Wells–Dawson heteropolyacid supported on silica: isobutane alkylation with C4 olefins

G. Baronetti [a], H. Thomas [b], C.A. Querini [a,*]

[a] *Instituto de Investigaciones en Catálisis y Petroquímica –INCAPE (FIQ,UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina*
[b] *Centro de Investigaciones y Desarrollo en Procesos Catalíticos, (CINDECA), Universidad Nacional de La Plata (CONICET), 3000 Santa Fe, Argentina*

Abstract

The alkylation of isobutane with C4 olefins is studied, using heteropolyacids (HPA) with Wells–Dawson (WD) structure supported on silica (WD/SiO_2). The catalytic performance of these catalysts is compared with a lanthanum-exchanged Y-zeolite catalyst. The loading of the HPA on silica was varied between 9 and 28 wt.%. These catalysts have activity for trimethylpentanes (TMP) production. The selectivity towards these products is not as high as in the case of the lanthanum containing Y-zeolite. The acidity of WD/SiO_2 catalysts increases as the loading increases, as seen by ^{1}H MAS-NMR. Correspondingly, a better TMP production is observed. The increase both in acidity and in the TMP production as a function of the WD content is more noticeable at low loading. The coke formed during the reaction requires high temperatures, 550°C approximately, in order to be fully removed with an oxygen containing carrier gas. The temperature-programmed oxidation (TPO) profile of this coke displays two peaks, the first one between 80 and 300°C associated with hydrocarbons that are released upon heating, and the second between 300 and 550°C, associated with coke that changed its structure during the heating. A regeneration at intermediate temperatures, e.g. 300°C, removes the coke that corresponds to the first peak, but does not restore the initial activity. If the regeneration is carried out at higher temperatures, e.g. 500°C, most of the coke is removed, but this treatment leads to changes in the structure of the HPA, as indicated by FTIR and MAS-NMR analysis. Regeneration with O_3 at low temperature (125°C) is effective both for coke removal and to recover the catalytic activity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isobutane alkylation; Heteropolyacids; Wells–Dawson; Regeneration

1. Introduction

The alkylation of isobutane with C4 olefins provides a high-quality gasoline, the alkylate, which is a component of the gasoline pool. This product has a high octane number, a low Reid vapor pressure, and a high H/C ratio. Industrially, this process is carried out in liquid phase using HF or H_2SO_4 acids as catalysts. The problems associated with the handling and disposal of these acids, and the environmental and potential hazards specially in the case of HF, have raised the interest in the development of an alternative process using solid acid catalysts.

Many different types of solids have been studied for the isobutane alkylation. Zeolites [1,2], heteropolyacids (HPA) [3,4], sulfated zirconia [5,6] among other materials have been studied. Industrial laboratories

* Corresponding author.
E-mail address: querini@fiqus.unl.edu.ar (C.A. Querini).

have carried out important efforts in the search for new processes [7–10]. In spite of all this research, the fast deactivation of the solid acid catalysts has not yet been solved. Activity and selectivity towards the trimethylpentanes (TMP) are adequate in many of the solids investigated, but the stability is generally very poor. This activity decay is associated with the formation of coke deposits, either by site coverage [11] or both site coverage and pore blockage [12].

We have previously reported about the coke characterization and regeneration of zeolite catalysts [12,13]. It has been found that those catalysts that show the better stability, are the catalysts that form more coke. This was associated with the deactivation mechanism that takes place on microporous materials such as mordenite and Y zeolite, where both site coverage and pore plugging occur. The more effective use of the internal surface, the better the stability and the higher the amount of coke deposited. On the other hand, if the acidity strength is too high, such as in mordenite catalysts, the deactivation occurs much faster due to a very strong adsorption of the olefins and a fast pore mouth plugging. Therefore, acidity should be perfectly balanced. The pore structure also plays a key role in determining the catalyst stability. The reaction is severely diffusion-limited for all practical catalyst particle sizes at a temperature of $100°C$ [14]. Therefore, a rational catalyst design for this reaction should consider a mesoporous or large-pore material as a starting point. This is also important, when trying to regenerate the catalyst using a solvent extraction procedure. In the case of microporous catalysts, the bulky coke molecules formed inside the cavities, cannot be extracted because their sizes are bigger than the pore mouth opening [12,15].

The HPA with Keggin structure have been studied for this reaction, both bulk [3,4] and supported [16,17]. In spite of the low thermal stability of these catalysts, no regeneration strategies were proposed.

In this work, we present a study carried out using HPA with Wells–Dawson (WD) structure supported on a large pore silica. The HPA with this structure has not been previously studied in the isobutane–butene alkylation reaction. The acid is deposited on a macroporous support in order to minimize the diffusional problems. The loading was varied between 9 and 28 wt.%. The catalysts were tested in the isobutane alkylation reaction in a fixed bed reactor, and characterized by

FTIR, ^{31}P and ^{1}H MAS-NMR and XRD, before and after thermal treatments. The coke was characterized by temperature-programmed oxidation (TPO) analyses. Reaction–regeneration cycles were carried out. The regeneration was carried out with air at different temperatures and with ozone at low temperature.

