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STRUCTURE AND REACTIVITY OF Zn-Cr MIXED OXIDES. ROLE OF NON-STOICHIOMETRY IN THE CATALYTIC SYNTHESIS OF METHANOL

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The catalytic behaviour of Zn/Cr mixed oxides with different compositions was investigated as a function of the bulk and surface properties. It was observed that non-stoichiometric spinel-type phases were stable also in the reaction conditions, in which zinc-surface enrichment did not occur. The maximum productivity in methanol was observed for monophasic non-stoichiometric spinel-type samples with a Zn/Cr ratio near to one, whereas the samples richest in zinc, for which a side phase, ZnO also was detected, showed a strong decrease in activity. The catalytic data support the hypothesis that non-stoichiometric spinel is the active phase for the synthesis of methanol on coprecipitated Zn-Cr catalysts.

1. Introduction

Zn-Cr mixed oxides have been well known for many years as active and selective catalysts for the synthesis of methanol at high temperature and pressure [1]. There is no definitive answer to the question, "what might the active phase actually be" [2–4] and, as a consequence, the optimum composition also is not known because these two parameters are related and depend on the preparation method adopted [1]. Maximum of activity has been found for zinc-rich compositions (about 75%, as atomic per cent), containing both ZnO and $ZnCr_2O_4$ [1]. ZnO has been generally identified as the active species and the promoting role of the chromium was attributed to the formation of spinel, which prevents the sintering of small ZnO crystallites [2] or acts as a high surface area support [3,4].

A further chemical promotor effect of chromium has also been hypothesized and attributed to ZnO doping [5,6]. On the other hand, renewed interest for these catalysts has resulted from the fact that modifications in their composition allow higher molecular alcohol mixtures to be obtained [7,8].

We have recently prepared by coprecipitation from aqueous solutions a series of catalysts with different Zn/Cr ratios, some of which (in the range from 33 : 67 to 50 : 50) are unambiguously monophasic and constitute examples of excess zinc, non-stoichiometric spinel-type phases. Taking into account the analogies observed between the X.R.D. patterns of our spinel-type phases and those reported for some non-stoichiometric mixed oxides [9,10], the general formula $Zn_xCr_{2/3(1-x)}O$ was adopted for these compounds, where x ranged from 0.25 (stoichiometric spinel) to 0.60, depending on the Zn/Cr ratio [11,12]. The characteristics of these solids have been reported in previous papers [11–13] and it has been shown that they form *via* chromate intermediates [14]. Furthermore, it has been found that the non-stoichiometric spinels have very different reactivities than ZnO and $ZnCr_2O_4$ towards CO and H_2 adsorption [15–17] and CH_3OH decomposition [16,18].

With the aim to verify if the non-stoichiometric spinels are the active species in the Zn/Cr mixed oxide catalysts or are only optimal precursors, the catalytic activity in the methanol synthesis was investigated and correlated with data for the characterization of bulk and surface properties.

2. Experimental

All the catalysts were prepared by coprecipitation at pH 8.0 ± 0.1 with $NaHCO_3$, dried at 363 K and calcined at 623 K for 24 h [13]. The X.R.D. powder patterns were collected by means of a Philips goniometer, using Nickel-filtered CuK_α-radiation ($\lambda = 0.15418$ nm). The crystal size was measured according to Scherrer's method; possible contributions to the broadening of disorder effects and/or lattice strains were not taken into account. A quantitative determination of crystalline ZnO was carried out using the method suggested by Klug and Alexander [19]. The XPS experiments were performed in a Perkin-Elmer PHI 5400 ESCA system [15] and a C.Erba Sorptomatic 1826 apparatus with N_2 adsorption was used to measure the surface area.

The catalytic tests were carried out in a copper-lined piston flow reactor, operating at 6.5 MPa and 540–600 K range, using a $H_2 : CO : CO_2 = 65 : 32 : 3$ (v/v) gas mixture. Before the catalytic tests, the catalysts were activated in-situ by hydrogen diluted in nitrogen; the hydrogen concentration and temperature were progressively increased during this pretreatment. Outlet gases were monitored on-line by gas-chromatography, while the liquid products were condensed in a cold trap at 253 K during the time on stream (6 h), then weighed and analyzed off-line by gas-chromatography. The total time of stream in the different reaction

conditions was about 50 h for each catalyst. In order to test the stability of the non-stoichiometric spinel-type phases, catalytic tests have been carried out for some samples also at 670 K for 50 h.

