

# Unsupported $\text{MoO}_3\text{--Fe}_2\text{O}_3$ catalysts: characterization and activity during 2-propanol decomposition

Shar S. Al-Shihry, Samih A. Halawy<sup>\*,1</sup>

Department of Chemistry, College of Education, King Faisal University P.O. Box 1759, Al-Hofuf 31982 Eastern Province, Saudi Arabia

Received 5 January 1996; accepted 5 April 1996

## Abstract

The catalytic decomposition of 2-propanol (2-PrOH) was studied as probe reaction, in the gas phase, over unsupported  $\text{MoO}_3\text{--Fe}_2\text{O}_3$  mixed catalysts. The samples were prepared by mixing  $\text{MoO}_3$  (as ammonium heptamolybdate) with different  $x$  mol%  $\text{Fe}_2\text{O}_3$  (as ferric nitrate) and calcined at  $500^\circ\text{C}$  in air for 5 h. All catalysts were characterized by TPR, IR, XRD and XPS analyses. The surface area of these samples were determined using the BET method. Also, the acidity and the basicity of all catalysts were estimated thermogravimetrically using the adsorption of pyridine and formic acid as probe molecules. The catalytic decomposition of 2-PrOH was studied over the catalysts in the temperature range of  $150\text{--}260^\circ\text{C}$ . A correlation between the catalytic activity and the acidity or the basicity of these catalysts has been made. The activation energies for both propene and acetone formation, over  $\text{MoO}_3\text{--Fe}_2\text{O}_3$  catalysts, were calculated.

**Keywords:** Acidity; Basicity; Decomposition;  $\text{Fe}_2\text{O}_3$ ; IR;  $\text{MoO}_3$ ; 2-propanol;  $S_{\text{BET}}$ ; TPR; XPS; XRD

## 1. Introduction

$\text{MoO}_3$ ,  $\text{Fe}_2\text{O}_3$  and Mo–Fe–O mixed oxides, as pure or supported materials, have emerged as a very important class of catalysts with many areas of industrial applications, such as the oxidation of propene [1], ammonia [2] and butene [3] and thiophene hydrodesulphurization (HDS) [4]. Mixtures of ferrimolybdate and  $\text{MoO}_3$  have been widely used in the selective oxidation of methanol to formaldehyde [5,6]. Several techniques have been used to characterize  $\text{MoO}_3$

[7,8],  $\text{Fe}_2\text{O}_3$  [9,10],  $\text{Fe}_2\text{MoO}_4$  and  $\text{Fe}_2(\text{MoO}_4)_3$  [11–14].

Decomposition of 2-propanol to propene and/or acetone is extensively used to characterize acid–base or redox properties of catalysts [15–18]. The dehydrogenation product (acetone) is preferentially formed on basic catalysts, e.g.  $\text{Fe}_2\text{O}_3$ , while the dehydration product (propene) is essentially formed when acid sites are available [15] as in case of  $\text{MoO}_3$  [19]. Recently Ouqour et al. [20] have studied the conversion of 2-propanol, over  $\text{CoMoO}_4$  and  $\text{NiMoO}_4$ , to investigate the redox and acid–base properties of such catalysts (in presence and absence of air respectively).

The purpose of this work was to characterize the unsupported  $\text{MoO}_3\text{--Fe}_2\text{O}_3$  mixed catalysts,

\* Corresponding author.

<sup>1</sup> Permanent address: Chemistry Department, Faculty of Science, South Valley University, Qena 83511, Egypt.

using different techniques, and an attempt has been made to correlate the catalytic activity of these catalysts, during the decomposition of 2-PrOH, with their structure and the acid–base properties.

## 2. Experimental

### 2.1. Materials and techniques

Pure  $\text{MoO}_3$  and  $\text{Fe}_2\text{O}_3$  were prepared by calcination of analytical grade ammonium heptamolybdate (AHM)  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (Fisons) and ferric nitrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Hopkin and Williams) at  $500^\circ\text{C}$  for 5 h in air. Samples of  $\text{MoO}_3$  containing  $x$  mol%  $\text{Fe}_2\text{O}_3$ , after calcination at  $500^\circ\text{C}$  (where  $x = 0.5, 5, 10, 30, 50, 70$  and  $90$ ) were prepared. Calculated amounts of (AHM) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were used to prepare sufficient amounts of the catalysts as explained previously [19], then the catalyst samples were calcined in air for 5 h at  $500^\circ\text{C}$ .

Temperature-programmed reduction (TPR) of the catalysts, calcined at  $500^\circ\text{C}$ , was done in apparatus described elsewhere [21]. TPR profiles were recorded at the same experimental conditions as indicated previously [22].

X-ray powder diffraction (XRD) analysis was performed using a Philips diffractometer (P.W. 2103/00) with Ni-filtered  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ).

IR absorption spectra were recorded by means of a Perkin-Elmer 599B IR spectrophotometer, adopting the KBr disc technique, in the region  $1600\text{--}200 \text{ cm}^{-1}$ .

X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos ES300 spectrometer. The aluminum  $\text{K}_\alpha$  line (1486.4 eV) was used for excitation. The X-ray power supply was run at 14 kV and 15 mA with a response time of 1 s and a range of  $10^{14}$  CPS.

Surface area measurements were performed using the BET method, using liquid  $\text{N}_2$  at

$-196^\circ\text{C}$  as adsorbate on a Carlo-Erba, single point, SORPTY 1750 unit.