2. Experimental

2.1. Catalysts

Dawson acid ($H_6P_2W_{18}O_{62}$ (aq.)) was synthesized elsewhere [18] from an aqueous solution of α/β $K_6P_2W_{18}O_{62}·10H_2O$ salt, which was treated with ether and concentrated HCl (37%) solution. The acid so released formed an addition compound with the ether, which allows it to be separated from the solution. The remaining solution was placed in a vacuum-desiccator until crystallization.

Silica-supported WD acid was prepared by wet impregnation of Grace Davison silica (Grade 59, specific area $= 250\,m^2/g$) with an aqueous solution of the synthesized Dawson acid. Three catalysts containing 9, 20 and 28.5 wt.% of WD were prepared (WD(9)/SiO$_2$, WD(20)/SiO$_2$ and WD(28)/SiO$_2$). After impregnation, samples were dried at room temperature in a vacuum-desiccator during 8 h.

Y-zeolite (UOP, Y-54), with a Si/Al ratio of 5.3 was used. The sodium form of the zeolite was exchanged with La(NO$_3$)$_3$ 0.58 M, in reflux for 4 h, drying at $100°C$, calcining at $550°C$, and then a second ionic exchange with NH$_4$NO$_3$ was carried out for 4 h at reflux, drying and then calcining at $550°C$. This catalyst is labeled LCH-Y. This catalyst has a good activity and selectivity towards TMP production [13]. The exchange degree of the zeolite obtained with La^{3+} was 68%.

2.2. Activity test

The alkylation reaction of isobutane with a mixture of C4 linear olefins was carried out in liquid phase at temperatures between 25 and $80°C$, and at $30\,kg/cm^2$, in a fixed-bed reactor. The weight hourly space velocity (WHSV) was $1\,h^{-1}$ referred to the olefins. The molar ratio isobutane/olefins in the feed was 15. The samples were pretreated under an inert gas.

2.3. Coke characterization

Coke was characterized by TPO analyses. These experiments were carried out using a modified unit. The CO_2 produced during the coke burning is converted to CH_4, in a methanator reactor. A H_2 stream is fed to this reactor, which is loaded with a Ni catalyst, in order to quantitatively convert CO_2 into CH_4. This compound is then continuously monitored by a flame ionization detector (FID). With this configuration the sensitivity and resolution of the classical TPO technique is greatly improved. Typically, 10 mg of coked catalyst is loaded into a quartz cell, heating at 12°C/min, using 5% O_2/N_2 as carrier gas. Additional details of the technique can be found elsewhere [19].

2.4. Regeneration

Regeneration experiments were carried out using air and ozone. The ozone was generated by flowing air between two electrodes at high electrical potential. The stream coming out of this equipment contains 1% O_3 approximately.

2.5. Catalyst characterization

The catalysts were characterized by ^{31}P and ^{1}H MAS-NMR, FTIR and XRD measurements.

^{31}P and ^{1}H MAS-NMR spectra were recorded in a Bruker MSL-300 equipment operating at frequencies of 121.496 and 300.13 MHz for ^{31}P and ^{1}H, respectively. A sample holder of 5 mm diameter and 17 mm height was used. The spin rate was 2.1 kHz and several hundreds of pulse responses were collected. Chemical shifts were expressed in parts per million with respect to 85% H_3PO_4 as an external standard for [31]P. Chloroform was used as an external reference in the case of ^{1}H spectra. Prior to ^{1}H measurements, the samples were dried at 100°C for 2 h.

Catalysts were analyzed by infrared spectroscopy with a FTIR Bruker IFS 66 equipment and X-ray diffraction spectra were recorded for 2θ values between 5 and 45° with a Philips PW 1390 equipment (Cu K radiation and Ni filter).

^{31}P MAS-NMR and FTIR measurements were carried out on fresh and calcined samples at different temperatures, and also after ozone treatment.

3. Results and discussion

3.1. Fresh catalyst characterization

Fig. 1 shows results of ^{31}P MAS-NMR of WD/SiO_2 catalysts. The chemical shift of bulk Dawson acid is −12.8 ppm (relative to 85% H_3PO_4, as external reference) [18]. The catalysts containing 9, 20 and 28 wt.% WD on silica display the main peak with a chemical shift between −12.6 and −12.7 ppm, which indicates that after the impregnation and drying, the acid maintains its Dawson structure, independent of the loading. Two new small signals at −12 and −11 ppm approximately are evident in the three samples. These signals could be related to the presence of different Dawson species, such as $H_6P_2W_{18}O_{62}$ strongly interacting with the Si–OH groups of the support and to species like $P_2W_{21}O_{71}{}^{6-}$, respectively [20].

