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Study of surface properties of dodecatungstophosphoric acid by means of ionization of aromatic hydrocarbons

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The surface properties of $H_3PW_{12}O_{40}$ are initially dependent on pretreatment temperature as can be deduced from the ionization of adsorbed aromatic hydrocarbons. Not only does surface dehydration proceed at a lower temperature than bulk dehydration but also highly reactive species (ionized benzene) are generated by the loss of protons of polyanions in special locations such as corner or edge positions.

Keywords: Hydrocarbon ionization; ESR; dodecatungstophosphoric acid

1. Introduction

Heteropoly acids and their salts represent an important class of inorganic compounds [1] with some very interesting properties in both redox and acid catalysis [2–4]. Most of the studies performed on these compounds involve Keggin structures, mainly because of their higher thermal stability. As they are well soluble in polar solvents, these catalysts can be used in both homogeneous and heterogeneous catalysis. Only few salts of alkaline or organic cations are non soluble in such media, nevertheless they present in the solid state a porous structure such as zeolites [5] allowing reactants to go through the solid and leading all active sites accessible. Due to their high solubility in polar solvents, the gas–solid catalysis of e.g. the alcohol dehydration by heteropolyacids cannot be undertaken as a reaction taking place only at the surface of the grain; it is necessary to assume that reactants go also in the bulk and react in the solid. Such a phenomenon was called the "pseudo-liquid" phase [2]. Unlike polar reagents, apolar compounds such as alkanes and alkenes can react only at the external surface of the grain. As a consequence, the reactivity of heteropolyacids with polar compounds will give informa-

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tion on the acidic (and/or redox) properties of the bulk while those of the surface will be obtained by reaction with apolar compounds. We developed studies in the latter subject as much information on the acidity of heteropolyacids in the bulk is provided [3,6,7], in contrast with almost few data on the properties of the surface, which could be quite different from those in the bulk. In preceding papers [8], we studied the *n*-hexane cracking reaction on heteropolyacids and showed that surface dehydration occurred at a lower temperature than that in the bulk. The present paper gives results of aromatic hydrocarbon ionization on dodecatungstophosphoric acid followed by ESR as a function of the pretreatment temperature.

2. Experimental

Dodecatungstophosphoric acid was a commercial product supplied by Prolabo. It was recrystallized before use. The polyacid was then kept during one night at 100°C in order to prepare its hexahydrate form which is relatively stable at room temperature. This treatment was undertaken in order to obtain a polyacid that always contained the same number of hydration molecules. The desired amount of polyacid was then weighted (typically 100 mg) and introduced in a classical ESR cell allowing the solid to react with the desired hydrocarbon after treatment. For each experiment, it was checked that the height of the catalyst in the tube was constant and higher than 2.5 cm. The polyacid was treated under vacuum (10^{-6} Torr) at the desired temperature during 2 h. A first ESR spectrum was then recorded prior to introduction of the hydrocarbons to ensure that no reduction of the solid occurred during the pretreatment (if grease is present, its vapors, even under secondary vacuum, can reduce the polyanion at temperatures between 300 and 450°C). The hydrocarbons were deoxygenated before use and kept in sealed capsules which were broken when necessary. Perylene was in solution in benzene.

The ESR spectra were recorded on a E-9 Varian spectrometer under the following conditions: frequency: 9.293 GHz (X band), power: 5 mW (experiments with other values showed that no saturation occurred in this case), recording at room temperature. The *g* values are referred to DPPH and quantitative information was achieved by recording the ESR spectra of the Varian pitch after each experiment.