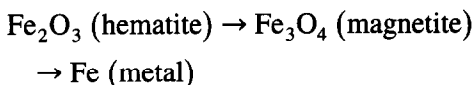
The acidity ( $\Psi$ ) and the basicity ( $\Phi$ ) of catalyst samples were determined thermogravimetrically, as described previously [23], using the adsorption of pyridine and formic acid as probe molecules. The weight loss was estimated as the acidity or basicity of the catalyst. The values of ( $\Psi$ ) and ( $\Phi$ ) were calculated [24] as  $[\text{H}^+]$  or  $[\text{OH}^-] \times 10^{18}$  ions/ $\text{m}^2$  catalyst, respectively.

Measurements of activity and selectivity of all catalysts, during the decomposition course of 2-PrOH, were conducted in a continuous flow system under atmospheric pressure. The detailed experimental procedure is described elsewhere [19]. Also, the reaction rates, catalytic activity, selectivity and the kinetic parameters of the decomposition of 2-PrOH were calculated as explained earlier [19].

## 3. Results and discussion

### 3.1. Temperature-programmed reduction (TPR)

The TPR profiles of  $\text{MoO}_3\text{--Fe}_2\text{O}_3$  catalysts calcined, in air, for 5 h at  $500^\circ\text{C}$  are shown in Fig. 1. The TPR pattern of  $\text{MoO}_3$  (Fig. 1a) displayed two reduction peaks with  $T_{\text{max}}$  at  $683$  and  $818^\circ\text{C}$ , corresponding to the reduction steps,  $\text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \text{Mo}$  [25,26], which is confirmed by a ratio of areas under the peaks of approximately (1:2). The experimental  $\text{H}_2$  uptake was calculated as  $2.14 \times 10^{-2}$  mol/g (which is in agreement with the theoretical value i.e.  $2.08 \times 10^{-2}$  mol/g). The TPR profile of  $\text{Fe}_2\text{O}_3$  (Fig. 1i) showed a small peak at  $353^\circ\text{C}$  and another big peak at  $537^\circ\text{C}$  which might be attributed to stepwise reduction of  $\text{Fe}_2\text{O}_3$  to metallic Fe [27] as follows:



This is in agreement with the reduction mechanism, reported previously [28–30], where

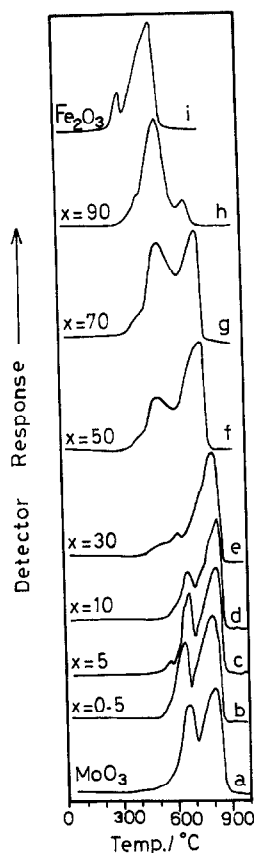


Fig. 1. TPR profiles of  $\text{MoO}_3$  (a),  $\text{MoO}_3$  mixed with  $x$  mol%  $\text{Fe}_2\text{O}_3$  (b–h) and  $\text{Fe}_2\text{O}_3$  (i), calcined in air at  $500^\circ\text{C}$  for 5 h, carried out at  $5^\circ\text{C}/\text{min}$  in 6%  $\text{H}_2/\text{N}_2$  ( $40\text{ cm}^3/\text{min}$ ).

no  $\text{FeO}$  (Wüstite) is encountered below  $575^\circ\text{C}$ . Also, this is consistent with the calculated area of the TPR peaks of  $\text{Fe}_2\text{O}_3$  (Fig. 1i). The hydrogen amount required for the complete reduction of  $\text{Fe}_2\text{O}_3$  is calculated theoretically [31] as  $1.87 \times 10^{-2}$  mol/g which is in close agreement with the  $\text{H}_2$  uptake found (ca.  $1.95 \times 10^{-2}$  mol/g). Evidence for  $\text{Fe}_3\text{O}_4$  intermediate in reduction of  $\alpha\text{-Fe}_2\text{O}_3$  has been given, previously, by Gazzarini and Lanzavecchia [32] and Colombo et al. [33].

The addition of 0.5, 5 and 10 mol%  $\text{Fe}_2\text{O}_3$  to  $\text{MoO}_3$  had little effect on the reduction of  $\text{MoO}_3$ , as the TPR profiles (Fig. 1b–d) have the same reduction peaks as those of  $\text{MoO}_3$  with  $T_{\text{max}}$  shifted to lower values and, in addition, a shoulder at  $567\text{--}590^\circ\text{C}$  which may be attributed to

