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Journal of Catalysis 217 (2003) 292–297

JOURNAL OF
CATALYSIS

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A study of the stability of tungstophosphoric acid, $H_3PW_{12}O_{40}$, using synchrotron XPS, XANES, hexane cracking, XRD, and IR spectroscopy

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Received 28 August 2002; revised 20 December 2002; accepted 4 February 2003

Abstract

Tungstophosphoric acid (HPW) has been investigated using different spectroscopic and chemical techniques. Bulk-sensitive techniques such as X-ray diffraction (XRD) and infrared (IR) spectroscopy indicate that the acid is stable at temperatures as high as 300 °C or higher. However, our work suggests that, besides the surface dehydration, HPW starts loosing stability at temperatures as low as 200 °C. For instance, P 2p peak was not detected in the synchrotron radiation XPS spectrum of HPW preheated at 100 °C, but was clearly observed after preheating the acid at 200 and 400 °C. This suggests the destruction of the molecules of the surface leading to the apparent enrichment of surface with phosphorous. These results may explain why HPW deactivates very fast, e.g., 8 min at 200 °C, in hexane-cracking experiments. This could limit the use of HPW in surface reactions that even require moderate temperatures. Detailed infrared spectroscopic investigation of the HPW as a function of temperature showed a gradual increase in absorbance of the W–O–W corner-shared vibration relative to the absorbance of the other bands. This indicates that the symmetry, and hence the stability, of the molecule was decreased upon heating.

1. Introduction

The utility of heteropoly acids (HPA) as catalysts has stimulated considerable interest in these compounds [1–17]. The tungstophosphoric acid ($H_3PW_{12}O_{40}$) is reported to be among the strongest acids in the series of heteropoly acids [1,5,6,16]. Some studies showed that HPW has super acid characteristics [5,6,16]. The Keggin structure of HPW as shown in the literature is composed of a central PO_4 tetrahedron surrounded by 12 WO_6 octahedra arranged in four groups of three-edge-sharing W_3O_{13} octahedra [1,2,4]. There are four types of oxygen sites: internal, edge sharing, corner sharing, and terminal.

When a heteropoly acid is used as a heterogeneous catalyst, the nature of the reactants often determines whether the reaction takes place on the surface or in the bulk of the heteropoly acid where they are activated and form the desired products. For example, the dehydration of propanol, a polar molecule, is believed to take place in the bulk of the HPW acid. However, alkylation of aromatics, nonpolar molecules, takes place on the surface of the catalyst.

Stability of the HPW is very important for its chemical activity, especially for high-temperature reactions. Although it is reported that HPW is a stable molecule up to 600 °C [1], other studies considered that the major drawback of HPA, in general, is its thermal stability [9]. In a previous work, we have found that preheating HPW at 350 °C deactivates it toward hexane cracking; the conversion was less than 1%, at 300 °C, compared to 28.5% without preheating [18]. Similar results were obtained by Oulmekki and Lefebvre [12,13]. However, in hexane-cracking experiments the HPW deactivated nearly completely after 20 min time on stream. Such fast deactivation prevents utilizing the catalyst in high-temperature reactions. It was also shown that at temperatures higher than 400 °C, the HPW is present as anhydrous phase [12] or could be in oxide form [9]. Any catalytic activity at higher temperature, e.g., 400 °C, could be attributed to the formation of unique types of oxides rather than to the presence of intact Keggin units [9].

Some chemical methods, e.g., slurry calorimetry [15] and hexane cracking [12–14,18], were used to study the solid acidity of HPW. Calorimetric studies gave same heat of pro-

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doi:10.1016/S0021-9517(03)00066-6

tonation upon heat treatments of HPW at 162 and 200 °C [5,15]. However, slurry calorimetry is not only a surface-sensitive technique but also a bulk-sensitive one [15]. Therefore, these results cannot explain the behavior of the reactions that only occur at the surface. Techniques that are more sensitive to the surface are needed for better understanding of the reactions that occur at the surface of HPW.

Some of the previous studies used conventional X-ray photoelectron spectroscopy (XPS) to investigate the structure of heteropoly acids [19–22]. In this work we report for the first time the use of synchrotron radiation XPS and XANES techniques as tools to study the surface of HPW preheated at different temperatures. The results are compared to the results of hexane-cracking reactions, IR spectroscopy, and powder X-ray diffraction (XRD) techniques.

