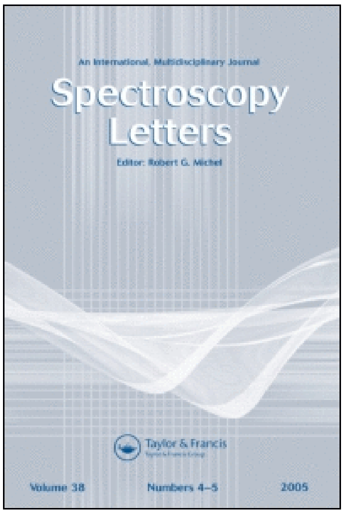

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FT-IR SPECTROSCOPY STUDY OF ISOPROPANOL REACTIVITY ON SILICA-SUPPORTED HETEROPOLYANIONS

Key words: FT-IR spectroscopy, isopropanol reactivity,
heteropolyanions, silica support

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ABSTRACT

FT-IR spectroscopy studies on the adsorption of pyridine on silica-supported heteropolyanions have shown the presence of surface acid sites, both Lewis and Brønsted ones, when starting from commercial phosphomolybdic acid, but only Lewis acid sites when starting from n-hexylammonium phosphododecamolybdate. A preferential formation of propene instead of acetone (i.e., a larger selectivity towards dehydration) has been observed during isopropanol decomposition, due to the strong surface acidity of the samples.

INTRODUCTION

Heteropolyoxometalates are ionic solids with discrete anions and cations. A special interest deserve those posessing the Keggin structures.[1] The anion $[PMo_{12}O_{40}]^{3-}$ belongs to this type, and its structure consists of a $[PO_4]$ tetrahedron surrounded by four $[Mo_3O_{13}]$ groups formed by three edge-sharing octahedra.[2] Organic salts of heteropolyanions with the Keggin-like structure provide outstanding features to be used as acid heterogeneous catalysts. PAS-FTIR studies[3-6] have shown that stoichiometric salts of the heteropolyoxometalates frequently possess residual quantities of protons, which are believed to be responsible for the activity of these salts in acid catalyzed processes. These catalysts are generally supported on inert supports, such as silica and alumina. In solution, heteropolyoxometalates form cation-anion molecular aggregates which stability is enhanced if protonated organic molecules (i.e., alkyl-ammonium) are used as countercations,[7] as the anion-anion interactions are then decreased, thus favouring a larger (uniform) dispersion when supported on a suitable support. The size of the countercation also modifies the dispersion. So, selection of the solvent and of the cation may provide an insight about the best experimental conditions to prepare a supported, Keggin-like catalyst. In the present paper, FT-IR spectroscopy has been used to analyze the properties of three catalysts obtained from organic (ammine) salts of $[PMo_{12}O_{40}]^{3-}$ supported on silica, using three different solvents during the impregnation. Qualitative testing of catalytic activity for isopropanol decomposition has been carried out by FT-IR spectroscopy.

EXPERIMENTAL

Preparation of the Samples

12-molybdophosphoric acid (hereafter HPMO12) was from Merck. The n-hexylammonium salt (hereafter HEX-PMO12) was obtained as a yellow powder from a solution of n-hexylamine, $Na_2MoO_4.2H_2O$ and Na_2HPO_4. This solution had been prepared by adding n-hexylamine (0.5 ml, 3.52 mmol) to a solution of $Na_2MoO_4.2H_2O$ (5 g, 24 mmol) and Na_2HPO_4 (0.5 g, 3.52 mmol) in water (200 ml), previously mixed with stirring during 30 min at room temperature, and vigorously stirred until dilution. The pH value was fixed at 3 with aqueous HCl. Results of chemical analysis for this compound were as follows: Found C, 9.12; H, 2.42; N, 1.94; Mo (MoO_3), 83.90; calculated for $C_{18}H_{52}Mo_{12}N_3O_{42}P$: C, 9.06; H, 2.47; N, 1.93; Mo (MoO_3), 84.01. The main IR bands were recorded in the following positions: ν(O-H) 3510m; ν(N-H) 3405m; ν(C-H) 3212m, 3070m and 2861m; ν(NH_3^+) 2930m; δas(NH_3^+) 1610m; ν(N-H) 1471m; ν(P-O), 1064vs; ν(Mo-O), 961vs, 870vs and 784vs; δ(O-P-O), 596w and δ(Mo-O_b), 496w cm^{-1}.