The FTIR also shows that after impregnation the acid maintains its Dawson structure. Fig. 2 shows the spectra for the bulk Dawson acid and for the $WD(20)/SiO_2$ and $WD(28)/SiO_2$ samples, after subtraction of the spectra that corresponds to the support. The characteristic bands of the HPA with Dawson structure are 1091 (stretching frequency of the PO_4 tetrahedron), 963 (W=O terminal bonds), 911, and 778 cm^{-1} ("inter" and "intra" W–O–W bridges, respectively) [18]. It can be observed that both catalysts containing 20 and 28 wt.% WD on silica, display the same characteristic bands. Nevertheless, for these
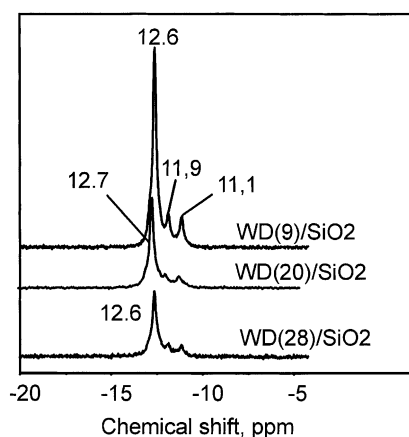

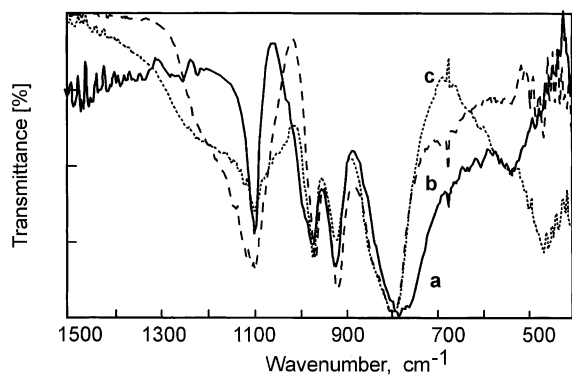Fig. 1. ^{31}P MAS-NMR spectra of WD/SiO_2, with 9, 20 and 28% acid.

Fig. 2. FTIR spectra, (a) bulk acid; (b) WD(20)/SiO$_2$; (c) WD(28)/SiO$_2$.

supported samples, a broadening of the band at 1091 cm^{-1} (stretching frequency of the PO$_4$ tetrahedron) must be noted. This fact can be due to a loss of tetrahedron symmetry [18] because of the interaction between WO$_6$ octahedrals and sylanol groups of the support. A slight shift of the 778 cm^{-1} band ("intra" W–O–W bridges), could also be observed which could be attributed to the same effect.

The maximum loading used in this study was 0.285 g of acid per gram of catalyst. The monolayer corresponds to a loading of 1.9 g of acid per gram of silica, i.e. 65 wt.%. Therefore, in all cases there is an uncompleted coverage of the surface. The XRD

analyses (not shown) indicate that there is no crystallinity of the HPA supported on silica up to 28.5 wt.%. Therefore, it can be inferred that large particles of WD were not formed on these catalysts.

3.2. Catalyst activity

3.2.1. Comparison with the LCH-Y zeolite

Fig. 3 shows activity results for the WD(20)/SiO$_2$ and the LCH-Y zeolite. The supported HPA is less selective for TMP production than the zeolite. The zeolite also displays a higher liquid yield (grams of C5+ fraction/gram of olefin fed) than the WD. However, the stability of the latter is better, maintaining a higher activity for dimethylhexenes (DMH) production. One major difference between these two catalysts is that in the case of the WD/SiO$_2$, the DMH are obtained from the beginning of the reaction. The pattern observed with the zeolite is typical of catalysts with good activity and selectivity for the isobutane alkylation reaction. When the catalyst is fresh, mainly TMP are obtained. After some time on oil, DMH start coming out with the products and the TMP production abruptly decreases. This change is associated with the loss of the hydrogen transfer capacity. The activity for hydrogen transfer is an essential factor in determining the quality of the product, leading to the production of saturated compounds. Therefore, according to these results of activity, the acidity of the
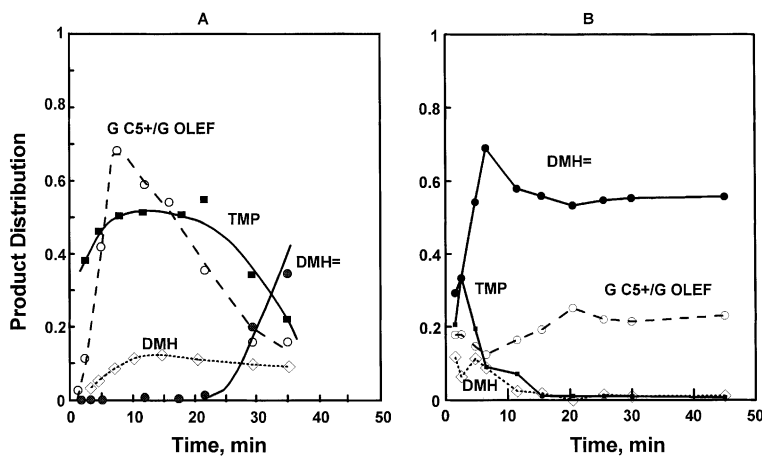