the reduction of  $\text{Fe}_2\text{O}_3$ . Increasing the mol%  $\text{Fe}_2\text{O}_3$  added (i.e. 30, 50 and 70 mol%  $\text{Fe}_2\text{O}_3$ ) gave different shapes of TPR patterns, (Fig. 1e–g). It is assumed that  $\text{Fe}_2(\text{MoO}_4)_3$  is formed in these samples, containing 30–70 mol%  $\text{Fe}_2\text{O}_3$ , then undergoes a complete reduction to the corresponding Fe and Mo metals in the final stage. These patterns (Fig. 1e–g) are characterized by a shoulder in the range  $416\text{--}538^\circ\text{C}$ , and a peak at  $524\text{--}615^\circ\text{C}$ . The shoulder can be due to the reduction of  $\text{Fe}_2\text{O}_3$  to Fe metal, while the peak located between 524 and  $615^\circ\text{C}$  can be related to the reduction of the residual  $\text{Fe}_2\text{O}_3$ , in  $\text{Fe}_2(\text{MoO}_4)_3$ , to metallic Fe as well as the reduction of  $\text{MoO}_3$  to  $\text{MoO}_2$ . There is another peak in the temperature range  $743\text{--}811^\circ\text{C}$  (patterns e–g), which is attributed to the reduction of  $\text{MoO}_2$  to Mo metal. It is worth noting here, that significant additions of  $\text{Fe}_2\text{O}_3$  to  $\text{MoO}_3$  ( $x = 30\text{--}70$  mol%) have resulted in a catalyzed reduction of  $\text{MoO}_3$ , to Mo metal, at lower temperatures as reported previously in case of  $\text{MoO}_3\text{--Co}_3\text{O}_4$  system [22,34]. Finally, the TPR profile of  $\text{MoO}_3\text{--}90$  mol%  $\text{Fe}_2\text{O}_3$  (Fig. 1h) shows a strong peak at  $T_{\text{max}} = 552^\circ\text{C}$ , with a shoulder at  $440^\circ\text{C}$ , corresponds to the reduction of  $\text{Fe}_2\text{O}_3$  to Fe metal, while the second small one is related to the reduction of  $\text{MoO}_3$  to Mo metal at  $T_{\text{max}} = 697^\circ\text{C}$ . The addition of  $\text{MoO}_3$  to  $\text{Fe}_2\text{O}_3$  inhibits the reduction of  $\text{Fe}_2\text{O}_3$  to Fe metal, because  $\text{Mo}^{6+}$  ions polarize Fe–O bonds in the same way as  $\text{Al}^{3+}$  ions do, making them more ionic, and consequently stronger and less reducible [35]. The values of  $\text{H}_2$  uptake of  $\text{MoO}_3\text{--Fe}_2\text{O}_3$  catalysts are cited in Table 1. These values increased gradually with the addition of  $\text{Fe}_2\text{O}_3$  to  $\text{MoO}_3$  and attained a maximum (i.e.,  $2.48 \times 10^{-2}$  mol/g), at Mo–Fe–V then decreased with increasing  $\text{Fe}_2\text{O}_3$  content.

### 3.2. X-ray diffraction analysis

Fig. 2 shows the XRD diffractograms of pure  $\text{MoO}_3$  (a), mixed with different  $x$  mol%  $\text{Fe}_2\text{O}_3$  (b–h) and pure  $\text{Fe}_2\text{O}_3$  (i) calcined at  $500^\circ\text{C}$  in

Table 1

Samples description,  $S_{\text{BET}}$ , acidity–basicity and  $\text{H}_2$ -uptake of  $\text{MoO}_3\text{-Fe}_2\text{O}_3$  catalysts calcined at  $500^\circ\text{C}$  for 5 h in air

Sample description	Mol% oxide at $500^\circ\text{C}$		$S_{\text{BET}}(\text{m}^2/\text{g})$	Acidity ( $\Psi$ ) ( $\times 10^{18}$ ions/ $\text{m}^2_{\text{cat}}$ )	Basicity ( $\Phi$ ) ( $\times 10^{18}$ ions/ $\text{m}^2_{\text{cat}}$ )	$\text{H}_2$ uptake ( $\times 10^{-2}$ mol/g)
	$\text{MoO}_3$	$\text{Fe}_2\text{O}_3$				
$\text{MoO}_3$	100	—	0.8	4.8	—	2.14
Mo–Fe-I	99.5	0.5	0.6	5.1	4.4	2.10
Mo–Fe-II	95.0	5.0	1.8	4.9	5.1	2.30
Mo–Fe-III	90.0	10.0	2.6	4.4	5.9	2.32
Mo–Fe-IV	70.0	30.0	4.2	2.7	6.1	2.39
Mo–Fe-V	50.0	50.0	10.6	2.5	8.3	2.48
Mo–Fe-VI	30.0	70.0	18.3	2.3	8.7	2.13
Mo–Fe-VII	10.0	90.0	29.0	2.0	8.9	2.06
$\text{Fe}_2\text{O}_3$	—	100	21.8	1.2	9.5	1.87

air for 5 h. The XRD pattern of Mo–Fe-I (Fig. 2b) had the same characteristic lines of pure  $\text{MoO}_3$  (Fig. 2a), especially the main intense lines at  $d = 3.818, 3.466, 3.267, 2.652, 2.309$  and  $1.852 \text{ \AA}$  (ASTM card No. 5-0508). The XRD patterns of Mo–Fe-II and Mo–Fe-III (Fig. 2c and d) were characterized by the appearance of a new diffraction line at  $d = 3.986 \text{ \AA}$  besides the same lines of  $\text{MoO}_3$ . The intensity of that line increased with increasing  $\text{Fe}_2\text{O}_3$  content,

and became the most intense line in patterns of Mo–Fe-IV and Mo–Fe-V (where  $x = 30$  and  $50$  mol%  $\text{Fe}_2\text{O}_3$ ), see Table 1 and Fig. 2 (patterns e and f). This can be due to the formation of the orthorhombic phase of  $\text{Fe}_2(\text{MoO}_4)_3$  [36,37], as it matches well the ferrimolybdate pattern (ASTM card No. 20-526). Our results are in good agreement with previously published work by Chen [38] on iron(III)molybdate, especially those lines at  $d = 4.439, 4.171, 3.969, 3.520,$

