STRUCTURAL AND CATALYTIC PROPERTIES OF MoO$_3$–NiO MIXED OXIDES SYSTEM

Abd El Aziz A. SAID*, Ehsan A. HASSAN, Ahmed M. El-AWAD
and Khalf-alla M. Abd EL-SALAAM

Chemistry Department, Assiut University, Assiut, Egypt

The unsupported MoO$_3$–NiO catalysts were investigated. The addition process of NiO was followed by electrical conductivity measurements, IR, XRD, surface area and finally catalytic activity measurements. The conductivity measurements revealed an increase in σ values when 2-propanol vapour was admitted in the gas feed. IR and XRD analysis detected a solid state reaction at about 500°C and its maximum was shown around 70 mole % Ni^{2+} where NiMoO$_4$ lattice diffraction type was detected. Parallel with these measurements, the catalytic activity was determined for the catalysts calcined at 500°C using the decomposition of 2-propanol. The conversion and the selectivity increased as Ni^{2+} was added to a concentration of 70 mole % Ni^{2+} ions. The results were discussed in respect to the creation of holes associated to Ni^{2+} addition.

MoO$_3$ catalysts as pure or mixed with other oxides play an important role in the partial or mild oxidation of organic compounds. The incorporation of NiO to MoO$_3$ forming solid spinel received a great attention in the field of heterogeneous reactions[1,2]. The catalytic behaviour of NiMoO$_4$ has been studied[3,4]. They concluded that the catalyst containing 55 at % Ni^{2+} showed the highest activity and the Mo^{6+} at anion vacancies are the active sites. Ozkan and Schrader[5] examined the selective oxidation of 1,3-butadiene over NiMoO$_4$ catalyst containing excess MoO$_3$. The activity and selectivity measurements indicated that the selective component was MoO$_3$ phase covered by NiMoO$_4$. Agarwal and Srivastava[3] prepared the NiMoO$_4$ catalyst for the oxidation of cumene in the liquid phase. They showed that NiMoO$_4$ has the capability for producing radicals due to the presence of Ni^{2+} ions on which the reaction has lower activation energy. Also, the extensive oxidation of olefins and alcohols over oxide based catalysts is usually ascribed to the presence of reactive adsorbed species of oxygen[6,7] or to the strength of the bond between the olefin and the cation on the surface according to the classical picture of π-complex[8] or to the lattice oxygen[9,10].

In this paper we aim to investigate how the changes in the structure and the electrical properties affect the catalytic activity of MoO$_3$–NiO mixed oxides system.

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* Present address: Chemistry Department, Faculty of Science, United Arab Emirates University Al-Ain, P.O. Box 1555, U.A.E.

EXPERIMENTAL

The procedure adopted to produce the starting materials of intimately dispersed mixed oxides covering the range from $0-100$ mole % was a continuous co-precipitation technique similar to that described by Andrushkevich et al.[11] Aqueous solutions of $Ni(NO_3)_2.6 H_2O$ and $(NH_4)_6.$ $.Mo_7O_{24}.4 H_2O$ (Analar) were continuously mixed in a stirred vessel at 80°C. Composition of the precipitate was controlled by choice of concentrations and flow rate of the two solutions. Total flow-rate was chosen to give residence time of one hour in the stirred vessel. The precipitate was removed continuously and washed in cold distilled water until no free nickel was detectable. Then the process was followed by drying overnight at 120°C and finally by calcination in air at 500°C for 4 h. This technique was chosen as it provides a uniform precipitation and it is mostly close to the commercial procedure used. The pure molybdene sample was prepared by precipitation from a solution of $(NH_4)_6 Mo_7O_{24}.4 H_2O$ by nitric acid addition.

The specific surface areas of the prepared calcined catalysts were determined by N_2 adsorption using a conventional volumetric adsorption apparatus.

The IR and XRD patterns of the calcined catalysts were obtained using Philips unit type PW 1010 with CuK_α radiation and Ni filter. The IR spectra were obtained using the KBr disc technique in the range of $1\,200-250$ cm^{-1} with the aid of Perkin–Elmer 599B IR spectrophotometer.

The electrical conductivity measurements were carried out using a conductivity cell described elsewhere[12]. Voltage was supplied via 240A high voltage supply and the current obtained was measured with 410A Picoameter (Kethley Instruments).

Testing the catalytic activity for 2-propanol decomposition was carried out at atmospheric pressure and 503 K. The reactor consists of a 9 mm i.d. stainless steel tube externally heated. For each run, 0·5 g of the catalyst was diluted with an equal volume of ground Pyrex glass in the reactor. Pure air was used as a carrier gas with a feed stream rate 300 ml (NTP) min^{-1}. The reaction mixture was analyzed chromatographically using Pye Unicam gas chromatograph with 20% PEC column coated on celite.

RESULTS AND DISCUSSION

Structural Measurements

X-ray diffraction patterns for MoO_3–NiO samples calcined at 500°C for 4 h are shown in Fig. 1. The results showed that for MoO_3 containing lower NiO ratios, the predominant diffraction lines corresponded to MoO_3 lattice. Increasing the NiO content to 70 mole % Ni^{2+} leads to the appearance of new lines. These lines assigned at $d = 0·5777, 0·4695$ and $0·3332$ nm correspond to the formation of $NiMoO_4$ spinel structure as a new phase.

