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Supported Heteropolyacid (HPW) Catalysts for the Continuous Alkylation of Isobutane with 2-Butene: The Benefit of Using MCM-41 with Larger Pore Diameters

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12-Tungstophosphoric acid (HPW) has been supported on three different carriers: a commercial silica, a high surface area amorphous aluminosilicate (MSA), and an all-silica mesoporous MCM-41; and their catalytic properties have been determined for the alkylation of 2-butene with isobutane at 33°C and 2.5 MPa. A maximum in activity, selectivity to TMP and stability with time on stream was found for the HPW/SiO$_2$ catalyst with 40 wt% acid loading, despite the higher acid dispersions achieved with the high surface area MCM-41 and MSA supports. The lower activity of the HPW/MSA samples is due to a stronger interaction of HPW with the surface sites of the aluminosilicate, which in turn decreased both the number and the average acid strength of the Brönsted acid sites of the heteropolyacid. When the HPW was supported on MCM-41 a continuous decrease of the catalytic activity with the HPW content was observed. This fact, together with the characterization results, suggests a partial blockage of the monodimensional pores of MCM-41, which decreased the accessibility of the reactants to the Brönsted acid sites of the heteropolyacid located inside the pores. We show that this pore blockage can be decreased, and the catalytic activity of HPW/MCM-41 catalysts increased, by using a MCM-41 sample with larger pore diameter. © 1998 Academic Press

1. INTRODUCTION

There is still a clear interest in replacing the hazard liquid acids HF and H$_2$SO$_4$ which are used in the commercial alkylation units by more environmentally friendly solid acids (1). Following this direction, both zeolites (2–5) and sulfated metal oxides (6–9) have been the most widely solid acids studied as potential alkylation catalysts although none of them have achieved, at present, commercial application, mainly due to the short life of the catalysts.

In the last two decades, the use of heteropoly compounds in acid catalyzed reactions has opened new expectations for processes requiring acidities higher than those present on zeolites (10–13). Heteropolyacids having the Keggin structure have been widely applied in catalysis due to their facile preparation, acceptable stability, and high acidity (14). Particularly the 12-tungstophosphoric acid, H$_3$PW$_{12}$O$_{40}$ (HPW), has shown the strongest acidity among the Keggin series (14). Unfortunately, in the solid state HPAs are nonporous materials with surface areas below 10 m^2 g^{-1}, and only the few acid sites present on the external surface are available when nonpolar molecules, like hydrocarbons, are reacted. In order to overcome this limitation one can prepare acid salts containing large cations such as Cs$^+$, K$^+$, Rb$^+$, and NH$_4^+$ which present surface areas in the order of 150 m^2 g^{-1} (15–17). On the other hand, when the use of the acid form is required, then the Keggin structure can be supported on a high surface area carrier, with amorphous silica the most frequently used for this purpose (18–21).

Recently, a new class of mesoporous materials generically known as M41S was discovered by the researchers at Mobil (22). The most known member of this family is the material named MCM-41 having an hexagonal array of mesopores. Owing to its very high surface area (typically 800–1000 m^2 g^{-1}) and its peculiar porosity, this material has been shown to be an excellent support for preparing bifunctional catalysts, presenting a superior activity and selectivity than conventional supports, such as alumina, silica-alumina, and even zeolites (23, 24). Heteropolyacids have been supported on all silica MCM-41 and, owing to the high dispersions achieved, the resultant catalysts showed an enhanced catalytic activity for liquid-phase organic reactions (25). Moreover, a patent assigned to Mobil (26) claims that this system could be adequate for carrying out the alkylation of butene with isobutane.

Taking into account the size of the Keggin ion (ca 12 Å) and the fact that the acid strength of the heteropolyacid strongly decreases when present in amounts below the theoretical monolayer (11), it was surprising to us that MCM-41 could be an adequate support for heteropolyacids. Then, in the present work we have prepared a series of HPW-supported catalysts with different acid loadings using amorphous silica, a mesoporous silica-alumina with a narrow

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pore size distribution (MSA) (27), and pure silica MCM-41 as supports. In the latter case we have used two MCM-41 samples with different pore diameter (ca 30 and 65 Å) in order to see the possible blocking of the pores by the Keggin ions, and the potential benefit of increasing the pore diameter. The HPW-supported catalysts have been studied for the alkylation of isobutane with 2-butene under liquid phase conditions (33°C, 2.5 MPa).