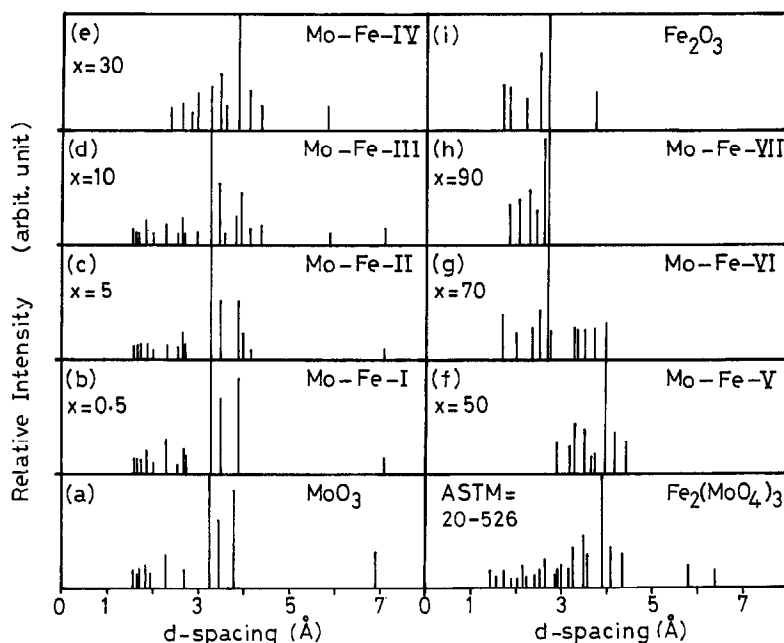


Fig. 2. XRD patterns of  $\text{MoO}_3$  (a),  $\text{MoO}_3$  mixed with  $x$  mol%  $\text{Fe}_2\text{O}_3$  (b–h) and  $\text{Fe}_2\text{O}_3$  (i), calcined in air at  $500^\circ\text{C}$  for 5 h.

3.290 and 2.885 Å. The XRD diffractogram of Mo–Fe–VI showed an observed decrease in the intensity of the diffraction line assigned to  $\text{Fe}_2(\text{MoO}_4)_3$  at  $d = 3.986$  Å, which has completely vanished from pattern (h) of Mo–Fe–VII (containing 90 mol%  $\text{Fe}_2\text{O}_3$ ). There is a new diffraction line appearing in patterns (Fig. 2g and h) of Mo–Fe–VI and Mo–Fe–VII at  $d = 2.730$  Å with  $I/I^\circ = 100$ , which is ascribed to the separation of  $\text{Fe}_2\text{O}_3$  in these mixtures. The XRD pattern of Mo–Fe–VII is almost identical with the pattern of pure  $\text{Fe}_2\text{O}_3$  (ASTM card No. 24-27A, see also (Fig. 2i), where the diffraction lines are at  $d = 3.728, 2.704, 2.515, 2.206$  and  $1.692$  Å.

From the XRD analysis, one can notice that the formation of  $\text{Fe}_2(\text{MoO}_4)_3$  has started in sample (Mo–Fe–II) containing 5 mol%  $\text{Fe}_2\text{O}_3$ , while samples Mo–Fe–IV and Mo–Fe–V (containing 30 and 50 mol%  $\text{Fe}_2\text{O}_3$ ) showed the maximum concentration of ferrimolybdate formed among these mixtures, as suggested from TPR analysis. Increasing the  $\text{Fe}_2\text{O}_3$  content up to 90 mol% in these mixtures gave identical XRD pattern of  $\text{Fe}_2\text{O}_3$ .

### 3.3. IR analysis

From the recorded spectra of  $\text{MoO}_3$ – $\text{Fe}_2\text{O}_3$  catalysts calcined at 500°C the spectra of  $\text{MoO}_3$ , Mo–Fe–I, Mo–Fe–II and Mo–Fe–III (Fig. 3a–d) have the same absorption band at  $990\text{ cm}^{-1}$ , which can be due to  $\text{Mo}=\text{O}$  stretching mode [38], followed by a group of bands in the range  $850$ – $555\text{ cm}^{-1}$  which are attributed to the stretching mode of the bridge oxygen  $\text{Mo}-\text{O}-\text{Mo}$  [39]. Also, the bands of the deformation mode of  $\text{O}-\text{Mo}-\text{O}$  in the region  $420$ – $230\text{ cm}^{-1}$  appear in these spectra (Fig. 3a–d). The IR spectra of samples Mo–Fe–IV, Mo–Fe–V and Mo–Fe–VI (containing 30, 50 and 70 mol%  $\text{Fe}_2\text{O}_3$ ) showed new bands at  $855$ – $840\text{ cm}^{-1}$  and  $550$ – $535\text{ cm}^{-1}$ , which are related to the formation of  $\text{Fe}_2(\text{MoO}_4)_3$  in these mixtures and assigned to  $\nu(\text{Fe}-\text{Mo}-\text{O})$  [40–42] as well as the frequencies assigned to  $\text{O}-\text{Mo}-\text{O}$ . The ob-

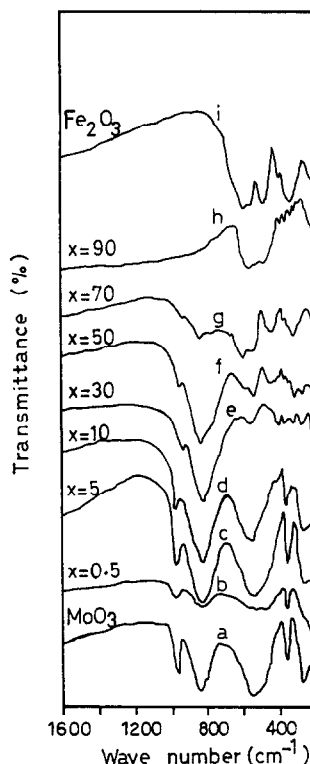


Fig. 3. IR spectra of  $\text{MoO}_3$  (a),  $\text{MoO}_3$  mixed with  $x$  mol%  $\text{Fe}_2\text{O}_3$  (b–h) and  $\text{Fe}_2\text{O}_3$  (i), calcined in air at 500°C for 5 h.

served frequencies of IR spectra of such samples (Fig. 3e–g) are consistent with those reported by Cord et al. [43]. The IR spectrum of  $\text{Fe}_2\text{O}_3$  (Fig. 3i) showed the characteristic frequencies of  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) [44] at 560, 470, 380 and  $395\text{ cm}^{-1}$ . Finally, the spectrum of Mo–Fe–VII (see Table 1) showed the similar bands of  $\alpha\text{-Fe}_2\text{O}_3$  besides a group of absorption bands at 665 and  $445$ – $225\text{ cm}^{-1}$  due to  $\text{O}-\text{Mo}-\text{O}$  deformation mode.

