SUPPORT EFFECT IN CARBON OXIDE(S) HYDROGENATION ON Cu-Cr SUPPORTED CATALYSTS

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Reducibility, adsorptive properties and catalytic properties of Cu-Cr supported on TiO_2, ZnO and Al_2O_3 were studied in carbon oxide(s) hydrogenation. ZnO is the best retardant for the reduction of copper, stabilizing more strongly Cu^+ species and retaining great amounts of H_2 during the reduction of the calcined precursors. A strong support effect is observed for the CO_2/H_2 reaction and good correlations are established between catalytic activities, Cu^+ species present in the reduced state and H_2 adsorption and storage. ZnO is the most active support but not the most selective one for this reaction. The support effect is not so important for the CO/H_2 reaction, but ZnO supported catalyst is again the most active and also the most selective.

It is now well established that the performance of the active phase of copper-based catalysts for methanol synthesis depends on the chemical environment and especially on the nature of the support and of the reactive atmosphere[1 – 5]. Thus, although ZnO and ZrO_2 supports are active in both CO/H_2 and CO_2/H_2 atmospheres, certain supports like Al_2O_3 are active only in a CO_2/H_2 atmosphere and others like MgO are active only in a CO/H_2 atmosphere[2]. However the quantitative results concerning this support effect are still debatable[1]. For Chinchen et al.[6,7] methanol activity in a $CO/CO_2/H_2$ atmosphere (523 K/50 bar) is proportional to the copper surface whatever the support and these results confirm those obtained by other authors[8 – 10]. A contrary conclusion is reported by Bartley and Burch[11] for whom copper activity in CO/H_2 and $CO/CO_2/H_2$ atmospheres (10 – 40 bar/523 – 543 K) depends greatly on the nature of the support and is proportional to the surface of copper for a given support only. Similar results were obtained by Sneeden et al.[12] in CO/H_2, CO_2/H_2 and $CO/CO_2/H_2$ atmospheres (493 K/bar).

These controversial data prompted us to study the support effect (TiO_2, ZnO, Al_2O_3) on the reducibility, H_2 thermodesorption, N_2O decomposition and catalytic properties for CO/H_2 and CO_2/H_2 reactions of copper-supported chromium modified catalysts[13,14].

EXPERIMENTAL

The catalysts were prepared by coprecipitating hydroxides (copper and chromium) with sodium carbonate at pH 7 and a temperature of 353 K in presence of the support. Copper nitrate and chromic acid were used as precursors. After the coprecipitation, solids were washed, dried at 393 K for 16 h, calcined under air flow at 623 K for 3 h and reduced with hydrogen at 573 K for 12 h before the catalytic test. The specific areas were determined by the BET method using a 2100D Coultronics apparatus.

The decomposition of N_2O, H_2 adsorption and thermodesorption were measured using a pulse chromatographic reactor[15] with 300 mg of catalyst. In both cases the solid was reduced under a H_2 stream (1.2 l h^{-1}), varying temperature from ambient to 573 K at 4 K min^{-1} and maintaining the latter temperature for 12 h (this procedure is similar to the reduction treatment before the catalytic test). Then the solid was flushed with argon at the same temperature for 3 h. After cooling down to 298 K, calibrated pulses of reactants were fed until the saturation of the solid was reached. The thermodesorption of hydrogen was carried out between 298 K and 623 K (at 15 K min^{-1}).

The catalytic tests were performed in a stainless steel fixed bed reactor[16] at 30 bar, 523 K, with a total flow rate of 15 l h^{-1} (H_2/CO_2 = 2 or H_2/CO = 2) in presence of 3 g of catalyst. The on line analyses were carried out by gas chromatography. Blank experiments have been carried out with an empty reactor (without catalyst) and we never noticed a significant activity neither in the CO nor in the CO_2 hydrogenation.

RESULTS AND DISCUSSION

N_2O decomposition. As reported in Table I, the amounts of N_2O decomposed into N_2 depended on the nature of the support and the order observed was (as a function of the support): ZnO > Al_2O_3 > TiO_2. (The metallic areas of copper were calculated assuming that the surface area of a copper atom was 0.67 . 10^{-19} m^2 (ref.[17]).)

Reducibility of the calcined precursors. The TPR of these precursors (Fig. 1) show that the reducibility of copper oxide depends very much on the nature of the support.

