Partial oxidation of methanol on TiO_2-supported 12-molybdophosphate catalysts

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Titania-supported 12-phosphomolybdic acid (HPMo/T) and their Ni- and Co-salts (NiPMo/T and CoPMo/T) have been prepared by impregnation and their acid properties tested by means of pyridine adsorption and by the heterogeneous partial oxidation of methanol with oxygen at atmospheric pressure. For sample HPMo/T, calcination at temperatures 523–723 K altered both methanol conversion and product distributions. At 523 K activity was high and reaction appeared to be dominated by acidity as CH_3OCH_3 was the major reaction product, however selectivity to CH_3OCH_3 decreased with the simultaneous increase of HCHO selectivity at 623 K indicating participation of redox properties of the catalyst. These changes have been interpreted as being due to the destruction of the supported heteropoly compound and the parallel change of the acid properties of the resulting catalyst.

Keywords: methanol oxidation, 12-molybdophosphates, MoO_3, pyridine adsorption

1. Introduction

Heteropoly acids and their salts are well known acidic and oxidative catalysts. Many potential applications have been proposed for these compounds, such as methanol conversion to hydrocarbons [1], hydration of olefins [2], modified Wacker reaction [3], synthesis of MTBE [4] and others [5–10]. Most of these reactions proceed not only on the acidic form of these compounds, but also on "neutral" salts even if the reaction is an acid-catalyzed one. As several advantages can be expected by salt formation, which may lead to a bifunctional catalyst and, in some cases, improved thermal stability, the study of catalytic behaviour of metal salts appears to be highly important.

As far as acid-site formation in neutral salts is concerned, several possibilities have been pointed out. Niiyama et al. [11] have postulated that the Lewis acidity of cation constitutes the origin of acid properties while the Brønsted acidity is a result of hydrolysis in the presence of water. Studies by means of photoacoustic spectroscopy revealed that the salts may also contain protons in the lattice [12]. Moreover, acid-site formation upon reduction under hydrogen and the nonstoichiometry of cation/polyanion have already been proposed. Although these considerations partially explain the results, additional information is required for a better understanding of the acid properties of metal salts.

In this paper, the acid behaviour of titania-supported heteropolymolybdates as well as their performance for the dehydration of methanol is reported. This reaction is a widely used "test reaction" for acid catalysis, and, therefore, general information regarding typical solid acid catalysts was obtained.

2. Experimental

Commercially available (Aldrich, 99.99 wt%, below 100 ppm metallic impurities) 12-molybdophosphoric acid, abbreviated as HPMo, was used as a starting material. Metal salts were prepared from aqueous solutions of the parent HPMo, to which the stoichiometric amounts of Ni- and Co-nitrates (Merck, reagent grade) were added, as described by Tsigdinos [13]. The content of molybdenum was 12.0 wt% and 1 wt% for Co and Ni. The titania-supported HPMo (denoted HPMo/T) and its Co and Ni salts (denoted as CoPMo/T and NiPMo/T, respectively) were prepared by impregnation of TiO_2 powder with aqueous solutions of purified HPMo and its corresponding salts, respectively. The TiO_2 support was prepared by hydrolysis of $TiCl_4$ followed by dehydration of $Ti(OH)_4$ xerogel at 373 K and then calcination at 723 K. The BET area of the powder sample was 70 m^2/g and phase proportion resulted in 85% anatase and 15% rutile.

Powder X-ray diffraction patterns of the samples were recorded on a Seifert 3000P diffractometer using nickel-filtered Cu $K\alpha$ ($\lambda = 0.15418$ nm) radiation and scanning 2θ angles ranging from 5 to 75°. The acidity of the samples was evaluated by recording the vibrational IR spectra of adsorbed pyridine. For this purpose, a special IR cell fitted with greaseless stopcocks and KBr windows was used. Self-supported samples of the catalysts were outgassed at 10^{-4} Torr at 523, 623 and 723 K for 1 h. After cooling to room temperature, the samples were exposed to about 1.5 Torr pyridine and the physically adsorbed fraction removed by outgassing at 393 K for 1 h before the spectra were recorded. The net spectrum of adsorbed pyridine is obtained by calculating the difference between the total and background spectra.