The IR results support the XRD results, where  $\text{Fe}_2(\text{MoO}_4)_3$  is clearly shown to be formed by the IR spectrum and XRD pattern of Mo–Fe–V (containing 50 mol%  $\text{Fe}_2\text{O}_3$ ) and  $\text{Mo}^{6+}$  ions are characterized in all spectra (Fig. 3), except for spectra (h) and (i), by two absorption bands at  $960$  and  $840\text{ cm}^{-1}$  [45].

### 3.4. XPS results

The values of the binding energies of Mo 3d and Fe 2p levels for  $\text{MoO}_3$ – $\text{Fe}_2\text{O}_3$  catalysts,

Table 2

Binding energies ( $\pm 0.5$  eV) relative to C 1s = 284.6 eV of Mo 3d and Fe 2p levels for MoO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> catalysts, calcined at 500°C for 5 h in air

Sample	Mo		Fe	
	3d <sub>5/2</sub>	3d <sub>3/2</sub>	2p <sub>3/2</sub>	2p <sub>1/2</sub>
MoO <sub>3</sub>	233.4	236.5	—	—
Mo-Fe-I	233.4	236.5	712.4	726.0
Mo-Fe-II	230.7	233.5	711.8	725.4
Mo-Fe-III	229.7	233.0	710.6	724.6
Mo-Fe-IV	230.7	233.0	710.1	724.4
Mo-Fe-V	230.3	233.2	712.6	727.6
Mo-Fe-VI	230.2	233.1	712.5	727.2
Mo-Fe-VII	230.2	233.2	713.4	725.6
Fe <sub>2</sub> O <sub>3</sub>	—	—	713.6	727.2

under investigation, are listed in Table 2. All binding energies were referenced to the contaminated carbon (C 1s = 284.6 eV). The binding energy of the Mo 3d<sub>5/2</sub> level was 233.4 eV, in case of MoO<sub>3</sub> and Mo-Fe-I, indicating the presence of higher Mo-O oxidation states which are characteristic of Mo<sup>6+</sup> [12,46]. The addition of  $x$  mol% Fe<sub>2</sub>O<sub>3</sub> (i.e.  $x = 5, 10, 30, 50, 70$ , and 90) has lowered the binding energy of Mo

3d level from 233.4 to about 230.0 eV. This new value indicated the presence of Mo<sup>5+</sup> and Mo<sup>6+</sup> in these mixtures, as reported by Patterson et al. [47] in MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> reduced catalysts.

In case of Fe<sub>2</sub>O<sub>3</sub>, the binding energies of Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> levels were calculated as 713.6 and 727.2 eV respectively. These values match those published by Armour et al. [48]. The binding energy of Fe 2p<sub>3/2</sub> level (ca. 713.6 eV) corresponds to Fe<sup>3+</sup> [49]. The addition of MoO<sub>3</sub> to Fe<sub>2</sub>O<sub>3</sub> has slightly changed the binding energy of Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> to lower values, see Table 2. Our results are consistent with those obtained by other workers [50,51] for Fe<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> catalysts.

### 3.5. Catalytic activity measurements

The effect of catalyst composition of MoO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> system, calcined at 500°C for 5 h in air, on the decomposition of 2-PrOH at 200°C are shown in Fig. 4. The activity of MoO<sub>3</sub> is greatly affected by the addition of 0.5 mol% Fe<sub>2</sub>O<sub>3</sub>,

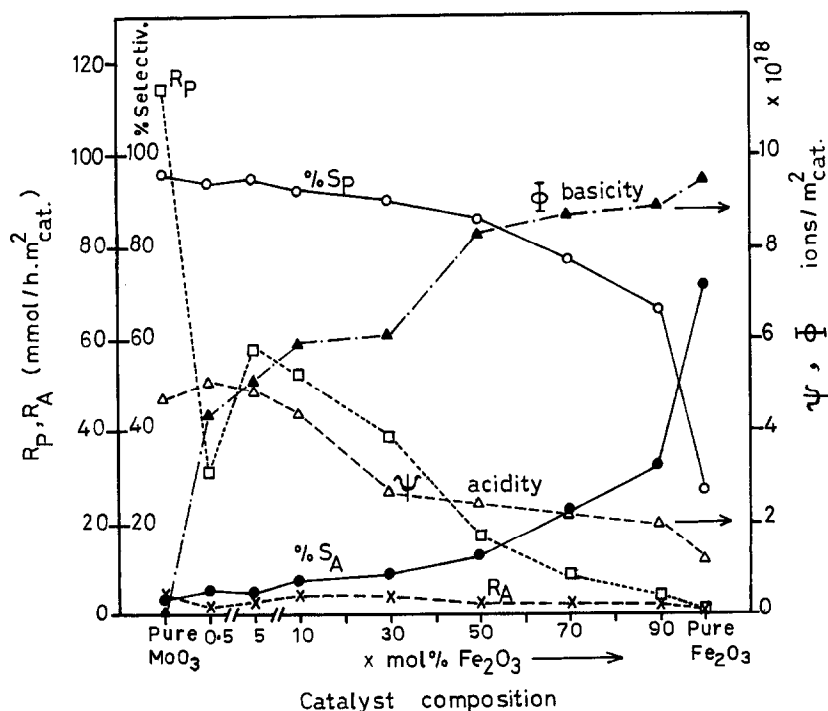


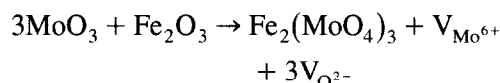
Fig. 4. Effect of catalyst composition on its acidic-basic properties and activity, during the decomposition of 2-propanol, of MoO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> catalysts calcined in air at 500°C for 5 h.

