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Characterization And Study Of Catalytic Activity Of Cu/Zno/Al$_2$o$_3$ Systems For Oxidative Steam Reforming Of Methanol

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$Cu/ZnO/Al_2O_3$ catalysts with different composition, prepared from LDH precursors, are studied for OSRM. The catalysts are characterizad by XRD, N_2 adsorption and TPR techniques. N_2O passivation/TPR method is used for the measurement of Cu dispersion. Redox properties are greatly influenced by the chemical composition. Cu dispersion is a function of Cu content: nanosized Cu particles are present up to Cu content of 18at.%. Catalytic activity appears not simply related to Cu content or Cu surface area. A role of the dispersing oxide matrix on the catalytic activity is hypothesized.

1. Introduction

The production of hydrogen for PEM fuel cells of electrical vehicles can be obtained directly on-board from methanol by oxidative steam reforming (OSRM), also called autothermal reforming (ATR), that is a combination of steam reforming (SRM) (1) and partial oxidation (POM) (2):

$$CH_3OH\,(g) + H_2O\,(g) = CO_2 + 3\,H_2 \qquad \Delta H° = 49.5\ kJ\ mol^{-1} \qquad (1)$$

$$CH_3OH\,(g) + ½\,O_2 = CO_2 + 2\,H_2 \qquad \Delta H° = -192.3\ kJ\ mol^{-1} \qquad (2)$$

Compared with SRM and POM, OSRM system has the advantages of an autothermal operation, with a smaller reactor volume and a simpler reactor design [1]. Unfortunately, this process produces appreciable amounts of CO, that is a poison for the platinum anodes of PEM fuel cells, thus highly selective catalysts are required.

The catalysts employed for SRM, POM and OSRM are mainly based on metallic Cu in the presence of ZnO [2,3] eventually with addition of Al_2O_3 [4,5]. Although several new systems were proposed for SRM, POM and OSRM, no decisive novelty appeared in the last years, therefore Cu/ZnO based catalysts still maintain a primary interest.

ZnO acts as a promoter of Cu catalysts, but its mechanism is still debated [6]. Alumina also behaves as a promoter by inhibiting the sintering of Cu(0) [7], but it could also play a direct role in the catalysis through adsorption and activation of methanol [8].

The effect of the chemical composition and the influence of the dispersing oxide matrix on the OSRM activity of $Cu/ZnO/(Al_2O_3)$ systems is still a question under debate and deserves further research. In the present work $Cu/ZnO/Al_2O_3$ catalysts are investigated with the aim of studying the effect of composition and redox properties on the OSRM activity. The catalysts are obtained from hydroxycarbonate precursors with layered double hydroxides (LDH) structure [8]. The precursors and the catalysts are characterized for structural and superficial properties and a correlation between kinetic parameters and chemical-physical properties is drawn.

2. Experimental

2.1 Preparation of precursors and catalysts

The $Cu/ZnO/Al_2O_3$ precursors were prepared with the urea method (0.5 M $CuCl_2$, $ZnCl_2$ and $AlCl_3$, urea/Al=10). The catalysts were obtained by thermal decomposition of the precursors in air at 450°C, heating at rate of 10° C min^{-1} and subsequent reduction in situ with 2% H_2/He mixtures at 450°C for 2h. Pure CuO and ZnO were prepared from $Cu(NO_3)_2{\cdot}4H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ respectively by urea method. The spinel $ZnAl_2O_4$ was prepared from Al_2O_3 and $Zn(NO_3)_2{\cdot}6H_2O$ according to a known procedure [9]. Al_2O_3 was a commercial product (high purity CK-300 type supplied by former AKZO).

2.2 Physical and chemical characterization

X-ray powder diffraction patterns were obtained by a Philips X'Pert APD diffractometer using Cu-Kα Ni-filtered radiation. Specific surface areas were measured by N_2 adsorption on samples degassed at 100°C using a Micromeritics 2010 apparatus. TPR measurements were carried out on samples treated in air flow at 450°C using a 5% H_2/Ar mixture and a heating rate of 10°C min^{-1} on a Micromeritics 2900 apparatus. Copper dispersion was measured by N_2O passivation method [8].