The silica support was from Merck (specific surface area 332 m^2/g). Catalysts were prepared by impregnating SiO_2 with solutions of $H_3PMo_{12}O_{40}$ and $(C_6H_{16}N)_3[PMo_{12}O_{40}].2H_2O$. The solvents used in the impregnation solutions were water, acetone and dimethylsulfoxide (DMSO). Impregnation was carried out at 303, 313 and 373 K, respectively, for acetone, water and DMSO, until dryness evaporation. Then the solids were dried at 433 K for 24 h and calcined in air at 598 K for 3 h, as higher temperatures would yield decomposition of the Keggin structure. The codes for the catalysts are listed in Table 1.

Characterization

Mo content was determined by Inductively Coupled Plasma Spectroscopy using an ICP ARL 3410 equipment with minitorch. Surface areas were determined by the BET method from nitrogen adsorption-desorption isotherms measured in a Micromeritics AcuSorb 2100E apparatus; samples (about 0.1 g) were pretreated at different temperatures (from 300-570 K) at vacuum pressure (10^{-4} mm Hg) prior to adsorption of N_2 at 77 K.

Surface acidity has been studied by FT-IR spectroscopy monitoring of pyridine (py) adsorption at room temperature (r.t.) and outgassing at increasing temperatures. A Perkin-Elmer 16PC spectrometer was used, coupled to a conventional high vacuum line; the samples were used in the form of self-supported discs, in a specially designed cell with CaF_2 windows. Surface acid distribution of catalysts H(CO) and H(DMSO) has

TABLE 1

Codes of the Samples Prepared and Summary of Physicochemical Properties

Sample	Precursor[a]	Solvent	% $H_3PMo_{12}O_{40}$	SSA[b]
H(H2O)	HPMO12	Water	11.5	278
H(CO)	HPMO12	Acetone	11.8	291
H(DMSO)	HPMO12	DMSO[c]	11.2	298
HEX(H2O)	HEX-PMO12	Water	4.2	319
HEX(CO)	HEX-PMO12	Acetone	12.2	293
HEX(DMSO)	HEX-PMO12	DMSO	14.2	302
SiO_2	-----	-----	-----	332

[a] HPMO12=commercial salt; HEX-PMO12= prepared in this work
[b] specific surface area, m^2/g
[c] DMSO=dimethylsulfoxide

been quantified from the differential adsorption heat of ammonia by using a diferential scanning calorimetry (Setaram DSC 111) and a FT-IR spectrometer (Nicolet 740) to measure the heat associated with the neutralization of the acidic sites and the amount of ammonia, respectively.

A qualitative study of the catalytic activity was carried out by FT-IR spectroscopy, in order to identify the adsorbed species formed along the catalytic reaction. This study was carried out in the same experimental system above described for py adsorption studies.

RESULTS

Characterization of the Samples

The specific surface areas of the catalysts and the content of active phase in each catalyst is shown in Table 1. The low content of $H_3PMo_{12}O_{40}$ in catalyst HEX(H2O) is due to the low solubility of the n-hexylammonium salt in water.

Quantitative determination of surface acidity indicates a larger surface acidity in sample H(DMSO), 26.9 mmol/g_{cat} (differential adsorption heat 156 kJ/mol) than in sample H(CO), 16.1 mmol/g_{cat} (differential adsorption heat 95 kJ/mol).

Adsorption of pyridine

The FT-IR spectra recorded upon adsorption of py at room temperature on samples H are rather similar. That recorded for sample H(CO) is shown in Fig. 1. Bands are recorded at 1610, 1594, 1540, 1490, 1452, and 1449 cm^{-1}, and have been ascribed (Table 2) to stretching modes of coordinated and protonated py, indicating the presence of both surface Lewis and Brønsted acid sites. Splitting of the band due to mode 8a of coordinated py (1610 and 1594 cm^{-1}) is probably due to the presence of two different types of surface Lewis acid sites.