IR spectra for the various samples are seen in Fig. 2; for spectrum *1*, the infrared absorption bands assigned at 940 cm^{-1} correspond to the presence of a double bonded oxygen, while the bands at about 840 and 400 cm^{-1} can be ascribed to Mo—O—Mo lattice vibration modes[3,13]. The broad band at about 650 cm^{-1} of the molybdenum rich samples indicates the formation of $NiMoO_4$ (ref.[14]).

Surface Area Measurements

Adsorption–desorption cycles of N_2 gas at 77 K on the different samples of MoO_3–
–NiO system are all of type IV of the Brunauer classification which have hysteresis
loops of simple type B. The surface area (S_{BET}) and the pore volume (V_p) for the
different catalysts are shown in Table I.

It is to be noted that doping of MoO_3 with 1 mole % Ni^{2+} will lead to an about
six-fold increase of S_{BET}. This increase can be ascribed to the defect formation
through the lattice points in MoO_3 which are mainly cationic vacancies and holes
as expressed by the following equations:

$$Mo^{6+} + O_2 + NiO \rightarrow Ni|Mo| + MoO_3 + 4|e| , \qquad (1)$$
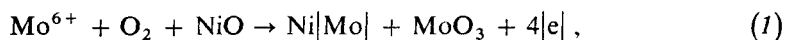
where $|e|$ is a defect electron (hole) and $Ni|Mo|$ is an Ni^{2+} ion replacing an Mo^{6+}
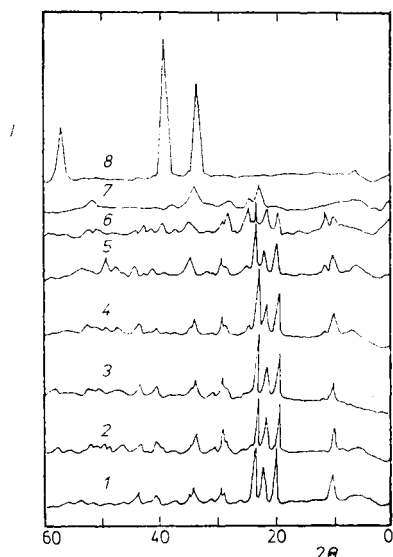ion in its lattice positions.

FIG. 1

XRD patterns for pure MoO_3 (1) and MoO_3
mixed with 10, 30, 40, 50, 70,90 mole % Ni^{2+}
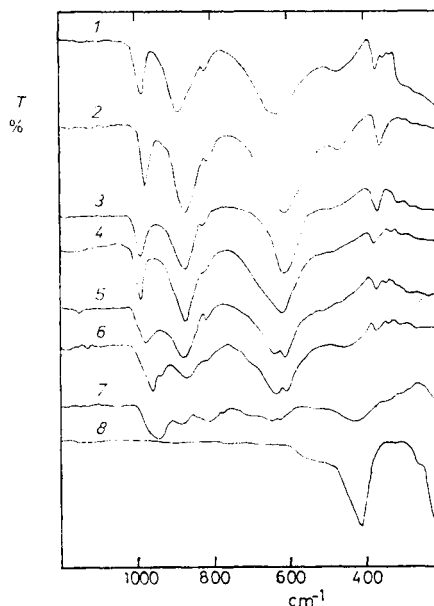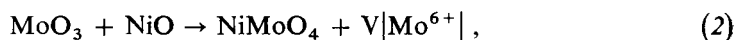(2−7) and pure NiO (8), catalysts calcined
at 500°C for 4 h

FIG. 2

IR spectra of MoO_3–NiO catalysts; symbols
as in Fig. 1

Also, the reaction takes place:

$$MoO_3 + NiO \rightarrow NiMoO_4 + V|Mo^{6+}|,$$ (2)

where $V|Mo^{6+}|$ is a cationic vacancy.

From the results in Table I, it appears that, up to 50 mole % Ni, the increasing content of Ni^{2+} ions leads to a noticeable increase of S_{BET}. At this Ni content, the concentration of $NiMoO_4$ seems to be high as the XRD and IR analyses show. Also, the diffusion of NiO into MoO_3 lattice to form $NiMoO_4$ spinel structure is associated with a high deviation of the S_t/S_{BET} values from unity.

Electrical Conductivity Measurements

Measurements of the electrical conductivity of MoO_3–NiO samples were carried out with and without 2-propanol in the gas phase. Data obtained are presented in Fig. 3, where $\log \sigma$ varies with the content of Ni^{2+} ions. It appears that conductivity values decrease abruptly when 10 mole % Mo^{6+} was admixed to Ni^{2+} ions, then is followed by a monotonous increase. Also, admission of 2-propanol in the feed will lead to a σ increase. This is an indicative result about the p-type site nature on the solid oxide[15].

