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Oxidation of methanol on sodium modified chromium–molybdenum catalysts

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Abstract

The effect of sodium on catalytic properties of the Cr–Mo-based catalysts for methanol oxidation was investigated. The samples were prepared by (i) - precipitation from 5 wt.% aqueous solutions of chromium nitrate and sodium molybdate (ii) - impregnation of preliminary synthesised catalyst with aqueous solutions of $NaNO_3$, vaporising, drying and calcination at 500°C in the course of 5 h. Formation of a new compound with composition $Na_2O.Cr_2O_3.3MoO_3$ was established. The results obtained allowed our conclusion that the sodium effects on the properties of the catalysts depended strongly both on the way of its introduction into the system and the composition and properties of the compounds it formed.

Keywords: Methanol oxidation; Chromium–molybdenum catalyst; Sodium influence

1. Introduction

It is known, that the presence of alkaline metal impurities has a negative effect on the conversion of methane and methanol to formaldehyde on silica-supported molybdenum oxide [1,2]. Popov et al [3] studied the influence of various sodium salts on the catalytic properties of Fe–Mo–O catalysts and have ascertained that the introduction of 0,4 wt. % Na by impregnation leads to a decrease in the activity of the samples by a factor of 10–12. The forming of sodium molybdates or of polymolybdates has been assumed, but no evidence of this has been given. On the contrary, according to Portela et al [4], introduction of small quantities of Na (up to 50 ppm) leads to an improvement of the catalytic properties of commercial iron–molybdenum catalysts. In both cases sodium is introduced by impregnation with a solution of soluble salts. Canavesi et al [5] have obtained an active and selective catalyst by precipitation from Na_2MoO_4 and $FeCI_3$ solutions. Our research showed that the introduction by precipitation of sodium in amounts up to 0,2% not only did not worsen, but on the contrary, improved the properties of the iron–molybdenum catalysts due to its locking in the form of $NaFe(MoO_4)_2$ [6].

It is known, that chromium–molybdenum and mixed chromium–iron–molybdenum are some of the most promising catalysts for selective oxidation of methanol [7,8]. In this paper, we are going to discuss the results of the oxidation of methanol over two series of sodium doped chromium molybdates. The aim is clarifying the influence of alkaline metals on the properties of these catalysts and specifying the nature of the compounds which are formed in the process of their preparation.

2. Experiment

The preparation of the sodium-doped catalysts was carried out in two ways: (i) - By precipitation from 5 wt.% aqueous solutions of chromium nitrate and sodium molybdate. Precipitation was carried out by slow addition, with continuous stirring, of aqueous solutions of nitrate to an aqueous solution of molybdate. At the end of sedimentation the pH was 5,5. The sediment was washed with distilled water, dried and calcinated at 500°C in the course of 5 h. Before and after each washing samples were taken from the sediments and the filtrate and analysed for content of Na, Mo and Cr. (ii) - Different amounts of sodium were incorporated into preliminary synthesised catalyst by impregnation with aqueous solutions of $NaNO_3$, vaporising, drying and calcination at 500°C in the course of 5 h.

Chemical analysis of the samples was performed by atomic absorption (AA) and atomic emission (ICP). X-ray diffraction patterns obtained to establish the phase com-

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position of the catalysts. Measurements of the catalytic activity and selectivity (S) towards oxidation of methanol were performed with a flow apparatus at a flow rate of 12 000 h^{-1}, with 6 vol. % methanol concentration in the alcohol–air mixture and temperatures between 200 and 400°C. In all cases the amount of the catalyst was 3 cm^3 and its particle size was 1.0 –1.6 mm. The formaldehyde content in the reaction products was determined by the bisulfite method. The amounts of CO, CO_2, $(CH_3)_2O$ (DME) and unreacted methanol were analysed by a gas-chromatography.