When the sample is outgassed at increasing temperatures, a decrease in the intensities of the bands is observed, mainly the band at 1540 cm^{-1} (mode ν_{19b} of pyridinium), that completely vanishes after outgassing at 573 K; however, the bands due to adsorption on Lewis sites are not removed if the sample is outgassed below 673 K.

Samples corresponding to series HEX show also similar spectra after adsorption of py at room temperature. That corresponding to sample HEX(CO) is shown in Fig. 2. Bands at 1607, 1594, 1489, 1452, and 1446 cm^{-1} are originated by modes 8a and 19b of coordinated py, i.e., only surface Lewis acid sites exist in the surface of these samples. Splitting of the bands due to modes 8a and 19b (Table 2) indicates the presence of, at least, two types of surface Lewis acid sites (coordinatively unsaturated cations, M_{cus}). When the sample is outgassed at increasing temperatures, the intensities of all bands decrease, but they are only removed after outgasing at 673 K (the maximum temperature attainable by our experimental instrument), indicating that py is adsorbed on strong surface Lewis acid sites.

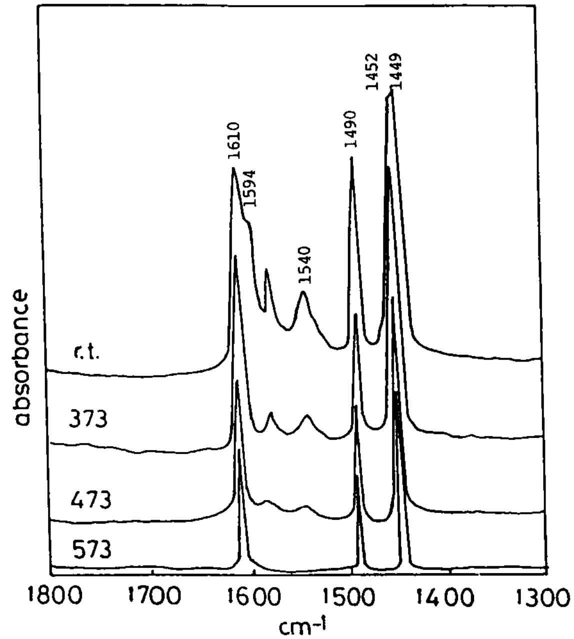

FIG. 1.-FT-IR spectra recorded after adsorption of py on sample H(CO) at room temperature and outgassing at the temperatures given (in K).

TABLE 2
Position (cm^{-1}) and Ascription of the FT-IR Absorption Bands Recorded upon Adsorption of Pyridine at Room Temperature on Samples H(CO) and HEX(CO)

	Bpy			Lpy			
Sample	ν_{8a}	ν_{19a}	ν_{19b}	ν_{8a}	ν_{8b}	ν_{19a}	ν_{19b}
H(CO)	-	1490	1540	1610 1594	1577	1490	1452 1449
HEX(CO)	-	-	-	1607 1594	1576	1489	1452 1443

Bpy (Lpy) = bands due to adsorption of py on Brønsted (Lewis) acid sites.

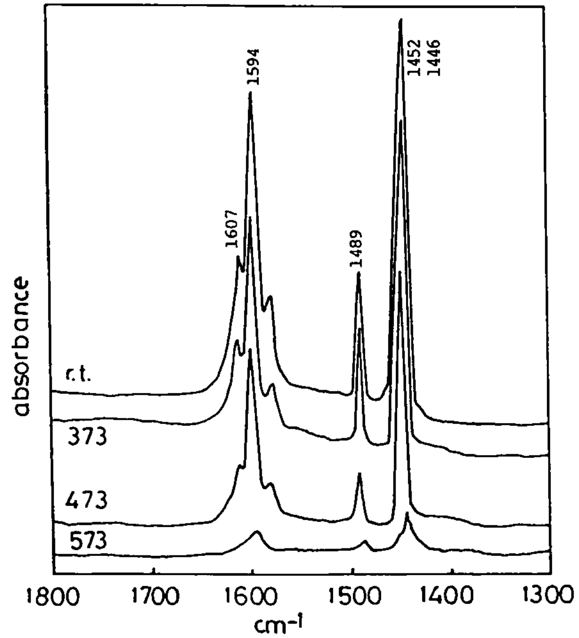

FIG. 2.-FT-IR spectra recorded after adsorption of py on sample HEX(CO) at room temperature and outgassing at the temperatures given (in K).

