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Studies on the Properties of Water in and Conversion of Methanol into Dimethyl Ether on $H_3PW_{12}O_{40}$

INTRODUCTION

The 12-heteropoly compounds having acidic and redox properties can be used to catalyze a wide variety of reactions including partial oxidation (*1, 2*), dehydration (*3*), oxidative dehydrogenation (*4*), and methanol to hydrocarbon conversion (*5–8*). As a new catalyst, it has excited researchers' interest in recent years. The conversion of methanol into hydrocarbons will be an important process for producing gasoline from coal. It now appears to be generally accepted that methanol undergoes a preliminary dehydration step, and the resulting DME is an intermediate in the formation of hydrocarbon. Because the temperature of dehydration is lower than that of hydrocarbon formation, the two-step reaction can be studied separately. The dehydration mechanism of methanol on $H_3PW_{12}O_{40}$ has been investigated using infrared photoacoustic spectroscopy (*5*), but to date, no direct IR studies have been reported. The present work studies the conversion mechanism of methanol into DME and the properties of water in $H_3PW_{12}O_{40}$ by *in situ* transmission IR, GC-TPD, MS-TPD, and activity measurements.

EXPERIMENTAL

Infrared Spectroscopy

Infrared measurements were performed with a Nicolet 5DX spectroscope. The spectral regions between 4600 and 400 cm^{-1} were examined. The sample $H_3PW_{12}O_{40}$ was dissolved in acetone and the resulting solution was dropped onto a very thin NaCl single crystal. After evaporation of the acetone, the deposited layer was placed into a quartz *in situ* IR cell which can be heated to around 873 K under vacuum.

Prior to adsorption the samples were evacuated to 10^{-4} Torr at 603 K for 30 min and then cooled to the temperature from which desorption was to be carried out. Background spectra were thus accumulated during programmed heating and were subtracted from all spectra so that the effects of adsorption could be more clearly seen.

MS-TPD

The apparatus consists of reaction and detection systems. The former includes a quartz reactor with 0.5 g of sample and an oil diffusion pump capable of being evacuated to 1×10^{-6} Torr. The latter includes a quadrupole mass spectrometer, a titanium pump, and a leak valve. There were two ways to carry out the experiment. One was static; i.e., after methanol adsorption the sample was evacuated to 10^{-6} Torr, and then the desorption curves were recorded during programmed heating. The other was dynamic; i.e., methanol vapor was flowing during programmed heating.

Activity Measurements

The reaction of methanol to DME was carried out using 2.6 g of catalyst placed in a fixed-bed continuous flow stainless reactor of 9 mm i.d. The reactor effluent was analyzed with a gas chromatograph under the following conditions: an organic support 408 (40–60 mesh) produced by Shanghai Chemical factory was used as a fixed phase at 343 K (column length 3 m, 3 mm i.d.). The flow rate of carrier H_2 was fixed at 25 $cm^3 \cdot min^{-1}$. The retention times for

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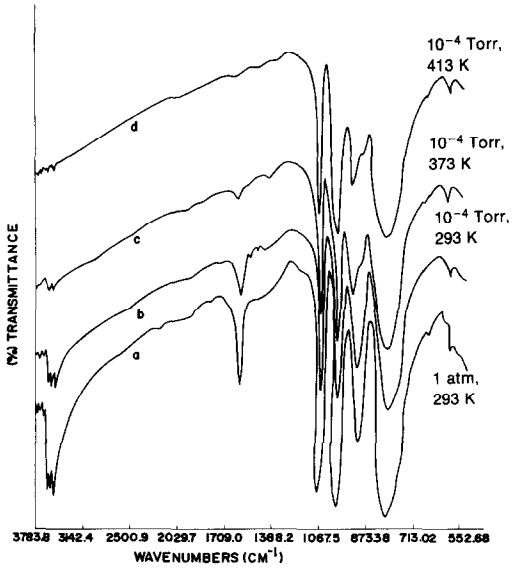


FIG. 1. IR spectra of 12-tungstophosphoric acid at varying temperatures. (a) 298 K, 760 Torr; (b) 298 K, 10^{-4} Torr; (c) 373 K, 10^{-4} Torr; (d) 413 K, 10^{-4} Torr.