Catalytic experiments for methanol oxidation were performed in a continuous flow system with a stainless steel tubular reactor 6.2 mm i.d., using 0.05 g of catalysts held between quartz glass wool portions. A $CH_3OH/O_2/He = 5/10/85$ (molar ratio) mixture was fed into the reactor at a flow of 100 cm^3/min and atmospheric pressure. Methanol was fed by means of a liquid pump (Becton-Dickinson) and then vaporized. The analysis of the effluents of the reactor was performed with an on-line gas chromatograph (Varian 3400 CX) provided with a TC detector and a Porapack N packed column. The samples pretreated in the temperature range 533–733 K were heated to the reaction temperature under helium flow. Two reaction temperatures were tested for each sample: 483 and 503 K and the runs extended for periods of time ranging from 5 to 12 h. In a blank experiment with no catalyst in the reactor, no methanol conversion was observed. Duplicate experiments gave dispersion of the results within ±5%.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of the titania-supported HPMo sample heated at 623 and 773 K are displayed in figure 1. The impregnated samples are largely amorphous as no diffraction peaks of HPMo or MoO_3 could be identified up to 523 K. However, upon heating at 623 K diffraction peaks of the monoclinic β-MoO_3 [14], with other much less intense ones of the orthorhombic α-MoO_3 are observed. Finally, the latter phase is the dominant one detected upon calcination at 773 K.

3.2. Pyridine adsorption

The IR spectra of pyridine adsorbed on the HPMo/T catalyst pretreated at different temperatures are displayed in figure 2. Also the spectra of the NiPMo/T and CoPMo/T catalysts outgassed at 523 K are included for comparison. It is well known that pyridine coordinatively bonded to Lewis acid sites exhibits bands in the region 1440–1500 cm^{-1} (ν19b) and 1590–1640 cm^{-1} (ν8a) [15]. The wavenumber of the former is sensitive to Lewis acidity, while the intensity of the latter is proportional to the number of acid sites. The IR spectra of pyridine on the HPMo/T sample outgassed at 523 K show bands at 1485, 1610 and 1635 cm^{-1} characterising the Lewis acidity (figure 2a). The Brønsted acid sites are identified by the band at 1540 cm^{-1} [15]. After calcination at 623 K a new band appears at ca. 1450 cm^{-1}, the intensity of which increases with increasing pretreatment temperature (figures 2b–d). This new band of Lewis acidity can be assigned to the presence of isolated Mo^{6+} cations of molybdenum oxide phase(s), formed at higher calcination temperature. On the basis of our previous study [9], the Lewis acid sites at 1440 cm^{-1} would be associated with coordinatively unsaturated molybdenum $Mo^{\delta+}$ ($4 < \delta < 6$) cations generated during the outgassing treatment. Both CoPMo/T and NiPMo/T samples display a strong band of Lewis acidity at ca. 1448 cm^{-1}, due to Co^{2+} and Ni^{2+} cations, in comparison with that for their HPMo/T counterpart outgassed at the same temperature (523 K). The observation of Brønsted acidity for the Co and Ni salts of HPMo could be related to the incomplete stoichiometry of cation/polyanion and/or to some hydrolysis of the molybdophosphate anion during its preparation [16].