3. Results

The experimental results are very dependent on the pretreatment temperature as it is shown in table 1 and fig. 1. However, the ESR spectra do not show special features (fig. 2): for perylene, the position and the hyperfine structure of the signal ($g = 2.002, A = 3.35$ G) allow us to attribute it to the $Pe^{\cdot +}$ radical cation. Only a small broadening is observed when the pretreatment temperature increases. For benzene, there is no formation of the benzene radical cation as on zeolites [9] but

Table 1
Color of the samples after addition of the aromatic hydrocarbon

Pretreatment temperature (°C)	Perylene addition	Benzene addition
25	white	white
100	gray blue	white
200	gray blue	brown
300	dark blue	dark blue
400	dark blue	dark blue

the signal ($g = 2.002$), which is sharp and has a peak-to-peak width of ca. 10 G, is similar to that observed by Akimoto et al. by reaction of C_6H_6 with heteropolymolybdates [10,11]. It can be attributed to the radical form of a polycondensed aromatic compound. Attempts to observe the formation of only the benzene radical cation (or its dimer form) by reaction of benzene vapor at 77 K failed, the ESR spectrum being always the same.

Fig. 1 and table 1 show that, as a function of the evacuation temperature, the following behaviors are observed:

– After treatment at room temperature, only a small amount of perylene radicals are formed, the benzene being not ionized.

– After evacuation at 100°C, there is also no ionization of benzene but the number of $Pe^{\cdot +}$ radicals is the highest.

– After evacuation at 200°C, both perylene and benzene are ionized and the number of $Pe^{\cdot +}$ radicals has slightly decreased.

– After evacuation at 300°C, the number of radicals is quite constant but the solid is now reduced as shown by its dark blue color.

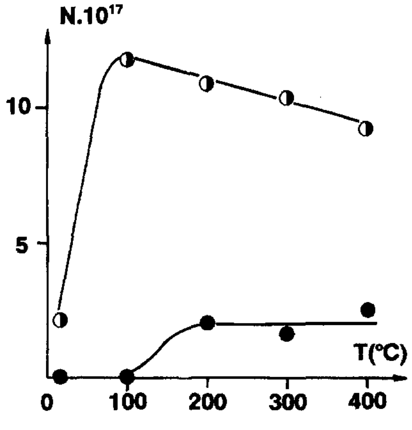

Fig. 1. Number of radical cations formed per gram of dodecatungstophosphoric acid as a function of the pretreatment temperature. Perylene (◐), benzene (●).

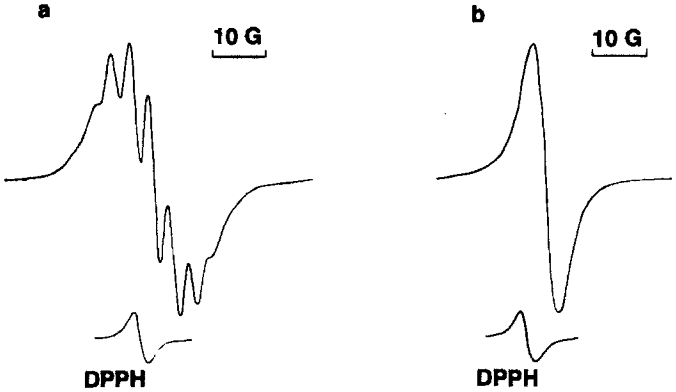

Fig. 2. Typical ESR spectra obtained after adsorption of (a) perylene and (b) benzene on dodecatungstophosphoric acid.

4. Discussion

It is well known that the dodecatungstophosphoric acid leads to the following species by dehydration [1,12]:

– $H_3PW_{12}O_{40} \cdot nH_2O, n = 12–30$ which is the compound purchased commercially and which can lose hydration water easily.

– $H_3PW_{12}O_{40} \cdot 6H_2O$ is formed by the dehydration of the above compound and can be kept at room temperature during some days, its rehydration being slow. Its structure has been refined by X-ray diffraction [13].

– $H_3PW_{12}O_{40}$, the anhydrous form of the phosphotungstic acid is prepared by heating the hexahydrate. It is not stable in presence of water and leads to the hexahydrate form.

– "$PW_{12}O_{38.5}$" is the anhydride phase formed by the loss of constitution water in the anhydrous acid, occurring between 350 and 400°C.

– Finally, the anhydride decomposes into oxides which recrystallize at ca. 600°C.