2.3 Catalytic activity measurements

Catalytic activity measurements were carried out in a laboratory flow apparatus with a fixed bed reactor operating at atmospheric pressure. The catalyst (size = 90-110 μm) was diluted in 1:10 ratio with fused quartz powder. Liquid feed (H_2O/CH_3OH) was regulated by a metering pump and gaseous feed (O_2, He) by electronic mass flow controllers. A GC HP 5890 with a Porapak-molecular-sieve column and a TCD detector allowed the analysis of H_2, CO, (detection limit = 0.01%) CO_2, O_2, CH_4, CH_3OH, H_2O. A mass spectrometer Hiden was employed for identification of products not detected by GC. The OSRM tests were carried out at T = 200-400°C, $H_2O/CH_3OH/O_2$ molar ratios = 1.1/1/0.12 (CH_3OH concentration = 17.8 %), GHSV = $6{\cdot}10^4$ h^{-1}. SRM tests were carried out in the same conditions, but without feeding O_2.

3. Results and Discussion

3.1 Chemical analysis and textural properties

Table 1 shows the composition of the catalysts expressed as metal atom percentage and the phase composition of the precursors. Some precursors contain, besides the hydrotalcite ($(Cu,Zn)_{1-x}Al_x(OH)_2(CO_3)_{x/2}{\cdot}mH_2O$), also a certain amount of paratacamite phase ($Cu_{2-x}Zn_x(OH)_3Cl$). The formation of paratacamite is clearly favoured by high Cu

Table 1. Composition of the catalysts and phase composition of the precursors.

	Metal composition, at%			Precursor phases, wt%	
Catalyst	Cu	Zn	Al	Hydrotalcite.	Paratacamite
H5	5	28	67	100	0
HP15	15	48	37	75	25
HP18	18	33	49	85	15
HP45	45	31	24	56	44
P75	75	25	0	0	100

content, confirming the difficulty of inserting high Cu contents in the hydrotalcite structure [10]. The sample P75, derived from a precursor of pure paratacamite, is also included in this study for comparison.

The treatment at 450°C causes the complete decomposition of hydroxycarbonates into CuO, ZnO and Al2O3, as observed from XRD patterns. The formation of amorphous Cu or Zn aluminates cannot be excluded [10]. Surface areas of samples heated at 450°C are reported in Table 2. All samples have high surface areas with exception of P75. The main contribution to surface area is probably given by Al_2O_3: the sample H5, having the highest Al content, has the highest surface area, while the sample P75 that is free of alumina, shows the lowest value. However a regular dependence of surface area on Al content is not recognizable, indicating that other effects must be taken into account. The increase of surface area from HP15 to HP45, suggests that some contribution can be due to CuO or Cu aluminate.

Table 2: Surface area, Cu surface area and Cu dispersion of the catalysts and the reference materials.

Sample	Surface area ([a]) $m^2\ g^{-1}$	Cu surface area $m^2\ g^{-1}$	Cu dispersion %	Cu crystal size ([b]) nm
H5	254	14.8	46	2.4
HP15	88	17.5	20	5.5
HP18	111	15.5	14	7.9
HP45	125	3.3	1.33	83
P75	9.4	4.8	1.25	88
CuO	1	-	-	-
ZnO	13	-	-	-
Al_2O_3	180	-	-	-
$ZnAl_2O_4$	112	-	-	-

(a) Samples treated in air at 450°C (not reduced).

(b) Calculated from Cu dispersion, assuming a spherical shape.

3.2 Temperature Programmed Reduction (TPR) and Cu dispersion measurements

TPR profiles of samples are reported in Fig. 1 together with the curve of pure CuO. The other reference materials (ZnO, Al_2O_3, $ZnAl_2O_4$) give no TPR signals. The amount of H_2 consumption indicates the presence of only Cu(II) in all samples. The shape and intensity of the curves appear strongly depending on the composition. Pure CuO gives a peak with maximum at 342°C. Sample H5 shows one peak at 287°C. The catalysts show composite signals with two components at about 300 and 350°C. P75 shows a very large and broad signal with maximum at 500°C.