2. Experimental

Polycrystalline tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot 25H_2O$) was obtained from Aldrich. Samples were preheated for 1 h at a given temperature just before XPS, XANES, XRD, and IR spectroscopy analyses.

2.1. XPS

High-resolution XPS spectra of the HPW samples were obtained using the Advanced Light Source at Lawrence Berkeley National Laboratory on beamline 9.3.2 [23]. The photon energy used was 650 eV and the base pressure in the analysis chamber was maintained at 10^{-10} Torr. The kinetic energy of the photoelectrons was analyzed by a Scienta-hemispherical energy analyzer with an energy resolution better than 0.2 eV. Conventional laboratory XPS spectra of the samples were also obtained, in order to clarify some questions raised during the data analysis, using nonmonochromatic Al-K_α photons (1486.6 eV) at 130 W as the incident beam. The binding energy of adventitious carbon 1s core level, which is 284.6 eV [24], was used to correct for the energy shift due to surface charging.

2.2. XANES

X-ray absorption near edge structure (XANES) measurements were also performed using the Advanced Light Source at Lawrence Berkeley National Laboratory on beamline 9.3.2. High-resolution XANES spectra were taken in the O K absorption edge region, while the monochromator was set at a resolving power ($E/\Delta E$) of $\geqslant 7000$. The photon flux at the sample was about 10^{10} photons/s. The base pressure in the experimental chamber was about 10^{-10} Torr. Since the size of the synchrotron radiation photon beam at the sample was $\leqslant 1$ mm, it was not difficult to align the system to make sure that only the sample was illuminated by the photon beam. XANES measurements were performed in total electron yield mode. I_0 signal from a freshly evaporated gold grid was used to normalize the spectra.

2.3. Hexane-cracking test

n-Hexane cracking was carried out in a fixed bed reactor using 0.30 g of fresh HPW ($H_3PW_{12}O_{40} \cdot 25H_2O$). Saturated nitrogen–hexane mixture is introduced at atmospheric pressure and flow rate of 3 ml/min using a bubbler at 0 °C. Under these conditions the partial pressure of n-hexane is 45 mm Hg. The reactor effluent was analyzed using gas chromatography. More details about hexane-cracking analysis can be found elsewhere [18].

2.4. XRD

X-ray powder diffraction measurements were carried out on a Siemen instrument. Each sample was ground in an agar pestle and mortar. The fine powder was packed into a sample holder having a diameter of 25 mm and depth of 3 mm. The surface of the packed sample was smoothed with a piece of flat glass. The diffraction pattern was recorded from $2\theta = 4$ to 50°. More details can be found elsewhere [18].

2.5. IR spectroscopy

KBr pellet technique was used to record the IR spectra. The IR spectra were taken immediately after the preheat treatment of the samples.

3. Results and discussion

Fig. 1 shows high-resolution XPS spectra of the P 2p region in HPW preheated at different temperatures. Surprisingly the phosphorous was not detected in the 100 °C sample even after 40 scans. However, it was detected in the

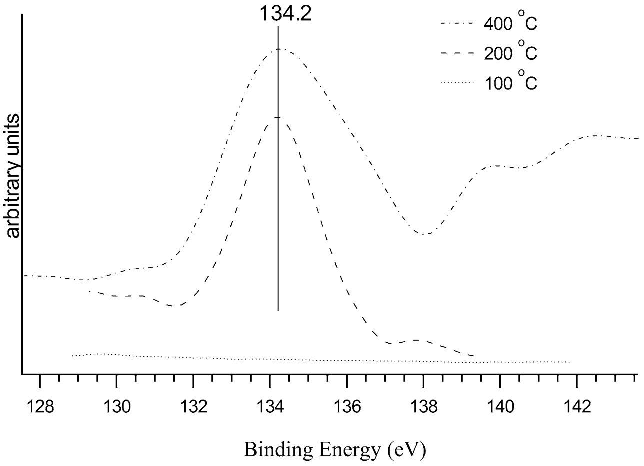

Fig. 1. High-resolution XPS spectra of the P 2p region in HPW preheated at different temperatures.

