence of Cu_2O which is due to the exposition of the $ZnAl_2O_4$ on the surface. On the other hand, $ZnAl_2O_4$ has been found to be a very efficient catalyst support in the methanol steam reforming reaction [17]. Fujitani et al. [18] agreed that Cu^{2+} is inactive and Cu^+ as well as Cu^0 are active species in the steam reforming reaction. While Idem et al. [19] found that for the steam reforming of methanol, the reaction efficiency strongly depends on the amount of Cu^+ species formed in the catalyst. This comes in correlation with our results where 5%Cu5Zn10Al have shown the highest hydrogen selectivity and the highest methanol conversion rate where $ZnAl_2O_4$ is the support in the presence of Cu^+ species.

The reduction peak of the 5Cu10Al catalysts before test (Fig. 1B) was observed at 230 °C and assuming theoretically, 5.52 mmol g^{-1} of H_2 are needed to reduce all copper species into Cu(0). But experimental H_2 consumption value has shown that a small part of copper presented, as $CuAl_2O_4$ spinels are not reduced by TPR. The reduction of copper species after test has taken place at a lower temperature (150 °C) and a very low hydrogen consumption (0.66 mmol g^{-1}) proving the reducibility of CuO after test. Some authors [20] found that highly dispersed CuO gave TPR signals at much lower temperature than bulk CuO. This result proves the XRD results and shows that a small amount of CuO remains on the catalysts after test after their reduction to Cu^0 and are highly dispersed over alumina so they are reduced at a lower temperature. TPR signals for the 5%Zn5Cu10Al before test (Fig. 1B) have shown that the H_2 consumption is much lower (1.55 mmol g^{-1}) than that theoretically needed (5.52 mmol g^{-1}) to reduce all the copper species. This means that the $CuAl_2O_4$ spinel form becomes stable by adding 5% of ZnO and tends not to be reduced during TPR. After test, the H_2 consumption value (0.13 mmol g^{-1}) shows that during the test most of the copper species such as CuO and $CuAl_2O_4$ detected by XRD were reduced into Cu^0 during test. Fig. 1B, has also shown that 5Zn10Al catalyst did not present any reduction peak before test, which is the

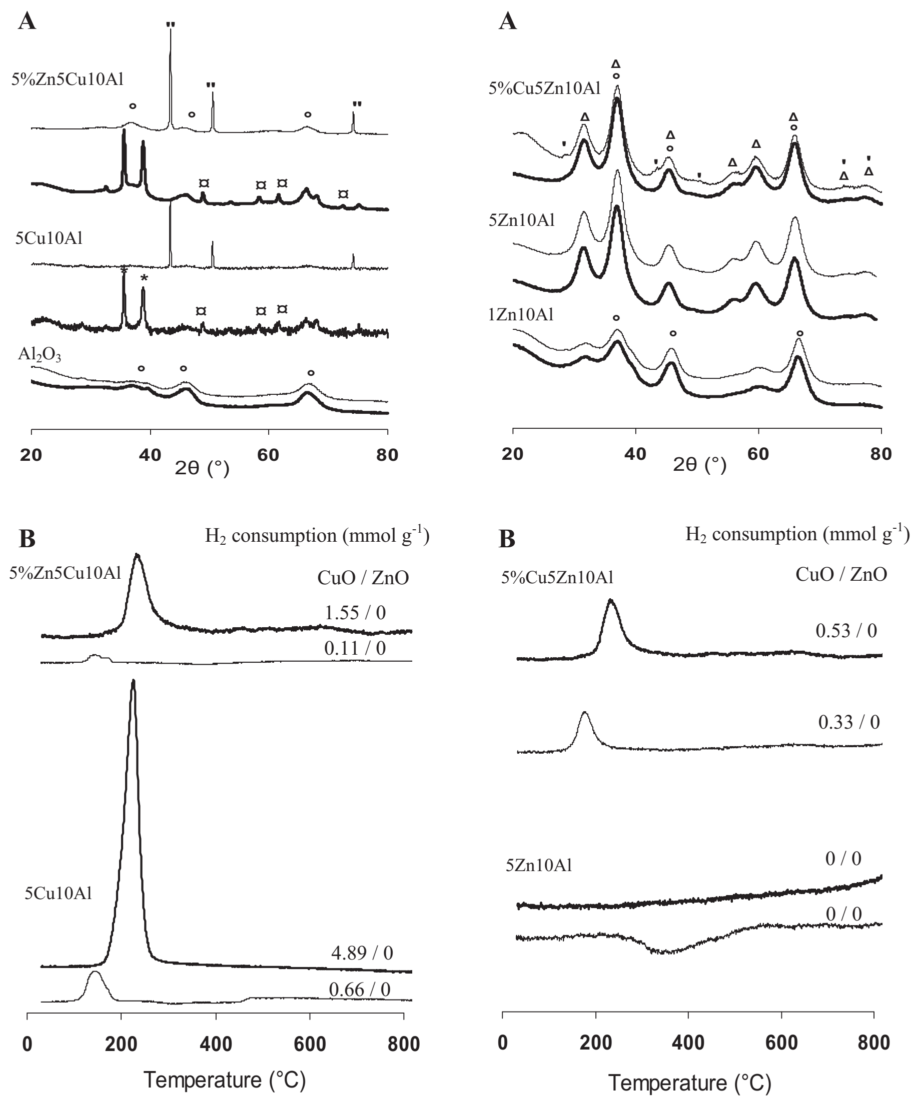

Fig. 1. (A) XRD patterns before test (▬) and after test (–). (B) TPR profiles before test (▬) and after test (–). (○) γ-Al_2O_3, (¤) $CuAl_2O_4$, (∗) CuO, (″) Cu^0, (′) Cu_2O and (△) $ZnAl_2O_4$.

result of high thermal stability of the Zn(II) species as demonstrated [21]. Moreover, a negative peak was detected between 280 and 500 °C for the 5Zn10Al catalysts after test. This peak could be linked to a surface reaction of pre-adsorbed H_2 [22], which explain the low H_2 and the high CH_4 (2) selectivity during the MSR test which is in correlation with our XRD results. The reduction behaviour of CuO in 5%Cu5Zn10Al catalyst examined by TPR after test (Fig. 1B) shows that all the CuO added over the 5Zn10Al were reduced into Cu^0 during TPR and no reduction peak assigned to ZnO species was shown in the spectra. After test, the low H_2 consumption (0.33 mmol g^{-1}) explains that 93% of Cu_2O formed during the test are reduced into Cu^0 during TPR.

4. Conclusions

The above results demonstrate that the presence of alumina enhances the dispersion of copper oxide species by the stabilization of isolated Cu^{2+} ions in their matrix, and moderately by the formation of spinel like $CuAl_2O_4$. By increasing the copper loading, the H_2 selectivity and the methanol conversion increase and 5Cu10Al shows the highest performance among the copper-based catalysts. Zinc-based catalysts show a lower hydrogen selectivity and methanol conversion than that of the copper-based ones with an important coke formation over the catalysts. This could be related to the high thermal stability of $ZnAl_2O_4$ spinel species. Knowing that the redox properties of Cu^{2+} ions play an important role in the catalytic activity, we distinguish that by adding 5% of CuO to 5Zn10Al we favour the formation of Cu^+ species and the suppression of the coke formation after the test. Consequently, in the case of 5%Cu5Zn10Al catalyst the hydrogen selectivity and the methanol conversion rate were the highest. This is attributed to the presence of $ZnAl_2O_4$ spinal form that stabilises the Cu^+ ions, assumed to be the most active species in the SRM reaction.

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