3. Result and discussion

3.1. Catalysts preparation and characterisation.

We synthesised two series of samples, containing different amount of An by precipitation and through impregnation. The results from the chemical analyses of the precipitates, presented in Table 1, indicate that washing with distilled water has a significant effect on their composition. The content of sodium decreases sharply from 7.1 to about a 0.2 wt. % and the ratio Mo/Cr decreases from 1.5 to 1.2 at the end of the process. Apparently the calcinated samples would be rather different and will differ in their composition, which would permit evaluating the influence of the quantity of the incorporated sodium on their properties.

Taking into consideration the similar properties of $Cr_2(MoO_4)_3$ and $Fe_2(MoO_4)_3$, it is quite probable that in this case similarly to the iron–molybdenum catalysts [6], the heat treatment leads to the formation of a new phase with the composition $NaCr(MoO_4)_2$. This necessitated the preparation of $NaCr(MoO_4)_2$ through mixing in an appropriate proportion of aqueous solutions of sodium and chromium nitrates and ammonium paramolybdate, vaporisation of water, drying and calcination at 550°C in the course of 6 h. The well defined phase obtained was used as a reference compound.

Fig. 1 shows the results from X-ray phase analysis of pure $Cr_2(MoO_4)_3$ (a) and $NaCr(MoO_4)_2$ (d) as well as those of samples 1(c) and 7 (b) from Table 1.

Table 1
Content of Na (calculated as Na_2O), Cr (calculated as Cr_2O_3) and Mo (calculated as MoO_3) in catalysts depending on the number of washings of the sediment

N°	Number of washings	Content of, wt %		
		Na_2O	Cr_2O_3	MoO_3
1	0	9.6	23.5	66.9
2	1	4.4	32.8	63.5
3	2	2.2	35.7	61.9
4	3	1.3	40.9	58.1
5	4	0.7	42.9	57.6
6	5	0.3	43.2	56.4
7	6	0.2	44.3	54.6

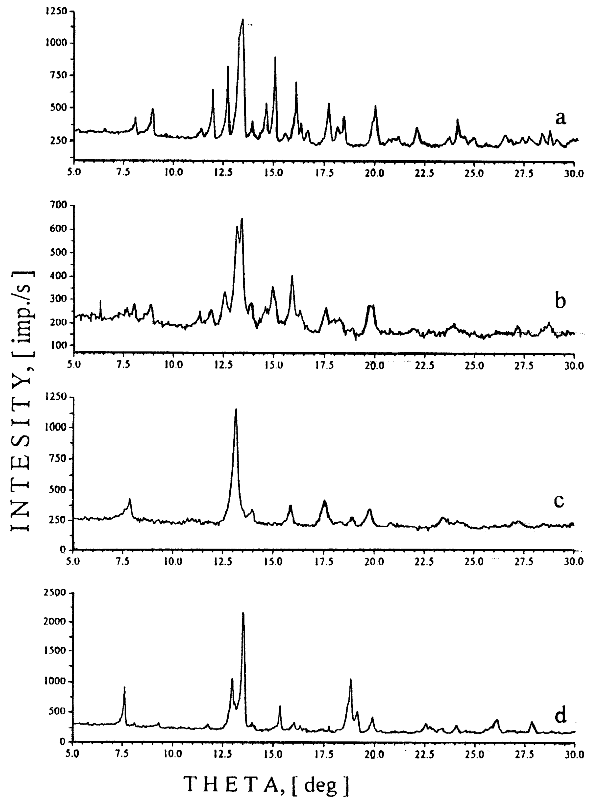

Fig. 1. X-ray diffraction patterns of pure $Cr_2(MoO_4)_3$ (a) and $NaCr(MoO_4)_2$ (d) and samples 1 (c) and 7 (b) from Table 1.

The visual comparison of the diffractograms shows that samples **a** and **d** are well-crystallised $Cr_2(MoO_4)_3$ and $NaCr(MoO_4)_2$. The angular position and the intensities of the lines of diffractogram **b** are very close to those of pure $Cr_2(MoO_4)_3$. Only the poor crystallisation suggests the presence of admixture.

A significant difference is noted in diffractogram **c** of the sample with sodium content of 9.6 wt. (calculated as Na_2O), which differs both in the positions and the intensities of the main lines. The precise comparison of the results obtained from the X-ray analysis, given in Table 2, shows the presence of completely different compounds.

