Catalysis Letters 18 (1993) 265–271

Iron–chromium–molybdenum oxide catalysts for methanol oxidation

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Received 15 October 1992; accepted 22 January 1993

The activity and selectivity of a precipitated iron–chromium–molybdenum oxide catalyst ($Mo/(Fe + Cr) = 2.5/(0.5 + 0.5)$) towards methanol mild oxidation have been studied by a flow-circulation method. Commensurable activity and selectivity with those of the industrial $Fe_2(MoO_4)_3$–MoO_3 catalysts as well as an enhanced stability have been found. The Mössbauer spectra of fresh and tested catalysts show that during the catalytic reaction a partial reduction occurs and a steady state composition differing from the initial one is formed.

Keywords: Methanol oxidation; iron–chromium–molybdenum oxide catalysts; formaldehyde synthesis; partial oxidation

1. Introduction

A $Fe_2(MoO_4)_3$–MoO_3-based system is the only catalyst which has found industrial application in the mild oxidation of methanol to formaldehyde [1–6]. Its thermal and mechanical stability and the duration of its industrial application are, however, still unsatisfactory. In order to improve these basic parameters, studies have been carried out during the past years on the synthesis and behaviour of multicomponent catalysts [4–11]. As the normal molybdates of iron and chromium are isostructural and the ionic radius of Fe^{3+} (0.79 Å) is close to that of Cr^{3+} (0.76 Å) [12], Popov et al. [7] have established the formation of continuous substituted solid solutions in the system $Fe_{1-x}Cr_xMo_{1.5}O_6$. Our studies of the same system have shown [9] the presence of an orthorhombic phase of the type $Me_2(MoO_4)_3$ ($Me = Fe, Cr$) and free MoO_3 in catalysts with a $Mo/(Fe + Cr)$ atomic ratio of $2.5/(0.5 + 0.5)$ after thermal treatment at 400–550°C.

The present paper contains results obtained by investigating the catalytic activity of iron–chromium–molybdenum oxide catalysts with $Mo/(Fe+Cr) = 2.5/(0.5 + 0.5)$ during oxidation of methanol.

2. Experimental

An iron–chromium–molybdenum catalyst with a Mo/(Fe + Cr) ratio of 2.5/(0.5 + 0.5) was prepared by coprecipitation from aqueous solutions of iron and chromium (III) nitrates and ammonium paramolybdate at room temperature and continuous stirring. Ammonium hydroxide was used to maintain a pH value of 3.8 at the end of the precipitation. The samples were dried in air and heated at 540°C in an air flow for 4 h.

The phase composition of the catalyst obtained was established by X-ray diffraction using a DRON1 apparatus with Cu Kα radiation. The specific surface area was determined by the BET method.

The Mössbauer study was performed on iron–chromium–molybdenum oxide samples heated in a methanol–air mixture under the conditions given in table 1. The sample heated at 360°C and cooled in nitrogen (N_{360}) was additionally calcined for 2 h in oxygen at 400°C (O_{400}) and 540°C (O_{540}).

The Mössbauer spectra were registered by a spectrometer with a constant acceleration at room temperature. A ^{57}Co matrix with an α-Fe standard was used, the center of its sextet being the reference point for calculating the isomeric shift.

Measurements of the specific catalytic activity and selectivity towards oxidation of methanol to formaldehyde were performed with a flow-circulation apparatus [13–15]. The specific rate of the methanol–air mixture ranged from 1.0 to 1.4 ml/g s at an initial methanol concentration of 1.6–2.0 μmol/ml. A fraction with grain sizes of 0.3–0.6 mm was used for kinetic measurements. The formaldehyde content was determined by the bisulphite method. The methanol concentration in the initial and the final mixture and the CO and CO_2 contents were established chromatographically.

3. Results and discussion

Chemical analyses of the precipitate and the filtrate have shown a practically complete coprecipitation. The X-ray phase analysis has allowed explicit determination of the catalyst phase composition. Two crystalline phases are identified: an

Table 1
Conditions of application of iron–chromium–molybdenum catalyst samples

Sample	Index	Heating in a CH_3OH–air mixture	Cooling (atmosphere)
fresh (before the catalytic test)	F		
used (after the catalytic test)	U	240–380°C	air
used	N_{240}	240°C 4h	nitrogen
used	N_{280}	280°C 4h	nitrogen
used	N_{360}	360°C 4h	nitrogen

orthorhombic phase with the structure of iron (III) molybdate and free MoO_3 ($d = 3.80, 3.50$ and 3.21 Å). The specific surface area was 11.5 m^2/g.

The temperature dependence of methanol conversion to formaldehyde under experimental conditions used is shown in fig. 1. The only reaction products are HCHO, CO and H_2O. Within the temperature range investigated (220–380°C), the conversion degree of methanol to formaldehyde passes through a maximum at 270–280°C. At this temperature evolution of carbon monoxide continuously increases. Catalyst selectivity towards oxidation of methanol to formaldehyde at 270–360°C is 99–70%. The activation energy of methanol oxidation to formaldehyde, as calculated from the temperature dependence of the specific reaction rate, is 15.8 kcal/mol.