where  $R_p$  (the rate of propene formation) decreased to about one quarter of its original value for  $\text{MoO}_3$ . Increasing  $\text{Fe}_2\text{O}_3$  content to 5 mol%  $\text{Fe}_2\text{O}_3$  improved the value of  $R_p$  to 57.8 mmol/h · m<sup>2</sup><sub>cat</sub>, then it decreased gradually with increasing the mol%  $\text{Fe}_2\text{O}_3$ .  $\text{MoO}_3$  is mainly selective towards propene formation but a continuous increase in mol%  $\text{Fe}_2\text{O}_3$  added to  $\text{MoO}_3$  results in a notable decrease in %  $S_p$  (% propene selectivity), see Fig. 4. The lessening of %  $S_p$  goes parallel with the decrease in the measured values of the acidity ( $\Psi$ ) of these catalysts, see Table 1.  $\text{Fe}_2\text{O}_3$  is highly selective towards acetone formation (i.e. %  $S_a = 72.3$ ), with a relatively lower value of propene selectivity (i.e. %  $S_p = 27.7$ ). The calculated values of  $R_a$  (the rate of acetone formation) of  $\text{MoO}_3$ - $\text{Fe}_2\text{O}_3$  system, Fig. 4 and Table 3, were very small related to the values of  $R_p$  of these catalysts. This is because the basic sites on  $\text{Fe}_2\text{O}_3$ , that are responsible for the formation of acetone [15], were still inactive at 200°C where the dehydrogenation of 2-PrOH was carried out, as in case of the selective oxidation of butene [3]. The gradual increase of %  $S_a$  with increasing the amount of  $\text{Fe}_2\text{O}_3$  in the catalysts, also, goes parallel with the measured values of the basicity ( $\Phi$ ) of such samples, see Fig. 4 and Table 1.

The % conversion over Mo-Fe-I is nearly one fifth of its value over  $\text{MoO}_3$ . Also, % conversion increased gradually with increasing

mol%  $\text{Fe}_2\text{O}_3$  added to  $\text{MoO}_3$ . The maximum value of % conversion (ca. 38.3%) is located at sample Mo-Fe-V, containing 50 mol%  $\text{Fe}_2\text{O}_3$ . The addition of 70 and 90 mol%  $\text{Fe}_2\text{O}_3$  to  $\text{MoO}_3$  decreased gradually % conversion of 2-PrOH over such samples.  $\text{Fe}_2\text{O}_3$ , on the other hand, has a very low activity towards 2-PrOH decomposition at the same experimental conditions (% conversion = 2.4%).

The dehydration reaction of 2-PrOH is catalyzed at acidic sites and the dehydrogenation reaction is catalyzed at both acidic and basic sites [52].  $\text{MoO}_3$  has Brönsted acidity [53] and its measured acidity ( $\Psi$ ) =  $4.8 \times 10^{18}$  ions/m<sup>2</sup><sub>cat</sub>, therefore it is mainly selective towards propene formation.  $\text{Fe}_2\text{O}_3$ , on the other hand, has Brönsted basicity ( $\Phi = 9.5 \times 10^{18}$  ions/m<sup>2</sup><sub>cat</sub>) with the presence of some acid sites [54] ( $\Psi = 1.2 \times 10^{18}$  ions/m<sup>2</sup><sub>cat</sub>), and consequently  $\text{Fe}_2\text{O}_3$  is selective towards both acetone and propene formation (see Table 3). The addition of  $\text{Fe}_2\text{O}_3$  to  $\text{MoO}_3$  has resulted in a gradual increase in its activity, due to the generation of new sites  $V_{\text{Mo}^{6+}}$  (molybdenum vacancies) and  $V_{\text{O}^{2-}}$  (oxygen vacancies) during the formation of  $\text{Fe}_2(\text{MoO}_4)_3$  according to the equation [36]:



Increasing the concentration of  $\text{Fe}_2(\text{MoO}_4)_3$ , in these mixtures, leads to the generation of

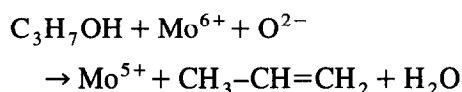
Table 3

Kinetic parameters for the decomposition of 2-PrOH over  $\text{MoO}_3$ - $\text{Fe}_2\text{O}_3$  catalysts, calcined at 500°C for 5 h in air as well as the activation energies for propene and acetone formation at the corresponding temperature ranges

Catalyst description	% conversion	$R_{2\text{-PrOH}}$ (mmol/h · m <sup>2</sup> <sub>cat</sub> )	$R_p$ (mmol/h · m <sup>2</sup> <sub>cat</sub> )	$R_a$ (mmol/h · m <sup>2</sup> <sub>cat</sub> )	Temperature range (°C)	$E_p$ (kJ/mol)	$E_a$ (kJ/mol)
$\text{MoO}_3$	17.7	118.2	113.8	4.4	180–210	75 ± 5	46 ± 8
Mo-Fe-I	3.7	33.0	31.2	1.8	200–250	67 ± 6	53 ± 10
Mo-Fe-II	20.4	60.8	57.8	3.0	160–200	102 ± 5	71 ± 3
Mo-Fe-III	27.5	56.7	52.0	4.7	150–200	109 ± 7	59 ± 6
Mo-Fe-IV	32.8	41.8	37.8	4.0	150–200	106 ± 8	58 ± 3
Mo-Fe-V	38.3	19.3	16.8	2.5	150–185	103 ± 4	65 ± 2
Mo-Fe-VI	36.2	10.6	8.2	2.4	150–200	101 ± 6	63 ± 9
Mo-Fe-VII	35.1	6.5	4.3	2.2	150–200	99 ± 2	75 ± 7
$\text{Fe}_2\text{O}_3$	2.4	0.6	0.2	0.4	220–260	110 ± 3	130 ± 8