2. EXPERIMENTAL

2.1. *Preparation and Characterization of Catalysts*

The two MCM-41 samples were synthesized as described in Ref. (28) from gels with the molar composition

$$SiO_2\text{: } 0.12 \text{ CTABr: } 0.28 \text{ TMAOH: } 26 \text{ } H_2O,$$

where CTABr is cetyltrimethylammonium bromide and TMAOH is tetramethylammonium hydroxide (25%, Aldrich). The gels were crystallized in teflon-lined autoclaves in static conditions at 135°C for 12 h and 150°C for 6 days for the samples with 30 Å (M41-A) and 65 Å (M41-B) pore diameters, respectively (28). Then, the solids were filtered, washed with deionized water, dried, and finally calcined at 540°C for 1 h in nitrogen flow, followed by 6 h in air at the same temperature with a gas flow rate of 140 ml/min.

The other supports were used without further treatment before incorporation of the heteropolyacid.

The $H_3PW_{12}O_{40}$ xH_2O (HPW, Aldrich, 99% pure) was incorporated onto the different supports by shaking the support with an aqueous solution containing the required amount of HPW acid at room temperature for 1–9 h to achieve different acid loadings. In the case of silica and MSA, 3 ml of solution per gram of total catalyst (support + HPW) were used, and then the excess water was evaporated in a rotary evaporator at ca 50°C and vacuum, followed by drying the solid at 100°C for 2 h. The HPW/MCM-41 samples were prepared in a similar way, but using 10 ml of the aqueous HPW solution per gram of support. Drying of the MCM-41-based catalysts was performed by introducing the suspension directly into the oven at 100°C overnight. In all cases the dried samples were stored in a desicator before used for characterization or catalytic testing. The prepared catalysts were denoted as xPW/“supp,” where x is the weight percent of HPW loaded and “supp” is Si, MSA, and M41 for SiO_2, SAM, and MCM-41, respectively.

The HPW phase and the mesoporous crystalline structure of MCM-41 was characterized by means of X-ray diffraction in a Philips PW 1830 equipment using Ni-filtered Cu K_α radiation. Patterns were recorded in the range of ca 2 to 40° (2θ).

The primary Keggin structure of the HPW on the different materials was studied by means of FT-IR spectroscopy. IR spectra were recorded in the range of 300–1900 cm^{-1} in a Nicolet 710 apparatus using the KBr pellet technique with a catalyst concentration of 0.5 wt%.

Thermogravimetric and differential thermal analysis (TG-ATD) were performed in a Nest instrument using 20 mg of sample and kaolin previously calcined at 1100°C as reference material, increasing the temperature from 25 to 800°C at a rate of 10°C/min in a controlled atmosphere of dry air (100 ml/min).

Textural properties were determined from the nitrogen adsorption isotherms at 77 K in an ASAP 2000 apparatus (Micromeritics) using 250 mg of sample previously pretreated at 400°C overnight in a vacuum in the case of the bare supports, and at 100°C overnight followed by heating at 300°C for 2 h in a vacuum for the HPW-supported catalysts.

^{31}P MAS NMR spectra were recorded at ambient temperatures on a Varian VXR-S 400-WB spectrometer using a 7-mm CP/MAS Varian probe equipped with zircona rotors. Samples were spun at a rate of 7 KHz. Standard inversion-recovery pulse sequence was applied to measure the ^{31}P longitudinal relaxation time T_1. Conventional ^{31}P Bloch decay spectra were acquired using pulses of 5.7 μs corresponding to a flip angle of 80° and a delay between two consecutive pulses long enough to ensure the total relaxation of the spin system.

2.2. *Isobutane/2-Butene Alkylation Experiments*

The alkylation of *trans*-2-butene (>99% pure) with isobutane (>99% pure) was carried out in an automated fixed bed stainless steel reactor at 33°C, 2.5 MPa total pressure, and an isoparaffin-to-olefin (I/O) molar ratio of 15. The weight of catalyst loaded into the reactor was varied, depending on the acid content in order to obtain a constant space velocity (WHSV) of 2 $g_{\text{2-butene}}\ g_{\text{HPW}}^{-1}\ h^{-1}$. Further details of the reaction system and experimental procedure have been described elsewhere (5). Before starting the run, the catalysts (0.59–0.84 mm particle size) were activated *in situ* at 300°C for 2 h in a nitrogen stream of 50 cm^3/min.