Fig. 3. Product distribution in the C5+ fraction. (A) LCH-Y catalyst; (B) WD(20)/SiO$_2$, pretreated at 200°C. DMH: dimethylhexanes; DMH: dimethylhexenes; TMP: trimethylpentanes, G C5+/G OLEFIN: grams of the C5+ fraction per gram of olefin fed.
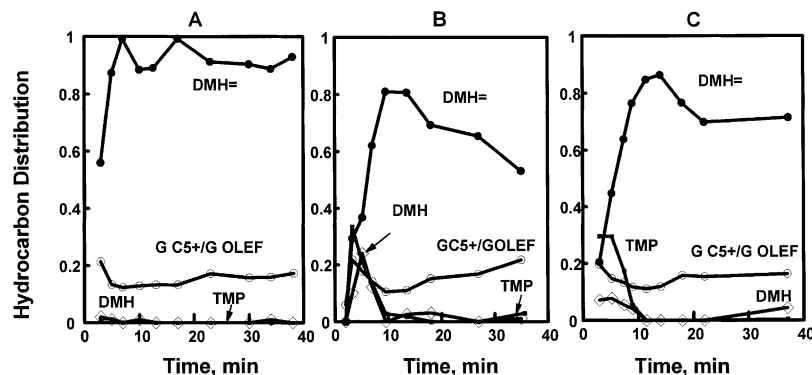
Fig. 4. Product distribution in the C5+ fraction. (A) WD(9)/SiO$_2$; (B) WD(20)/SiO$_2$; (C) WD(28)/SiO$_2$. DMH: dimethylhexanes; DMH: dimethylhexenes; TMP: trimethylpentanes, G C5+/G OLEFIN: grams of the C5+ fraction per gram of olefin fed.

WD/SiO$_2$ seems to be lower than the acidity of the zeolite, and lower than the acidity required in order to effectively promote the hydrogen transfer reaction. As known, this reaction takes place starting with protonation of a hydrocarbon in an acidic OH group, followed by a hydride abstraction from the isobutane. The pore size apparently allows the catalyst to maintain the activity for DMH production longer than in the case of the zeolite, in which the pore plugging inhibits the reactant to reach the active sites.

3.2.2. Influence of the heteropolyacid loading and pretreatment

The bulk WD acid does not have any activity, neither TMP nor DMH are obtained when the WD is not supported. However, Fig. 4 shows that the three WD/SiO$_2$ supported catalysts are active for the production of TMP and DMH. The behavior of the WD(20) and WD(28) are very similar, having a higher activity and selectivity than the WD(9). The latter has a negligible TMP production. Due to the isobutane alkylation being a "surface-type" reaction the catalyst activity could be directly related to the number of the surface acid sites accessible to the reactants [16]. Therefore, the higher activity of the supported Dawson acid is a consequence of an increment in the number of acidic sites for the supported samples.

Changing the pretreatment temperature from 80°C up to 200°C there is no significant change in the catalytic behavior (result not shown). These materials release water when heated above 100°C [18]. The activity data indicate that after a pretreatment at

temperatures in the range of 150–200°C, when the temperature is decreased to the reaction temperature (80°C), the solid is rehydrated and the initial composition is restored. It has to be emphasized that the inert gas was not flowed through a water trap, and therefore the little water contained in this gas rehydrates the solid.

3.3. Coke characterization

The TPO profiles of the WD/SiO$_2$ catalysts display two well-defined peaks, as shown in Fig. 5A. The first is related to hydrocarbons that desorb upon heating. The amount of coke deposited on the LCH-Y zeolite is 13% approximately [12]. Fig. 5B shows the result of an experiment carried out heating the coked WD(20)/SiO$_2$ catalyst under helium, from room temperature up to 600°C (TPHe). After this treatment, a normal TPO is carried out to the same sample. The dash line in Fig. 5B corresponds to the profile of this latter TPO. The first peak of the original TPO profile is completely removed by the treatment in helium. Besides, the second peak is now located at a higher temperature. The TPO of the coked catalyst finishes at 530–540°C approximately, and the TPO carried out after the TPHe, finishes at 570°C. This agrees with results obtained with zeolite catalysts [13]. For these catalysts it was proposed that the second peak in the TPO profile corresponds to coke that changed from the original aliphatic structure with high H/C ratio, to a highly polymerized aromatic coke, with a low H/C ratio. The latter requires higher temperatures to
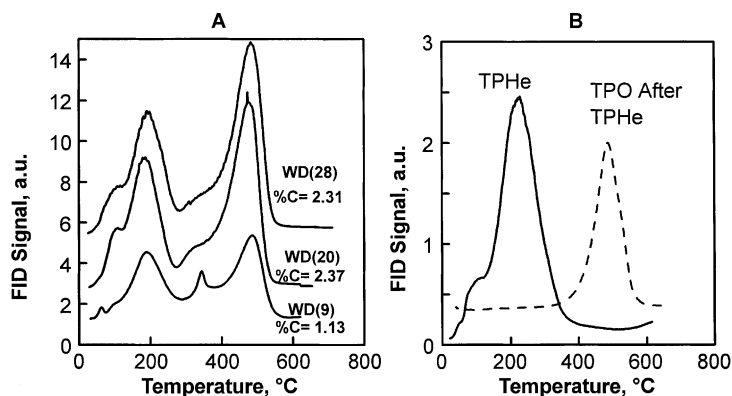
Fig. 5. (A) TPO profiles of WD/SiO$_2$ catalysts; (B) stripping in He of WD(20)/SiO$_2$ (TPHe), and TPO after the TPHe (dashed line).

be burnt. The second peak shifts to higher temperatures after the TPHe, because of the high temperature reached during the initial treatment in helium, which leads to a more dehydrogenated coke.