$R_{2\text{-PrOH}}$  = total rate of removal of 2-PrOH; % reactant = 1.2%;  $W/F = 1.87$  g cat mol/L · h; total flow rate = 100 mL/min; reaction temperature = 200°C.

more cation–anion pair sites in the catalysts. Sample Mo–Fe–V, containing 50 mol% Fe<sub>2</sub>O<sub>3</sub>, showed the maximum concentration of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, as confirmed by XRD and IR analyses (see Figs. 2 and 3); then Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> diminished gradually in samples containing > 50 mol% Fe<sub>2</sub>O<sub>3</sub>. This is consistent with the above equation and the experimental data (Table 3 and Fig. 4). Also, % S<sub>p</sub> decreased gradually due to the replacement of Mo<sup>6+</sup> by Fe<sup>3+</sup> in these mixtures and consequently the expected yield of the dehydration reaction of 2-PrOH will decrease [36]:



The activation energy for propene and acetone formation ( $E_p$  and  $E_a$ ) was calculated from the Arrhenius plots of  $\log R_p$  (rate of propene formation) or  $\log R_a$  (rate of acetone formation) against  $1/T$  as explained previously [19]. The values of  $E_p$  increased gradually from  $67 \pm 6$  to  $99 \pm 2$  kJ/mol with increasing mol% Fe<sub>2</sub>O<sub>3</sub> in these mixtures and, also, with decreasing the acidity of the catalysts, see Tables 1 and 3. The values of  $E_a$  is ranging between  $53 \pm 10$  and  $75 \pm 7$  kJ/mol for the mixed catalysts. The calculated values of  $E_p$  and  $E_a$  in this work, are in great agreement with those published recently, on CoMoO<sub>4</sub> and NiMoO<sub>4</sub>, by Ouqour et al. [20]. From the values of  $E_p$  and  $E_a$  of pure Fe<sub>2</sub>O<sub>3</sub> (Table 3) one can notice that the higher values of the activation energy (and low % conversion) suggests that Fe<sub>2</sub>O<sub>3</sub> is still an inactive catalyst at the applied range of temperature (220–260°C) compared with other catalysts in this series. Fe<sub>2</sub>O<sub>3</sub> is known to be a very active catalyst at higher temperatures (> 350°C) as in case of the selective oxidation of butene to butadiene [3].

#### 4. Conclusions

Finally, it is concluded that the decomposition of 2-PrOH over MoO<sub>3</sub>–Fe<sub>2</sub>O<sub>3</sub> catalysts,

calcined at 500°C for 5 h in air, depends mainly on two factors: (i) the composition of the catalysts, where the sample with the composition of (MoO<sub>3</sub>–50 mol% Fe<sub>2</sub>O<sub>3</sub>) in this series was shown to be the most active one. It contains the highest concentration of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, accompanied by the generation of more cation–anion pair sites, as confirmed by XRD and IR analyses; and (ii) the surface acidic–basic characters of these catalysts. The addition of increased amounts of Fe<sub>2</sub>O<sub>3</sub> (as mol%) to MoO<sub>3</sub> have resulted in a continuous decrease of the concentration of Brönsted acidic sites and, consequently, an increase in the concentration of the basic Brönsted sites on their surfaces. This is parallel with the increments of (% S<sub>a</sub>) selectivities of the catalysts towards acetone production.

#### Acknowledgements

We gratefully acknowledge Professor G.C. Bond and the staff of his laboratory, Department of Chemistry, Brunel University, UK, for their valuable help in TPR measurements.

#### References

- [1] B. Benaichouba, P. Bussiere and J.C. Vedrine, Appl. Catal. A: Gen. 130 (1995) 31.
- [2] J.J.P. Biermann, F.J.J.G. Janssen, M. de Boer, A.J. Van Dillen, J.W. Geus and E.T.C. Vogt, J. Mol. Catal. 60 (1990) 229.
- [3] B.L. Yang, F. Hong and H.H. Kung, J. Phys. Chem. 88 (1984) 2531.
- [4] J.M. Lewis and R.A. Kydd, J. Catal. 136 (1992) 478.
- [5] Y. Matsuoka, M. Niwa and Y. Murakami, J. Phys. Chem. 94 (1990) 1477.
- [6] C.J. Machiels, W.H. Cheng, U. Chowdhry, W.E. Farneth, F. Hong, E.M. McCarron and A.W. Sleight, Appl. Catal. 25 (1986) 249.
- [7] S. Rajagopal, H.J. Marini, J.A. Marzari and R. Miranda, J. Catal. 147 (1994) 417.
- [8] P.A. Spevack and N.S. McIntyre, J. Phys. Chem. 96 (1992) 9029.
- [9] S.A. Halawy and M.A. Mohamed, Collect. Czech. Chem. Commun. 59 (1994) 2253.



