

Acidic Cs⁺, NH₄⁺, and K⁺ Salts of 12-Tungstophosphoric Acid as Solid Catalysts for Isobutane/2-butene Alkylation

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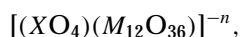
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The caesium, ammonium, and potassium salts of 12-tungstophosphoric acid (HPW) have been prepared with different stoichiometries ($1 \leq x \leq 3$), and their catalytic behavior measured for the liquid phase alkylation of isobutane with 2-butene at 80°C. The salts with a cation content of $2.5 \leq x \leq 3$, and that of Cs⁺ with $x = 2$, showed a much higher surface area than the parent acid, which is partially due to the formation of micropores. The micropores presented a fairly homogeneous distribution, with an average diameter in the range of 6–11 Å, depending on the type of cation and cation content. The activity of the heteropoly acid and their monovalent type B salts for isobutane alkylation could be correlated with the surface acidity of the solids. Thus, the initial (1 min TOS) olefin conversion went through a maximum for the NH₄⁺ and K⁺ salts with a cation content of $x = 2.5$, and in the range of $2 \leq x \leq 2.5$ in the case of the Cs⁺ compounds. (NH₄)_{2.5}PW showed a very high initial cracking activity (ca. 72 wt% C₅–C₇ in C₅₊), suggesting the presence of surface acid sites of a higher acid strength in the ammonium salt, as compared to the caesium and potassium salts with similar composition. In all cases the desired trimethylpentanes (TMPs) were the predominant compounds in the C₈ fraction formed in the initial reaction stages. The deactivation rate also depended on the nature of the cation exchanged in the heteropoly salts. © 1996 Academic Press, Inc.

INTRODUCTION

Heteropoly acids (HPAs) and related compounds have attracted increased interest in catalysis, owing to their ability to catalyze both acidic and red-ox processes (1–4). HPAs can be prepared with a wide variety of structural and chemical compositions, but those of the Keggin structure have been more extensively studied (4–6) because of their easier availability, higher stability, and better catalytic performance.

The Keggin-type HPAs are formed by heteropoly anions having the general formula



where X is the central atom or heteroatom, typically Si or P,

M is the peripheral atom, such as W or Mo, and n depends upon the oxidation numbers of X and M . In the primary structure the central atom is tetrahedrally linked to four oxygens (XO_4) and surrounded by 12 edge-sharing metal-oxygen octahedra (MO_6) (7). In the secondary structure the fundamental polyanions described above are bound to each other to form a solid. In the case of the Keggin compounds, the polyanions are organized in a *bcc* crystalline structure, in which the protonated water dimer $(H_2O)_2H^+$ is connected to four anions by hydrogen bonding at the more accessible terminal oxygen atoms of the anions (8).

The most stable and strongest acid in the Keggin series is H₃PW₁₂O₄₀ (abbreviated as HPW) (9), and for this reason it has been extensively studied as a catalyst for many acid-catalyzed organic reactions, both in homogeneous and heterogeneous systems (1–4, 10–12). In the solid acid form, HPAs have low surface areas and no explicit pore structures. In this case, nonpolar molecules such as hydrocarbons are unable to penetrate the bulk structure and react on the surface acid sites (surface-type reactions). However, polar molecules, such as water, alcohols, and esters can easily penetrate the bulk structure between the anion and the counteranions (H^+) accessing to all the protons and giving rise to the so-called “pseudoliquid phase” behavior (2, 11).