H_2O, DME, and CH_3OH were found to be 5.17, 11.73, and 15.23 min, respectively.

RESULTS AND DISCUSSION

The Properties of Water in 12-Tungstophosphoric Acid

The 12-tungstophosphoric acid dissolved in acetone was dropped onto an NaCl single crystal; the transmission IR spectrum (cf. Fig. 1) measured showed bands at 1076, 982, 919, and 818 cm^{-1} representing the absorption bands of the Keggin structure (*9*). This revealed that the 12-tungstophosphoric acid still kept its original structure of the Keggin unit (KU).

At room temperature and atmospheric pressure, two bands at 3613 and 1619 cm^{-1} which characterize the stretching and bending vibration of the hydroxyl group in water (*10*) were observed as shown in Fig. 1. As the system was evacuated to 10^{-4} Torr the bank strength decreased rapidly. When the sample temperature progressively increased, they continued to decrease and vanished at 413 K.

The results showed that a great part of water could be pumped out and the remaining water would desorb with increasing temperature. When the temperature reached 413 K the water was lost completely. The MS-TPD spectrum (cf. Fig. 2a) showed that there are two water desorption peaks at 455 and 643 K, the first peak starting at 373 K. Using the GC-TPD method the water desorbed from the two peaks was analyzed and found to be 4.0 H_2O/KU. From the above results, the water contained in 12-tungstophophoric acid would be lost as the process

$$(H_3O)_3PW_{12}O_{40} \cdot XH_2O \xrightarrow[298\ K]{10^{-4}\ Torr}$$

$$(H_3O)_3PW_{12}O_{40} \xrightarrow[455\ K]{10^{-6}\ Torr}$$

$$H_3PW_{12}O_{40} \xrightarrow[643\ K]{10^{-6}\ Torr} HPW_{12}O_{39}. \quad (1)$$

The x moles of water contained in 12-tungstophosphoric acid will disappear at first under pumping conditions. the remaining 3 moles of protonized water will also disappear as the sample is heated to 455 K; 1 mole of structural water from $H_3PW_{12}O_{40}$ will do the same at 643 K. Thus the GC detected 4 moles of water. Hodett and Moffat (*11*) also found and considered that the structural water in $H_3PW_{12}O_{40}$ can be lost without destroying the original Keggin structure.

The adsorption isotherm of water on

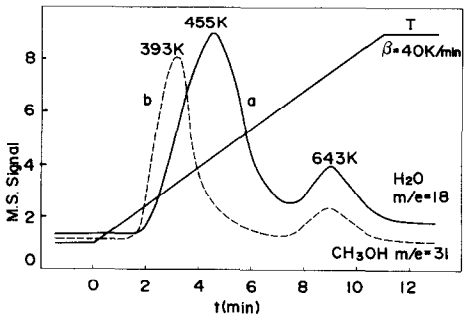


FIG. 2. The MS-TPD spectrum of (a) water in $H_3PW_{12}O_{40} \cdot 3\ H_2O$; (b) methanol adsorbed on $H_3PW_{12}O_{40}$.

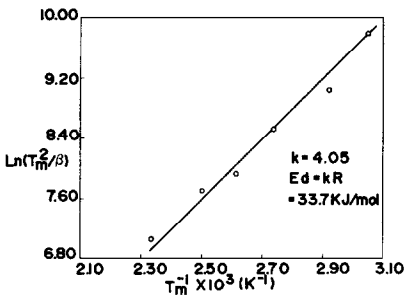


FIG. 3. $\mathrm{Ln}(T_m/\beta)$ vs $1/T_m$.

$H_3PMo_{12}O_{40}$ at 573 K was measured by Misono *et al.* (*9*) and the amount of equilibrium adsorption was found to be 1.0 H_2O/KU. The result can be explained by the fact that at 573 K a part of structural water in $H_3PMo_{12}O_{40}$ was lost and $HPMo_{12}O_{39}$ formed. By interaction with water vapor it can be recovered slowly to $H_3PMo_{12}O_{40}$. Thus, the final equilibrium adsorption amount is just 1.0 H_2O/KU. This result is consistent with the last step of the pathway (*1*) suggested above.

