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Oxidation of methanol on different silica supported lithium molybdates

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Abstract

The adsorption, the temperature programmed desorption and the oxidation of methanol were studied on different silica supported Li_2MoO_4. It was found that after adsorption of methanol methoxy species were formed in all cases, but the thermal stability of these species were different. The lowest value was found on Li_2MoO_4/aerogel. Oxygen in the gas phase stabilizes the surface methoxy groups up to 600–650 K. TPD spectra of adsorbed methanol show that up to 620 K only CH_3OH and HCHO desorbed but at higher temperatures CO_2, CH_4 and H_2 were also formed. In the oxidation of CH_3OH the rate of HCHO formation was the highest on aerogel supported Li_2MoO_4 at 533 K, and the selectivity was more than 70%.

Keywords: Oxidation of methanol; Lithium molybdate; TPD spectra

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1. Introduction

Silica supported molybdenum catalysts are widely used in the partial oxidation of methane [1] and methanol [2], but less attention has been paid to the effect of alkali metal molybdates. It was found that adding Na to MoO_3/SiO_2 significantly increased the HCHO and CH_3OH yields in the CH_4 oxidation [3] and Na_2MoO_4 is an active catalyst at high temperature for the dehydrogenation of CH_3OH to produce water free HCHO [4]. Alkali metal molybdates were active in the partial oxidation of methane [5], ethane [6] and in the conversion of methane to benzene [7]. In contrast to these observations, it has been shown that alkali metal impurities lead to the formation of alkali metal molybdates, which inhibit the conversion of methane and methanol to HCHO [1]. Recently we have found that the catalytic activity for methane conversion was the highest on Rb_2MoO_4/SiO_2 due to its surface structure [5], but in the methanol oxidation Li_2MoO_4/SiO_2 shows the best efficiency among the silica supported alkali metal molybdates [8]. In the present work, the oxidation of methanol and surface methoxy species were investigated on silica supported lithium molybdates. In particular, we focused on the correlation between the type of the silica support and the activity and selectivity of the catalysts and on the intermediates formed during the adsorption of reactant and during the catalytic reaction.

2. Experimental

Catalyst was prepared by impregnating the SiO_2 (Cab-O-Sil) with a basic solution (pH $\sim$ 11) of Li_2MoO_4 to yield a nominal 2% loading of MoO_3. The suspension was dried at 373 K. Samples were prepared by sol–gel method from Li_2MoO_4 and tetraethoxysilane. The gel was dried either at 373 K in air (xerogel) or by supercritical carbon dioxide (aerogel). All samples were calcined at 873 K.

The samples were characterized by XP (Kratos XSAM 800) and FT Raman (Bio-Rad) spectroscopies, NH_3 TPD, pyridine adsorption, pore size and pore volume distribution.

The oxidation of methanol was carried out in a fixed-bed continuous-flow reactor. Generally 0.5 g sample was used as catalyst. The amount of methanol introduced into the reactor was that resulting after bubbling a mixture of $Ar + O_2$ through methanol cooled to 273 K. In the reacting gas mixture the methanol oxygen molar ratio was usually 1:1. The space velocity was $6000\,h^{-1}$. The gases were analyzed by gas chromatography (Chrompack 9001) or by an online mass spectrometer (Pfeiffer QMS 200). The adsorption and temperature programmed desorption of methanol were carried

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out in a microbalance (Netzsch STA 409 PC) coupled to a mass spectrometer (Pfeiffer QMS 200). The adsorption of methanol and the surface stability of methoxy groups were studied by FTIR spectroscopy (Bio-Rad FTS 135).

3. Results and discussion

3.1. Characterization of the catalysts

The BET surface of the calcined silica supported Li_2MoO_4 samples increased in the order of impregnated sample (150 m^2/g), xerogel (220 m^2/g), and aerogel (550 m^2/g). The pore volume of the xerogel (0.2 cm^3/g) was more than seven times less than that of the aerogel (1.5 cm^3/g). The features of the TPD curves of adsorbed NH_3 were nearly the same; the amount of it decreased in the order of aerogel $>$ impregnated sample $>$ xerogel. IR spectra of adsorbed pyridine show that only weak Lewis acidic centers are on the catalysts. The Raman frequency of the Mo–O band in the Li_2MoO_4/SiO_2 samples (901 cm^{-1}) was the same in all cases as on the unsupported Li_2MoO_4. It means that the molybdate bonded to the support in the original tetrahedral structure.