The protons in Keggin HPAs can be readily exchanged, totally or partially, by different cations without affecting the primary Keggin structure of the heteropoly anion. When large monovalent cations, such as NH₄⁺, Cs⁺, K⁺, and Rb⁺, are introduced (type B salts), the solids obtained are characterized by an increased surface area, higher thermal stability, and lower water solubility than the parent acid (6, 11, 13–15). Furthermore, the high surface area type B salts possessed a well defined microporous structure (15–17). The micropore structure was found to depend on the size of the alkali cation, as well as on the extent of ion-exchange and the preparative conditions (17–20). In addition, some of the partially exchanged monovalent salts showed high catalytic activity for a number of red-ox and acid-catalyzed reactions. In particular, the Cs_{2.5}H_{0.5}PW₁₂O₄₀ salt (abbreviated as Cs_{2.5}PW) was found to be more active than the pure acid (HPW) and even other strong solid acids, such as

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zeolites, Nafion-H, and sulfated zirconia (21–23), despite the fact that the acidity of Cs_{2.5}PW was lower than that of sulfated zirconia when measured by Hammett indicators (22). This striking behavior of the Cs_{2.5}PW salt was attributed to its high surface acidity and the high acid strength of the protons associated to the heteropoly anion.

Owing to their interesting catalytic properties, solid HPAs and the related high surface area monovalent salts have been explored as catalysts in processes where replacement of harmful liquid mineral acids, such as HF and H₂SO₄, is highly desired, as is the case of isobutane/butene alkylation (24). Unfortunately, the literature concerning the use of heteropoly compounds as solid catalysts for this process is very scarce. Okuhara *et al.* (23) reported that the Cs_{2.5}PW salt was even more active and selective than a sulfated zirconia superacid for the alkylation of isobutane with butene at room temperature. However, the SO₄²⁻/ZrO₂ sample used in that work, which was prepared from Zr(OH)₄ and H₂SO₄, was finally calcined at 650°C for 5 h prior to the alkylation experiments, and according to the results obtained in our laboratory (25) this is not the optimum calcination temperature for this reaction. Moreover, the activity data reported in (23) corresponded to 7 h on stream, and were probably affected by deactivation, making a direct comparison of the activity of the two catalysts quite difficult.

In this work we have studied the activity, selectivity, and deactivation behavior of solid HPW and their ammonium, caesium, and potassium salts with different degree of exchange ($x=1, 2, 2.5, \text{ and } 3$) during the liquid phase alkylation of isobutane with 2-butene at 80°C reaction temperature and 2.5 MPa total pressure.

EXPERIMENTAL

Preparation and Characterization of Catalysts

The parent 12-tungstophosphoric acid (HPW) was purchased from Aldrich and used without further purification (BET surface area of 6 m² g⁻¹). The Cs⁺, NH₄⁺, and K⁺ salts of HPW with different stoichiometries (M_xH_{3-x}PW₁₂O₄₀, $x=1, 2, 2.5, \text{ and } 3$) were prepared by slowly adding predetermined amounts of a 0.025 M aqueous solution of the corresponding carbonates to a 0.08 M solution of HPW at room temperature and under agitation, following the procedure reported by Nishimura *et al.* (21). The precipitates obtained together with the solution were subsequently evaporated to dryness at 40°C. In the case of the K⁺ and Cs⁺ salts, the degree of exchange of protons in the parent acid (x) was in good agreement with the expected theoretical value, whereas it was lower for the NH₄⁺ salts. In this latter case, an excess of cation (NH₄⁺/PW₁₂ molar ratio of 4) was used during the precipitation step in order to obtain the stoichiometric ammonium compound, (NH₄)₃PW₁₂O₄₀.

The larger deviation of the ammonium salts with respect to the expected degree of exchange as compared to the caesium and potassium compounds has also been observed by others (26).

The K⁺ and Cs⁺ contents of the salts were determined by atomic absorption spectrophotometry (AAS), after dissolving the solids in aqueous NaOH. For the ammonium salts, the cation composition was calculated from the nitrogen content determined by elemental analysis. The stoichiometry of the different salts, given by the cation content per Keggin unit (x), was referred to the W content as calculated by inductive coupled plasma (ICP) spectrophotometry.

IR spectra were recorded on a Nicolet 710 FTIR spectrometer at room temperature using KBr disks. X-ray diffractograms were obtained in a Phillips PW 1830 diffractometer using nickel-filtered CuK α radiation and a 2θ range of 5–60°.