The results, given in Table 2, show that the diffraction lines typical of MoO_3 and Cr_2O_3, are found in none of the samples examined. In samples 1 and 3, only the lines, typical for pure $Cr_2(MoO_4)_3$ and $NaCr(MoO_4)_2$were observed. Of highest interest are the results obtained for sample 2. The analysis made showed that no Na, Cr and Mo- containing compound with such characteristics was obtained. Obviously, a new compound, with composition $Na_2O.Cr_2O_3.3MoO_3$ was prepared. Additional investigations are needed to determine the parameters of its crystal lattice.

The amount of $NaNO_3$ used to introduce sodium by impregnating of pre-synthesised chromium–molybdenum

Table 2
Angle of reflectance (Q,°), inter-plane spaces (D_{HKL}, A) and relative intensity (I/I_0, %) of the diffraction lines of $Cr_2(MoO_4)_3$, $NaCr(MoO_4)_2$ and samples 1 from Table 1

θ [deg]	D_{HKL}, (A)	I/I_0, %		
		$Cr_2(MoO_4)_3$	Sample $\mathrm{N}^{\hat{\imath}}$ 1	$NaCr(MoO_4)_2$
1	2	3	4	5
7.60	6.763	0	0	34
7.85	6.549	0	21	0
12.74	4.056	60	0	0
12.95	3.991	0	0	43
13.10	3.946	0	0	24
13.15	3.932	0	100	0
13.35	3.874	0	0	100
13.40	3.860	100	0	0
13.78	3.755	5	0	0
13.95	3.710	31	14	6
14.63	3.541	17	0	0
15.08	3.438	69	0	0
15.35	3.379	0	0	21
15.90	3.265	0	18	0
16.15	3.216	49	0	0
16.37	3.174	16	0	0
16.69	3.114	11	0	0
17.55	2.966	0	23	0
17.72	2.939	33	0	0
18.34	2.843	14	0	0
18.48	2.822	23	0	0
18.80	2.776	0	0	44
18.85	2.768	0	8	0
18.95	2.754	0	9	0
19.15	2.727	0	0	17
19.80	2.641	0	16	0

catalysts, was selected so that the sodium content in the catalysts varied between 0,5 to 1,5% wt. Fig. 2 shows the comparison of the diffractograms of pure $Cr_2(MoO_4)_3$ and a catalyst obtained by impregnation with a sodium content of 1.5% wt.

