ESR, FT-Raman spectroscopic and ethanol partial oxidation studies on MoO_3/SnO_2 catalysts made by metal oxide vapor synthesis

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A series of SnO_2-supported MoO_3 catalysts were prepared by the metal oxide vapor synthesis (MOVS) technique. ESR studies indicated the presence of highly dispersed Mo^{5+} species in both octahedral and tetrahedral coordination environments at all the loadings studied. At the highest MoO_3 loading of 12 wt%, the formation of MoO_3 microcrystallites was indicated from the lower intensity of the ESR signal. Raman studies also showed the presence of well dispersed surface molybdate species up to 4.4 wt% MoO_3 loading, and the peaks corresponding to microcrystallites of molybdena were observed at 12 wt% MoO_3 loading. The ethanol partial oxidation activities of the catalysts increased with increase in MoO_3 loading and the catalyst with 4.4 wt% molybdena content showed the highest activity; all the MOVS catalysts showed 100% selectivity to acetaldehyde at low conversions.

Keywords: MOVS, MoO_3/SnO_2, characterization, XRD, ESR, FT-Raman, ethanol partial oxidation

1. Introduction

SnO_2 is a versatile material since it finds application as a gas sensor [1] and as a carrier in supported metallic and oxide catalysts. SnO_2-supported Pt and Pd catalysts have been employed for CO oxidation [2]. Unlike the conventional inert supports such as α-Al_2O_3, SiO_2, etc., SnO_2 exhibits redox properties acting as a promoter. SnO_2-supported and mixed-oxide vanadia catalysts have been utilized for catalyzing various industrially important oxidation [3] and ammoxidation [4,5] reactions. V_2O_5/SnO_2 catalysts were found to exhibit higher activities and selectivities in the above mentioned reactions, which was attributed to the promoting action of SnO_2 facilitating the easier removal of terminal oxygen of V=O surface species in the catalysts. MoO_3/SnO_2 catalysts were earlier employed for the oxidation of methanol to formaldehyde [6] and ethanol oxidation to either acetaldehyde [7] or acetic acid [8]. The oxidic active components like molybdena and vanadia are known to form monolayers on SnO_2 support, just as on other supports such as Al_2O_3, TiO_2 and ZrO_2 [9]. In the present investigation a unique method of metal oxide vapor synthesis (MOVS) was employed for the preparation of SnO_2-supported molybdena catalysts. MOVS is a novel technique of synthesis of the molybdena precursor, involving cocondensation of molybdena vapors (achieved by resistive heating) with anhydrous methanol [10]. This method was proved to be a facile technique in order to achieve higher molybdena dispersion and catalytic activity and selectivity. Our earlier investigations [11–13] on the activity studies of these catalysts for the partial oxidation of alcohols such as methanol and ethanol, alcohol synthesis from syngas, and for isomerization reactions indicated enhanced activity and selectivity in comparison with commercial catalysts. Isopropyl alcohol decomposition to determine the acid–base properties of the MoO_3/TiO_2 catalysts made using the MOVS method indicated predominance of the basic properties of the catalysts over the acid–base characteristics [13]. In the present study, the MoO_3/SnO_2 catalysts synthesized using the MOVS method were characterized by employing the spectrophysical techniques such as X-ray diffraction, electron spin resonance and FT-Raman spectroscopy. The oxidation activities of the catalysts were tested using the ethanol partial oxidation reaction.

2. Experimental

SnO_2-supported molybdena catalysts with MoO_3 content varying between 0.4 and 12 wt% were prepared by metal oxide vapor synthesis (MOVS) using the Torrovap apparatus that has been described in detail elsewhere [10]. Molybdenum trioxide (Aldrich) vaporization was achieved by resistive heating at a pressure of 3×10^{-6} Torr and the oxide vapors were cocondensed at 77 K with a 250-fold molar excess of anhydrous methanol (Fisher HPLC grade). The cocondensate was allowed to slowly come to room temperature and formed a clear colorless solution, which was removed from the reaction flask via a Schlenk tube. Calculated amounts of the molybdena MOVS solution were added to the SnO_2 support (Aesar, S.A. 10 m^2/g) precalcined at 773 K for 5 h. The samples were stirred for 1 h to ensure even deposition on the support surface. The excess solution was removed by vacuum evaporation. The samples were dried overnight at 383 K followed by calcination at 723 K for 4 h. The molybdena contents in the calcined

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catalysts were determined by inductively coupled plasma (ICP) analysis on a Varian Liberty 100-OES spectrometer after calibrating the instrument with NIST traceable standards. All of the MoO_3/SnO_2 catalysts had surface areas (determined by the BET method) which were experimentally indistinguishable from the SnO_2 support itself.