Thermogravimetric (TG) and differential thermal (DTA) analysis of the parent acid and related salts were carried out on a Nest instrument using 0.02 g of sample, and heating in air gas flow (100 ml min⁻¹) from 25 to 800°C, and taking kaolin previously ignited at 1100°C as reference material.

Textural properties were measured by nitrogen adsorption–desorption at 77 K in an ASAP 2000 equipment (Micromeritics). The distribution of micropores in the range 0–60 Å of the high surface area salts was also studied by adsorption of Ar at 87 K in the same apparatus, and the mean size of the micropores was calculated using the Horvath–Kawazoe equation (27). In all cases the samples were outgassed at 100°C overnight and 300°C for 2 h under vacuum prior to the measurements of the isotherms.

Reaction System and Procedure

The alkylation experiments were carried out in an automated fixed-bed stainless steel reactor at 80°C reaction temperature, 2.5 MPa total pressure, a space velocity (WHSV) of 1 h⁻¹ referred to the 2-butene, and an isobutane/2-butene molar ratio of 15. Under these conditions both reactants and products are in liquid phase. Liquid isobutane (225 cm³ h⁻¹) and 2-butene (13 cm³ h⁻¹) are fed by means of two independent piston-type pumps. Preliminary experiments were carried out changing the total flows of isobutane and butene between 340 and 20, and 170 and 10 cm³ h⁻¹ respectively, always keeping constant the isobutane/butene molar ratio (15/1), and space velocity (1 h⁻¹). The results showed that under the conditions used in this work the reaction is not controlled by external diffusion effects. Catalyst particles of 0.59–0.84 mm diameter (8 g) were diluted with inert silica (50/50 by weight) before being loaded into the reactor, and activated at 300°C for 2 h in nitrogen flow prior to the catalytic measurements. Reaction products were depressurized at the reactor outlet,

diluted with a nitrogen stream ($50 \text{ cm}^3 \text{ min}^{-1}$), and vaporized before going to a heated 8-loop sampling valve connected to a gas chromatograph. This system allows collection of samples from very short (1 min or less) to larger times on stream at desired intervals, and to analyze them automatically in the GC at the end of the run. The first sample was collected within the first minute after products were detected at the reactor outlet. Therefore, the one minute time corresponds to $t = t_0 + 1$, t_0 being the time needed to fill up the system and which varies depending on flows. A GC with a 100 m capillary column (fused silica, Supelco) and a FID was used for the analysis of reactants and products. Individual C_4 – C_8 paraffins were identified by GC-MS and reference mixtures. A more detailed description of the reaction system and procedure can be found elsewhere (28).

RESULTS AND DISCUSSION

Catalyst Characterization

The chemical composition and textural characteristics of the ammonium, potassium, and caesium salts of HPW prepared with different stoichiometries are given in Table 1. It can be seen that all the three salts with $x > 2$ show increased surface area as compared to the parent acid. In the case of Cs_2PW a relatively high surface area is also obtained, as compared to the NH_4^+ and K^+ compounds with the same theoretical stoichiometry ($x = 2$). Furthermore, as already reported by Moffat *et al.* and based

TABLE 1

Chemical Composition and Textural Properties of the Ammonium, Caesium, and Potassium Salts of HPW Prepared with Different Stoichiometries

Sample	Cation/ K.U. ^a x	S_{BET}^b ($\text{m}^2 \text{ g}^{-1}$)	S_{micro}^b ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ^b ($\text{cm}^3 \text{ g}^{-1}$)	V_{micro}^b ($\text{cm}^3 \text{ g}^{-1}$)	AMD ^c (Å)
$(\text{NH}_4)_1\text{PW}$	0.84	11	6	0.0086	0.0031	—
$(\text{NH}_4)_2\text{PW}$	2.05	13	4	0.0086	0.0019	—
$(\text{NH}_4)_{2.5}\text{PW}$	2.40	70	51	0.0593	0.0256	7.7
$(\text{NH}_4)_3\text{PW}$	3.09	69	50	0.0659	0.0249	6.9
Cs_1PW	0.92	1	—	0.0051	—	—
Cs_2PW	1.89	63	46	0.0426	0.0229	8.3
$\text{Cs}_{2.5}\text{PW}$	2.33	119	43	0.0896	0.0211	10.6
Cs_3PW	2.81	92	33	0.0736	0.0163	10.4
K_1PW	0.99	3	—	0.0067	—	—
K_2PW	1.95	11	—	0.0088	—	—
$\text{K}_{2.5}\text{PW}$	2.41	60	45	0.0508	0.0223	7.2
K_3PW	2.72	52	44	0.0420	0.0219	6.9

^a Cation content per Keggin unit as calculated from chemical analysis.