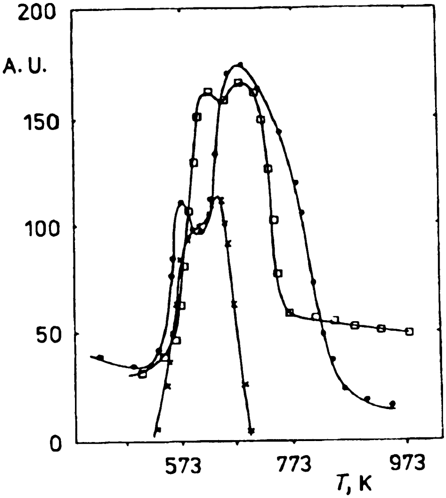

FIG. 1

Temperature programmed reduction of the supported Cu-Cr catalysts. A. U. denotes arbitrary units. □ Cu-Cr/ZnO, ● Cu-Cr/Al_2O_3, × Cu-Cr/TiO_2

We observe two steps of the reduction for the catalysts supported by TiO_2 (573 K and 633 K), Al_2O_3 (573 K and 673 K) and three steps for the catalysts supported by ZnO (623 K, 673 K and 773 K). If the amounts of H_2 consumed during these reductions reflect mainly the reduction of copper(II) oxide, this oxide is reduced significantly on Al_2O_3 (90%), moderately on ZnO (77%) and relatively feebly on TiO_2 (47%) (Table I). These results are similar to our previous data concerning the reducibility of copper-zinc oxide(s) catalysts supported on Al_2O_3 and SiO_2 (ref.[18]). The two principal steps of reduction concerned the formation of partly and of totally reduced copper species[18]. The first species were stabilized on an Al_2O_3 support and not on a SiO_2 support[18]. In the present case of Cu-Cr supported catalysts, it is tempting to attribute also the two principal peaks to partly and totally reduced states of copper (Fig. 1). The third step concerned the superficial ZnO reduction, the hydrogen storage or the reduction of mixed species formed specifically on ZnO supported catalysts.

The first step is reached at a lower temperature (573 K) on TiO_2 and on Al_2O_3 and at a higher temperature (623 K) on ZnO. Thus ZnO retards the reduction of copper(II) oxide and favours the partly reduced state of copper. These conclusions are in good agreement with literature data which indicates that ZnO interacts significantly with copper, stabilizing copper(I) species[1,19]. On the other hand, the high percentage of the totally reduced copper on Al_2O_3 seems to indicate more a structural than a chemical effect of this support[19]. On the contrary the lower reducibility of copper oxide in TiO_2 indicates a more significant metal-support interaction[20,21].

Moreover it is interesting to compare these conclusions with those concerning Cu-Cr bulk catalysts. In fact, for these catalysts it has been shown that the formation of "CuCrOy" species ("copper chromite") ensures a good stabilization of part of the copper as Cu^+ species[22–24]. Besides, the stabilization of Cu^+ species is better with a

TABLE I

N_2O decomposition, H_2 adsorption and thermodesorption of supported catalysts

Property	Catalysts		
	Cu-Cr/TiO_2	Cu-Cr/ZnO	Cu-Cr/Al_2O_3
Composition (%Cu-%Cr)	14.9-14.8	13.6-13.1	11.6-10.7
Specific area (m^2 g^{-1})	50.0	77.5	126.6
N_2O decomposition (μmol g^{-1} Cu)	22.4	48.2	26.0
Metallic area (m^2 g^{-1} Cu)	1.8	4	2.1
Dispersion (%)	1.9	4.5	2.8
H_2 adsorption (μmol g^{-1})	4.3	6.7	3.4
H_2 desorption (μmol g^{-1})	6.9	31.8	12.8
Percentage of reduction	47.7	76.9	91.3

Cu-Cr system than with Cu-Zn or with Cu-Zn-Al systems[22]. This implies that in the case of our supported Cu-Cr catalysts, chromium favours also the formation of Cu^+ species and the phenomenon is amplified when the support is ZnO.