The Adsorption of Methanol on $H_3PW_{12}O_{40}$ Catalyst

The MS-TPD spectrum revealed two methanol desorption peaks at 393 and 643 K, respectively (cf. Fig. 2b). The desorption activation energy of the lower temperature peak was found to be 33.7 kJ/mole by varying the temperature-programmed rate (β) from 6 to 132 K/min (cf. Fig. 3). The transmission IR spectrum of CH_3OD adsorbed on $H_3PW_{12}O_{40}$ showed that there are absorption bands at 2970, 2860, 2645, and 1464 cm^{-1} which characterize the adsorption state of methanol at room temperature (*7*). When the temperature was raised under high-vacuum conditions ($<10^{-4}$ Torr), the bands started to decrease at 353 K and almost disappeared at 393 K. This indicated that the adsorbed methanol was mainly desorbed. But at low vacuum ($>10^{-1}$ Torr), it can be seen that as the temperature increases, the 2645 cm^{-1} band decreases and the 2970 and 2860 cm^{-1} bands increase very little; finally at 643 K all bands corresponding to the adsorbed species were missing. According to the results of PAS-FTIR Highfield and Moffat (*7*) considered that the 2970 and 2860 cm^{-1} bands are assigned to the symmetric and unsymmetric stretching vibrations in CH_3 and the 2645 cm^{-1} band to the stretching vibration in O–D (*12*). Thus it can be concluded that as the temperature increased, the dissociated adsorption state (CH_3,a) of methanol was formed under the condition of a low vacuum. According to the results of IR and MS-TPD, we consider that methanol adsorbed on $H_3PW_{12}O_{40}$ could be desorbed or dissociated as the temperature increases. Under high-vacuum conditions, the adsorbed methanol mainly desorbed, but at low vacuum, it dissociated. Thus the desorption peak at 393 K may correspond to its molecular adsorption state and the peak at 643 K can be considered the desorption of dissociated methanol.

Methanol Conversion to DME on $H_3PW_{12}O_{40}$

Figure 4 shows the yield of DME with reaction temperature and space time. The selectivity of DME is almost 100%. For the reaction

$$2CH_3OH = CH_3OCH_3 + H_2O$$

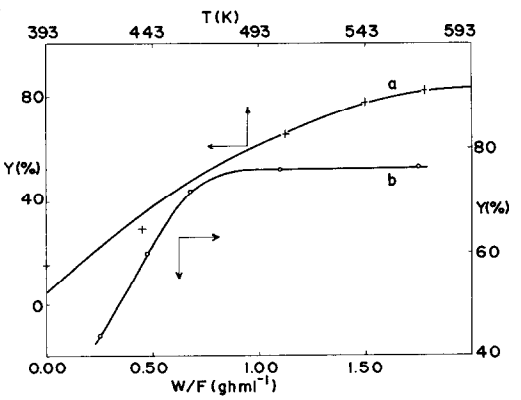


FIG. 4. The effects on DME yield. (a) Variation with temperature, W/F = 0.694 g h ml $^{-1}$. (b) Variation with space time, T = 513 K.

the equilibrium constant K_p can be written as

$$K_p = \tfrac{1}{4}(X_{ac}/(1 - X_{ac}))^2,$$

where X_{ac} is the equilibrium conversion of methanol or the yield of DME. The following equation gives the temperature dependence of K_p (*6*),

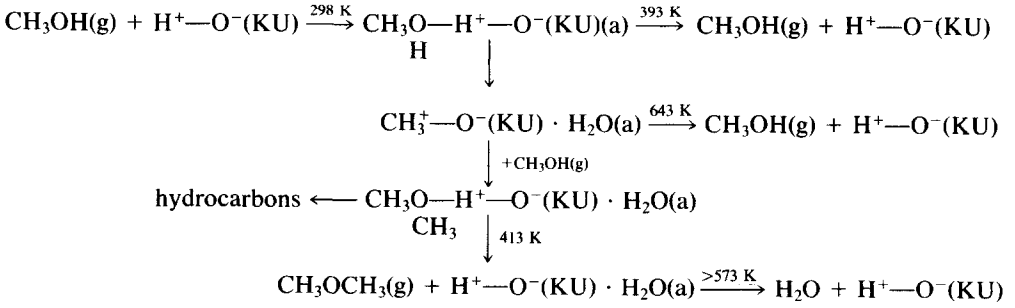
$$-R \ln K_p = \Delta G^\circ/T = -6836/T + 3.32 \ln T - 4.75 * 10^{-4}T - 1.1 * 10^{-7}T^2 - 10.92;$$