XP spectra show that the binding energy of the Mo $3d_{5/2}$ orbital (232.5 eV) does not change significantly when Li_2MoO_4 is supported on different silicas. Taking into account the XPS peak area ratios of the Mo 3d and Si 2p peaks for different silica supported samples, we can state that the amount of surface Mo atoms is the highest on impregnated sample ($Mo/Si = 0.019$). This value is about 35% more than that on the aerogel and more than double than on the xerogel.

Wachs and co-workers developed a method for the quantitative determination of the number of active surface sites for methanol oxidation by methanol chemisorption [9]. They supposed that methanol desorbed till 573 K bonded to the molybdenum sites. Using this technique the amount of active sites was the highest on the aerogel. This value (2.72 mg/g adsorbed methanol) was more than one and a half times higher than on the xerogel (1.54 mg/g) or on the impregnated sample (1.22 mg/g). When these data were related to the BET surface of the samples an opposite order was obtained. The Mo/Si ratio determined by XPS is characteristic for the amount of Mo atoms in the top layers. By means of methanol adsorption the number of active sites could be measured. So the difference between these two data is ambiguous.

3.2. Infrared spectra of adsorbed methanol

The adsorption of methanol on different silica supported Li_2MoO_4 at 298 K produced IR bands at 2998, 2955, 2923, 2855 and 2846 cm^{-1} which can be assigned as C–H stretching vibrations of adsorbed methanol and those of methoxy groups bound to the catalysts [10] (Fig. 1). On both pre-treated Li_2MoO_4/SiO_2 and on SiO_2 a very intense band of isolated Si–OH groups was observed at 3740 cm^{-1}, but methanol adsorption resulted in the consumption of OH groups on the silica surface. This points to the fact that the surface OH groups on the silica interact with the adsorbed methanol in this process. At the same time, a broad band appeared at 3420–3360 cm^{-1} which refers to the formation of hydrogen bridge bonding. After evacuation the intensities of the bands at 2923 and 2846 cm^{-1} decreased significantly and the latter peak shifted to 2829 cm^{-1}. These bands disappeared from the spectra when the sample was heated to 473 K. Increasing the evacuation temperature the intensities of the absorption peaks decreased continuously, but even after evacuation at 923 K the bands at 2998, 2960 and 2858 cm^{-1} were still detectable when the impregnated sample was used. On aerogel or on xerogel the same spectral features were observed as mentioned above, but the stability of the methoxy species were higher in these cases, the bands disappeared from the spectra only after evacuation above 1000 K.