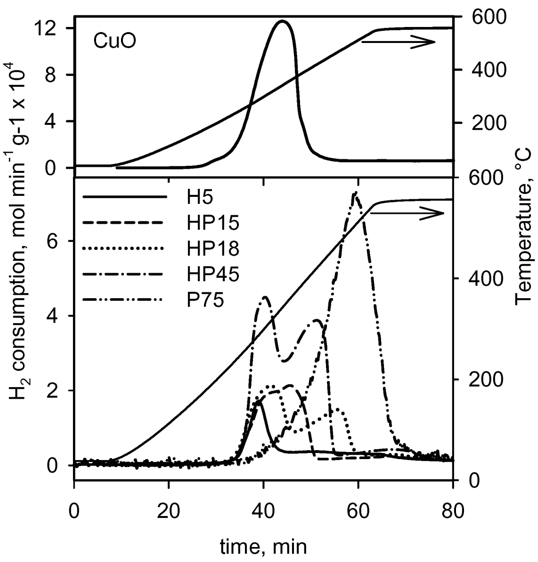

Fig. 1. TPR profiles of the samples

The presence of more than one reduction signal in TPR profiles was related to different Cu(II) species, such as CuO, Cu aluminate or Cu(II) species included in the octahedral sites of Al_2O_3 or vicariant in zinc oxide or zinc aluminate [11]. In the present case, it can be noted that only the samples derived from two phases precursors give rise to two well evident TPR signals. This suggests that hydrotalcite and paratacamite produce CuO phases with different behaviour towards H_2 reduction. Probably hydrotalcite produces a more disperse CuO phase, while the paratacamite phase generates, after thermal treatment, a more compact and less reducible CuO.

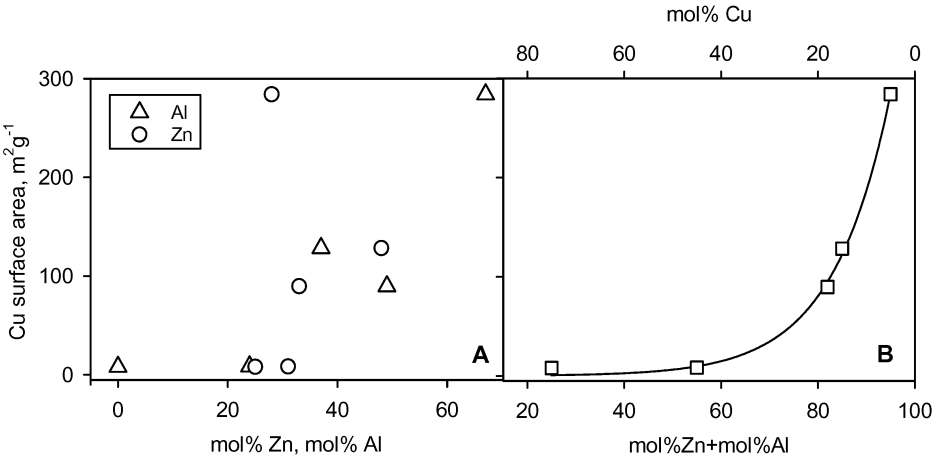

Fig. 2. Cu surface area as a function of (**A**) Zn, Al and (**B**) (Zn+Al) content.

Cu dispersions and Cu surface areas are reported in Table 2. The values of Cu diameter for samples with low Cu content are lower than 10 nm showing that LDH precursors allow to obtain catalysts with nanosized Cu particles. Specific Cu surface area has been plotted as a function of Zn, Al or (Zn+Al) content in Fig. 2. It can be noted that Cu dispersion is not related in a regular way to Zn or Al content, while it is related to the sum (mol% Al + mol% Zn), that is the complement of mol% Cu, suggesting that Al and Zn have a cumulative effect, in other words Cu area is simply related to Cu content. The strong decrease of Cu surface area with Cu mol% at low Cu contents can be related to a strong tendency to coalescence of the nanosized particles. It can also be hypothesized that the presence of paratacamite phase in the precursor, leading to formation of more compact CuO, gives rise to less dispersed metal phase This could explain the very low dispersion observed for the samples HP45 and P75.