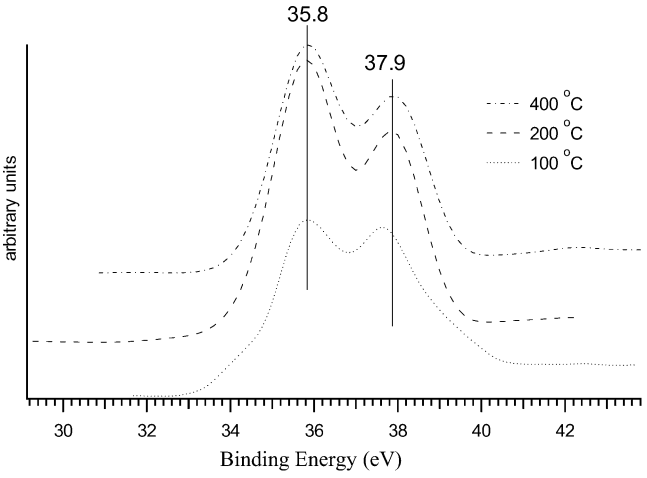

Fig. 2. High-resolution XPS spectra of the W 4f region in HPW preheated at different temperatures.

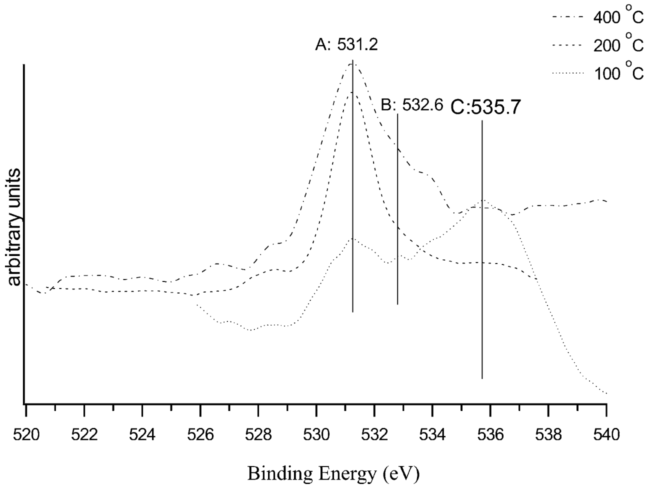

Fig. 3. High-resolution XPS spectra of the O 1s region in HPW preheated at different temperatures.

200 and 400 °C samples. Note that the P 2p peak in a well-crystallized structure consists of a doublet with 0.84 eV separation due to the spin-orbit splitting. Although the energy resolution in our case was better than 0.2 eV, only a single broad phosphorous peak was detected in 200 and 400 °C samples. Furthermore, the FWHM of the observed peak increases from 2.4 eV at 200 °C to 3.8 eV at 400 °C. These observations suggest deterioration of surface crystallinity as a result of the destruction of the Keggin structure of the HPW molecule and an apparent enrichment of the surface with phosphorous. The absence of the phosphorous signal in the 100 °C sample may also be due to the presence of a thin water-enriched layer on the surface of the sample as discussed below.

Fig. 2 shows high-resolution XPS spectra of the W 4f region in 100, 200, and 400 °C samples. Note the presence of two shoulders besides the main doublet in the 100 °C sample. This spectrum was fitted with three different doublets of W 4f with $4f_{7/2}$ located at 34.3, 35.8, and 37.3 eV. The major contribution is from the second peak. The spectra of 200 and 400 °C samples show only one form of W having $4f_{7/2}$ binding energy at 35.8 eV. Therefore, we conclude that the first and the third peaks are related to the presence of water on the sample surface.

Fig. 3 shows high-resolution XPS spectra of O 1s region in 100, 200, and 400 °C samples. The spectrum of 100 °C sample shows two strong peaks at 531.2 eV (labeled A) and at 535.7 eV (labeled C). Note that peak C is broad and is skewed toward lower binding energy. This suggests the existence of at least one more peak at about 532.6 eV (labeled B) between A and C. This suggestion is reinforced by the observation of an asymmetric tail of peak A toward higher binding energy in the 200 and 400 °C spectra. Peak A is assigned to W–O–W, and to carbonates [24]. Peak B is assigned to W–O–P and W–O–H. The broad peak C is assigned to water species on the sample surface. Recent high-pressure XPS studies on water show that the binding energy of O 1s in water precipitates is about 535.5 eV [25,26]. The peak C at 535.7 eV disappeared in the 200 and 400 °C samples, in agreement with our assignment.