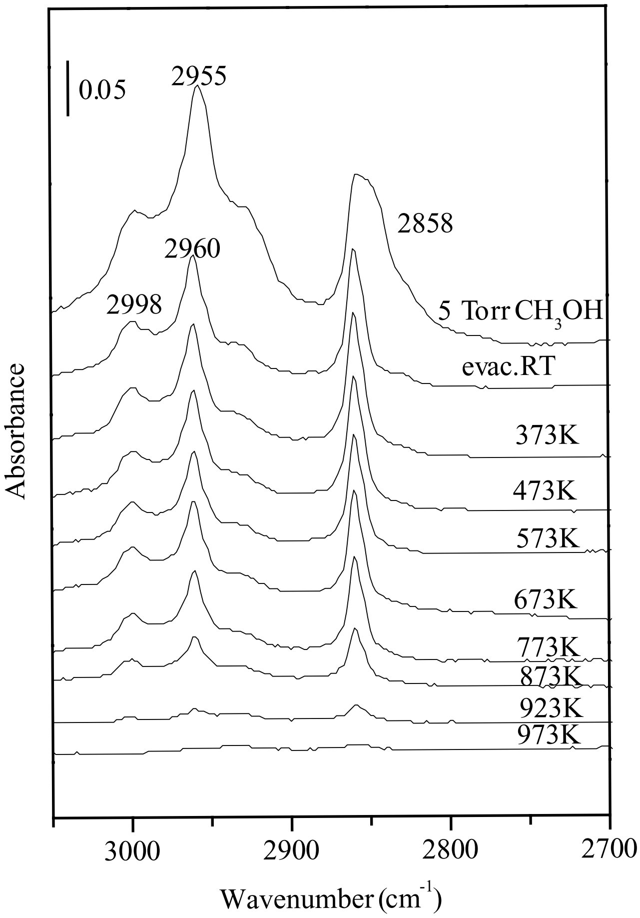

Fig. 1. Infrared spectra of adsorbed methanol (0.665 kPa) on Li_2MoO_4/SiO_2 impregnated samples and evacuated at different temperatures.

There were no significant differences between the IR spectra of adsorbed methanol on different Li_2MoO_4/SiO_2 and on silica support, although the surface contains Li_2MoO_4, these sites are slightly basic towards methanol, which is mildly

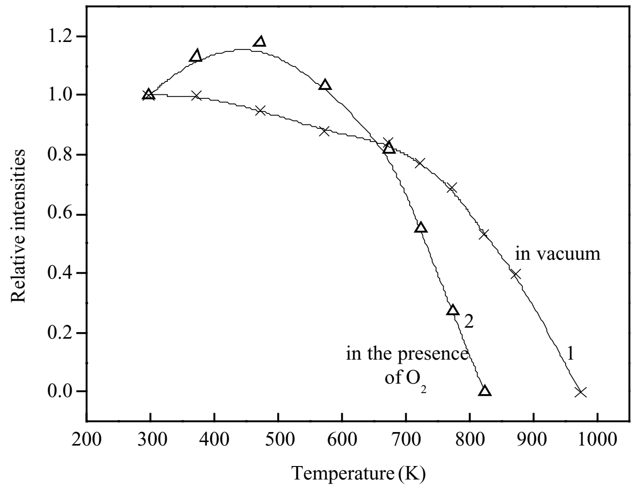

Fig. 2. Changes of relative intensity of the IR band of methoxy species at 2858 cm^{-1} as a function of temperature in vacuum (1) and in the presence of 1.33 kPa of oxygen (2) on the impregnated sample.

acidic and this would be the reason for the formation of surface alkoxy species other than produced on the somewhat acidic Si–OH sites. It is possible that bands that appeared at 2923 and 2846 cm^{-1} can be assignated as C–H stretching of methoxy bonded to the molybdates, but we have no other evidence to declare it.

When the adsorbed methanol was evacuated at room temperature and then the sample was heated in 1.33 kPa of oxygen, new absorption peaks were not detected. The intensities of IR bands in the presence of O_2 did not decrease up to 550 K as in vacuum. Above this temperature, the thermal stability of the absorption bands was much lower, at about 800 K all peaks disappeared from the spectra (Fig. 2). Wachs and co-workers found [9] and our TPD results also show that at low temperature only the molybdate bonded methoxy species desorbed from the surface. Our IR spectra revealed that the intensities of absorption bands of surface methoxy species decreased in vacuum but when oxygen was present in the gas phase, the intensities rather increased than decreased. This stabilizing effect can be explained that in the presence of oxygen a stable Mo–OCH_3 complex can be formed. These species can be produced only by adsorbed oxygen.

3.3. Temperature programmed desorption of methanol

After adsorption of CH_3OH at 373 K the chamber was flushed with Ar and then the catalyst was heated in Ar flow up to 1173 K. A typical TPD spectrum is shown in Fig. 3. Methanol desorption occurred in the temperature range 390–670 K. The TPD spectrum of this product exhibits a maximum at 470 K. This peak has a broad shoulder towards higher temperatures. The shape of the curve suggests that methanol adsorbed in multilayer. Above 520 K appears HCHO. This product desorbs as a broad signal in the range of 520–920 K without a sharp maximum. It is well known that HCHO can be produced from methoxy species.

