Non-stoicheiometric Zn–Cr Spinel as Active Phase in the Catalytic Synthesis of Methanol

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Zn^{2+} ions octahedrally co-ordinated in a non-stoicheiometric Zn–Cr spinel-like phase are the active sites in the catalytic synthesis of methanol from syngas at high temperature.

Zn–Cr mixed oxides are well known catalysts for the synthesis of methanol from syngas at high temperature and pressure.[1] The structure of these catalysts and the nature of the active species have not been fully explained, but generally the active component was considered to be ZnO with a very low crystal size.[2—4] The aim of this work was to clarify the nature of the active species in this catalytic synthesis of methanol.

We have prepared by coprecipitation with $NaHCO_3$ at 333 K and pH 8.0 ± 0.1 three catalysts with Zn : Cr ratios of 0.5, 1.0, and 3.0, respectively, from a solution of the corresponding nitrates of the elements.[5] After calcination in air at 653 K, the Zn : Cr = 0.5 sample showed practically the same *X*-ray diffraction (X.R.D.) pattern as that of pure $ZnCr_2O_4$ (NBS 22–1107). In the Zn : Cr = 1.0 catalyst only a spinel-like phase

Table 1. Characterisation and catalytic results for the catalysts calcined at 653 K for 24 h.

(a) Characterisation results

			ZnO Percentage			Crystal size (nm)	
Zn : Cr atomic ratio	x^a	a (nm)	Calculated	Observed	Δ	Spinel phase	ZnO
75 : 25	0.507	0.841	63.5	37.0	26.5	8.0	15.0
50 : 50	0.400	0.836	25.8	0	25.8	4.0	—
33.3 : 66.7	0.250	0.834	0	0	0	8.2	—

(b) Catalytic results[b]

		Productivity ($g\ h^{-1}\ kg_{catalyst}^{-1}$)			
Zn : Cr atomic ratio	Reaction temperature (K)	MeOH	CH_4	H.A.[c]	H.M.W.[c]
75 : 25	623	188.4	0	0.6	1.0
"	673	59.1	3.4	1.7	0.2
50 : 50	623	392.6	4.6	10.9	3.6
"	673	194.4	7.2	17.1	1.5

[a] x in $Zn_xCr_{2/3(1-x)}O$. [b] *Reaction conditions:* P = 8.0 MPa; reaction time = 8 h; gas hourly space velocity = 8000—9000 h^{-1}. [c] H.A. = Higher alcohols; H.M.W. = other higher molecular weight compounds.

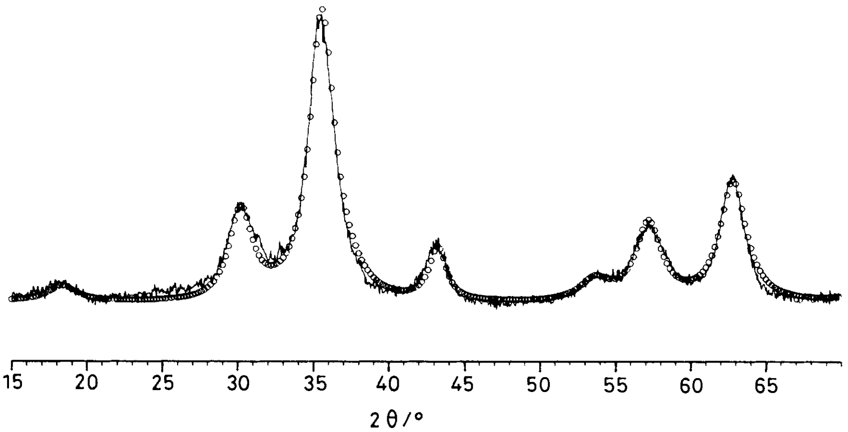

Figure 1. X.R.D. patterns observed (——) and calculated (oooo) for the Zn : Cr = 1.0 catalyst.

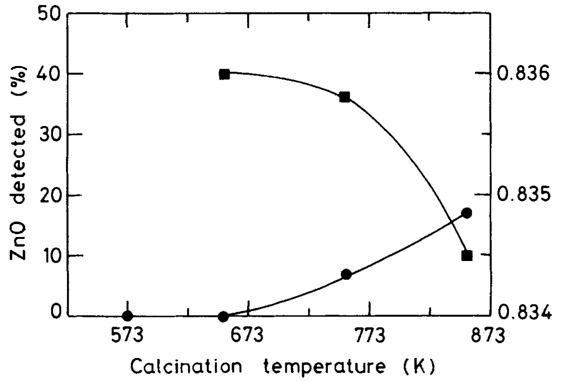

Figure 2. Lattice parameter *a* (■) of the spinel-like phase and amount of ZnO detected (●) for the Zn : Cr = 1.0 catalyst calcined at different temperatures.