In order to verify that some of the features observed above are related only to the sample surface, we repeated some of the experiments using laboratory XPS. This is due to the fact that at higher photon energy and thus higher kinetic energy of photoelectrons, the inelastic mean free path of the photoelectrons is larger. This allows one to probe relatively deeper in the sample with higher photon energy. Indeed the P 2p signal was observed even in the 100 °C sample unlike in the case of synchrotron XPS (see Fig. 4). This confirms our explanation suggesting that a thin hydrated adlayer masks the signal when low photon energy is used as in the case of synchrotron XPS ($h\nu = 600$ eV). Note that the 200 °C spectrum shows a broad shoulder at about 132 eV, suggesting the presence of another form of P, possibly phosphate [24].

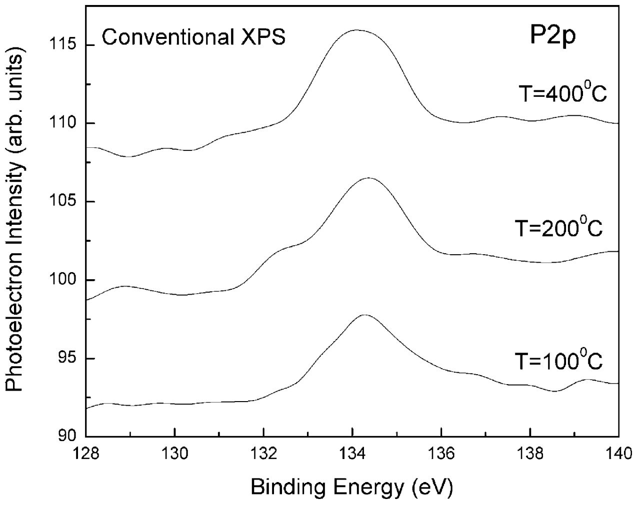

Fig. 4. Conventional XPS spectra of the P 2p region in HPW preheated at different temperatures.

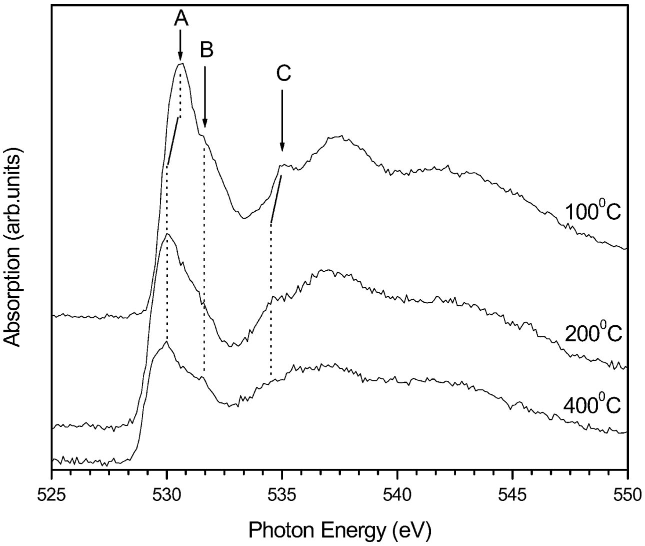

Fig. 5. XANES at the O K edge of HPW preheated at different temperatures.

The laboratory XPS data showed only one form of W with $4f_{7/2}$ binding energy at 35.9 ± 0.3 eV for all three samples. This confirms our earlier conclusion, based on the synchrotron XPS results, that the first and the third peaks in the W 4f region of the 100 °C sample are related to the water species on the surface. As the sample is heated to 200 and 400 °C, the water is removed from the surface. The laboratory XPS data also showed only two O 1s peaks A and B at 531.2 ± 0.3 and 532.6 ± 0.3 eV, respectively, for all three samples. This again confirms our assignment of the broad peak C at 535.7 eV in the O 1s region of the 100 °C sample, seen in the synchrotron XPS spectra, to water species on the sample surface.