The appearance of new diffraction lines at $Q=13.2$ and

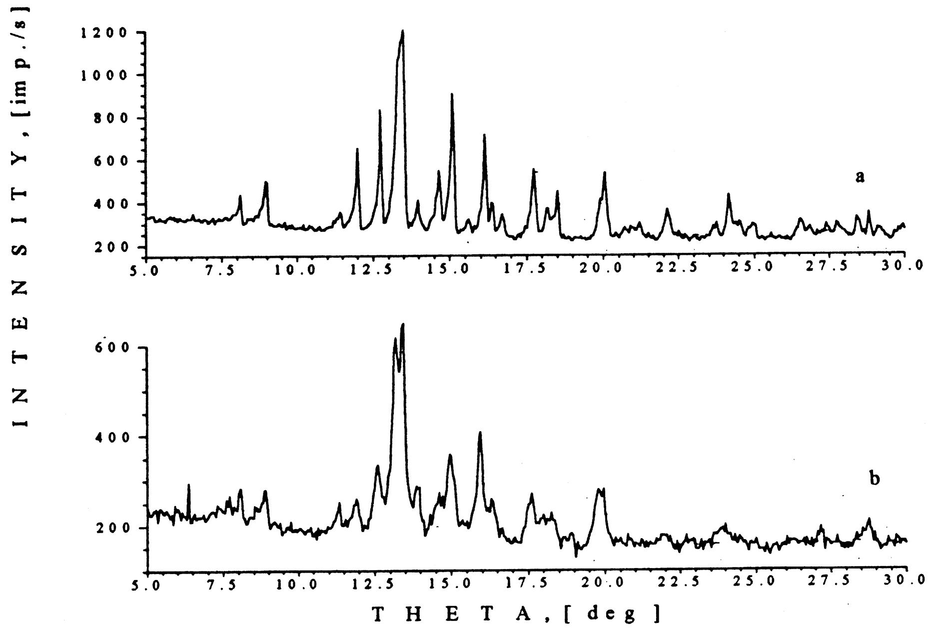

Fig. 2. X-ray diffraction patterns of $Cr_2(MoO_4)_3$ and prepared by impregnation sample with 1.5 wt.% sodium.

Table 3
Dependence of the process rate over precipitated Cr–Mo–O catalysts on sodium content at 300 and 350°C

N°	Number of washings	T,°C	Content of, %				S, %
			CH_2O	CO	DME	Total	
1	0	350	21.9	0.3	<0.1	22.2	98.6
		300	4.8	<0.1	<0.1	4.8	100.0
2	1	350	48.6	1.0.	0.4	50.0	97.2
		300	9.0	0.2	0.3	9.5	94.7
3	3	300	71.0	1.8	1.0	73.8	96.2
	350	26.5	0.7	1.3	28.5	93.0	
4	6	350	89.2	2.8	1.5	93.5	95.4
		300	84.1	1.9	2.8	88.8	94.7

19.8 also confirmed the formation of $Na_2O.Cr_2O_3.3MoO_3$ in the impregnated samples.

3.2. Methanol oxidation

Table 3 shows the results from methanol oxidation on samples obtained by precipitation.

It is seen that with the chromium–molybdenum catalysts some dependence of the catalytic activity on the sodium content of catalysts is observed, as in the iron–molybdenum. This result is expected since $Fe_2(MoO_4)_2$ and $Cr_2(MoO_4)_4$ are iso-structural compounds, and the mechanism of methanol oxidation is the same on both compounds. One is, however, impressed by the significantly lower activity of the sample with the highest sodium content (N°1 of Table 1). This is explainable by taking into account that in this case a pure $Na_2O.Cr_2O_3.3MoO_3$ with a low activity for methanol oxidation, is formed. In all cases with iron–molybdenum catalysts, some amount of $Fe_2(MoO_4)_2$, is found along with $NaFe(MoO_4)_2$ providing for their higher total activity. The sample containing less than 0.2% wt. sodium (sample 4 of Table 3) showed high activity and a very good selectivity, i.e. $Na_2O.Cr_2O_3.3MoO_3$ plays the role of a mechanical admixture and its presence in such amounts does not exert any significant effect on the catalytic properties of the samples.

Table 4
Dependence of the process rate over impregnated catalysts on sodium content at 300 and 350°C

N°	Na, %	T,°C	Conversion to,%				S, %
			CH_2O	CO	DME	Total	
1	0.10	350	79.3	2.0	1.1	82.4	96.2
		300	40.3	1.3	1.5	43.1	93.5
2	0.25	350	64.7	1.8	0.9	67.4	96.0
		300	32.7	1.0	1.2	34.9	93.7
3	0.50	350	48.6	1.1	0.4	50.1	97.0
		300	26.2	0.9	1.1	28.2	92.9

Table 4 shows the results of methanol oxidation on samples obtained by impregnation.

In this case, as with iron–molybdenum catalysts, insignificant amounts of sodium introduced by impregnation provoked a sharp decrease in activity. Obviously, the reason for that again is the sodium concentration on the surface of samples and the blocking of their active centres.

4. Conclusions

1. The results from the performed research show, that small quantities of sodium, introduced during precipitation, do not influence in a negative way the properties of the chromium–molybdenum catalysts. However, its introduction by impregnation leads to a sharp deterioration of their catalytic properties.

2. It is established that during the interaction of sodium molybdate and chromium nitrate at pH at the end of the sedimentation 5,5, a new, compound with composition $Na_2O.Cr_2O_3.3MoO_3$ is obtained.

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