Adsorption of isopropanol

Samples H: Adsorption of isopropanol at room temperature on samples H leads to bands in the high wavenumbers range at 2979, 2937, and 2897 cm^{-1} (C-H stretching modes), and also in the medium wavenumbers range at 1467, 1388, 1377, and 1090 cm^{-1}, ascribed to $\delta_{as}(CH_3)$, $\delta_s(CH_3)$ and $\nu(CO)$ of iso-propoxide species formed upon dissociative adsorption of isopropanol, Fig. 3.A. A band at 1620 cm^{-1}, due to δH_2O, is recorded, but no band due to molecularly, unreacted, adsorbed isopropanol is recorded. Adsorption is reactive, as the band at 1692 cm^{-1} is due to νCO of acetone coordinated to surface Lewis acid sites existing on these samples. Upon outgassing at increasing temperatures, the band due to molecular water vanishes rapidly, while the intensities of the bands originated by isopropoxide decrease and

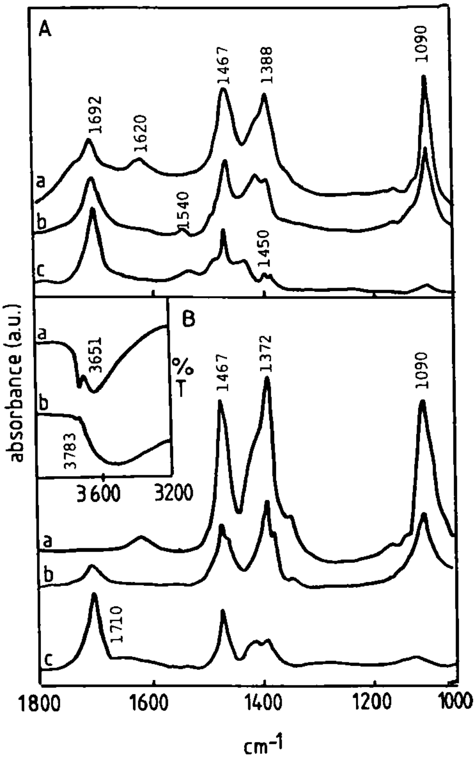

FIG. 3.-FT-IR spectra recorded after adsorption of isopropanol at room temperature and outgassing at (a) room temperature, (b) 373 K, and (c) 573 K on samples (A) H(CO), and (B) HEX(CO). Inset: FT-IR spectra of sample HEX(CO) in the vOH region for (a) outgassed sample and (b) after adsorption of isopropanol and outgassing at room temperature.

those bands due to acetone are strengthened. After outgassing at 373 K, weak bands similar to those found after adsorption of acetic acid on these samples are detected at 1540 and 1450 cm^{-1}, and are ascribed to modes $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ of surface acetate species; the intensities of these bands slightly increase when the outgassing temperature is raised up to 573 K.

Samples HEX: The spectra recorded after adsorption of isopropanol on these samples at room temperature are rather similar (that for sample HEX(CO) is included in Fig. 3.B) to those described above, with bands at 2979, 2937, and 2897 cm^{-1} (νCH), and 1467, 1455, 1372, and 1090 cm^{-1}, due to antisymmetric and symmetric deformations of $-CH_3$ and νCO. Although the band due to molecular water is also recorded at 1626 cm^{-1}, it disappears immediately as the sample is outgassed even at room temperature. No band due to carbonyl nor carboxylic species is registered. When the outgassing temperature is raised, the intensities of the isopropoxi species decrease, and a band due to νCO of coordinated acetone develops at 1710 cm^{-1} when the sample is outgassed at 573 K. It should be noted that reactive adsorption takes place on samples HEX at higher temperatures than for samples H.