Fig. 5 shows XANES data of 100, 200, and 400 °C samples of HPW at the O K edge. It shows three prepeaks labeled A, B, and C at about 530.5, 531.5, and 535.0 eV, respectively, for the 100 °C sample. Peak A is attributed to the W 5d(t_{2g})–O 2p hybridized band [23,24]. Peak B is related to the anisotropy of the t_{2g} band caused by nonequivalent O atoms present in the Keggin structure [27,28]. It was suggested that the intensity of peaks A and B in the H_xWO_3 compound is a measure of W–O covalency strength; the higher the intensity the higher the covalency [27]. Note, in Fig. 4, that the peak intensity in HPW decreases as the preheating temperature increases. This means that the covalency strength of W–O bonds in HPW becomes weaker as the temperature increases. In other words, the Keggin structure of the HPW molecule has been changed upon heating at 200 and 400 °C. This supports the conclusion derived from our XPS results that HPW becomes unstable at temperatures as low as 200 °C. While the peak position of B does not change significantly, peak A shifts to lower energy values by about 0.5 eV for the samples preheated at 200 and 400 °C. It is interesting to note that Purans et al. have observed that the peak position of A shifted to lower binding energy by 0.4 eV while the peak B position was almost unchanged when they moved from monoclinic WO_3 to layered hexagonal WO_3 [28]. This analogy further supports our conclusion that structural rearrangement takes place, at least at the surface, upon heating HPW at temperatures as low as 200 °C. Peak C is attributed to the W 5d(e_g)–O 2p hybridized band strongly influenced by the O 2p–H 1s interaction. Increased intensity of peak C means partial covalent interaction between O and H atoms [27,28]. It was also reported that the resonance of W–O bonds of WO_3 in this energy range is strongly dependent on the geometric structure. Note that the intensity of peak C decreases as the sample is heated at higher temperatures.

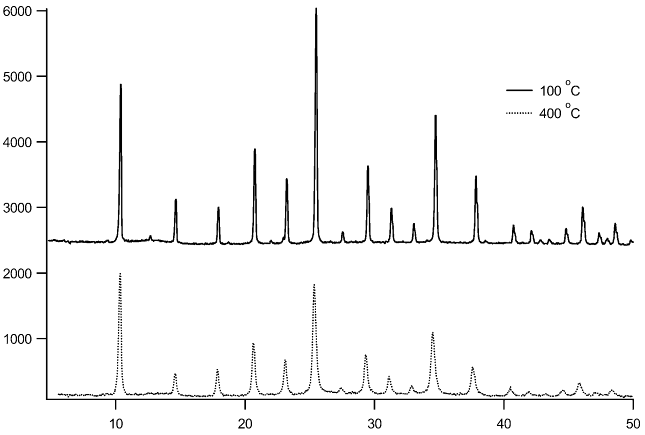

Fig. 6. XRD spectra of the preheated HPW at 100 and 400 °C.

The XRD spectra of the heated HPW at different temperatures are shown in Fig. 6. As can be seen, the crystallinity of HPW is maintained even at 400 °C. However, there is a considerable broadening upon heating at 400 °C, indicating a reduction of the crystallinity of the acid in the bulk. In contrast to the XPS and XANES results, XRD suggests that the crystallinity is maintained even upon heating at 400 °C. This is due to the fact that XRD is not a surface-sensitive technique.

The infrared spectra of the fresh and the heated HPW are shown in Fig. 7. As in the case of XRD, the IR features of the acid did not change upon heating, indicating the stability of the bulk even at 400 °C from an IR point of view. However, detailed investigation of the HPW bands as a function of temperature shows a gradual increase in the absorbance of the W–O–W corner-shared vibration relative to the absorbance of the other bands. Table 1 shows that the maximum percentage difference among the ratios of the fresh and the heated HPW is 25% for A_{892}/A_{800}, 2% for A_{984}/A_{800}, and 6% for A_{1082}/A_{984} bands. These results reveal that the relative proportion of corner-shared bonds increased as a result of the destruction of the acid upon heating.

n-Hexane (C_6H_{14}) cracking is a very useful technique for studying the surface acidity of solid catalysts. n-Hexane, a nonpolar molecule, is expected to occur on the surface of the HPW acid. The catalyst has no chemical activity in hexane cracking at 100 °C. On the other hand, it is active at 200 °C, but dies completely (conversion $< 0.01\%$) after