The reason for the conductance decreased of NiO upon addition of the n-type MoO_3 (ref.[16]) up to 10 mole % may be attributed to a decrease in the number of positive holes responsible for the conductance in the p-type NiO (ref.[17]). The fol-

TABLE I

Texture data for MoO_3–NiO system calcined at 500°C for 4 h in air

Ni^{2+} mole %	S_{BET} $m^2 g^{-1}$	S_t $m^2 g^{-1}$	V_p $ml g^{-1}$	S_t/S_{BET}
pure MoO_3	1·5	1·3	0·018	0·86
0·5	2·2	2·0	0·071	0·91
1	8·9	6·9	0·132	0·78
10	11·9	8·5	0·170	0·71
30	19·3	13·6	0·212	0·70
40	20·8	14·7	0·237	0·71
50	27·1	23·2	0·277	0·85
70	28·1	26·9	0·285	0·96
90	29·0	28·1	0·291	0·97
99	30·1	28·9	0·339	0·96

lowing mechanism can be proposed:

$$Ni^{2+} + MoO_3 + 4|e|^{\bullet} \rightarrow Mo|Ni|^{\cdots\cdots} + NiO + O_2 \qquad (3)$$
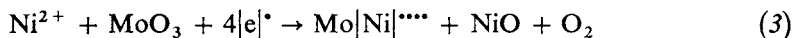
On the other hand, with the molybdenum-rich samples an addition of Ni^{2+} causes a decrease in the MoO_3 conductance via neutralizing their electron charge carriers by the created holes, as described above by mechanism (1), this can be represented by Eq. (4)

$$|e|^{\bullet} + e = \text{zero} \qquad (4)$$

Catalytic Activity

The catalytic activity for 2-propanol decomposition has been measured in constant flow experiments. Before each run, the catalyst was activated by passing air at 230°C for 4 h. Then the carrier gas was charged with 2·1% 2-propanol vapour at space time $W/F = 0.028\ g_{cat}\ l^{-1}\ h^{-1}$, where W is the weight of the catalyst and F is the total flow rate. The steady state conditions were attained after 2 h. The reaction products were mainly propene with a minor yield of acetone. Results of the experiments are shown in Fig. 4. Analysis of the results reflects that, under our experimental conditions, the activity of pure NiO catalyst is low as compared with the mixed oxide catalysts, with a predominant dehydrogenation process. Addition of Mo^{6+} increases the conversion reaching a maximum value at 30 mole % Mo^{6+} followed by a gradual decrease. The increase of dehydration with addition of MoO_3 suggests that de-

FIG. 3

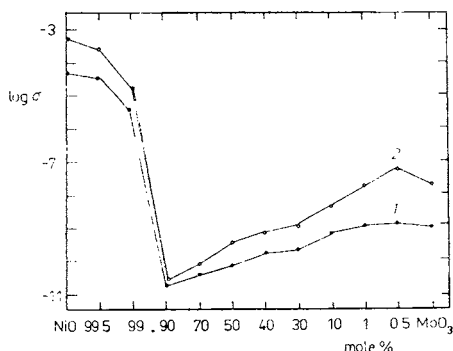Variation of log σ vs composition of MoO₃–
–NiO system (samples were calcined at
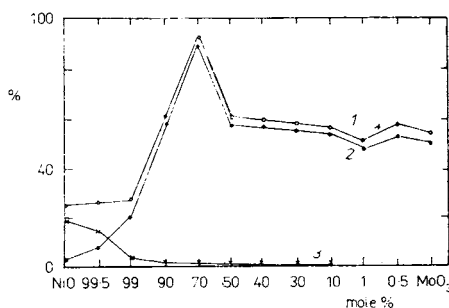500°C for 4 h in air). 1 In air, 2 in the
presence of 2-propanol

FIG. 4

Variation of conversion (%) with composi-
tion of MoO₃–NiO system (samples were
calcined at 500°C for 4 h in air). 1 Total
conversion, 2 yield of propene, 3 yield of
acetone

composition of 2-propanol is a donor reaction[18] as detected by the increase of σ values when 2-propanol was admitted in the feed.

As seen in Fig. 4, the catalytic activity of MoO_3 catalysts containing Ni^{2+} is nearly constant for catalysts containing more than 30 mole % Mo^{6+}. This is due to the effect of n-type character of MoO_3 containing p-type sites and the donor nature of the decomposition reaction of 2-propanol.

Previous XPS work conducted by Ozkan and Schrader[19] reported that the bond energies of the non-stoichiometric $NiMoO_4$ with different Mo/Ni ratios are the same, a situation indicating that the oxidation state of Mo^{6+} does not change in these samples. This gave a plausible explanation for the constant catalytic activity of molybdenum-rich catalysts which have the structure closely resembling $NiMoO_4$ as detected by IR absorption vibrational bands.

The crucial role of the specific structural arrangements (namely MoO_3 surface covered by $NiMoO_4$) is that $NiMoO_4$ selectively blocks the complete oxidation sites on MoO_3 surface which can explain why the dehydrogenation reaction diminished over catalyst surface with high MoO_3 compared with those containing high NiO concentration.

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