The X-ray diffractograms were recorded on a Rigaku Geigerflex DMAX II diffractometer using Co K_α radiation. ESR spectra were recorded at ambient temperature on an E-line century series EPR spectrometer operating in X-band with 100 KHz modulation frequency. g values were referenced to DPPH. The samples calcined at 723 K were sealed in quartz tubes to prevent exposure to the ambient conditions. FT-Raman spectra were recorded on a Bruker FRA 106 FT-Raman module interfaced to a Bruker IFS-66 FT-IR bench.

Activity studies for ethanol partial oxidation were carried out at atmospheric pressure in a fixed-bed microcatalytic reactor interfaced to a gas chromatograph with a six-way gas sampling valve in the temperature range 423–523 K, with a residence time $W/F = 35$ g-cat./h mol of ethanol.

200 mg of the catalyst was packed in a fixed-bed tubular glass reactor of 10 mm i.d. and was pretreated in a stream of purified dry air for 30 min at the maximum reaction temperature 523 K. After reducing the temperature to 423 K, ethanol was introduced into the reactor by flowing air (40 ml/min) through a saturator maintained at 298 K. The outlet of the reactor to the gas chromatograph was heated at 423 K to avoid condensation of the products. A lower-temperature reaction run was repeated for all the catalysts after the highest-temperature run to observe if there is any catalyst deactivation while obtaining the activity data. After a steady-state period of 30 min the products were analyzed on-line using a Varian 3400 gas chromatograph employing Porapaq QS (stainless steel column, 80/100 mesh, 6 ft. $\times$ 0.125 ft. in. diameter) and a thermal conductivity (TC) detector. The product stream was comprised mainly of acetaldehyde up to a reaction temperature of 498 K; at this temperature selectivity to acetic acid is significant, whereas only trace amounts of other products such as ether, diethoxyethane, ethyl acetate and CO and CO_2 were identified.

3. Results and discussion

Electron spin resonance is commonly employed [15–18] to identify the presence of paramagnetic molybdena species on the support surface. In addition to some lower various oxidation states of molybdenum present in the catalyst, different coordination environments around molybdenum can also be detected by ESR spectroscopy. Mo(V) in a suitable environment clearly shows resonance even at ambient temperature. Louis et al. [15,16] observed clear resolution of the ESR signals due to Mo^{5+} in different coordination environments such as tetra-, penta- and hexa-coordination in the MoO_3/SiO_2 catalysts made by their grafting method. Broader ESR signals were observed in some MoO_3/Al_2O_3 catalysts [17], which was attributed to spin–spin interaction/shorter relaxation times. The molybdena contents of the MoO_3/SnO_2 catalysts and the catalyst codes are given in table 1. The ESR spectra of Mo–Sn samples recorded at ambient temperature are shown in figure 1. The resonance spectra resemble those reported by Louis et al. [15,16]. A sharp signal with $g_\perp$ value of 1.958 can be attributed to six-coordinated Mo^{5+} (Mo^{5+}_{6c}) species. The parallel component, $g_\parallel = 1.884$, of this species is also identified in the spectra and shown in the figure. The other signal corresponding to a g value of 1.909 is assigned to the perpendicular component of the four-coordinated Mo^{5+} species. The hf1 and hf2 are the hyperfine lines of the five- and

Table 1
Molybdena contents and turnover numbers of ethanol partial oxidation for various catalysts.

Catalyst	MoO_3 (wt%)	Mo (atoms/nm^2)	TON[a] (s^{-1})
SnO_2	–	–	–
Mo–Sn 1	0.4	1.9	0.163
Mo–Sn 2	1.3	5.4	0.059
Mo–Sn 3	3.1	12.9	0.027
Mo–Sn 4	4.4	18.4	0.025
Mo–Sn 5	12.0	50.2	0.0029

[a] Based on the number of moles of ethanol reacted per mole Mo atom per second.