The TPO profiles that correspond to the WD(20) and WD(28) are very similar, as well as the total amount of coke (Fig. 5A). This is in agreement with the activity behavior of these catalysts, which is also practically the same. It has been observed that the better the catalyst stability, the higher the amount of coke deposited during the reaction [12]. This is because in microporous materials, the faster the pore mouth plugging, the lower the use of the internal surface, and therefore the lower the coke formation. The WD/SiO$_2$ catalysts have larger pore diameter than the zeolites, and a deactivation mechanism due to site coverage could be expected. The SiO$_2$ used as support has a pore diameter of 140 Å. The WD molecule (H$_6$P$_2$W$_{18}$O$_{62}$) has an ellipsoidal shape whose main dimensions are 10 Å × 11 Å approximately [21]. Since the XRD pattern indicate that there is no aggregate formation in these catalysts, the minimum effective pore opening would be 118 Å. Therefore, the diffusional problems will be less significant in these catalysts, and coke deposition will be related only to the acidity. In the case of the WD(9), the TPO profile is similar to the profile obtained with the WD(20) and WD(28), but the amount of coke is less than half. It is known that chemical shifts obtained from ^{1}H MAS-NMR measurements can be related to the acid strength of the sample [22]. The ^{1}H MAS-NMR of supported WD/SiO$_2$ catalysts showed a single peak with a continuous increase

Table 1
Chemical shifts (δ_H) ^{1}H MAS-NMR results on WD/SiO$_2$ catalysts

Catalyst	δ_H (ppm)
WD(9)	4.4
WD(20)	5.6
WD(28)	5.9

in the chemical shift (δ_H) as the WD loading increases. The δ_H values are shown in Table 1. This result indicates a change in the environment of the protons and therefore the change in its acidic strength. It has been shown that increasing value of the chemical shifts (δ_H) correspond to an increase in the acid strength [22]. The TPO profile and coke amount are very similar for both catalysts with a higher loading of WD. This also suggests that their acidity is very similar, in agreement with ^{1}H MAS-NMR measurements, as discussed above. Therefore, the lower activity and lower coke formation of the WD(9) as compared to WD(20) and WD(28) is due to a low acidity of the former.

A very important conclusion that can be obtained from these TPO is that this catalyst also requires high temperatures, well above 500°C, in order to fully remove the coke. However, as it is known for the HPA with Keggin [23] and Dawson [18] structure, and we also show below for the latter, these materials change its structure when heated, the changes being more dramatic above 400°C. In spite of this, the regeneration of these catalysts, whenever studied in acid-catalyzed reactions such as isobutane alkylation [3,4,16,17], has been completely neglected.
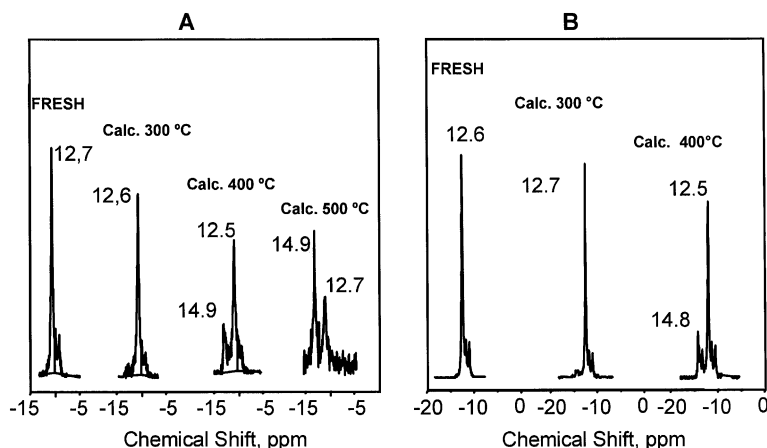
Fig. 6. ^{31}P MAS-NMR spectra of WD/SiO$_2$ catalysts pretreated at different temperatures, (A) WD(20)/SiO$_2$; (B) WD(28)/SiO$_2$.

3.4. Thermal stability

The WD/SiO$_2$ catalysts were treated at different temperatures in the range of 300–500°C and then analyzed by ^{31}P MAS-NMR and FTIR. Fig. 6 shows the ^{31}P MAS-NMR spectra of WD(20) and WD(28)/SiO$_2$. After calcination at 300°C in air, the NMR spectra shows only a well-defined signal around −12.7 ppm, indicating that the acid maintains its structure intact, both when loaded at 20% and 28%. However, at higher calcination temperature (400°C), two signals appear in the NMR spectrum, one at −12.7 ppm, and the other signal with a lower intensity at −14.9 ppm. This fact indicates the presence of at least two species with different phosphorous structure.

When the calcination temperature increases up to 500°C, (Fig. 6A) the intensity of the peak at −14.9 ppm notably increases while the peak at −12.7 ppm decreases. As mentioned above, the resonance at −12.7 ppm corresponds to a phosphorous of the Dawson acid structure. The other resonance around −14.9 ppm indicates a decomposition or modification of the Dawson structure. The signal at −14.9 ppm does not correspond neither to lacunary or unsaturated species like PWO_{11} and $P_2W_{17}O_{71}$, nor to $P_2W_{21}O_{71}$ [20]. However, this value is very close to the phosphorous resonance at −15 ppm reported for $(SiOH_2)^+(H_2PW_{12}O_{40})^-$ species. These species would correspond to a HPA with Keggin structure

having a strong interaction with the sylanol groups present on silica surface [16,20].

