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Note

Temperature-programmed reduction of $FeVMoO_7$

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Temperature-programmed reduction (TPR) is considered a successful method for the characterization of oxidic systems in the field of catalysis. It provides information about bonding states and interactions among the components [1, 2].

Molybdic anhydride is a very selective catalyst for a large number of oxidation reactions but, due to its low activity, it is usually employed in a mixture with some other metallic oxides [3].

However, the recently studied Fe_2O_3–V_2O_5–MoO_3 system includes several phases of particular interest as catalysts [4–11]. Although some new compounds in this system, such as $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$, have been synthesized by solid state reaction and characterized by XRD and other additional techniques, their structures are as yet unknown [12, 13].

This note describes the application of TPR in the study of the $FeVMoO_7$ reduction process in order to obtain additional information on the chemical nature and reactivity of this phase.

The TPR results are discussed in comparison with those obtained for other related oxidic systems using X-ray diffraction, IR spectroscopy and scanning electron microscopy (SEM).

The $FeVMoO_7$ phase was obtained by heating the corresponding oxides according to the literature method [7]. The purity of the sample was checked by XRD analysis.

The TPR studies were carried out in a reactor fed with 10% H_2 (as reducing agent) in an N_2 stream. The temperature was raised to 1100°C at a heating rate of $10°C\,min^{-1}$. The hydrogen consumed was detected by a thermal conductivity cell.

The XRD analyses were performed in a Philips PW-1714 diffractometer, with Cu $K\alpha$ radiation (Ni filter).

The IR spectra were recorded with a Perkin-Elmer 580-B spectrometer using the KBr pellet technique.

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The scanning electron microscopical characterization was carried out in a Philips 505 instrument (with an EDAX 9100).

In general, the temperature of reduction can be used as a measure of the strength of the oxygen bond in metal oxides [14]. Using this parameter, the reducibility of the isolated oxides of this system have been extensively studied. Their reactivities seem to be influenced by a great number of factors, in particular, by the presence of dopants. For example, the Fe_2O_3 reactivity in H_2 decreases when the sample is doped with Mn, Co or Ni, while the inverse behaviour is found for spinel-magnetite [15].

Figure 1 shows the TRP pattern of the $FeVMoO_7$ phase, together with those of $FeVO_4$ and MoO_3 which were included for comparative purposes.

The $FeVMoO_7$ pattern shows two important peaks at 704 and 1008°C, while the $FeVO_4$ has only one peak at 745°C, associated with the FeV_2O_4 spinel-phase formation. It is interesting to note that the reduction of pure Fe_2O_3 occurs between 260 and 400°C, leading to the formation of non-stoichiometric "$Fe_{3-x}O_4$" spinel-phase. This process implies that some metallic Fe has been formed in the surface layers which is easily accessible to the reducing gas [15].

The MoO_3 pattern shows a very weak peak at $\approx$500°C corresponding to the formation of Mo_4O_{11}, although this phase is rather difficult to obtain in a pure state. Although the subsequent reduction to MoO_2 is total at 800°C, in fact the process seems to begin at lower temperatures; a small proportion of this oxide is already observed at 500°C [16]. This oxide is further reduced to the metallic state between 860 and 910°C.

In this study, the reduction process can be elucidated from the XRD data of $FeVMoO_7$ samples heated under conditions similar to those used in the TPR measurement, with the aid of IR spectroscopy.

Figure 2 shows the diffraction patterns of the original sample (which is unchanged up to 400°C (A)), the samples heated to 800°C (B) and 1000°C (C), and the FeV_2O_4-spinel, MoO_2-monoclinic, and Mo phases.

From 800°C, the formation of MoO_2 and FeV_2O_4 oxides is evident. Although a small amount of metallic Fe might be formed in this reduction stage, it has not been clearly detected by XRD analysis: the Fe microcrystals are evidently very well dispersed in the oxidic matrix.

