Mössbauer study of modified iron-molybdenum catalysts for methanol oxidation

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Abstract. The preparation and catalytic properties of mixed Fe-Mo-W catalysts toward methanol oxidation are investigated. Mössbauer spectroscopy, X-ray diffraction and chemical studies revealed the formation of two types of solid solutions with compositions Fe₂(MoₓW₁₋ₓO₄)₃ and (MoₓW₁₋ₓ)O₃. The solid solutions formed are characterized by high activity and selectivity upon methanol oxidation and are of interest in view of their practical application. Sodium-doped iron-molybdenum catalysts are also investigated and the NaFe(MoO₄)₂ formation was established.

1. Introduction
The most important results of the investigations of oxide catalysts for selective oxidation of methanol, carried out during the last two decades, lead to the conclusion that the system Fe₂(MoO₄)₃-MoO₃ has no alternative [1, 2]. Mössbauer spectroscopy is an excellent technique for investigation of these catalysts [1, 3]. According to Pernicone [4] and Ivanov [5], attention should be focused on the enhancement of the activity, selectivity and stability of the catalysts by the introduction of suitable additives. The present work deals with a Mössbauer study of tungsten and sodium modified iron-molybdenum catalysts.

2. Experimental
The tungsten modified catalysts were obtained by precipitation from 5 mass % aqueous solutions of FeCl₃ and of mixtures of ammonium heptamolybdate and Na₂WO₄ in various ratios, at pH values by the end of the process ranging from 1.6 to 2.0. The precipitates obtained were washed, dried and annealed at 500°C for 5 hours.

The preparation of the sodium-doped catalysts was being carried out in two ways: (i) by precipitation from 5 mass % aqueous solutions of iron nitrate and sodium molybdate and (ii) different amounts of sodium were incorporated into preliminary synthesized catalysts by impregnation with aqueous solutions of NaNO₃, vaporizing, drying and calcination at 500°C in the course of 5 hours.

Chemical analysis of the samples was performed by atomic absorption (AA) and atomic emission (ICP) measurements. X-ray and Mössbauer spectra were obtained to establish the phase composition of the catalysts. The X-ray analysis of the annealed specimens was performed by a TUR-M 62 diffractometer with Co-Kα radiation. The exact positions of the lines and their breadths were determined according to a program for decomposition and profile analysis of the diffractograms [6].
The Mössbauer spectra were recorded on an electromechanical spectrometer Wissenschaftliche Electronic GmbH, (Germany) operating at a constant acceleration mode at room temperature. A $^{57}$Co/Cr (activity of about 50 mCi) source and an $\alpha$-Fe standard were used. The experimentally obtained spectra were mathematically treated by the least squares method. The parameters of the isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field ($H_{\text{eff}}$) were determined. The relative weight of the partial components (G) of the spectra was calculated on the basis of the intensity of the respective lines.

3. Results and discussion

3.1. Tungsten modified catalysts

The results of X-ray investigation suggest that the addition of tungsten leads to considerable changes in the phase composition and structure of the precipitated specimens: (i) the increase of the WO$_3$ content causes changes in the position and intensity of the basic lines in the diffractograms; (ii) the lines characteristic of Fe$_2$(MoO$_4$)$_3$ are slightly shifted to higher values of d (nm); (iii) the most considerable change is observed in the intensity of the lines belonging to MoO$_3$ (interplanar distances d = 0.685, 0.386, 0.347, 0.327 and 0.230 nm) - some of them almost disappear at high tungsten content. These changes in the X-ray diffractograms suggest that the replacement of some of the molybdenum atoms in the Fe$_2$(MoO$_4$)$_3$.MoO$_3$ catalyst by tungsten leads to the formation of two types of solid solutions. The drastic decrease of the intensity of the lines characteristic of MoO$_3$ and the absence of lines related to the formation of WO$_3$ lead to the conclusion that during precipitation and subsequent thermal treatment, compounds of the type (Mo$_x$W$_{1-x}$)O$_3$ are formed, the latter being described in powder diffraction files PDF 9-0224, PDF 9-0225, PDF 28-0667 and PDF 28-0669. At x < 0.5, the diffraction lines correspond in the best way to a compound with the composition (Mo$_{0.68}$W$_{0.32}$)O$_{3.5}$ [7].

On the other hand, the interplanar distances, characteristic of Fe$_2$(MoO$_4$)$_3$, increase with the rise of the WO$_3$ content. This indicates that a portion of tungsten participates in the formation of solid solution having a Fe$_2$(Mo$_{1-x}$W$_x$O$_4$)$_3$ composition. The results described above lead to the conclusion that some of the Mo$^{6+}$ ions in Fe$_2$(MoO$_4$)$_3$ and the free MoO$_3$ are isomorphically substituted by W$^{6+}$ ions. This is confirmed by the Mössbauer spectra of the specimens.