Table 1
The ratio of some IR absorbance bands of fresh and heated HPW

	$A_{892}{}^{a}/A_{800}{}^{b}$	$A_{892}/A_{984}{}^{c}$	A_{984}/A_{800}	$A_{1082}{}^{d}/A_{984}$
Fresh HPW	0.64	0.70	0.92	0.79
HPW heated at 300 °C*	0.72	0.79	0.91	0.80
HPW heated at 350 °C*	0.80	0.85	0.94	0.84
Maximum % difference**	25%	21%	2%	6%

[a] Corner-shared bridged bond W–O–W.
[b] Edge-shared bridged bond W–O–W.
[c] Terminal W–O.
[d] P–O bond.
* Heated for 1 h.
** [{Maximum value − minimum value}/minimum value] × 100.

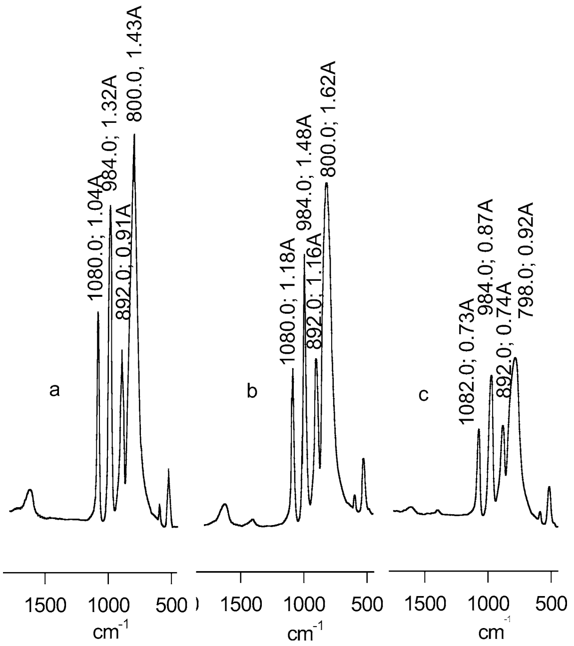

Fig. 7. Infrared spectra of (a) parent HPW, (b) heated HPW at 300 °C for 1 h, and (c) heated HPW at 350 °C for 1h.

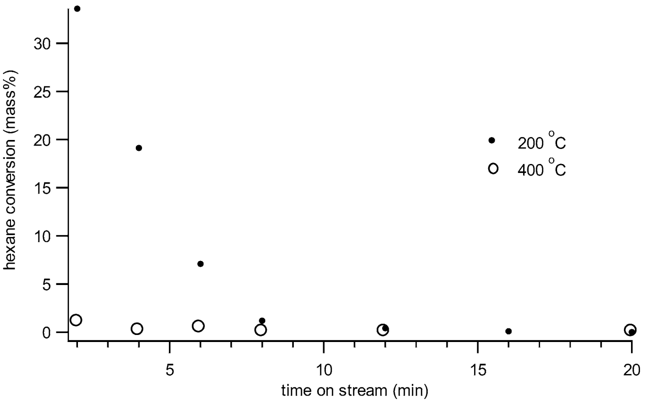

Fig. 8. Conversion of hexane over HPW at 200 and 400 °C.

20 min. As could be seen in Fig. 8, the catalyst lost most of its activity after 8 min of the reaction. This deactivation could be related to the formation of coke and/or to the destructive reduction of HPW. However, at 400 °C, the reactivity of the catalyst almost equals to zero, even at the beginning of the reaction. This means that the surface is no more acidic enough to crack *n*-hexane, indicating the destruction of the surface.

Some studies used ^{31}P NMR or IR spectroscopy to study the stability of the pure and supported HPW [6,8,12–14,17]. Based on the above discussion, we believe that the results of bulk techniques should be analyzed carefully to explain the behavior of HPW.

4. Conclusions

High-resolution XPS and XANES results show the deterioration of surface crystallinity at temperatures as low as 200 °C due to the destruction of the Keggin structure of the HPW molecule. As a result, the chemical stability and activity of the acid molecules are decreased, which limits their use in high-temperature surface reactions. Indeed, the catalyst died very fast at 200 °C and was almost inactive at 400 °C in hexane cracking.

Acknowledgments

This work was supported by the US Department of Energy under Contract No. DE-AC03-76SF00098. P.J., M.F., and N.T. thank KFUPM for its support.

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