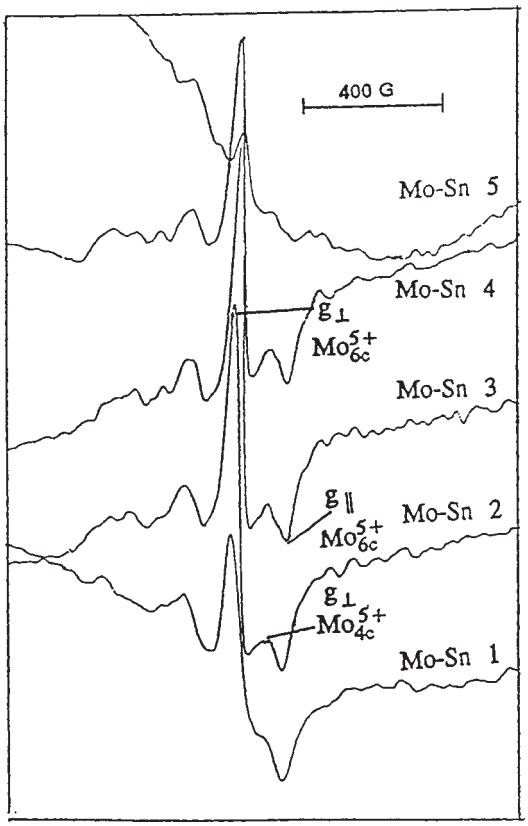

Figure 1. ESR spectra of the catalysts recorded at ambient temperature. (Peaks are assigned and labeled according to [15,16].)

Table 2
ESR parameters – parallel and perpendicular g components of Mo^{5+} in different coordination environments in MoO_3/SnO_2 catalysts.

Catalyst	Mo^{5+}_{6c}		Mo^{5+}_{4c}
	$g_\perp$	$g_\parallel$	$g_\perp$
Mo–Sn 1	1.9585	1.8861	1.9096
Mo–Sn 2	1.9585	1.8814	1.9048
Mo–Sn 3	1.9585	1.8796	1.9048
Mo–Sn 4	1.9585	1.8814	1.9048
Mo–Sn 5	1.9129	1.8722	1.9039

six-coordinated Mo^{5+} species, respectively [15]. The g values of both tetra- and hexa-coordinated Mo^{5+} are given in table 2 for the various catalysts. The values are close to those of MoO_3/SiO_2 samples as reported by Louis and coworkers [15]. There is not much variation in the ESR spectral pattern with increase in molybdena loading, except in the sample Mo–Sn 5 with a MoO_3 loading of 12 wt%. In this sample the hyperfine lines hf1 and hf2 observed in the other catalysts are not present and the intensity of the signal corresponding to Mo^{5+} is also much less, indicating fewer reducible molybdena sites, i.e., molybdena crystallites. ESR spectra of the samples exposed to the atmosphere under ambient conditions did not exhibit clear hfs lines and the resolution of the parallel and perpendicular g components was also not clear indicating the absorption of moisture under these conditions. These results are in conformity with FT-Raman and activity studies, as discussed below.

Figure 2 shows the Raman spectra of the catalysts recorded at ambient temperature in the range 1200–0 cm^{-1}. The Raman spectrum of the SnO_2 support is included in figure 2. A large number of studies [19–23] by Raman spectroscopy concerning the surface structures of supported molybdenum oxide species have been reported, as this technique can differentiate between the different molecular states of supported metal oxide since each state exhibits a characteristic vibrational spectrum that directly corresponds to its structure. Stampfl et al. [22] also noticed Raman peaks at similar shifts for SnO_2 support. In the sample Mo–Sn 1 only the support peaks at 775 and 632 cm^{-1} could be seen due to the extremely low loading of MoO_3. In the sample Mo–Sn 2 Raman peaks corresponding to dispersed molybdate species at about 950 cm^{-1} and peaks at 995 and 818 cm^{-1} corresponding to MoO_3 microcrystallites could be seen. Stampfl et al. [22] observed a peak at 950 cm^{-1} for the MoO_3/SnO_2 sample when the spectra was recorded at ambient temperature, upon calcination of the sample the peak shifted to 1000 cm^{-1}. In the present study the spectra were recorded at ambient temperature for the precalcined samples. Kim et al. [23] observed that Raman intensities of crystalline MoO_3 species will mask the peaks of surface molybdate species. With further increase in MoO_3 loading in the samples Mo–Sn 3 and Mo–Sn 4 there is an increase in the intensities of the peaks corresponding to microcrystalline species indicating their formation at the expense of the dispersed surface molybdate species. It can also be noted that the peaks of SnO_2 support at 775 and 632 cm^{-1} decreased in intensity indicating the coverage of the sup-