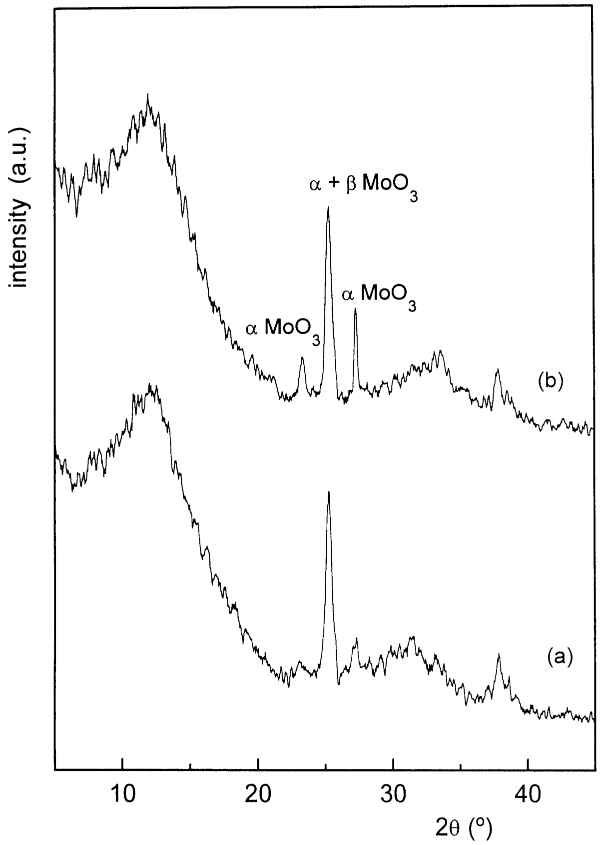

Figure 1. X-ray diffraction patterns of sample HPMo/T subjected to different calcination temperatures: (a) 623 K; (b) 773 K.

3.3. Catalyst activity

The oxidation of methanol over the catalysts produced dimethyl ether, formaldehyde and methyl formate. Only minor amounts of CO_2 were detected at higher temperatures. The methanol conversion and the yields to different products at a reaction temperature of 503 K over titania-supported HPMo, CoPMo and NiPMo catalysts are compiled in table 1. Selectivities to dimethyl ether, and formaldehyde over titania-supported HPMo catalyst at various pretreatment tempera-

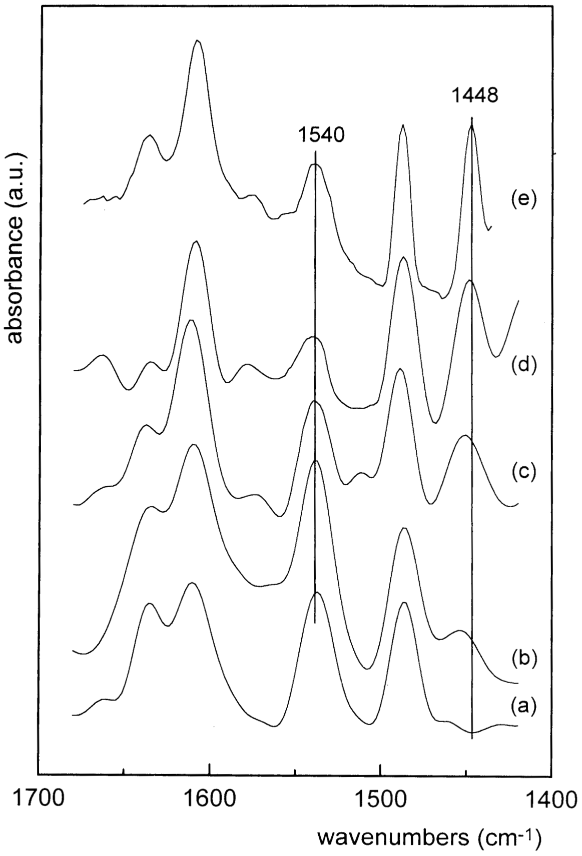

Figure 2. Infrared spectra of pyridine adsorbed on sample HPMo/T calcined at different temperatures: (a) 523 K; (b) 623 K; (c) 723 K; and on samples NiPMo/T (d); and CoPMo/T (e).

tures are displayed in figure 2. The HPMo/T sample calcined at 503 K showed the highest dimethyl ether selectivity and yield, as well as the largest methanol conversion. Upon increasing calcination temperature from 523 to 623 K for the HPMo/T catalyst (table 1, figure 3), a significant decrease in both selectivity and yield to CH_3OCH_3 was observed, which was much less marked at higher calcination temperatures. A similar trend was found in methanol conversion (table 1). The changes in the yields of HCHO and $HCOOCH_3$ were parallel to that of CH_3OCH_3 although less marked. For a given calcination temperature, less CH_3OCH_3 yield was obtained on the substituted Co^{2+} and Ni^{2+} samples (table 1).