However, the dehydration phenomena do not appear at well defined temperatures and a progression is observed inside the grain. Indeed, they cannot be considered as thermodynamic effects but as kinetic ones and so the transformation of a compound to one another can occur at various temperatures, depending on the experimental conditions. So, we can reasonably suppose that in our experiments, there is formation of the hexahydrate after treatment under vacuum at room temperature, while after evacuation at 100°C the anhydrous acid is obtained.

In addition, it is also easy to understand that the dehydration level is not the same along the depth of the grain. This was well characterized by the *n*-hexane cracking reaction which occurs at the external surface of the catalyst: a decrease of the number of Brønsted acid sites is observed between 200 and 250°C while the bulk loses them at 350–400°C [8].

Taking into account the above observations, the experimental results can therefore be explained assuming the following assumptions:

(1) The hexahydrate heteropolyacid does not ionize perylene and benzene by itself.

(2) The anhydrous acid can ionize perylene but not benzene.

(3) Highly reactive surface acid sites formed by dehydration can ionize both perylene and benzene.

It is reasonable to suppose that after evacuation at room temperature the surface acid sites are dehydrated more completely than the others. For example, they can correspond to the protons of polyanions located in edge or corner positions at the surface of the crystals and they should be responsible of the small perylene ionization. After treatment at 100°C, all surface sites are dehydrated, leading to protons not surrounded by water molecules, the number of $Pe^{\cdot +}$ radical cations is the highest. After treatment at 200°C, in agreement with the *n*-hexane cracking results, some Brønsted acid sites are lost due to dehydration. During this process some highly reactive sites are generated, probably by a partial degradation of polyanions in special positions. Indeed, as the dehydration process of the anhydrous acid is described as the junction of polyanionic entities by oxygen bridges and loss of water, it seems not reasonable to suppose that such an arrangement can lead to a Lewis acidity. However, at the surface of the grain some protons do not have neighbours, so their degradation could give highly reactive species.

After calcination at higher temperature the surface is not modified but the core (which represents most of the compound) is dehydrated, leading to the formation of the bulk anhydride phase. This phase allows delocalization of the electrons and is characterized by its dark blue colour, due to charge transfer bands.

Only one question remains: Indeed, as the "highly reactive" sites generated by dehydration can ionize benzene, they should also react with *n*-hexane and an activity increase should be expected in cracking, contrary to the experimental results. However, these sites, as highly reactive ones, should deactivate very rapidly and due to the method used for the study of the reaction (modelization of the experimental deactivation curves in order not to describe the first times of the reaction but to simulate the decrease during many hours), it is not surprising that they were not observed.

Finally, it can also be pointed out that the number of radicals generated by benzene adsorption at temperatures higher than 200°C corresponds to the number of perylene radicals formed after evacuation at room temperature. If we suppose that one site could lead to one radical cation, then the highly reactive sites should have been formed from polyacids in particular position which did not retain water and led to the formation of radicals by perylene adsorption.

The nature of the "highly reactive sites" generated by desorption is not clear, although the ionization of aromatic hydrocarbons has been proposed as a measure of Lewis acidity [14] and that of benzene as a probe of superacidity [15], it seems more reasonable to correlate it with the ionizability of the solid, i.e. its ability to capture electrons. However, with benzene adsorption, phosphomolybdic acid gives less radicals (their number is ca. one order of magnitude lower) [10], so it can be assumed that acidic properties do not interfere during the ionization process. As a conclusion, it seems difficult to separate acidic and redox properties for solids without protons, as Brønsted acidity can be created by reduction of the solid. This does not allow us to propose a structure for these highly active sites but it must be pointed out that superacidic catalysts were prepared by impregnating oxides with metatungstate ion [16] or with the silico-tungstic acid [8]. In the latter case, the number of superacidic centers was correlated with the number of surface-exchanged (and isolated) polyanions, but it was not possible to determine from these results whether the structure of the polyanion was retained or not. However, if the present data do not allow to answer to this latter question, it seems that isolated polyanions (where some protons are not bridged between two polyanionic entities) lead to solids which can be considered as precursors of superacids.

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