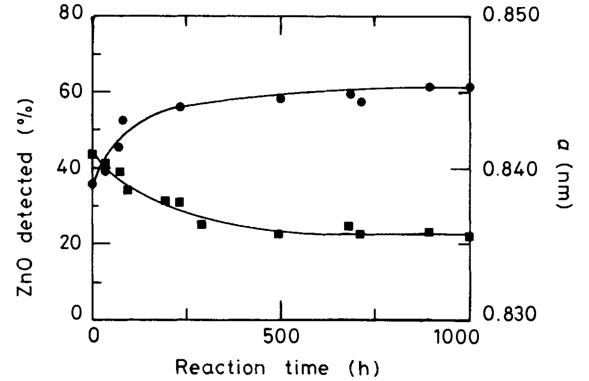

Figure 3. Variations in the lattice parameter *a* (■) of the spinel-like phase and the amount of ZnO detected (●) for the Zn : Cr = 3.0 catalyst as a function of the reaction time.

was present, with an X.R.D. pattern analogous to those reported for non-stoicheiometric mixed oxides of general formula $M_xM_{2/3(1-x)}O$.[6,7] In the case of the Zn : Cr = 3.0 catalyst the X.R.D. analysis revealed the presence of the spinel-like phase and ZnO, the last with the same X.R.D. pattern as that reported in the literature (NBS 5-0664). For the Zn : Cr = 1.0 and 3.0 catalysts the amount of ZnO detected was always smaller than that expected for a simple phase mixture of ZnO and $ZnCr_2O_4$ (Table 1). Assuming that this undetected ZnO was inside the spinel-like mixed oxide phase, the formula $Zn_xCr_{2/3(1-x)}O$ was adopted for this phase.

In Table 1 we have reported the characterisation and catalytic results for the catalysts studied; it must be noted that the Zn : Cr = 0.5 sample showed, in accordance with the literature,[1,8] very low catalytic activity even at the lower reaction temperature and therefore, results for it have not been reported. Our results suggest that the presence of the free ZnO is not necessary and that the spinel-like phase must be considered as the active species in the synthesis of methanol at high pressure. For all the catalysts, increase in the reaction temperature resulted in a decrease in the catalytic activity.

For a more accurate determination of the crystal structure of the spinel-like phase of the Zn : Cr = 1.0 catalyst an *X*-ray full profile fitting method was used. The mathematical model reported by Allegra and Ronca was adopted,[9] together with a structural model based on a faced-centred cubic spinel-like cell. The profile fitting has an appreciable goodness of fit as shown in Figure 1. The Zn^{2+} ions are located in octahedral sites in a random substitution of the Cr^{3+} ions, leaving some of the tetrahedral sites vacant. The structure, then, may be regarded as intermediate between a spinel and a rock salt structure.

The lattice parameter *a* was greater than that of pure $ZnCr_2O_4$ (0.8327 nm) and varied as a function of the Zn : Cr ratio and of the calcination temperature (Figure 2). Therefore the deactivation observed on increasing the reaction temperature can be explained on the basis of movement of the spinel-like phase towards its stoicheiometric form (evidenced by the lowering of the lattice parameter *a*) accompanied by an increase of the percentage of crystalline ZnO detected (together with its crystal size). We observed a similar trend with the reaction time: also in this case the deactivation was accompanied by a decrease in the non-stoicheiometry of the spinel-like phase and a corresponding increase in the amount of crystalline ZnO detected (Figure 3). It is worth noting that the methanol productivity decreased in the same way with decrease in the lattice parameter *a* of the spinel-like phase.

We conclude that the non-stoicheiometric spinel-like phase must be considered as the active species in the synthesis of methanol from syngas at high pressure. The reason why zinc inside the spinel-like phase should be more active than that in pure ZnO lies in the different co-ordination of the Zn^{2+} ions. They occupy octahedral sites in the spinel-like phase, an unusual co-ordination for zinc which in ZnO has tetrahedral co-ordination. The zinc ions at the surface of the spinel-like phase can co-ordinate both the reagents in syngas which favours the synthesis of methanol.

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