The reactants and products were analyzed by gas chromatography in a Varian 3400 GC equipped with a capillary column (fused silica, Supelco, 100 m length) and a FID. Individual C_4–C_8 isoparaffins were identified by GC-MS and commercially available reference mixtures.

3. RESULTS AND DISCUSSION

3.1. *Characterization of HPW-Supported Catalysts*

All the catalysts prepared show the typical IR bands at ca 1080 (P−O in the central tetrahedra), 982 (terminal W=O), 893 and 812 (W−O−W) cm^{-1} asymmetric vibrations associated to the Keggin ion, indicating that the primary

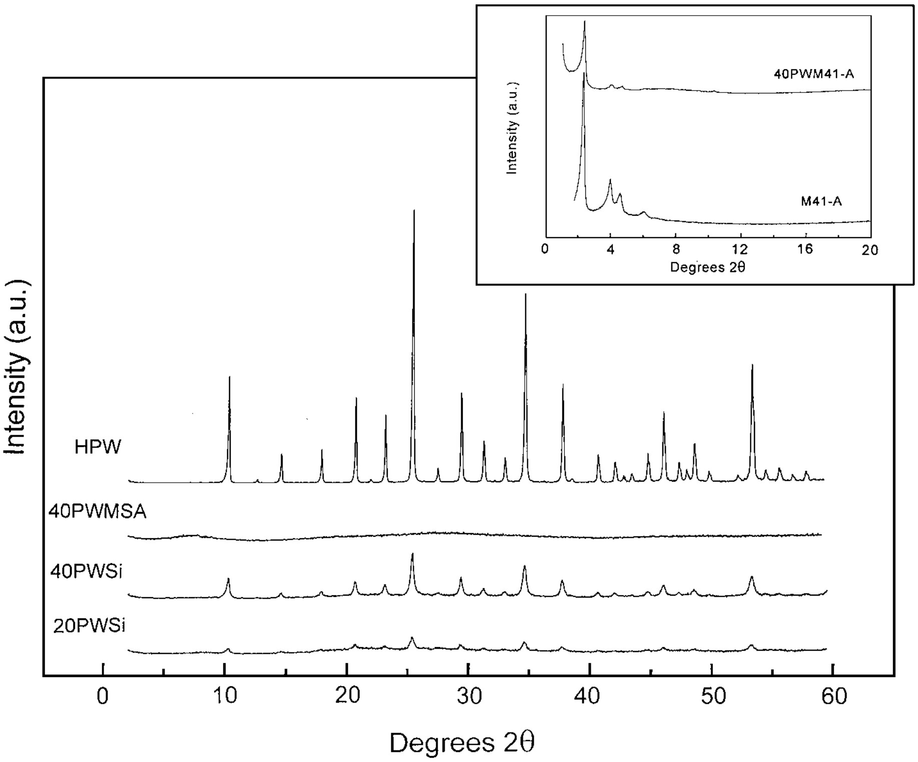

FIG. 1. XRD patterns of free HPW and different HPW-supported catalysts.

structure of the heteropolyacid is preserved after supporting it on the different carriers used.

The dispersion of the heteropolyacid on the catalyst surface can be inferred from the XRD patterns. It is seen in Fig. 1 that the secondary crystalline structure of the HPW readily develops at acid contents as low as 20 wt% for the SiO_2 support. As expected, the intensity of the peaks associated to crystalline hexahydrated HPW grows as the acid content increases. We have estimated the mean crystallite size of HPW in the HPW/SiO_2 catalysts from the XRD patterns by using the equation developed by Scherrer as proposed in (29). Following this methodology the estimated diameter of the HPW crystallites were 250, 300, and 350 Å for the HPW/SiO_2 catalysts with ca 20, 40, and 60 wt% acid loading, respectively, suggesting a decrease of the dispersion of the heteropolyacid when increasing acid loading. On the other hand, the approximate crystallite size of the heteropolyacid in a physical mixture of HPW and SiO_2 (40% acid content) was found to be of ca 600 Å, indicating a higher dispersion of the acid in the supported catalysts.