^b Measured from the nitrogen adsorption measurements.

^c Average micropore diameter calculated from argon adsorption isotherms using the Horvath–Kawazoe equation (27).

on nitrogen adsorption-desorption isotherms and X-ray diffraction analysis (17–19), the micropores strongly contribute to the high surface area of type B salts. The average diameter of the micropores, as determined from N_2 adsorption-desorption measurements, was reported to be in the range of ca. 15–30 Å for the stoichiometric type B salts of HPW (18, 29). Recently (30), these authors have applied the ^{129}Xe NMR method developed by Ito and Fraissard (31) to characterize the microporosity of these materials, and concluded that they have a quite homogeneous and organized porosity as is the case for zeolites. The average micropore diameters determined from Xe NMR were lower relative to those obtained from the N_2 adsorption-desorption isotherms, but the Xe NMR data were in better agreement with the lattice parameters obtained from the XRD of the microporous heteropoly salts (30). Here we have applied the adsorption-desorption isotherms of argon to study the microporosity of our samples by using the Horvath–Kawazoe equation (27). This method has been successfully applied for characterizing the microporous structure of zeolites (32). Our Ar adsorption-desorption results confirmed the presence of a fairly homogeneous distribution of micropores with a mean diameter in the range 6–11 Å, depending on the nature of the cation and cation content (Table 1). These results were in good agreement with the values determined from Xe NMR (30). The Cs^+ salts show, in general, micropores of a higher diameter than the NH_4^+ and K^+ samples. Moreover, the contribution of mesopores to the total surface area, as determined from N_2 adsorption-desorption isotherms (Table 1), was also higher for the Cs^+ compounds, which is explained by the larger size of the Cs^+ cation, whereas the NH_4^+ salts were more microporous, in accordance with previous published data (17, 29). The micropores in type-B salts can result from a rotation and translation of the heteropoly anions, so that the barriers between the interstitial voids present in the parent acid are partially removed, allowing the formation of channels between the anions and the counter cations. Moreover, the increase of mesoporosity observed when increasing the cation size could be explained by an increase of the cubic lattice parameter of the heteropoly salt leading to wider interstitial voids (16, 19).

The IR spectrum of all samples showed the characteristic bands at ca. 1080 and 980 cm^{-1} assigned to the asymmetric stretching vibration of the P–O bond in the central PO_4 tetrahedron, and the stretching vibration of $\text{W}=\text{O}_t$ (terminal oxygen in the Keggin structure), respectively, which indicates the presence of the $\text{PW}_{12}\text{O}_{40}^{3-}$ anion after the exchange of protons in the parent acid by the different cations. In addition to these bands, the ammonium salts show a band at ca. 1420 cm^{-1} characteristic of the NH_4^+ cation, whose intensity increases as the cation content increases. As an example, the IR spectra of the parent acid HPW and the stoichiometric salts ($x = 3$) are shown in Fig. 1.