After reaction, the catalysts were cooled at r.t. under a flow of hydrogen diluted in nitrogen. At r.t. the samples were stable and the reoxidation of their surface was not observed.

3. Results and discussions

The X.R.D. powder patterns of the samples after the catalytic tests are reported in fig. 1: for the Zn/Cr ratios $\leqslant 50:50$ only one spinel-type phase is present, whereas in the Zn/Cr $> 50:50$ samples a crystalline ZnO phase is also detectable. The main data arising from the X.R.D. results are reported in table 1: the distribution ratio between the tetrahedral and the octahedral sites of the cubic cell of the spinel-type phase arises from the diffraction power of the 400 plane relative to that of the 440 plane. In our case, according to Miller data of the octahedral site preferences energies [20], we have hypothesized that the Cr^{3+} ions are all located at octahedral sites, whereas the Zn^{2+} ions are present at both tetrahedral and octahedral sites, according to results previously reported [8,11–13]. It is possible to observe that for all catalysts the amount of ZnO detected is always smaller than that expected for a simple phase mixture of ZnO and $ZnCr_2O_4$. Therefore, also after the catalytic tests there are non-stoichiometric spinel-type phases present having general formula $Zn_xCr_{2/3(1-x)}O$, where the difference between the value of x and 0.25 can be taken as an index of the non-stoichiometry (this formula is equivalent to $Zn_{1+y}Cr_{2-2/3y}O_4$, with $y = 4x - 1$). The higher the value of x, the more Zn^{2+} ions are located in octahedral sites, randomly substituted by Cr^{3+} ions, and, consequently, more tetrahedral sites are left vacant. The highest values of the cell volume (table 1) support this hypothesis and take into account the higher steric requirement of the octahedral Zn^{2+} ions in comparison with the Cr^{3+} [21]. Table 1 shows also the values of surface area for the samples after reaction; these values are very similar to those previously reported for the calcined samples [13,18].

Furthermore, it must be pointed out that all the catalysts with Zn/Cr $< 50:50$ ratio were stable when investigated at 690 K; only for the Zn/Cr $= 50:50$ sample (i.e. the sample at the upper limit of the monophasic non-stoichiometric range) was a small segregation (13% of the theoretical ZnO value) observed when it was tested in the most severe operating conditions (fig. 1f and table 1), in agreement with the effect of the temperature on it [13].

In table 2 are reported the results of the XPS analyses for the samples investigated before and after reaction. Before reaction, in all samples Cr^{6+} ions are present at the surface and a chromium enrichment in comparison with the bulk value may be observed. As the Zn/Cr ratio is increased, the surface

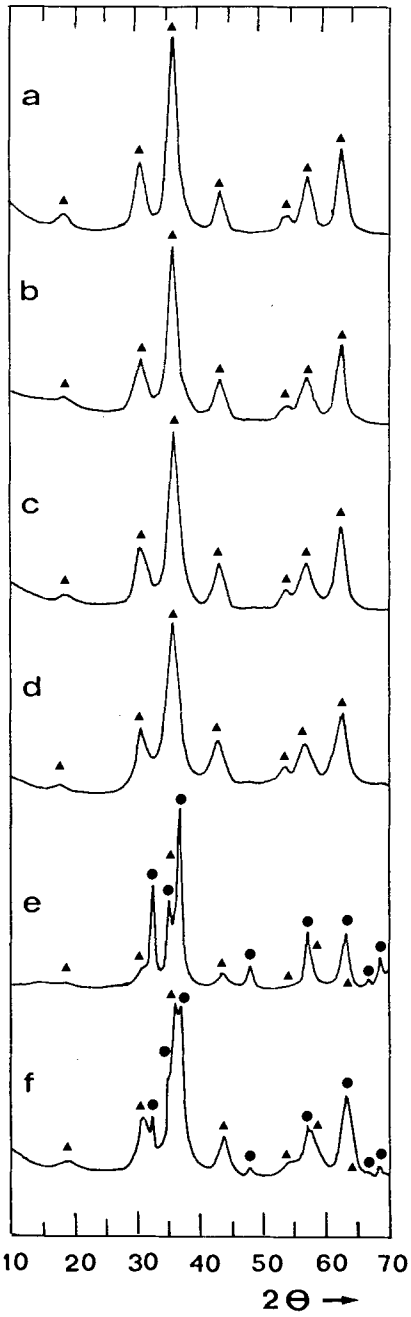

Fig. 1. X.R.D. powder patterns of the samples with different Z/Cr atomic ratios after the catalytic tests: (a) 33:67, (b) 41:59, (c) 44:56, (d) 50:50, (e) 75:25, (f) 50:50, tested in the most severe reaction conditions; (●) ZnO, (▲) spinel-type phase.