![Mössbauer spectra](image)

**Figure 1.** Mössbauer spectra of Fe$_2$(MO$_4$)$_3$+xWO$_3$, where x=0.0(1), 1.9(2), 8.0(3) and 15.9(4)
The spectra of the specimens containing tungsten are processed as composed of two doublets having the same IS values and differing in the QS values (Fig. 1). The parameters obtained and the relative weights of the areas corresponding to the doublets for Fe₂(MoO₄)₃,MoO₃ + xWO₃ catalysts, where x = 0.0, 1.9, 8.0 and 15.9 are given in Table 1. The parameters shown in Table 1 suggest that the Fe³⁺ ion are high-spin ones and are situated in a slightly deformed octahedral field. The higher QS values of the lower-intensity doublets (Fig.1, component B) are attributed to the ferric ions having a different ligand surrounding, composed of both Mo⁶⁺ and W⁶⁺ ions.

Table 1. Isomeric shift (IS), quadrupole splitting (QS), line width (FWHM) and relative weight of the components (G) of specimens with composition Fe₂(MoO₄)₃,MoO₃ and Fe₂(MoO₄)₃,MoO₃ + xWO₃, where x = 0, 1.9, 8.0 and 15.9

| Samples                        | IS, mm/s | QS, mm/s | FWHM, mm/s | G, %  |
|--------------------------------|----------|----------|------------|-------|
| Fe₂(MoO₄)₃,MoO₃                | 0.41     | 0.187    | 0.32       | 100   |
| 1 doublet                      |          |          |            |       |
| Fe₂(MoO₄)₃,MoO₃ +1.9 % WO₃    | 0.416    | 0.198    | 0.315      | 98.2  |
| 2 doublet                      | 0.395    | 0.463    | 0.320      | 1.8   |
| 1 doublet                      | 0.415    | 0.190    | 0.313      | 96.3  |
| Fe₂(MoO₄)₃,MoO₃ +8.0 % WO₃    | 0.415    | 0.190    | 0.313      | 96.3  |
| 2 doublet                      | 0.392    | 0.469    | 0.316      | 3.7   |
| 1 doublet                      | 0.416    | 0.189    | 0.306      | 96.3  |
| Fe₂(MoO₄)₃,MoO₃ +15.9 % WO₃   | 0.416    | 0.189    | 0.320      | 3.7   |
| 2 doublet                      | 0.392    | 0.460    | 0.320      | 3.7   |

The fact that the ratio of the relative weights of the doublets remains unchanged with the rise of the WO₃ content over 5% allows the assumption that the components of the system considered here have restricted solubility.

3.2. Sodium modified catalysts
The results from the chemical analyses of the precipitates indicate that washing with distilled water has a significant effect on their composition. The content of sodium decreases sharply from 6.5 to about 0.3 wt. % (presented as Na₂O).

The calcination of the precipitates prepared in the described way leads to the formation of well defined phases with composition Fe₂(MoO₄)₃ and MoO₃. The presence of a considerable amount of sodium in some of the samples, however, could lead to the formation of a new phase with composition NaFe(MoO₄)₂. This expectation was clearly confirmed by the results presented in Fig. 2. The catalytic activity and selectivity (S) for oxidation of methanol were determined on standard flow equipment at a volumetric rate of 1200 h⁻¹, methanol concentration in the alcohol-air mixture of 6% and temperature of the catalyst layer of 200 - 350°C. The amount of catalyst was 3 cm³ and a fraction of 1.0-1.6 mm was used in all cases. The formaldehyde content in the off-gases was determined by means of the bisulfite method, while the amounts of CO, CO₂, (CH₃)₂O and unreacted methanol were defined by gas chromatography.

The results for tungsten modified catalysts confirmed the expectation that solid solutions formed are characterized by high activity and selectivity upon methanol oxidation and are of interest in view of their practical application.

No negative effect up to 0.2 wt. % sodium content was indicated at the precipitated catalysts. On the contrary, a dramatic change in the catalytic activity of the impregnated catalysts was established at sodium content even under 0.05 wt. %.
4. Conclusions

1. The coprecipitation of aqueous solutions of FeCl₃ and of a mixture of ammonium heptamolybdate and Na₂WO₄ leads to the formation of a mixture of two types of solid solutions with compositions Fe₂(MoxW₁₋ₓO₄)₃ and (MoxW₁₋ₓ)O₃. The solid solutions formed are characterized by high activity and selectivity upon methanol oxidation and are of interest in view of their practical application.

2. A strong nucleation effect of sodium to form new compounds takes place. Regardless of the way of its introduction, NaFe(MoO₄)₂ formation after calcination was proved.

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