Table 1
Methanol oxidation[a] at 503 K over XPMo/T (X = H, Co, Ni) catalysts subjected to different calcination temperatures

Catalyst	$T_{calc.}$ (K)	CH_3OH conv. (%)	Yields[b]		
			CH_3OCH_3	HCHO	$HCOOCH_3$
HPMo/T	523	27.3	11.7	10.0	5.6
HPMo/T	623	15.5	3.2	8.6	3.7
HPMo/T	723	14.1	3.0	7.7	3.3
CoMoP/T	523	12.0	2.0	5.7	4.3
NiPMo/T	523	13.5	3.2	7.9	2.4

[a] Feed: $CH_3OH : O_2 : He = 5 : 10 : 85$, 100 ml/min.
[b] Carbon in products/carbon fed.

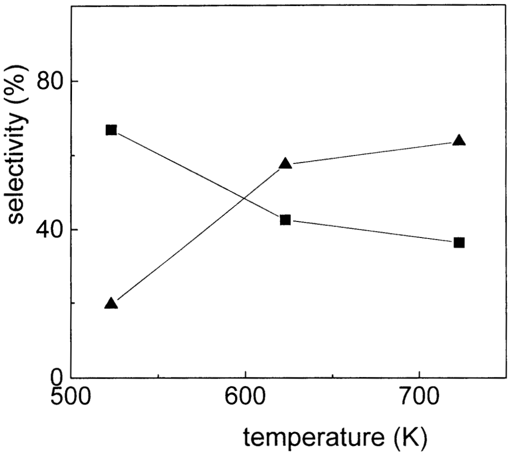

Figure 3. Dimethyl ether (■) and formaldehyde (▲) selectivities in methanol oxidation over sample HPMo/T calcined at different temperatures.

An examination of the changes of methanol conversion and product distributions as a function of pretreatment temperature reveals that methanol transformation proceeds in two directions: (i) at 523 K activity is high and reaction is dominated by acidity as CH_3OCH_3 is the major product; (ii) at 623 K selectivity to CH_3OCH_3 decreases while that to HCHO increases, thus indicating participation of redox properties of the catalyst; (iii) product distribution was essentially unchanged at higher temperatures. This behaviour is quite similar to that found by Rocchioccioli-Deltcheff et al. [17] on HPMo/SiO_2, although the acid–redox character was exhibited in a narrow temperature window.

The change in the catalytic properties of SiO_2- and TiO_2-supported HPMo catalysts could be related to the stability of the HPMo phase on the carrier. While the decomposition of HPMo/SiO_2 begins at temperatures below 523 K and ends at 623 K [18], the HPMo/T counterpart decomposes at a somewhat higher temperature. According to the classification of carriers concerning the isoelectric point, TiO_2 is more basic than SiO_2 [19]. This fact might be responsible for a stronger interaction of HPMo on the TiO_2 surface, as already revealed by the shift of the 960 and 1065 cm^{-1} bands of the supported HPMo phase with respect to that of the unsupported HPMo [20]. IR spectra provided evidence on preservation of the HPMo structure up to about 723 K. It can be noted that partial degradation of the Keggin unit into two morphologically distinct phases, α-MoO_3 and β-MoO_3, begins at 623 K and ends at 773 K with the formation of the dominant phase α-MoO_3.