The FTIR spectra shown in Fig. 7 also suggest a change in the Dawson structure when the supported samples are calcined at 400°C. There is a broadening in all characteristics of Dawson acid bands. Furthermore, for the catalyst calcined at 500°C this effect is more noticeable and it can be observed for an additional band at 986 cm^{-1} (spectrum not shown). Considering the above mentioned NMR results, this band could be due to the presence of Keggin-type species. In fact, the characteristics bands of Keggin ion, $PW_{12}O_{40}^{3-}$, are 1080, 982, 888 and 801 cm^{-1}.
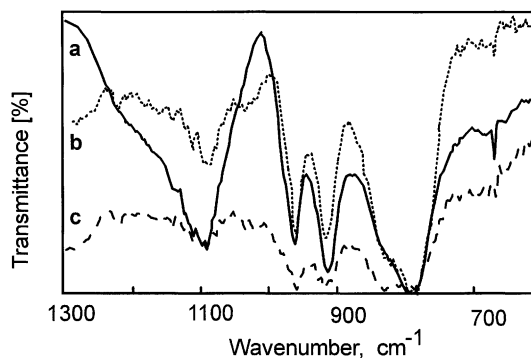

Fig. 7. FTIR spectra of WD(20)/SiO$_2$, (a) fresh; (b) calcined at 300°C; (c) calcined at 400°C.

If we compare these bands with that corresponding to the Dawson acid (1091, 963, 911 and 778 cm^{-1}) the broadening of the bands and the additional band at 986 cm^{-1} (ν W–O) also suggest the presence of species with Keggin-type structure after calcination at temperatures above 400°C.

In previous works [18,21], the thermal stability of bulk acid and potassium–tungsten Dawson salt was studied. In the case of bulk Dawson acid, it has been shown that the loss of crystallization water occurs between 150 and 400°C, and the acid keeps its HPA structure even after calcination at 600°C [18]. Besides, the bulk potassium–tungsten Dawson salt [21] loses water up to 280°C and then these structures also are stable up to 600°C. For these salts the Dawson structure is destroyed after calcination at 600°C, giving rise to three new phases by solid–solid reaction, one being a Keggin salt among these phases [21].

The temperatures at which these changes occur are lower when the Dawson acid is supported on silica, and the MAS-NMR and FTIR results indicate that the supported Dawson acid is stable up to 400°C. For temperatures higher than 400°C, a structural change in the supported Dawson acid on silica occurs. The above results would indicate the presence of Keggin-type species with strong interaction with the support besides the Dawson-type species. Nevertheless, although the NMR and the FTIR point towards a Keggin-type specie, it might be necessary to carry out additional studies to obtain conclusive evidences about this. In any case, what is relevant for our study, is that after the treatment at temperatures above 400°C, the catalyst modifies its structure irreversibly, leading to a loss in activity.

According to the TPO data and the thermal stability of the WD/SiO$_2$ catalysts, it seems that regeneration in air would not be possible since the temperature needed to completely remove the coke is higher than the HPA decomposition temperature.

3.5. Catalyst regeneration

3.5.1. Regeneration in air

The WD(20)/SiO$_2$ catalyst was regenerated at 300°C after the first reaction cycle. The catalyst was again regenerated at 300°C after the second reaction cycle, but in this case it was pretreated in helium saturated with water at room temperature. Results
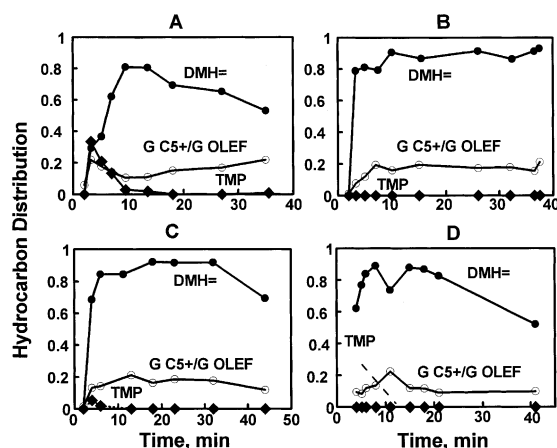

Fig. 8. Regeneration in air of WD(20)/SiO$_2$. Activity results: (A) 1st reaction cycle; (B) 2nd reaction cycle, after regeneration at 300°C; (C) 3rd regeneration cycle, after regeneration at 300°C, and pretreatment with wet helium; (D) 2nd reaction cycle, after regeneration at 500°C.