- [10] P.A. Chernavskii, V.V. Kiselev and V.V. Lunin, *Zh. Fiz. Khim.* 66 (1992) 2717.
- [11] M.M. Gasik and P.N. Ostrik, *J. Therm. Anal.* 40 (1993) 313.
- [12] B. Domenichini, B. Gillot and P. Tailhades, *Thermochim. Acta* 205 (1992) 259.
- [13] M. Karroua, J. Ladrrière, H. Matralis, P. Grange and B. Delmon, *J. Catal.* 138 (1992) 640.
- [14] Y.L. Xiong, R. Castillo, Ch. Papadopoulou, L. Daza, J. Ladrrière, P. Ruiz and B. Delmon, *Catalyst Deactivation*, C.H. Bartholomew and J.B. Butt (Eds.) (Elsevier, Amsterdam, 1991) p. 425.
- [15] J.M. Campelo, A. Garcia, J.F. Herencia, D. Luna, J.M. Marinas and A.A. Romero, *J. Catal.* 151 (1995) 307.
- [16] S.A. Halawy, M.A. Mohamed and S.F. Abd El-Hafez, *J. Mol. Catal.* 94 (1994) 191.
- [17] F. Pepe, C. Angeletti and S. De Rossi, *J. Catal.* 118 (1989) 1.
- [18] H. Pines, in: *The Chemistry of Catalytic Hydrocarbon Conversions* (Academic Press, New York, 1981) p. 127.
- [19] G.C. Bond, S.A. Halawy, K.M. Abd El-Salaam, E.A. Hassan and H.M. Ragih, *J. Chem. Technol. Biotechnol.* 59 (1994) 181.
- [20] A. Ouqour, G. Coudurier and J.C. Vedrine, *J. Chem. Soc. Faraday Trans.* 89 (1993) 3151.
- [21] S. Flamerz, Ph.D. thesis, Brunel University, U.K., 1988.
- [22] S.A. Halawy, M.A. Mohamed and G.C. Bond, *J. Chem. Technol. Biotechnol.* 58 (1993) 237.
- [23] S.A. Halawy and M.A. Mohamed, *J. Mol. Catal. A: Chem.* 98 (1995) 63.
- [24] M.A. Makarova, E.A. Paukshtis, J.M. Thomas, C. Williams and K.I. Zamaraev, *J. Catal.* 149 (1994) 36.
- [25] J. Brito, J. Laine and K.C. Pratt, *J. Mater. Sci.* 24 (1989) 425.
- [26] P. Arnoldy, J.C.M. de Jonge and J.A. Moulijn, *J. Phys. Chem.* 89 (1985) 4517.
- [27] E.E. Unmuth, L.H. Schwartz and J.B. Butt, *J. Catal.* 63 (1980) 404.
- [28] M. Shimokawabe, R. Furuichi and T. Ishii, *Thermochim. Acta* 28 (1979) 287.
- [29] J. Bessières and J.J. Heizmann, *Int. J. Hydrogen Energy*, 5 (1980) 585.
- [30] M.V.C. Sastri, R.P. Viswanath and B. Viswanathan, *Int. J. Hydrogen Energy* 7 (1982) 951.
- [31] R. Brown, M.E. Cooper and D.A. Whan, *Appl. Catal.* 3 (1982) 177.
- [32] F. Gazzarini and G. Lanzavecchia, *Proc. 6th Int. Symp. on Reactivity of Solids*, Schenectady, NY, August 1968.
- [33] Y. Colombo, F. Gazzarini and G. Lanzavecchia, *Mater. Sci. Eng.* 2 (1967) 125.
- [34] J.M. Zabala, P. Grange and B. Delmon, *CR Acad. Sci. Paris C* 561 (1974) 279.
- [35] P. Arnoldy and J.A. Moulijn, *J. Catal.* 93 (1985) 38.
- [36] A.A. Said, *Bull. Chem. Soc. Jpn.* 65 (1992) 3450.
- [37] V. Massarotti, G. Flor and A. Marini, *J. Appl. Cryst.* 14 (1981) 64.
- [38] M. Niwa, M. Kizutani, M. Takahashi and Y. Murakami, *J. Catal.* 70 (1981) 14.
- [39] F. Trifiro, S. Notarbartolo and I. Pasquon, *J. Catal.* 22 (1971) 324.
- [40] P. Forzatti, P.L. Villa, N. Ferlazzo and D. Jones, *J. Catal.* 76 (1982) 188.
- [41] P.L. Villa, A. Szabo, F. Trifiro and M. Carbuicchio, *J. Catal.* 47 (1977) 122.
- [42] T.S.R. Prasada Rao and K.R. Krishnamurthy, *J. Catal.* 95 (1985) 209.
- [43] P.P. Cord, P. Courtine, G. Pannetier and J. Guillermet, *Spectrochim. Acta A* 28 (1972) 1601.
- [44] N.T. McDevitt and W.L. Baun, *Spectrochim. Acta* 20 (1964) 799.
- [45] B. Gillot, B. Domenichini, Ph. Tailhades, L. Bouet and A. Rousset, *Solid State Ionics* 63–65 (1993) 620.
- [46] Y. Okamoto, K. Oh-Hiraki, T. Imanaka and S. Teranishi, *J. Catal.* 71 (1981) 99.
- [47] T.A. Patterson, J.C. Carver, D.E. Leyden and D.M. Hercules, *J. Phys. Chem.* 80 (1976) 1700.
- [48] A.W. Armour, P.C.H. Mitchell, B. Folkesson and R.J. Larsson, *Less-Common. Met.* 36 (1974) 361.
- [49] C.R. Brundle, T.J. Chuang and K. Wandelt, *Surf. Sci.* 68 (1977) 459.
- [50] B.I. Popov, A.V. Pashis and L.N. Shkuratova, *React. Kinet. Catal. Lett.* 30 (1986) 129.
- [51] Y. Okamoto, F. Morikawa, K. Oh-Hiraki, T. Imanaka and S. Teranishi, *J. Chem. Soc. Chem. Commun.* (1981) 1018.
- [52] M. Ai, *J. Catal.* 50 (1977) 291.
- [53] T. Fransen, O. Van der Meer and P. Mars, *J. Phys. Chem.* 80 (1976) 2103.
- [54] C.P. Bezouhanova and M.A. Al-Zihari, *Catal. Lett.* 11 (1991) 245.