The calcined MCM-41 samples present the typical low angle diffraction peak characteristic of MCM-41 materials (22), as observed in Fig. 1 for the M41-A sample with lower pore diameter. The approximate pore diameter of the calcined MCM-41 samples estimated from the XRD reflections, assuming the typical 9 Å value for the wall thickness (30), is 29 and 66 Å for the M41-A and M41-B samples, respectively. As seen in Fig. 1, no HPW crystals were observed in the XRD of the PW/MSA and PW/M41-A catalysts with 40 wt% acid loading, suggesting a higher dispersion of the heteropolyacid on these supports as compared to silica.

The textural properties of the three series of HPW-supported catalysts are presented in Table 1. The data corresponding to the free supports are also included, together with the real HPW concentration (determined by ICP) and the fraction of surface of the support theoretically occupied by the heteropolyacid (Φ) with respect to the monolayer ($\Phi = 1$).

As seen in this table, the surface area and pore volume determined from the N_2 adsorption isotherms decrease after supporting the heteropolyacid on the three supports, the decrease being larger as the amount of supported acid increases. This is not surprising considering the very low surface area of bulk HPW (ca 5 m^2/g). However, the relative decrease of surface area and pore volume observed at similar HPW loadings are greater for the MCM-41 catalysts, and even more so for the M41-A sample with a lower pore diameter. This seems surprising, considering the high dispersion of the HPW on the latter sample, as observed by XRD (Fig. 1). The results presented in Fig. 1 show that even if the intensity of the XRD peaks of MCM-41 decreases after supporting the heteropolyacid, the mesoporous structure is almost preserved, and this cannot account for the sharp decrease of surface area and pore volume observed in

TABLE 1

Composition and Textural Properties of HPW-Supported Catalysts

Sample	wt% HPW	Φ^a (m^2/m^2)	$S_{B.E.T.}$ (m^2/g)	S_{micro} (m^2/g)	PV (cm^3/g)
SiO_2	0	—	137	8.9	0.61
20PWSi	20.1	0.43	79	14.4	0.33
40PWSi	37.8	1.04	67	12.7	0.25
60PWSi	60.0	2.57	54	10.5	0.15
MSA	0	—	719	254.1	0.46
20PWMSA	20.0	0.08	535	116.2	0.53
40PWMSA	40.8	0.23	429	109.5	0.50
60PWMSA	62.5	0.54	210	74.6	0.23
M41-A	0	—	1024	3.9	1.13
40PWM41-A	31.8	0.11	325	112.0	0.22
60M41-A	57.3	0.31	159	50.2	0.11
M41-B	0	—	720	81.0	0.84
40PWM41-B	34.6	0.17	414	89.2	0.44
50PWM41-B	43.8	0.25	325	91.0	0.32
60PWM41-B	65.1	0.61	156	52.5	0.13

[a] Fraction of support surface occupied by HPW ($\Phi = 1$ for monolayer).

the HPW/MCM-41 catalysts. Thus, we believe that this decrease is, rather, produced by blocking of the monodimensional channels of MCM-41 by small aggregates of HPW, which is not surprising, taking into account the size of the keggin anion (approx. 12 Å). Indeed, when the HPW is supported on a MCM-41 sample with pores of ca 66 Å of diameter (M41-B), the relative decrease in surface area was, at similar acid loadings, lower as compared with the catalysts prepared from sample M41-A. This further supports our hypothesis of pore blockage as the main cause of the strong decrease in surface area and pore volume observed for the HPW/MCM-41 catalysts.

It is also seen in Table 1 that by supporting the heteropolyacid the microporosity increases for M41-A, decreases for MSA, and has little effect for M41-B catalysts. This suggests that the mechanism of pore volume modification must be different in these systems, and, therefore, it should have a different influence on the activity of the HPW-supported catalysts.