are shown in Fig. 8A–C. The first regeneration at 300°C only leads to the recovery of the activity for DMH, i.e. for olefins oligomerization. There is no TMP formation (Fig. 8B). If after the regeneration at 300°C the catalyst is treated with wet helium, it is possible to recover a very small fraction of the initial activity for TMP production (Fig. 8C). The regeneration at 300°C removes the fraction of the coke represented by the first peak of the TPO profile, this quantity being less than half of the total amount. The results shown in Fig. 8 indicate that the amount of coke not removed from the catalyst is the main reason of the incomplete activity recovery. It is not the loss of water during the regeneration, or a change in structure since it occurs at higher temperatures. If higher regeneration temperatures are used such as 500°C at which most of the coke was removed as will be shown below, there is no recovery of activity for TMP formation (Fig. 8D). In this case, the change in structure as pointed out above, could be the reason. The decomposition of Dawson structure would produce a Keggin-type surface species, which is active for the isobutane alkylation reaction as reported by Essayem et al. [4]. Both species are strong acids. In spite of this, the catalyst after thermal treatment at 500°C does not recover the activity towards TMP formation. Blasco et al. [16] have reported for

the isobutane alkylation reaction using Keggin acid supported on silica, that the activity strongly depends on the acid loading. They found the lower activity for the lower acid loading, because of the acidity of $(SiOH_2)^+(H_2PW_{12}O_{40})^-$ surface species decreases, due to a strong interaction with the sylanol groups of the support. Kozhevnikov et al. [20] studied the trans-de-*t*-butylation of 2,6-di-*t*-butyl-4-methyphenol reaction in liquid-phase. They found that the acid strength of the surface dimeric species (like Dawson structures) decreases to a lesser extent compared to the surface Keggin species, due to the stronger interaction with Si–OH groups of the latter.

Even if after regeneration at 500°C, the catalyst is treated in air saturated with water at 25°C during 12 h, there is no recovery of activity for TMP production (result not shown). Recently, Essayem et al. [24] concluded that the $H_3PW_{12}O_{40}$ bulk acid dehydrated at 400°C can be re-hydrated almost to its original state after 48 h of exposure to the air. On the other hand, after dehydration at 500°C the sample gives a tetragonal structure, which only partially recover its hydration degree, being necessary for this partial rehydration much longer times. Therefore, the strong interaction of the Keggin-type species with the support, what leads to species with lower acidity, and the uncompleted rehydration of the catalyst after the regeneration at high temperature, might be the reason of the deactivation observed during the regeneration at 500°C.

The TPO profiles after the reaction–regeneration cycles also provide information regarding catalyst modifications. Fig. 9 shows the TPO after one reaction cycle (curve A), after the two reaction cycles with one regeneration at 500°C (curve B) and after the three reaction cycles with two regenerations at 300°C (curve C). The TPO profiles of the catalysts regenerated in air are quite different from that one obtained after one reaction cycle. Since as previously discussed the coke is strongly related to the acidity of the catalyst for a given pore structure, it can be concluded that the regeneration at 500°C led to a notorious decrease in acidity. On the other hand, the regeneration at 300°C led to the accumulation of heavy coke, which is not removed during the regeneration at low temperature. During the second and third cycles after regeneration at 300°C, there is a negligible formation of TMP. Therefore, it can be expected that the formation of coke will be correspondingly low, with no fresh coke
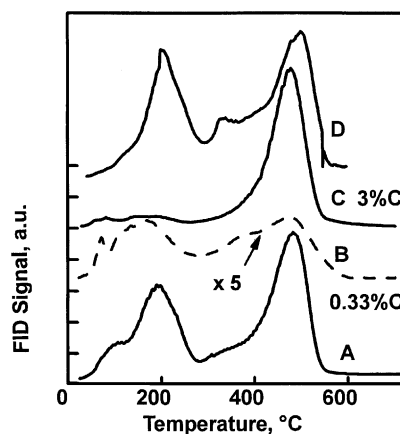

Fig. 9. TPO profiles of WD(20)/SiO$_2$, (A) after one reaction cycle; (B) after two reaction cycles with regeneration at 500°C; (C) after three reaction cycles with two regenerations at 300°C; (D) after two reaction cycles with regeneration with O$_3$ at 125°C.

being formed during these two last reaction cycles. This is the reason why only the second peak of the TPO profile is observed.

During the regeneration at 500°C almost all the coke was removed. However, only 0.33% C is left on the catalyst after the regeneration at 500°C followed by a second reaction cycle. Again, there is a correlation between the activity and the coke formation. In this case, there is no activity for TMP production and the coke deposition is negligible.

3.5.2. Regeneration in ozone

It has been previously shown that the ozone is active for coke removal at low temperatures, for acid catalysts used in the isobutane alkylation reaction [13]. Fig. 10 shows the activity of the catalyst WD(20)/SiO$_2$ during the second reaction cycle, after regeneration in ozone at 125°C (Fig. 10A) and the TPO of the regenerated catalyst (Fig. 10B). The activity during the second cycle is the same as that of the first cycle (compare Fig. 3B and 10A). This indicates that the very small amount of coke left after the ozone treatment (0.12%) does not influence the activity. The TPO profile after the second cycle is the same as that of the first cycle (curves D and A respectively, Fig. 9). Therefore, according to previous discussion, it can be inferred that the catalyst has exactly the same acidity and therefore the same activity before and after the ozone treatment.
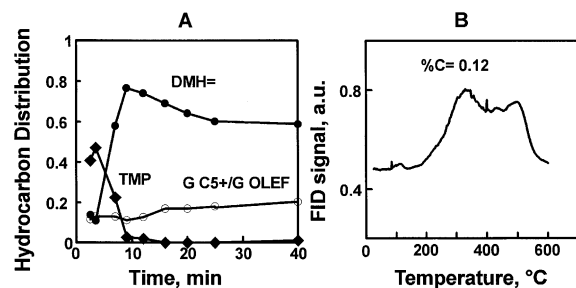
Fig. 10. Regeneration with O_3 of WD(20)/SiO$_2$: (A) Product distribution in the second reaction cycle, after regeneration with ozone at 125°C for 13 h; (B) TPO profile after the regeneration with ozone.
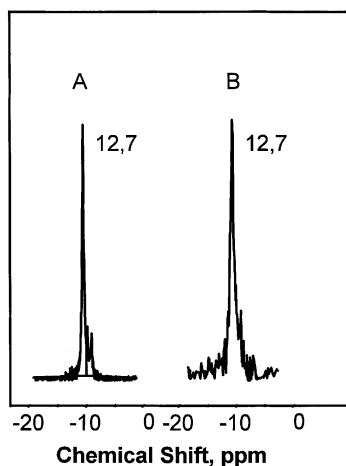