when $T = 513$ K it follows that $X_{ac} = 0.72$. The measurement of catalytic activity showed that at about 520 K the maximum yield of DME was 76% and the selectivity nearly 100% which were consistent with the results calculated from thermodynamics. XPS measurements confirmed that the composition and element valence of $H_3PW_{12}O_{40}$ were not changed after the reaction, indicating that no oxidation and reduction took place in $H_3PW_{12}O_{40}$.

Reaction Mechanism of Methanol Conversion to DME on $H_3PW_{12}O_{40}$

At room temperature DME was adsorbed on $H_3PW_{12}O_{40}$ and the system was then pumped to 10^{-4} Torr; the bands at 2935, 1450, 1345, and 1170 cm^{-1} were observed. At programmed heating to 413 K, these four bands were missing. This suggests that DME adosrbed on $H_3PW_{12}O_{40}$ and desorbed at 413 K. The desorption peak for methanol was at 393 K; thus the basicity of DME is greater than that of methanol, and this is in accord with pK_a values for methanol (−4.5) (*9*) and DME (−3.83) (*13*).

At 10^{-4} Torr methanol was adsorbed on $H_3PW_{12}O_{40}$ and then heated to 643 K; the adsorbed state of DME was not observed. While in the presence of methanol vapor (60 Torr) and at constant temperature (373 K), the 1201 cm^{-1} band which characterizes the band vibration of C–O–C in DME and is analogous with that of gaseous DME appeared (*14*). DME was not observed by the static MS-TPD experiments, but was detected at 373 K by the flowing MS-TPD method (cf. Fig. 5). Figure 5 shows that the amount of DME formed increases with temperature and reaches its peak at 593 K, whereas above 593 K, production of DME decreases while those of H_2O and CH_4 increase rapidly. These two experiments indicate that the adsorbed methanol cannot be dehydrated directly to form DME. However, in the presence of gaseous methanol, DME can be formed by the reaction of adsorbed methanol with the methanol in the gas phase. According to the results mentioned above, the reaction mechanism of dehydration of methanol on $H_3PW_{12}O_{40}$ may be expressed as



There are two adsorbed states of methanol existing on $H_3PW_{12}O_{40}$, the molecular state and the dissociated state. Perhaps there exists a slow equilibrium between the molecular and the dissociated state. At 393 K the adsorbed molecular state is desorbed and thc desorption activation energy (E_d) is found to be 33.7 kJ/mole. At 643 K the dis-

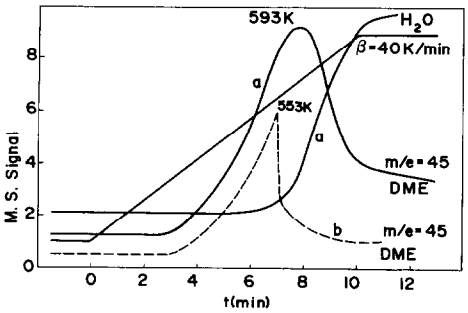


FIG. 5. The MS-TPD spectrum of flowing methanol. (a) CH_3OH flowing at 2×10^{-5} Torr, DME and H_2O detected. (b) CH_3OH flowing at 2×10^{-5} Torr, as the sample was heated to 553 K, CH_3OH was turned off suddenly, and DME detected.

sociated state is desorbed into $CH_3OH(g)$. Above 373 K, the dissociated state reacts rapidly with gaseous methanol to form DME. The DME also adsorbs on $H_3PW_{12}O_{40}$ and desorbs at 413 K; as temperature becomes higher than 593 K, DME further reacts to form hydrocarbons. This mechanism is similar to that of Highfield and Moffat (*7*), but they did not measure the desorption temperature of various species or suggest an equilibrium between the molecular and the dissociated state of methanol. The mechanism suggested here can explain the results of catalytic activity.

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