Catalytic tests further indicate that the interaction with the support does not only lead to some stabilization of the HPMo structure, but also to modification of its acid–redox properties. The changes of CH_3OCH_3 selectivity in the 523–623 K range on HPMo/T catalyst could be related to the parallel changes in its acidic properties. This is revealed by the relative change of the Lewis to Brønsted band intensity ratio upon increasing pretreatment temperature (figure 2). It is well known that with increasing pretreatment temperature of the heteropoly compounds there is a gradual dehydration of the HPMo structure, with the formation of the so-called "anhydrous" phase, which is accompanied by a loss of protons [21]. According to Serwicka et al. [22], the high degree of heteropolyanion hydration provides the existence of Brønsted acid sites (BAS), and a gradual rising of the calcination temperature reduces the number and strength of BAS. Tatibouet et al. [23] have also shown that for methanol oxidation the decrease in concentration of mobile protons in HPMo resulted in a decrease of the CH_3OCH_3 yield and a rise of HCHO selectivity. We could also assume that the high CH_3OCH_3 selectivity on the sample heated at low temperature (523 K) is caused mainly by adsorption of methanol on strong BAS. Since CH_3OCH_3 and HCHO have a common intermediate, methoxy species [24], the sample with more BAS produces the higher yields to dehydration (CH_3OCH_3) and dehydrogenation (HCHO) products.

The influence of the change in BAS in the case of replacement of H^+ in the HPMo by metal cations, Co^{2+} and Ni^{2+}, on the selectivities of CoPM/T and NiPMo/T, respectively, is illustrated in figure 4. The total methanol conversion and the CH_3OCH_3 selectivity decrease, whereas the HCHO selectivity increases with respect to that of HPMo/T. This trend agrees with the difference in the acidic properties of HPMo/T and Ni- or CoPMo/T samples. The intensity of the Lewis band at 1450 cm^{-1} increases upon incorporation of Ni^{2+} or Co^{2+} cations while the Brønsted acidity slightly decreases. The catalytic behavior of samples calcined at 623–723 K would mainly be related to the change in phase composition. As shown in figure 1, calcination at 723 K leads to the formation of α-MoO_3 phase which may act as a redox system, which is confirmed by the increase in HCHO selectivity. Irrespective of the development of redox properties in catalyst HPMo/T calcined at 723 K, selectivity to CH_3OCH_3 is still high (a decrease not less than 20–40%) as a consequence of the remaining Brønsted acidity (figure 2). It is likely that the water by-product may be responsible for the acid character of the sample. Some restructuring of the decomposition products of HPMo at 723 K would be expected in the presence of water vapor at the reaction temperatures. It has been shown that in the presence of steam the bulk 12-molybdophosphoric acid heated at 673 K, giving a mixture of P_2O_5, α- and β-MoO_3, was again transformed into a mixture of HPMo and α-MoO_3 [18]. In addition, the constancy of CH_3OCH_3 and HCHO selectivities at temperatures in the range 623–723 K would correspond to some equilibrium existing between the surface species, responsible for their formation. This can be promoted by the presence of steam produced during the methanol conversion.

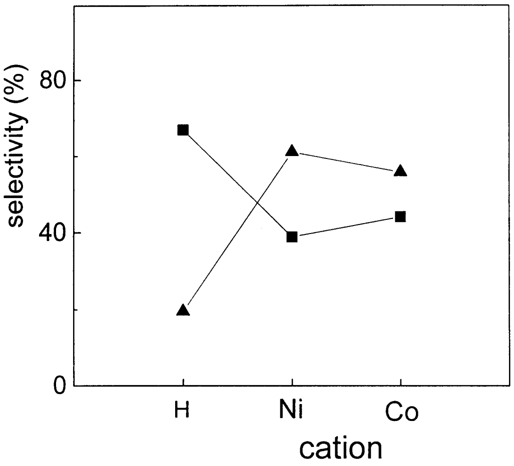

Figure 4. Comparison of dimethyl ether (■) and formaldehyde (▲) selectivities in methanol oxidation over samples XPMo/T (X = H, Co, Ni) calcined at 523 K.

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