Adsorption and thermodesorption of H_2. As expected[17,18,25,26] the amounts of adsorbed H_2 are lower than those of thermodesorbed H_2 (Table I). Cu-Cr supported on ZnO adsorbs and desorbs greater amounts of H_2 than the two other catalysts (Table I). The thermodesorbed H_2 is due to the existence of a reservoir formed during the reduction of the calcined precursors[18,26 - 29]. Whatever the nature of the stored hydrogen – dissociative or associative – still in discussion[1,30,31], the amount of it depends on the nature of the support in copper based catalysts[18,28]. Indeed we observe that the amounts of H_2 retained vary with the nature of the support: ZnO stores 2.5 times more H_2 than Al_2O_3 and about 5 times more H_2 than TiO_2 supported catalyst. It must be noted however that the Cu 11.6-Cr 10.7/Al_2O_3 catalyst stores more H_2 (12.8 μmol g^{-1}) (Table I) than Cu 10-Zn 12/Al_2O_3 (0.8 μmol g^{-1}) (ref.[18]). This clearly indicates the greater influence of chromium on copper in comparison with zinc for H_2 storage. If we now compare these results with the storage of H_2 (31.8 μmol g^{-1}) by Cu 13.6-Cr 13.1/ZnO (Table I), the influence of chromium on copper seems to be more significant when ZnO is used as a support. This is in good agreement with the reduction experiments (Fig. 1) and emphasizes the significance of the support in the determination of the properties of copper. Moreover, Fig. 2 shows the effect of the support on the H_2-TPD. We can observe two types of hydrogen, one desorbing at low temperature (470 K) and the other corresponding to a high desorption temperature between 573 K and 623 K. On ZnO supported catalyst the hydrogen desorbing at the low temperature preponderates.

Catalytic activity. The catalytic results of the CO_2/H_2 and CO/H_2 reactions (Table II) indicate that the activities depend both on the nature of the support and of the nature of

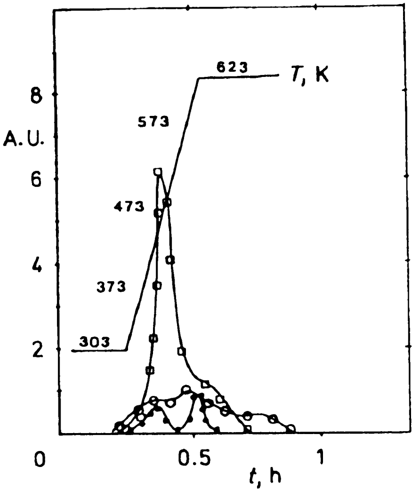

FIG. 2

Hydrogen TPD from catalysts. For A. U. see Fig. 1. ☐ Cu-Cr/ZnO, ● Cu-Cr/Al_2O_3, × Cu-Cr/TiO_2

the reactive atmosphere. As expected[1] conversion are higher with the CO_2/H_2 reaction than with the CO/H_2 reaction (Table II). However, methanol selectivities are greater in the CO/H_2 reaction than in the CO_2/H_2 reaction.

Thus, the CO_2/H_2 reaction is sensitive to the nature of the support: The rates of methanol formation are 8.7, 2.4 and 1.2 (10^{-4} mol h^{-1} m^{-2} Cu) when Cu-Cr species are supported on ZnO, TiO_2 and Al_2O_3, respectively. These results corroborate the redox and adsorption properties observed: The catalysts supported on ZnO are the most active (Table II). That can be related to low energetic hydrogen adsorption (Table I) and stabilization of copper(I) species (Fig. 1).

The results of the CO/H_2 reaction show that there was a low support effect: the rates of methanol formation are 4.2, 2.9 and 2.9 (10^{-4} mol h^{-1} m^{-2} Cu) when Cu-Cr species are supported on ZnO, TiO_2 and Al_2O_3, respectively (Table II). Moreover, no correlation was observed between the redox, the adsorption properties and the activity or the selectivity. These results are different from those obtained with Cu supported catalyst for which in the CO/H_2 reaction there was a strong support effect[11]. They are also different from the results obtained with bulk Cu-Cr catalysts for which a good correlation was observed between copper(I) species and the methanol activity in the CO/H_2 reaction[22]. The simultaneous effects of chromium and of the support bring different catalytic properties depending on the carbon oxide (CO or CO_2) which is hydrogenated.