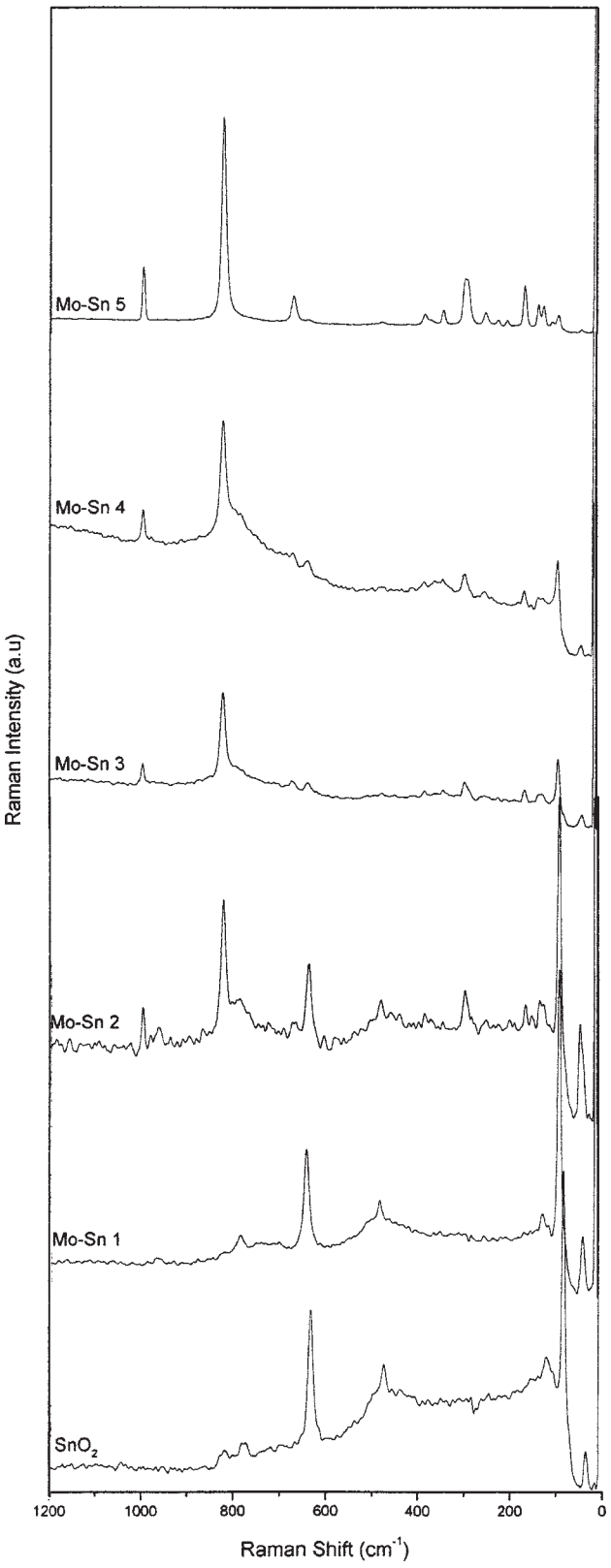

Figure 2. FT-Raman spectra of SnO_2 support and Mo–Sn catalysts in the range 1200–0 cm^{-1}.

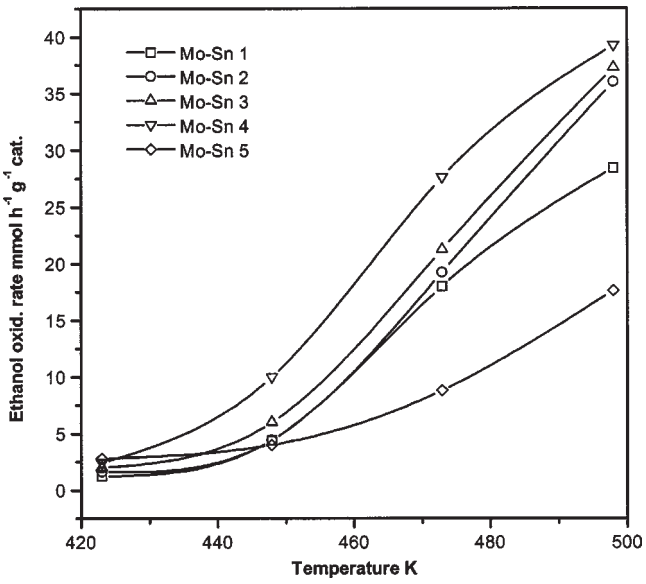

Figure 3. Ethanol partial oxidation rates of MoO_3/SnO_2 catalysts as a function of reaction temperature.