Table 1
Physical-chemical characteristics of the catalysts after reaction

Zn/Cr atom. ratio (%)	33:67	38:62	41:59	44:56	50:50	65:35	75:25	50:50 [a]
ZnO detected (w/w%)	–	–	–	–	–	9.5	38.8	3.5
ZnO detectable [b] (w/w%)	0	7.1	11.7	16.8	25.9	48.7	63.5	25.9
V [c] spinel-type phase (nm^3)	0.583	0.582	0.588	0.589	0.589	0.602	0.592	0.589
c.s. [d] spinel-type phase (nm)	5.5	8.0	5.5	5.0	4.0	3.5	6.5	4.5
x [e]	0.250	0.286	0.315	0.345	0.400	0.515	0.496	0.384
Occupancy factor x_T [f]	0.215	0.219	0.214	0.209	0.222	0.202	0.229	0.223
Occupancy factor x_O [f]	0.035	0.066	0.101	0.136	0.178	0.313	0.266	0.161
Occupancy factor x_C [f]	0.500	0.476	0.457	0.437	0.400	0.323	0.336	0.411
Occupancy ratio of tetrahedral/octahedral sites	0.401	0.405	0.383	0.366	0.383	0.318	0.381	0.390
Surface area (m^2g^{-1})	75	106	100	101	110	79	92	107

[a] After catalytic tests at 690 K.
[b] Referred to a phase composition ZnO and $ZnCr_2O_4$.
[c] Unit cell volume.
[d] Crystal size.
[e] On the basis of the general formula $Zn_xCr_{2/3(1-x)}O$.
[f] On the basis of a structural formula: $(Zn^{2+}_{x_T})^{\text{tetrahedral}}\ (Zn^{2+}_{x_O}Cr^{3+}_{x_C})^{\text{octahedral}}O$.

composition tends towards the value of the bulk; surface values higher than bulk ones were never detected. Furthermore, it should be pointed out that increased amount of zinc in the surface compositions as a function of the Zn/Cr ratio, is in agreement with the hypothesized formation of spinel-type phases that are progressively richer in zinc. The presence of chromates, already evidenced on the basis of chemical [14] and infrared [8,18] analyses, is related to the mechanism of formation of the spinel-type phases [14] and is not in contradiction with the proposed structure, considering that $ZnCrO_4$ has a crystal structure closely related to the spinel structure and has the same oxygen lattice.

After reaction, for the stoichiometric spinel and the Zn/Cr = 38:62 sample higher surface amounts of chromium are still present, whereas for the other samples the surface Zn/Cr ratios approach the bulk values, indicating that zinc-rich surfaces phases were not formed during the catalytic tests. Furthermore,

Table 2
Bulk (a) and surface composition of some Zn/Cr samples before (b) and after (c) the catalytic tests

Zn/Cr			Cr(VI)/[Cr(VI)+Cr(III)]×100	
(a)	(b)	(c)	(b)	(c)
33:67	22:78	23:77	33	0
38:62	23:67	24:76	33	0
41:59	32:68	38:62	26	0
44:56	41:59	44:56	28	0
50:50	47:53	48:52	32	0

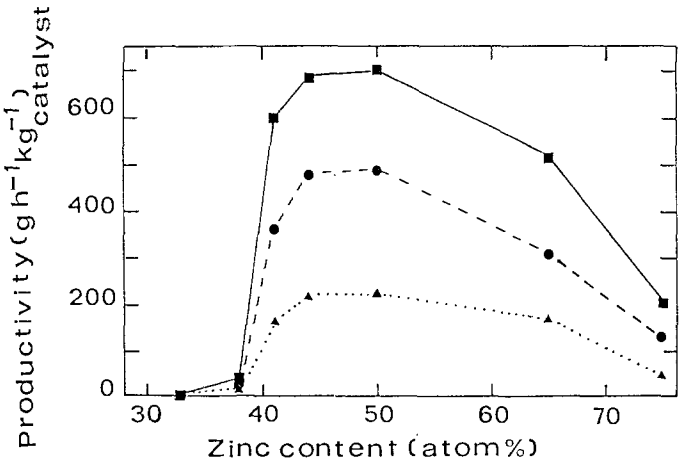

Fig. 2. Methanol productivity as a function of catalyst composition. Reaction temperature: (▲) 565 K, (●) 575 K and (■) 585 K.

the absence of surface Cr^{6+} ions shows that the stability of the non-stoichiometric spinel-type phases cannot be attributed to the presence of surface chromates.