At 1000°C, the MoO_2 has been practically reduced to metallic Mo and the intensity of the diffraction lines of the FeV_2O_4 spinel-phase has decreased slightly.

It is clear in Fig. 1 that the MoO_2 obtained from the studied sample has a significantly lower reactivity to hydrogen reduction than that observed for pure MoO_2; in the first case the reduction reaction proceeds at nearly 100°C above the second. To explain this difference, the possibility of obtaining solid solutions must be considered. In fact, the substitution of octahedral Mo(IV) ($r = 0.65$ Å) by Fe(III) ($r = 0.645$ Å) or V(III) ($r = 0.64$ Å) to form a non-stoichiometric, substituted phase is possible. The incorporation of a

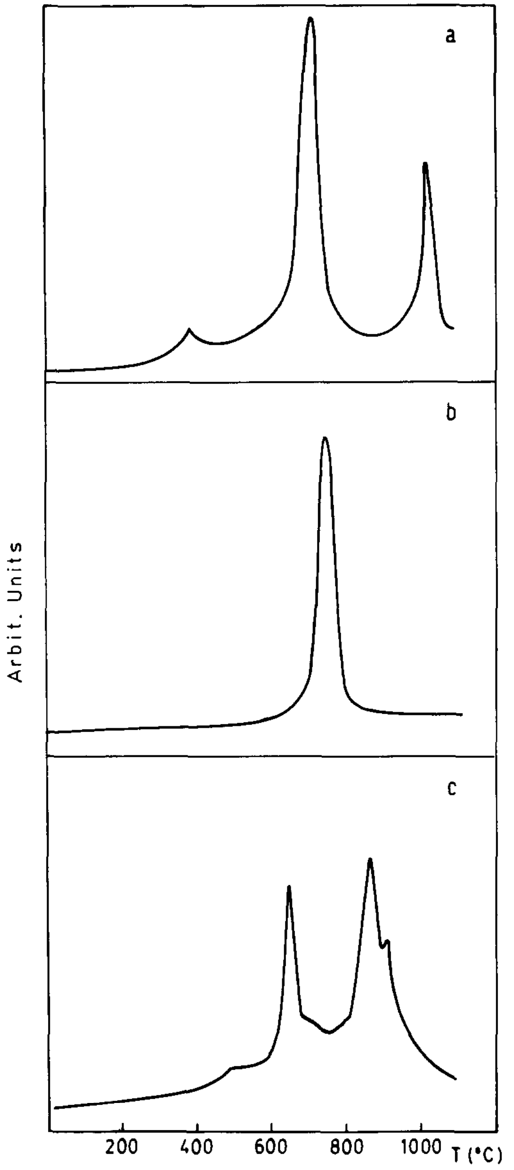

Fig. 1. TPR patterns of a, $FeVMoO_7$; b, $FeVO_4$; c, MoO_3.

small proportion of these ions in the MoO_2 lattice does not produce an appreciable change in its monoclinic cell parameters.

A similar behaviour can also be suggested in the spinel phase where V(III) can easily be substituted by Fe(III) and, especially, by Mo(III) [17]. Evidence of solid solution formation has also been obtained from the IR spectrum of the sample heated at 1100°C where the "FeV_2O_4" spinel compound is the unique oxidic phase.