Fig. 2 presents the experimental results from a comparative catalytic investigation on iron–molybdenum and iron–chromium–molybdenum ($Mo/(Fe + Cr) = 2.5/(0.5 + 0.5)$) catalyst samples.

Results given in fig. 2 evidence that under identical experimental conditions, the catalytic activity of the chromium–iron–molybdenum catalyst is commensurable with that of industrial iron–molybdenum catalyst samples. In addition, when the process takes place under extreme conditions ($T = 400$–420°C, methanol concentration about 4 vol%), the activity of the chromium–iron–molybdenum catalyst remains practically constant for 100 h, while the activity of the industrial iron–molybdenum catalyst (sample I) decreases by about 20%. This is indicative for a favourably enhanced catalyst stability.

Fig. 3 shows the Mössbauer spectra of a fresh Fe–Cr–Mo–O catalyst and a typi-

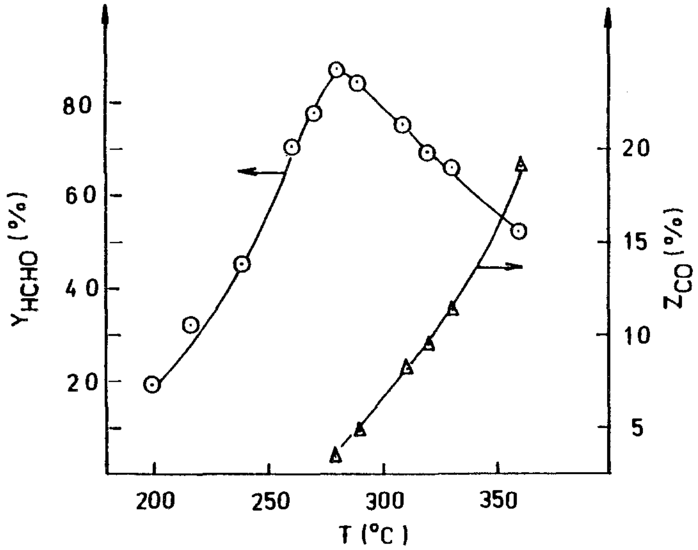

Fig. 1. Temperature dependence of the degree of conversion of methanol to formaldehyde (Y_{HCHO} (%)) and carbon monoxide (Z_{CO} (%)).

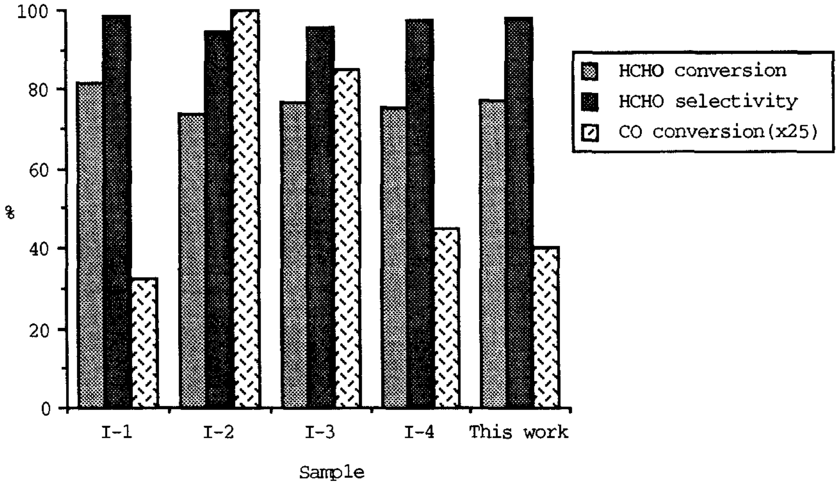

Fig. 2. Experimental results on industrial samples of Fe–Mo–O (I-1 to I-4) and Fe–Cr–Mo–O ($Mo/(Fe+Cr) = 2.5/(0.5+0.5)$) catalysts.

cal spectrum of the same sample obtained after a catalytic test under nonisothermal conditions (sample U) during methanol oxidation.

Both spectra contain a very intense component due to Fe^{3+} ions occupying octahedral sites in the monoclinic structure of Fe(III) molybdate. The isomeric shift values (table 2) of this component of the spectrum evidence that the Fe^{3+} ions are in a high-spin state. In the spectrum of the used catalyst there is also a low-intensity component, which indicates that when the catalyst is acting, new states for iron ions appear in its structure. Their appearance cannot be associated with the presence of Cr^{3+} ions in the catalyst because this component is absent from the spectrum of the fresh catalyst; it is not found in the fresh catalyst either [9]. The appearance of these new states of Fe^{3+} ions is most probably a consequence of the interaction between the catalyst and the components of the gas mixture during formation of the steady-state catalyst composition. Comparison of this new complex with that observed at low reduction degrees of the Fe(III) molybdate prior to formation of Fe(II) molybdate [9] reveals their similarity. Therefore, formation of new states of iron ions in this case cannot be ascribed to accumulation of anionic vacancies at the expense of the participation of oxygen from the molybdenum lattice in a chemical interaction with CH_3OH.