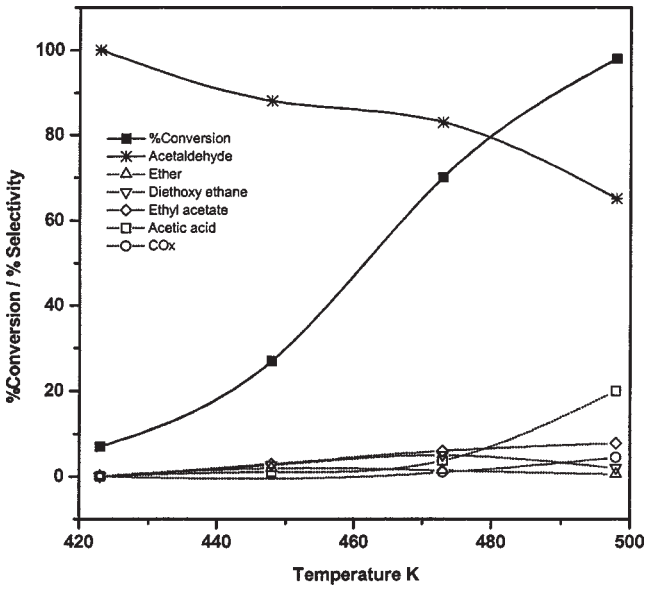

Figure 4. % conversions and % selectivities to various products for the Mo–Sn 4 catalyst at different reaction temperatures.

port. In the sample Mo–Sn 5 with highest loading of MoO_3 only the peaks corresponding to crystalline MoO_3 could be seen.

The ethanol partial oxidation reaction has been employed previously to assess the activity of supported molybdena catalysts [7,8,10,24]. Oyama and Somorjai [25] in their ethanol oxidation studies on V_2O_5/SiO_2 catalysts have proposed that ethanol oxidation is a structure-insensitive reaction. The turnover numbers (TON, s^{-1}) of the catalysts calculated from the number of moles of ethanol converted per mole of molybdenum atom per second are given in table 1. All the molybdenum atoms were assumed to be on the surface and participating in the reaction. The ethanol partial oxidation rates of the Mo–Sn catalysts are shown in figure 3 as a function of reaction temperature. The activities of the catalysts increased with increase in molybdena loading up to 4.4 wt% MoO_3 (sample Mo–Sn 4). Considering the monolayer loading of 0.16 wt%, as suggested by Bond et al. [26] for the MoO_3/TiO_2 catalysts, the 4.4 wt% in Mo–Sn 4 catalyst is close to three monolayers. In another study, Bond et al. [27] have shown that the activity of the supported molybdena catalysts increased with increase in MoO_3 content with three to four monolayers in the isopropanol decomposition reaction. Thus the higher catalyst Mo–Sn 4 can be explained based upon these observations of Bond et al. [27] due to the presence of molybdena monolayers in the dispersed form. The activity of the sample Mo–Sn 5 is lowest, which is due to the presence of molybdena in highly crystalline form, as reflected in ESR and FT-Raman studies. The activities of the catalysts increased with increase in the temperature range of 423–523 K. The % ethanol conversions and % selectivities towards various products of the Mo–Sn 4 catalyst, which exhibited highest activity in the series, are shown in figure 4. At lower conversions, total selectivity to dehydrogenated product acetaldehyde was observed, while at higher conversions the selectivity to acetic acid is ∼20% with trace amounts of ether, diethoxyethane, ethyl acetate and CO_x. SnO_2 support by itself exhibited very low conversions with total selectivity to acetaldehyde under the reaction conditions. MoO_3 by itself exhibited noticeable activity only at 498 K and above with total selectivity to acetaldehyde; with an increase in temperature from 498 to 548 K, trace amounts of ether, diethoxyethane and ethyl acetate were observed. Niwa et al. [28], from their *in situ* ESR studies on a MoO_3/SnO_2 catalyst during methanol oxidation studies, proposed that oxidation occurs primarily at Mo^{5+} sites. In the present investigation the increase in the ESR signal intensity of the Mo^{5+} species up to 4.4 wt% MoO_3 loading and then a decrease in the sample Mo–Sn 5 with 12 wt% molybdena loading is in agreement with the above observation.

In summary, ESR spectra indicated the presence of four- and six-coordinated Mo^{5+} species in our MOVS catalysts. Raman studies showed highly dispersed surface molybdate species up to 4.4 wt% MoO_3 loading. Highest ethanol partial oxidation activity and total selectivity to acetaldehyde was obtained on this latter sample, which is consistent with the conclusions drawn from the spectroscopic studies.

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