The thermal stability of the HPW in the supported catalysts was studied by thermogravimetry and differential thermal analysis (TG-DTA). The DTA of the unsupported HPW shows two sharp peaks, one endothermic peak at ca 192°C and another exothermic at ca 602°C, associated to the loss of crystallization water and to the decomposition of the HPW structure into the corresponding single oxides, respectively (31). For the PW/Si samples decomposition of the heteropolyacid was seen to occur at a temperature ca 20°C lower than for the free acid (exothermic peak at ca 580°C), suggesting a decrease of the thermal stability of HPW when supported on silica, which can be related with the interaction of HPW with the surface sylanols of silica (32–34). The decomposition of HPW when supported on the two MCM-41 samples was observed at temperatures between 590–600°C, depending on the acid content, which is very close to that of the pure HPW. However, a significantly lower stability of HPW was observed in the case of the mesoporous aluminosilicate MSA, where the T_{max} of the high temperature exothermic peak was observed at 552 and 564°C for the PW/MSA samples with 40 and 60 wt% acid loadings, respectively. This may be ascribed to a stronger interaction of the heteropolyacid with the bridging Si–OH–Al groups associated to tetrahedral Al in MSA (27), as compared to the surface sylanols present in silica and MCM-41.

Thouvenot *et al.* (35) used the ^{31}P MAS NMR relaxation time as a probe to determine the dispersion of the HPMo heteropolyacid supported on silica. The mean relaxation time reaches a minimum for a given concentration of HPA that should correspond to the exact "saturation" of the silica surface by the Keggin anions and remains unchanged for further dilutions. This conclusion was reached assuming the presence of two types of $[PMo_{12}O_{40}]^{3-}$ anions with different ^{31}P NMR properties, as derived from similar observations on the $HSiMo/SiO_2$ system (36). Some of the anions are forming microcrystals on the silica surface and display a relaxation time similar to that of macrocrystals, while others are directly interacting with the surface Si–OH groups of the silica support and possess a much shorter T_1 relaxation time (35).

We have applied this methodology to study the dispersion and state of the $[PW_{12}O_{40}]^{3-}$ anions in the HPW/SiO_2 samples with different acid loadings. Figure 2 shows the

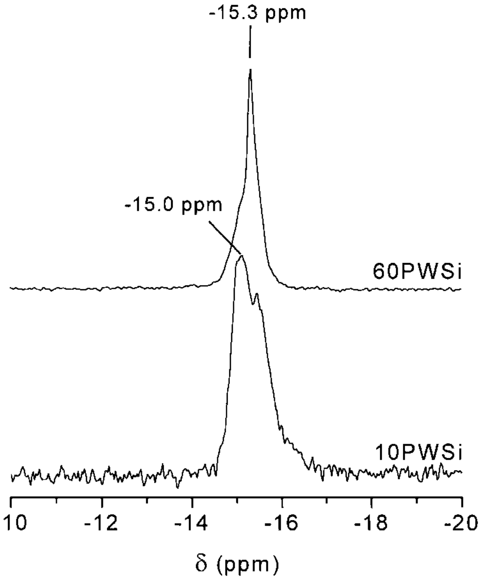

FIG. 2. ^{31}P MAS NMR spectra of two HPW/SiO_2 catalysts with low (10 wt%) and high (60 wt%) acid loadings.

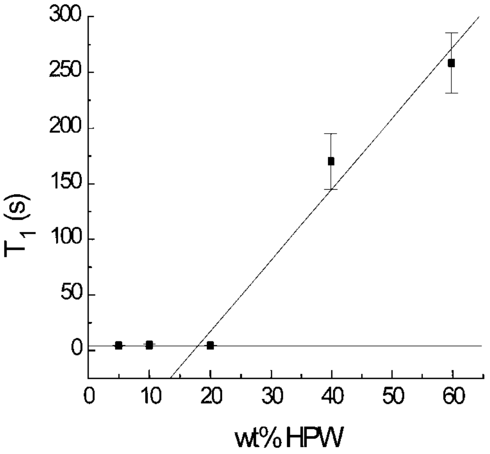

FIG. 3. ^{31}P MAS NMR relaxation times (T_1) of HPW/SiO_2 catalysts as a function of HPW content.