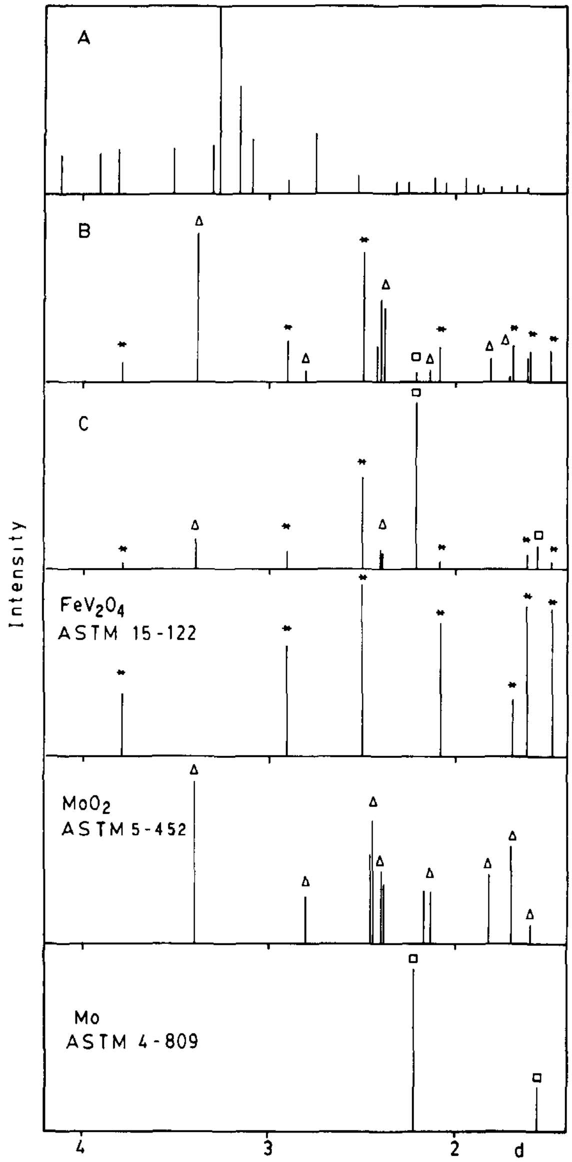

Fig. 2. XRD patterns of A, $FeVMoO_7$; B, $FeVMoO_7$ heated to 800°C; C, $FeVMoO_7$, heated to 1000°C; *, FeV_2O_4; △, MoO_2; □, Mo.

The IR spectra of normal II–III spinels exhibit four regions of absorption corresponding to the four IR-active modes [18]. The two high-frequency bands (ν_1 and ν_2) are strong or very strong, and depend on the nature of the octahedra cations [19]. Likewise, the symmetry of these bands is related to the order of the cationic species in the lattice [20].

The IR spectrum of the $FeVMoO_7$ sample heated in a reducing

Fig. 3. Scanning electron micrographs (original magnification ×1620; scale bar, 10 μm); A, $FeVMoO_7$; B, $FeVMoO_7$ heated at 800°C; C, $FeVMoO_7$ heated at 1100°C.

atmosphere at 1100°C shows these two typical ν_1 and ν_2 bands centred at 587 and 460 cm^{-1}, while the IR spectrum of "FeV_2O_4" obtained from the $FeVO_4$ reduction shows bands located at 581 and 450 cm^{-1}.

The TPR measurement of an Fe_2O_3–V_2O_5 stoichiometric mixture, which forms FeV_2O_4, presents a strong peak at 578°C, while its spectrum shows two bands at 591 and 455 cm^{-1}.

Scanning electron micrographs (SEM) of the original $FeVMoO_7$ phase, as well as those of samples heated at 800 and 1100°C, are shown in Fig. 3. The morphology of the $FeVMoO_7$ crystals is shown in Fig. 3A. Important alterations are observed in Fig. 3B, where the crystals are now poorly developed. The electron microprobe analysis reveals the presence of the spinel (S) and MoO_2 (M) phases. Finally, the spinel phase is covered with tiny crystals of metallic Mo at 1100°C.

In conclusion, the formation of the FeV_2O_4 spinel phase occurs at lower temperature than in the $FeVO_4$ reduction process. However, the formation of this spinel by reaction of the physical mixture of Fe_2O_3 and V_2O_5, in similar conditions, occurs 70°C lower.

A more marked effect is found in the second reduction step, where the MoO_2 from the $FeVMoO_7$ is reduced to the metallic state at approximately 100°C above the pure MoO_2 reduction. The reduction reaction is retarded by the incorporation of metallic species in this monoclinic lattice.

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