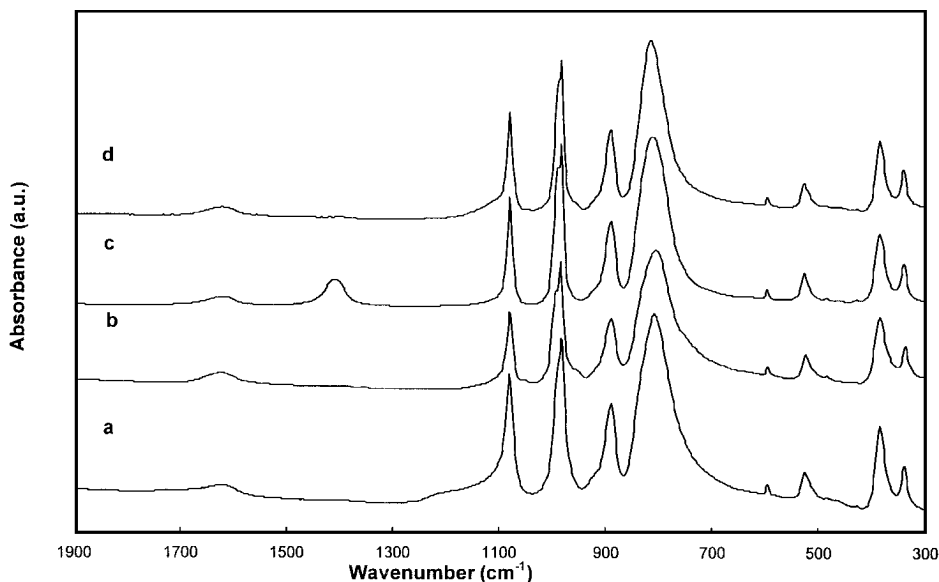


FIG. 1. FTIR spectra of the HPW acid (a) and their stoichiometric ($x=3$) salts: Cs_3PW (b), $(\text{NH}_4)_3\text{PW}$ (c), and K_3PW (d).

The X-ray diffractogram of the parent HPW reflecting the secondary crystalline structure of the heteropoly acid is known to depend on the amount of hydration water (33), and therefore on the pretreatment conditions. In our case, the XRD of HPW obtained from a 0.08 M aqueous solution after evaporation of water at 40°C (Fig. 2a) coincides with the XRD pattern reported for the hexahydrated HPW, corresponding to a cubic $\text{Pn}3\text{m}$ crystalline structure (8). The diffractograms of the stoichiometric salts are also shown in Figs. 2b–2d, and are in concordance with previously published data (34, 35). However, the XRD of the NH_4^+ and K^+ compounds with $x=1$ showed additional peaks, besides

the typical peaks of the stoichiometric salts shown in Fig. 2, whose position coincides with some of the peaks in the XRD of the parent HPW (Fig. 2a). These results may suggest that the solids obtained by precipitating the salt with a theoretical cation/anion ratio of 1 are a mixture of the parent acid and a crystalline salt. According to the results reported by Tatematsu *et al.* (36) for Cs^+ salts prepared in the same way as our samples (drying together the precipitates and solution) and mainly based on XRD data, the solids obtained with a composition of $0 \leq x < 2$ were a mixture of the free acid HPW and the Cs_2PW salt, whereas the solids prepared with $2 \leq x \leq 3$ were formed by a mixture of the Cs_2PW and