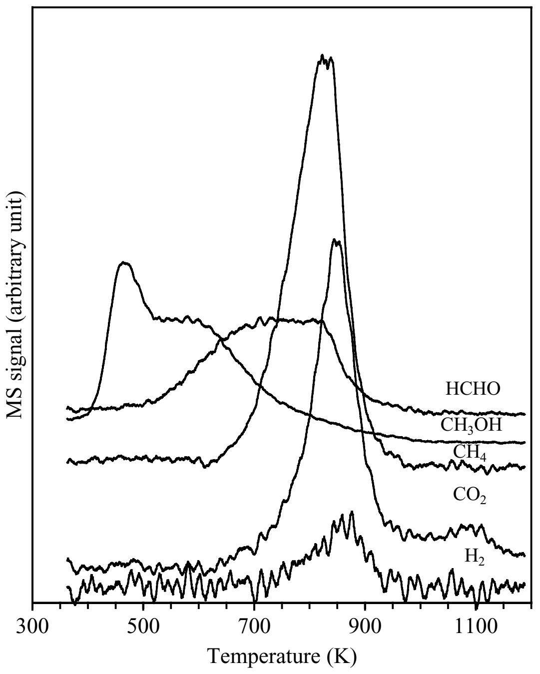

Fig. 3. Temperature programmed desorption of methanol adsorbed on Li_2MoO_4 supported on xerogel.

Evolution of CO_2 and CH_4 were observed in the same temperature range (650–920 K). The amount of methane is higher than that of carbon dioxide in all cases. Traces of hydrogen formation were also observed together with CO_2 and CH_4. Water desorbed all along the spectra while both surface methoxy formation and decomposition generate it.

The TPD curves and the product distribution were almost the same in the case of other Li_2MoO_4/SiO_2 samples. The largest quantity of methanol adsorbed on the aerogel, but the surplus of it comparing with the other samples desorbs mainly as methanol.

For comparison the methanol TPD was studied on clean silica supports, too. In these cases methanol desorption was detected between 373 and 473 K and CO_2 evolution was observed above 873 K. When the methanol was adsorbed on Li_2MoO_4/SiO_2 in addition to methanol and carbon dioxide, HCHO and at high temperatures methane was also desorbed. These results suggest that although the methoxy species bonded to the silica at this temperature, the decomposition of it is influenced by the molybdate. It means that the surface methoxy species have to spill over from the silica to the molybdates or at least to the silica molybdate interface. Methane can be formed in the decomposition of methyl formate which is the possible product of the formyl produced on the molybdates and methoxy bonded to the silica.

The low temperature methanol desorption shows that methoxy species can take up hydrogen from their surroundings from the surface, so they can desorb as methanol. This hydrogen could come from the –OH of silica or from the previously adsorbed –H.

Table 1
Some characteristic data for methanol oxidation on different silica supported Li_2MoO_4 at 533 K

Catalysts	BET surface (m^2/g)	Mo/Si ratio[a]	Adsorbed methanol[b] (mg/g)	Conversion (%)		Selectivity (%)						Rate of HCHO formation (μmol/g s)	
				20 min	170 min	HCHO		CO		CO_2		20 min	170 min
						20 min	170 min	20 min	170 min	20 min	170 min		
Impregnated sample	150	0.019	1.22	13.4	7.7	77.8	72.8	2.3	4.3	19.9	22.9	0.91	0.44
Xerogel	220	0.0088	1.54	10.2	5.1	74.5	64.6	5.5	9.2	20.0	26.2	0.56	0.23
Aerogel	550	0.014	2.72	17.0	10.8	72.1	70.2	10.6	14.1	17.3	15.7	0.87	0.53

[a] The Mo/Si ratio determined from the XPS peak area.
[b] The amount of adsorbed methanol on the molybdenum site.