^{31}P MAS NMR spectra of two samples with low (ca 10 wt%) and high (ca 60 wt%) acid contents. It is clear from Fig. 2 that the spectra are constituted by the contribution of at least two peaks at −15.3 and −15.0 ppm, which have been previously attributed to $H_3PW_{12}O_{40}$ and $(SiOH_2)^+(H_2PW_{12}O_{40})^-$ species, respectively (38). The former peak, narrower than the high frequency component, increases with the HPW content and becomes predominant at high loading. The T_1 values measured here are represented in Fig. 3 as a function of the HPW content in the HPW/SiO_2 samples. At low loading, highly dispersed anion species interacting with the silica surface are predominant, leading to very short ^{31}P longitudinal relaxation times. At HPW loadings above ca 20 wt%, which should correspond to the true saturation of the silica surface, the anions aggregate to form $H_3PW_{12}O_{40}$ crystallites, giving rise to T_1 values that increase linearly with the HPW content. Accordingly, the relaxation time measured for the pure HPW has a minimum value of 450 s. These results show that the true saturation of the silica surface occurs at much lower acid loadings (ca 20 wt% HPW) than the ca 40 wt% loading theoretically predicted when considering the surface area of the silica and the area occupied by a HPW molecule (Table 1).

3.2. Isobutane/2-Butene Alkylation on HPW-Supported Catalysts

The initial (1 min TOS) 2-butene conversion obtained at 33°C on free and supported HPW catalysts is presented in Fig. 4 as a function of the acid loading. It is worth noting that the activity of the supported heteropolyacid is higher than that of the unsupported HPW. As we have previously shown (37) isobutane/2-butene alkylation is a "surface-type" reaction, and therefore the catalyst activity should be directly proportional to the number of the surface acid sites which are the ones accessible to the reactants. Then, the higher activity of the supported HPW with respect to the free acid can be ascribed to an increase in the number of surface acid sites when dispersed on the support surface.

In the case of SiO_2 and MSA catalysts a maximum activity is observed at HPW loadings of ca 40 wt%. In both cases a much lower activity is obtained for the simple physical mixtures of HPW and the supports (40 wt% HPW). Nevertheless, a higher activity is observed for the physical mixtures as compared to the free acid. This fact is not surprising, taking into account that the mean crystallite size of the heteropolyacid in the physical mixtures is much lower than that of the free HPW due to the crushing of the mixture of HPW with either SiO_2 or MSA during the homogenization of the mixture, as confirmed by SEM (not shown). Besides that, the relatively high activity observed for the physical mixture of HPW with MSA is also explained by the contribution of the aluminosilicate support to the overall activity. In fact, when the alkylation reaction is carried out over the HPW-free MSA material, about 40 wt% of the initial 2-butene was converted at TOS = 1 min, but the selectivity to TMP was very low (only ca 3% of the C_8 fraction).

At low acid loadings the number of surface acid sites increases, owing to a higher dispersion of the HPW (as deduced from XRD), but at the same time the average acid strength of the Brönsted sites decreases, owing to a stronger interaction with the support, as has been described in the literature for the HPW supported on silica (38) and on MCM-41 (39). It is concluded from these works that one proton of the heteropolyacid will react with the OH of sylanol groups present on the surface of the support leading to a $SiOH_2^+$ group, which should act as a counter ion for the

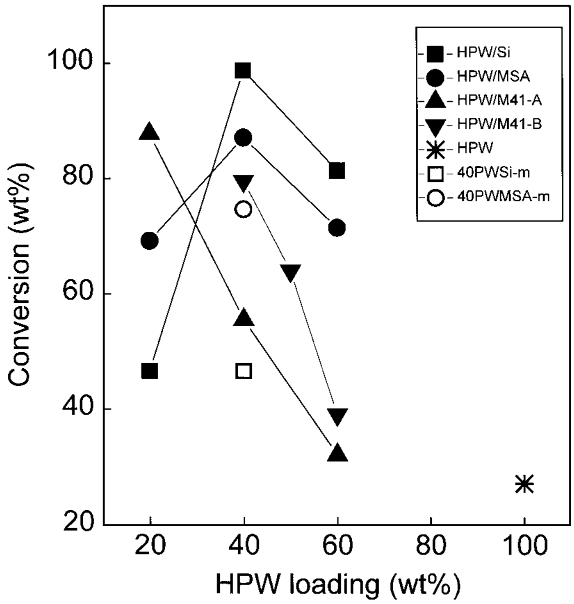

FIG. 4. Initial (1 min T.O.S.) 2-butene conversion of HPW-supported catalysts as a function of acid loading.