3.3 Catalytic activity

H_2 yield for the catalysts and P75 is reported in Fig. 3. H_2 yield increases with temperature according to S shaped curves and varies markedly among the different catalysts, but a simple correlation with the Cu content cannot be drawn. The most active catalyst is HP18 up to 300°C, while at 350-400°C the highest H_2 yields are given by the sample H5 with values close to 100%. The catalysts HP15 and HP45 give significantly lower H_2 yields. The reference material P75 shows a different behavior, because it gives very low H_2 yield at all temperatures, showing a maximum of about 0.9 at 300°C. These data indicate that the activity is not related only to the metallic Cu phase but is also influenced by the properties of the dispersing oxide phase.

Kinetic constants of OSRM and SRM are evaluated from conversion data assuming a first order rate equation and are plotted as a function of Cu surface area in Fig. 4. It can be noted that kinetic constants for OSRM are much higher than those for SRM: the higher activity in the presence of O_2 can be explained by the reaction mechanism involving a partially oxidized Cu surface [12]. It is reported that the adsorption of methanol occurs on a (partially) oxidized Cu, such as a surface Cu-O-Cu group. Methanol reacts with this site producing adsorbed methoxy that is further dehydrogenated, giving rise to adsorbed formaldehyde with simultaneous reduction of the Cu site. Formaldehyde can desorb from the surface or be further oxidized to formate species. Under SRM conditions, adsorbed formate decomposes to CO_2. The oxidized Cu sites are restored by reaction with H_2O In this way Cu undergoes an oxidation-reduction cycle, allowing abstraction of hydrogen atoms from the adsorbed species and their recombination to gaseous H_2. The likely determining step in this mechanism is dehydrogenation of adsorbed methoxy groups. As a consequence the catalytic activity depends

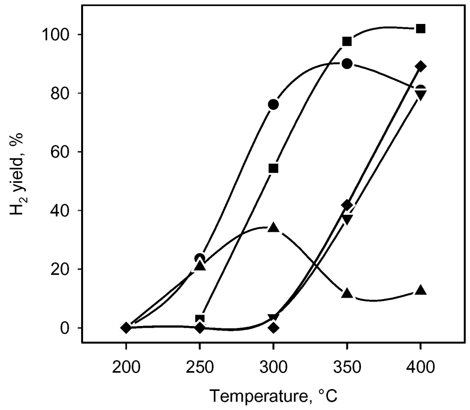

Fig. 3. H_2 yield as a function of temperature

not only on Cu surface area but also on Cu redox properties that are influenced by the presence of the dispersing oxides. This could explain why a simple relation between k and Cu area cannot been derived, since other factors affect the kinetics of OSRM reaction. On the other and, the k values for SRM show a clear increase with the Cu area, suggesting that this reaction is less influenced by the properties of the oxide matrix. However the k value observed for HP15 is lower than that expected from the correlation and is probably related to the lower total surface area compared to those of H5 and HP18, suggesting that some influence of the oxide matrix is present also under SRM conditions.

The above results point to an important role of the oxide matrix of Cu/ZnO/Al$_2$O$_3$ catalysts in determining the activity for OSRM reaction.

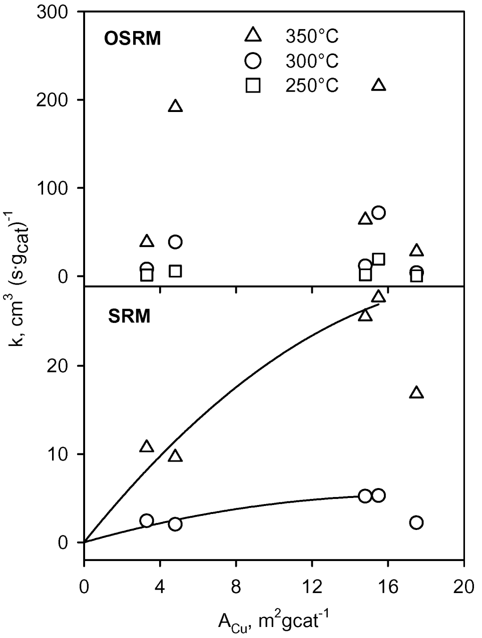

Fig. 4. Kinetic constants of OSRM and SRM as a function of Cu area.

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