The catalytic behaviour as a function of the catalyst composition is reported in fig. 2 and 3. All the catalysts were very selective in methanol in our conditions, the main by-product being water coming from the reverse water gas shift reaction. For all the temperatures investigated the maximum activity was found for samples containing 44 to 50% zinc (i.e. for samples in which only a non-stoichiometric spinel-type phase is present even after reaction); furthermore, all the catalysts had apparent values of the activation energy of 113 ± 5 kJ mol^{-1}. On the other hand, the presence of a side ZnO phase (samples with Zn/Cr > 50 : 50) gives rise to a decrease in activity.

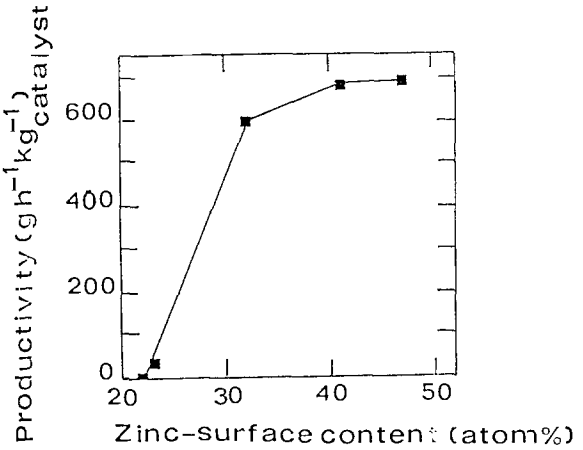

Fig. 3. Methanol productivity as a function of the surface composition of the catalysts. Reaction temperature 585 K.

4. Discussion

The inactive catalysts are therefore those in which excess Cr^{3+} are also present at the surface after reaction. The activity increases up to Zn/Cr = 50 : 50 with increasing non-stoichiometry of the spinel-type phase, while the formation of a ZnO side phase causes a further decrease in activity.

However, the catalytic data do not show a linear correlation with the excess zinc inside the non-stoichiometric spinel-type structure up to Zn/Cr = 50 : 50, as previously observed in the CH_3OH TPD experiments [16,18]. Therefore, the octahedrally coordinated zinc ions, active in the adsorption of CH_3OH on the surface of Zn/Cr mixed oxides, cannot be assumed to be the only source of the catalytic activity. On the other hand, if the methanol productivity is plotted as a function of the zinc surface content (as determined by XPS analysis), a linear correlation is obtained up to a Zn/Cr ratio = 41 : 56, and a further increase in the surface zinc does not give rise to a corresponding increase in activity (fig. 3). This behaviour may be explained taking into account the following factors:

a) Deviation from stoichiometry causes considerable modifications in the CO adsorption capacity, which shows a maximum when the Zn/Cr ratio is 38 : 62 and decreases with increasing zinc content of the samples [13,15,16]. The active sites have been identified as "modified" Cr^{3+} ions present at the surface of the non-stoichiometric spinel-type phases [15].

b) Heterolytic dissociative adsorption of H_2 occurs only on the non-stoichiometric spinel-type phases [17], involving surface octahedrally coordinated Zn^{2+} ions. Recently, it has been reported that the Cu/Cr system with a ratio 50 : 50 also forms only a cubic spinel phase, in which the cupric ions exist in both tetrahedral and octahedral environments [22]. This sample is much more active in the hydrogenation of olefins than the phase with Cu/Cr = 33 : 67 and this higher activity can be attributed to the presence of cuprous ions in octahedral environment [23].

In our non-stoichiometric spinels, the zinc also is located both in tetrahedral and in octahedral sites and the activity of the non-stoichiometric spinels may be related to the presence of zinc in the octahedral environment. These ions, directly involved in the hydrogen activation [17], also modify the "collective" properties of the samples and increase the amount of sites active in CO coordination [15,16]. The low activity of the Zn/Cr = 38 : 62 sample may be attributed to the small amount of surface octahedral zinc ions, and the small increase in activity in the zinc range 41 → 50% to the decrease of surface "modified" chromium ions. This hypothesis also agrees with the decrease in activity in the biphasic systems (Zn/Cr > 50 : 50), for which partial coverage of the active surface by the ZnO also must be taken into consideration. Therefore, the catalytic data reported here support the hypothesis that non-stoichiometric spinel is the active phase for the synthesis of methanol on the coprecipitated Zn/Cr catalysts.

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