polyanion (38). This interaction should decrease not only the number, but also the strength, of the acid sites of the heteropolyacid molecules directly interacting with the support. Indeed, Gao and Moffat (40) consider the continuous increase in the ^{1}H MAS NMR chemical shift observed when increasing the acid loading as indicative of the changing environment of the proton and the acid strength. This change is particularly notorious up to acid loadings of about 30%, being the increase smaller for further loadings. Similar conclusions on acid strength were reached for HPW supported on carbon using microcalorimetry of NH_3 adsorption (41). On the other hand, at high HPW loadings the concentration of surface protons will be strongly reduced, due to the formation of large HPW crystallites, as has been estimated here from XRD data, even though the acid strength of those sites increase and approach that of the free heteropolyacid (38, 42). The opposite trends of a number of surface acid sites and their acid strength when increasing the acid loading can explain the maximum in catalytic activity observed in Fig. 4 for the HPW/silica and HPW/MSA catalysts. The fact that the maximum activity occurs at the same acid loading (ca 40 wt%) for both supports, despite their very distinct HPW dispersions (see Fig. 1) can be explained, on one hand, by the different extent of HPW-support interaction, and on the other, by the contribution of the Brönsted acid sites associated to framework Al present in the MSA support of the overall catalyst activity (see above).

Results in Fig. 4 show that, contrary to what has been observed for the silica and MSA supports, the activity of the HPW/MCM-41 catalysts (prepared from sample M41-A) continuously decreases when increasing the acid content from ca 20 to 60 wt%. Moreover, the activity significantly increases when increasing the pore diameter of the MCM-41 (catalysts prepared from sample M41-B). These results can be explained by a partial blockage of the unidimensional pores of MCM-41 produced by small aggregates of heteropolyacid, as already discussed.

The initial product distribution obtained on the HPW-supported catalysts displaying maximum catalytic activity, as well as that obtained on the unsupported heteropolyacid, is given in Table 2. As observed, the unsupported HPW gives a relatively high concentration of cracking products, C_5–C_7, and trimethylpentanes (TMPs) in spite of its much lower conversion (ca 27%), suggesting that the acid strength of its surface Brönsted sites should be higher than those present in the supported catalysts. When the HPW-supported catalysts are compared, it is seen that the silica-based sample produces a higher amount of cracking products, suggesting a higher strength of its surface acid sites as compared to MSA and MCM-41, in agreement with the lower acid dispersion and therefore larger HPW crystallites, as discussed before. The 40HPWSi catalysts gives the highest concentration of the desired TMPs within the C_8 fraction, being the 2,2,4-TMP the predominant isomer formed on this catalyst at the initial reaction stages. Furthermore, the lower amount of cracking products and TMPs produced at exactly the same conversion level by the 20PWM41-A as compared to the 40PWMSA sample suggests that the former possess Brönsted acid sites of lower acid strength. This fact is consistent with the lower amount of heteropolyacid in the MCM-41 catalyst, which as discussed above, should result in a higher HPW-support interaction.

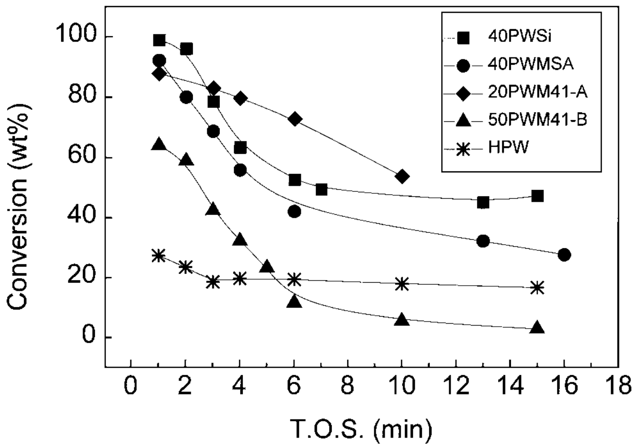

FIG. 5. Evolution of the 2-butene conversion with T.O.S. for unsupported and HPW-supported catalysts.