3.4. Partial oxidation of methanol

The oxidation of methanol was first followed at 533 K. The initial conversion of methanol was about 9–12%, which decreased during the conditioning period. The main products at this temperature were HCHO, CO and CO_2, but traces of methyl formate and dimethyl ether were also formed. The selectivity of HCHO formation was about 70% in all cases, but after 3 h of reaction these values were slightly lower. Some characteristic data for methanol oxidation were summarized in Table 1. The steady state activity was attained after a reaction time of 120–140 min. The highest conversion in the steady state was observed on aerogel and this value decreased in the order of impregnated sample and xerogel. The rate of HCHO formation in the steady state was the highest on aerogel (Table 1). When the rates were related to the Mo/Si ratio determined by XPS the high efficiency of this sample is also observable. This value was about twice higher than on xerogel, although the Mo/Si ratio determined by XPS was only about 60% higher in the latter case. On the impregnated sample the rate of HCHO formation was only slightly lower than on aerogel.

To achieve higher conversion the reaction was carried out at higher temperature. In this case the product distribution was completely different. At 593 K, the conversion was more than 50%, the main product were dimethyl ether, CO and methyl formate, a small amount of CO_2 and traces of HCHO were also formed.

Earlier it was found [11] that the silica support gave rise to CO_x and dimethyl ether and did not yield any redox products (formaldehyde, methyl formate). The CO_x was produced from the oxidation of the Si–OCH_3 species. The dimethyl ether is produced by some acidic impurities present in the catalyst. The addition of Li_2MoO_4 to the silica resulted in the production of HCHO. When the reaction was carried out above 573 K significant amount of methyl formate was detected. Methyl formate production requires the reaction between HCHO produced on redox sites and adjacent surface methoxy species on the silica support. The rate of HCHO formation at lower temperature, at 533 K, was higher than at 593 K, although the methyl formate formation was much higher in the latter case. From these results, we may conclude that the mobility of surface methoxy group on the silica is the rate determining step for the methyl formate formation at about 530–600 K.

This observation supported our assumption that the silica surface is a reservoir for methoxy species from where they can migrate to the molybdates which are the active centers for the HCHO formation. Seman and co-workers suppose [12] that two kinds of methoxy species exist on the surface of MoO_3/SiO_2: spectators and active intermediates. Only the active intermediates could be oxidized at temperatures lower than 573 K, and these are the actual participants in the reaction.

The best efficiency of the aerogel for HCHO formation could be attributed to the highest amount of active sites determined by CH_3OH adsorption.

Acknowledgements

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References

[1] N.D. Spencer, C.J. Pereira, R.K. Grasselli, J. Catal. 126 (1990) 546.
[2] M.A. Banares, H. Hu, I.E. Wachs, J. Catal. 150 (1994) 407.
[3] A.W. Sexton, E. MacGiolla Coda, B.K. Hodnett, Catal. Today 46 (1998) 127.
[4] M.R. Prairie, S. Su, A. Renken, P. Ruterana, P. Buffat, Appl. Catal. 57 (1990) 84.
[5] A. Erdőhelyi, K. Fodor, R. Németh, A. Hancz, A. Oszkó, J. Catal. 199 (2001) 328.
[6] A. Erdőhelyi, F. Máté, F. Solymosi, J. Catal. 135 (1992) 563.
[7] A. Szőke, F. Solymosi, Appl. Catal. A: General 142 (1996) 361.
[8] A. Erdőhelyi, A. Hancz, M. Tóth, É. Novák, Appl. Catal., submitted for publication.
[9] L.E. Briand, W.E. Farneth, I.E. Wachs, Catal. Today 62 (2000) 219.
[10] M.A. Natal-Santiago, J.A. Dumesic, J. Catal 175 (1998) 252.
[11] J.-M. Jehng, H. Hu, X. Gao, I.E. Wachs, Catal. Today 28 (1996) 335.
[12] M. Seman, J.N. Kondo, K. Domen, R. Radhakrisnan, S.T. Oyama, J. Phys. Chem. B 106 (2002) 12965.