TABLE II
Activity and selectivity of supported Cu-Cr catalysts in carbon oxide(s) hydrogenation (reaction conditions: P = 30 bar, T = 523 K, catalyst weight W = 3 g, total flow F = 15 l h^{-1}, $H_2/CO(CO_2)$ = 2)

Parameter		Catalysts		
		$Cu\text{-}Cr/TiO_2$	Cu-Cr/ZnO	$Cu\text{-}Cr/Al_2O_3$
		CO_2/H_2 reaction		
Total conversion, %[a]		3.5 (4.22)	15.5 (87.5)	5.6 (58.4)
Selectivity, % in	CH_3OH[b]	16.3 (2.4)	30.0 (8.7)	6.3 (1.25)
	CO	83.3	69.0	93.0
	CH_4	0.4	0.1	0.5
		CO/H_2 reaction		
Total conversion, %[a]		0.9 (11.2)	3.1 (17.4)	1.7 (17.3)
Selectivity, % in	CH_3OH[b]	73.8 (2.9)	73.0 (4.2)	51.0 (2.9)
	CO_2	22.7	26.4	46.0
	CH_4	2.0	0.3	1.0
	C_2H_6	1.0	0.2	0.6

[a] Total activity (mol h^{-1} m^{-2} Cu . 10^4) in brackets; [b] methanol activity (mol h^{-1} m^{-2} Cu . 10^4) in brackets.

CONCLUSIONS

The principal conclusions of this work are: (i) the reducibility of copper(II) oxide depends on the nature of the support. Copper(II) oxide is significantly reduced on Al_2O_3 but not completely reduced on TiO_2, (ii) an hydrogen storage during the reduction of the solids conjugated with a slow desorption for hydrogen strongly adsorbed which modify the adsorption properties and we observed a little adsorption of hydrogen on all these solids. Moreover, the hydrogen amounts stored in the catalysts depend on the support and the biggest are observed with ZnO supported solids, (iii) a significant support effect is observed for the CO_2/H_2 reaction but not for the CO hydrogenation, (iv) a Cu-Cr/ZnO catalyst is active in both reactions but methanol selectivity is more significant from CO/H_2 than CO_2/H_2 reaction. Nevertheless, it is the inverse for methanol productivity. Thus, as proposed by other authors these results could also show that there are two ways of obtaining methanol, namely with CO/H_2 and with CO_2/H_2 (ref.[2]).

1) However, in the CO/H_2 reaction it will be noticed that Cu-Cr catalysts with the same metallic surface and deposited on TiO_2 and on Al_2O_3 have not the same selectivity for methanol. The former is much more selective. This behaviour is in relation with the amount of H_2 adsorbed and the total rate of reduction of the catalyst rather than with the dispersion of the metal.

2) In the CO_2/H_2 reaction although the selectivity for methanol is not as high as above the order of reactivity is the same. Here again the ZnO support is particularly suitable for activating CO_2 or/and intermediate species leading to methanol. It can also favour the water gas shift reaction and the formation of CO and H_2O. In fact, in our experiments, one can notice that carbon monoxide is the major product. In comparison to the CO/H_2 reaction, the CO environment in the carbon dioxide hydrogenation is modified by the presence of oxygen species and hydroxyl groups which will be further transformed into water. As an example Chinchen et al.[6] view the overall methanol synthesis mechanism from CO_2 and H_2 as,

$$CO_2(a) + H(a) \longleftarrow\!\!\!\longrightarrow HCO_2(a)$$

$$HCO_2(a) + 3H(a) \longleftarrow\!\!\!\longrightarrow CH_3OH(g) + O(a)\,.$$

Each copper site at which methanol is formed becomes oxidized during the synthesis reaction and the steady state between oxidixed and no oxidized surface is maintained by the reaction of CO or/and H_2 with O(a). Then, the hydrogen coverage and the presence of specific sites for hydrogen activation in the vicinity of CO_2 adsorption sites will have a determining role in the methanol formation and the regeneration of the catalyst during the (CO_2/H_2) reaction. A peculiarity of copper chromium catalyst and of a ZnO support would be the role of various surface chromite or zinc sites in the activation and storage of hydrogen in the hydride form, desorbing at low temperature. In a further work we shall attempt to define the nature and the localization of the hydrogen involved in methanol formation and the effect of CO or CO_2 on the adsorption states.

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