The decrease of 2-butene conversion with time on stream (TOS) is presented in Fig. 5 for the above catalysts. In all cases the olefin conversion decreases during the first 5–10 min TOS and then tends to reach a steady conversion at higher times. As observed in this figure, the catalyst based on MCM-41 with 20 wt% HPW loading deactivates at a lower rate during the initial period, but reaches a conversion similar to that of the 40PWSi sample after 10 min TOS. The lower deactivation rate of the MCM-41 based catalyst loaded with 20 wt% HPW may be related with the lower acid strength of its Brönsted acid sites, as discussed before. Indeed, it is known that very strong acid sites responsible for cracking and alkylation reactions deactivate faster than those of weak-medium strength which remain active for olefin oligomerization (7, 9). In fact, the 20PWM41-A catalysts produces more octenes in the C_8 fraction and gives a lower alkylation/dimerization ratio, as deduced from the lower $TMP/(DMH + C_8{=})$ ratio, from the beginning of the reaction as compared to the other HPW-supported samples (Table 2). At higher acid loadings, where blockage of the monodimensional pores is more important, the HPW/MCM-41 catalysts were the fastest decaying ones, as observed in Fig. 5 for the 50PW/M41-B sample. Furthermore, the chemical analysis of the catalysts before and after use showed that in all cases the loss of conversion with time on stream was not due to a loss of the HPW during the alkylation reaction, but to heavy hydrocarbons deposited on the

TABLE 2

Initial (1 min TOS) Product Distribution Obtained on the Free Heteropolyacid and Different HPW-Supported Catalysts

Catalyst	HPW	40PWSi	40PWMSA	20PWM41-A
2-$C_4^=$ conversion (wt%)	27.2	98.8	87.1	87.8
C_{5+} distribution (wt%):				
C_5–C_7	15.1	29.5	13.3	9.3
Total C_8s	71.6	59.5	70.2	74.6
C_{9+}	13.3	11.0	16.5	16.1
C_8's distribution (wt%):				
TMP	55.4	85.3	73.8	63.7
DMH	9.2	12.9	14.8	13.7
Octenes	35.4	1.8	11.4	22.6
TMP/(DMH + $C_8^=$) ratio	1.24	5.81	2.82	1.75
TMP's distribution (%):				
2,2,4-TMP	29.3	45.5	30.8	29.9
2,2,3-TMP	14.3	17.8	11.2	5.2
2,3,4-TMP	29.3	14.9	29.1	38.1
2,3,3-TMP	27.1	21.8	28.9	26.8

catalyst surface as observed by infrared and quantified by carbon analysis.

The evolution of the different reaction products as the catalysts deactivated were seen to follow a similar trend, irrespectively of the nature of support and acid loading; the concentration of C_5–C_7 and TMPs rapidly decreases during the first 3–5 min on stream in favor of octenes and heavier C_{9+} compounds. This trend in the product distribution with TOS indicates a change in the reaction pathway from alkylation to olefin oligomerization as a consequence of the faster deactivation of the strongest acid sites. Similar trends have been observed for other solid acid catalysts, such as zeolites (5) and sulfated metal oxides (7, 8), although the rate at which these changes occur obviously depended on the nature of the catalyst and reaction conditions.

4. CONCLUSIONS

We have shown that HPW-supported catalysts are active and selective for carrying out the alkylation of butene with isobutane at relatively low reaction temperatures. A higher alkylation activity is observed when amorphous silica is used as the support as compared to the mesoporous MSA aluminosilicate and all-silica MCM-41 materials. A maximum in activity, TMP's selectivity and catalyst stability is obtained for the silica-based catalyst with 40 wt% acid loading.

All silica MCM-41 should combine the good properties of silica with the high dispersions attainable owing to its high surface area. Unfortunately, a partial blockage of the monodimensional channels of MCM-41 by small aggregates of HPW occurs, decreasing the accessibility of the acid sites to the reactants. The pore blockage is more significant as the amount of heteropolyacid in the catalyst increases and can be minimized by increasing the mean pore diameter of the mesoporous molecular sieve. This may be one direction to follow in order to increase the catalytic performance of HPW/MCM-41 catalysts. We did not detect in the duration of the run any leaching of HPW.

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