Fig. 11. ^{31}P MAS-NMR of the fresh (A) and the ozone regenerated (B), WD(20)/SiO$_2$ catalyst.

The WD(20)/SiO$_2$ catalyst was analyzed by ^{31}P MAS-NMR after 13 h in ozone at 125°C. Fig. 11 shows the spectra for both the fresh catalyst and the catalyst treated with ozone. They are identical, which also proves that after this regeneration procedure the catalyst retains the Dawson structure and the acidity, in agreement with the activity and TPO data.

4. Conclusions

The HPA with Dawson structure supported on silica presents activity for isobutane alkylation with C4 olefins. The activity increases when the acid loading

increases from 9 to 20%, but further increase in the amount up to 28% does not lead to a significant improvement either in activity or in stability. The catalytic performance of these catalysts is not as good as the Y-zeolite partially exchanged with lanthanum.

The acid is well dispersed when loaded up to 28%, and retains its structure up to 300°C. An increase in the acid strength is observed by ^{1}H MAS-NMR when increasing the loading of the HPA. Calcination at higher temperatures leads to a modification in the Dawson acid structure as seen by NMR and FTIR. This modification probably generates species like Keggin-type structure, with lower activity for isobutane alkylation due to a stronger interaction with the support coupled with a very slow rehydration capacity.

The TPO profile of the coke indicates that temperatures of 550°C are needed in order to fully remove it with oxygen. This is a serious complication for this type of thermosensitive materials.

The regeneration with ozone is effective to remove the coke at low temperature (125°C) without changing the structure of the Dawson acid.

References

[1] A. Corma, A. Martínez, C. Martínez, J. Catal. 146 (1994) 185.
[2] F. Cardona, N.S. Gnep, M. Guisnet, G. Szabo, P. Nascimento, Appl. Catal. A: General 128 (1995) 243.
[3] T. Okuhara, M. Yamashita, K. Na, M. Misono, Chem. Lett. (1994) 1451.
[4] N. Essayem, S. Kieger, G. Coudurier, J. Vedrine, St. Surf. Sci. Catal. 101 (1996) 591.
[5] C. Guo, S. Yao, J. Cao, Z. Qian, Appl. Catal. A: General 107 (1994) 229.
[6] A. Corma, M.I. Juan-Rajadell, J. López-Nieto, A. Martínez, C. Martínez, Appl. Catal. A: General 111 (1994) 175.
[7] US Patent 5,414,187.

[8] US Patent 5,157,197.

[9] EP Patent 650,394.

[10] US Patent 5,220,095.

[11] M.F. Simpson, J. Wei, S. Sundaresan, Ind. Eng. Chem. Res. 35 (1996) 3861.

[12] C.A. Querini, E. Roa, Appl. Catal. A: General 163 (1997) 199.

[13] C.A. Querini, E. Roa, C.L. Pieck, J.M. Parera, St. Surf. Sci. Catal. 111 (1997) 407.

[14] M.F. Simpson, J. Wei, S. Sundaresan, in: P. Anastas, T. Willianson (Eds.), ACS Symposium Series No. 626, American Chemical Society, 1996, p. 105.

[15] C.A. Querini, Catal. Today 26 (2000) 135–143.

[16] T. Blasco, A. Corma, A. Martínez, P. Martínez-Escolano, J. Catal. 177 (1998) 313.

[17] K.J. Del Rossi, G.A. Jablonski, C.T. Kresge, G.A. Kuehl, US Patent 5,475,178 (1995).

[18] G.T. Baronetti, L. Briand, U. Sedran, H. Thomas, Appl. Catal. A: General 172 (1998) 265.

[19] S.C. Fung, C.A. Querini, J. Catal. 138 (1992) 240.

[20] I.V. Kozhevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zanbergen, H. Van Bekkum, J. Mol. Catal. A 114 (1996) 287.

[21] L.E. Briand, H.J. Thomas, G.T. Baronetti, Appl. Catal. 201 (2000) 191.

[22] S. Gao, J.B. Moffat, Catal. Lett. 42 (1996) 105.

[23] M. Mioc, R. Dimitrijevic, M. Davidovic, Z. Nedic, M. Mitrovic, P. Colomban, J. Mater. Sci. 29 (1994) 3705.

[24] N. Essayem, Y.Y. Tong, H. Jobic, J.C. Vedrine, Appl. Catal. A 194 (2000) 109.