The interpretation of the steady state of the catalyst is associated with the idea [7] about activation of the Fe(III) molybdate crystal during the catalytic reaction. This activation requires breaking in the crystal of the initial bonds which differ in lengths and energies [17]. This inevitably leads to transformation of the subsurface layers in the crystallites and formation of new states for the iron ions.

Previous studies [17,18] by Mössbauer spectroscopy have reported defects appearing during the catalyst synthesis (biographical reduction) or under the effect

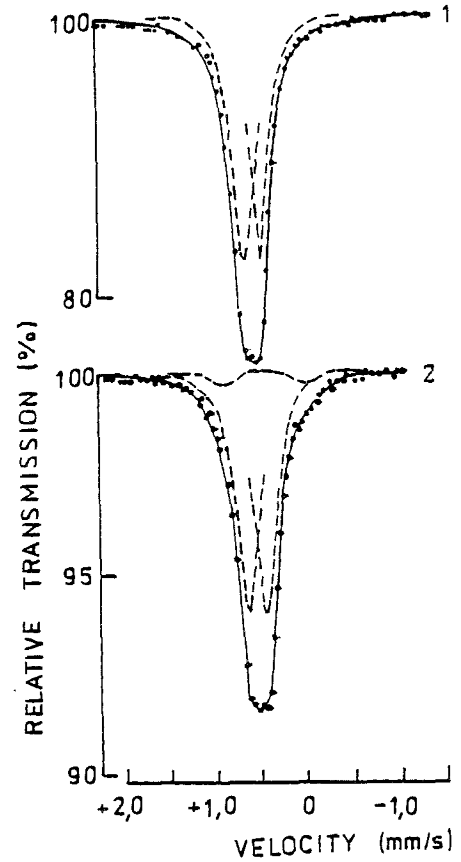

Fig. 3. Mössbauer spectra of a fresh Fe–Cr–Mo–O catalyst (1) and a catalyst after the test reaction (2).

of the reaction medium. The cited papers of other authors concerning Fe(III) molybdate and our investigations on the iron–chromium–molybdenum catalyst reveal the possibility of partial reduction of the catalyst during its application.

All spectra of used catalysts recorded by us exhibit a low intensity doublet indicating partial reduction of the catalysts. The reduction degree increases with increasing temperature of the isothermal treatment of the samples from 240 to 360°C. The relative weight of the low-intensity doublet increases from 12 to 21% (table 2). Samples heated at 400 and 540°C in an oxygen flow for 3 h after the catalytic reaction followed by cooling under nitrogen (table 2) have been subjected to Mössbauer investigation. The results evidence that oxidation of the catalyst at 400°C only leads to a decrease (from 21 to 16%) of the relative weight of the low-intensity doublet, whereas oxidation at 540°C restores the initial state of the catalyst: a low intensity component is absent, as in the case of the fresh catalyst.

It may, therefore, be concluded that, during the catalytic reaction, when the reaction components interact with the catalyst surface, partial reduction occurs and a

Table 2
Parameters of the Mössbauer spectra of the Fe–Cr–Mo–O catalysts treated under different conditions[a]

Sample	Main component $Fe_2(MoO_4)_3$				Low-intensity component $Fe_2Mo_3O_{12-x}$			
	δ (mm/s)	Eq (mm/s)	FWHM (mm/s)	G %	δ (mm/s)	Eq (mm/s)	FWHM (mm/s)	G (%)
F	0.413	0.182	0.286	100	–	–	–	–
U	0.406	0.191	0.281	93.8	0.318	0.879	0.294	6.2
N_{240}	0.410	0.188	0.281	87.6	0.300	0.927	0.657	12.4
N_{280}	0.412	0.187	0.283	84.9	0.319	0.842	0.681	15.1
N_{360}	0.411	0.191	0.288	79.2	0.315	0.811	0.714	20.8
O_{400}	0.405	0.188	0.295	83.9	0.343	0.911	0.726	16.1
O_{540}	0.415	0.184	0.288	100	–	–	–	–

[a] δ = isomer shift; Eq = quadrupole splitting; FWHM = linewidth.

steady state composition differing from the initial is formed. Oxidation of methanol proceeds with high rate and selectivity which are commensurable with those of industrial iron–molybdenum catalysts. The catalytic data have shown that iron–chromium–molybdenum catalysts have an increased stability and can be used for a longer time.

Acknowledgement

DK Acknowledges a sabbatical grant (SAB 92-0302) from Ministerio de Educacion y Ciencia (Madrid, Spain).

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