The spectra in the νOH region (4000-3200 cm^{-1}) is shown as an inset in Fig. 3. Characteristic νOH bands are recorded at 3783 and 3651 cm^{-1}, although the first band is removed upon isopropanol adsorption, then turning up again when the sample is outgassed.

Preliminary catalytic activity studies[8] have shown that isopropanol is mostly decomposed through dehydration, yielding mainly propene; formation of acetone increases with the reaction time on catalysts HEX, but not on catalysts H. As no change is observed for other products, the lack of increase in acetone production on catalysts H should be due to its oxidation to carbon oxides, in agreement with the above FT-IR results, which showed that isopropanol is reactively adsorbed on samples H, and forms acetate species at 370 K, which undergo oxidation to carbon oxides; however, such an oxidation is not observed for samples HEX.

With regards to the effect of the solvent used for preparation of the catalysts, our results show that sample H(H2O) yields intermediate values (if compared to the results obtained with H(CO) and H(DMSO)), both for propene and acetone.[8] The catalyst prepared in DMSO is more selective towards production of acetone and diisopropylether, while that prepared in acetone is more selective for propene production.

DISCUSSION

Dissociative adsorption of isopropanol can be written as:

$$(CH_3)_2CHOH + L^{n+}(s) + OH^- \rightarrow (CH_3)_2CHO^- \text{---} L^{n+}(s) + H_2O \quad (1)$$

or

$$(CH_3)_2CHOH + L^{n+}(s) + O^{2-} \rightarrow (CH_3)_2CHO^- \text{---} L^{n+}(s) + OH- \quad (2)$$

where $L^{n+}(s)$ stands for a surface acid Lewis site (a coordinatively unsaturated surface-exposed metal cation). Reaction (1) accounts for developing of the δH_2O band close to 1620 cm^{-1}, for broadening of the vOH band at 3500-3000 cm^{-1} (hydrogen-bonded hydroxyl groups), and for removal of the band at 3783 cm^{-1}, due to vOH of free hydroxyl groups. Reaction (2) takes place only on highly dehydroxylated surfaces.

Dehydrogenation can be explained on the basis of oxidation of surface-adsorbed alkoxides,[9,10] as our FT-IR results clearly demonstrate formation of acetone coordinated to surface Lewis acid sites. Only on samples H, a small amount of acetone is oxidized to acetate species (FT-IR bands at 1540 and 1450 cm^{-1}) which undergo further oxidation to carbon oxides, thus accounting for the decrease in acetone formation.

The FT-IR results also indicate that adsorbed alkoxide species may alternatively undergo dehydroxylation, leading to propene through dehydration of original isopropanol:

$$(CH_3)_2CHO^- \text{---} L^{n+}(s) \rightarrow CH_3\text{-}CH{=}CH_2 + OH- + L^{n+}(s) \quad (3)$$

although Knözinger et al.[11] had proposed alternative routes to propene without intermediate formation of alkoxides.

In our case intermediate alkoxide is clearly formed, as it has been undoubtedly detected by FT-IR spectroscopy; when the sample is heated and outgassed at higher temperatures, its characteristic bands disappear, while those due to acetone develop. However, data are not clear enough to ascertain if surface alkoxide species giving rise to propene are the same as those leading to acetone.

Although both dehydration and dehydrogenation processes take place simultaneously, our data indicate that decomposition of isopropanol takes place mainly through dehydration, as a larger amount of propene than of acetone is formed. This fact is related to the larger concentration of strong surface acid sites existing on all samples, but mainly on samples H, possessing Lewis and Brønsted sites, as several authors[11,12] have proposed that surface acid sites are required for dehydration, while surface basic sites would account for dehydrogenation through abstraction of protons.

The difference between the behaviour of samples H and HEX on the selectivity during decomposition of isopropanol is clearly related to the increasing formation of acetone with the reaction time on catalysts HEX as the oxidation process decrease in these catalysts. In addition, the solvent used during the impregnation step seems to play also an important role, as both samples H(CO) and HEX(CO) are more selective to propene formation than the other samples.

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