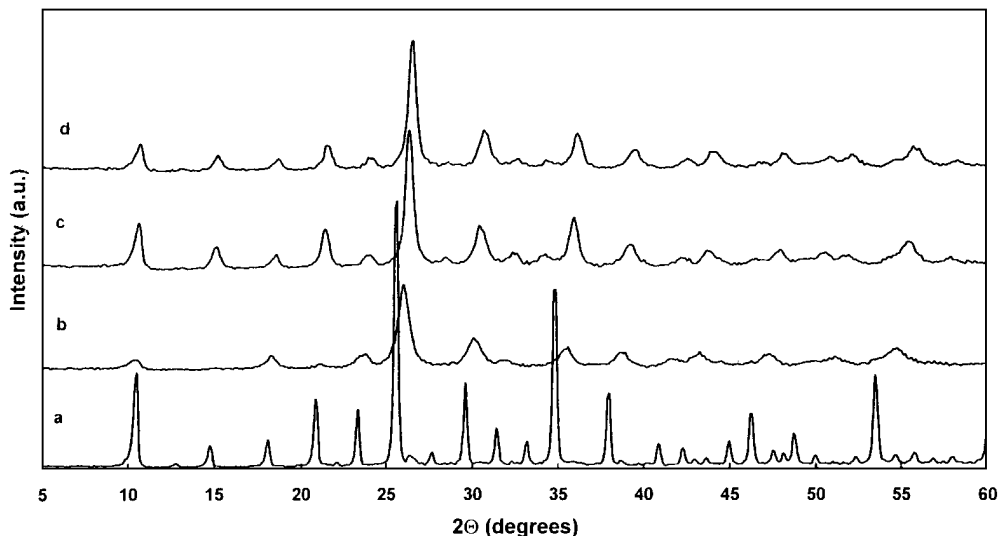


FIG. 2. XRD of the HPW (after evaporation of water at 40°C from a 0.08 M aqueous solution of HPW) (a), and their stoichiometric salts: Cs_3PW (b), $(\text{NH}_4)_3\text{PW}$ (c), and K_3PW (d).

Cs₃PW salts. The subsequent thermal treatment at 300°C would make possible the diffusion of Cs⁺ and H⁺, and probably would transform the mixture into more homogeneous acidic salts (36). Our XRD data seem to support the above hypothesis also in the case of the K⁺ and NH₄⁺ salts, and probably also for Cs⁺, although the XRD peaks of the latter samples are less intense and broader. Moreover, the diffractograms of the salts with a composition of $2 \leq x \leq 3$ show the same pattern, indicating that they would have the same crystalline structure. Furthermore, the XRD peaks of the three stoichiometric salts ($x = 3$) are shifted to lower angles, indicating an expansion of the unit cell volume, as the size of the cation increases, i.e., Cs⁺ > NH₄⁺ > K⁺ (Figs. 2b–2d).

Finally, the thermal stability of HPW and their salts was studied by TG-DTA analysis. HPW showed several endothermic peaks, with the most intense at ca. 53 and 188°C, associated to the loss of water of crystallization (33, 37) (ca. 5% mass loss up to 200°C), and an exothermic peak at ca. 602°C ascribed to the decomposition of the acid into the corresponding single oxides (38, 39). The Cs⁺, NH₄⁺, and K⁺ salts show a single endothermic peak at ca. 100°C and an endothermic peak in the range 580–600°C. In the case of the ammonium salts, the temperature of decomposition increases from 585 to 598°C as the cation content increases from $x = 1$ to $x = 3$ (theoretical).

Isobutane/2-butene Alkylation

Initial activity and selectivity. The reaction system used in this work allows to collect samples of products at very short times on stream (TOS), and therefore to compare the activity and selectivity of the different catalysts in the absence of deactivation. In this way the initial 2-butene conversion (1 min TOS) obtained on the different salts of

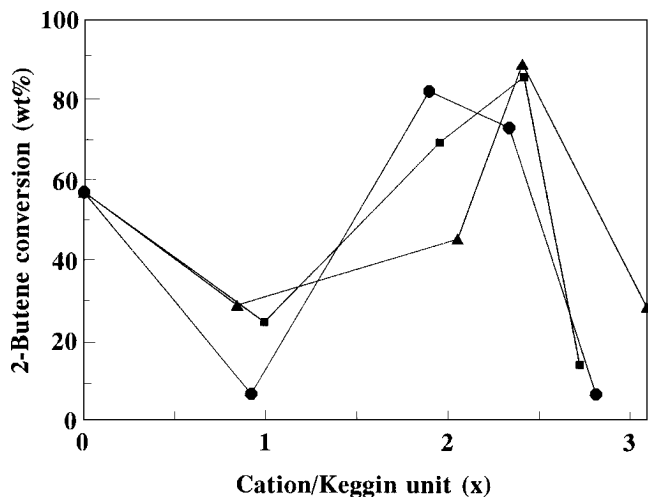


FIG. 3. Initial (1 min TOS) 2-butene conversion as a function of the cation content per Keggin unit (x) in the monovalent salts of HPW: (●) Cs _{x} PW, (▲) (NH₄) _{x} PW, and (■) K _{x} PW.

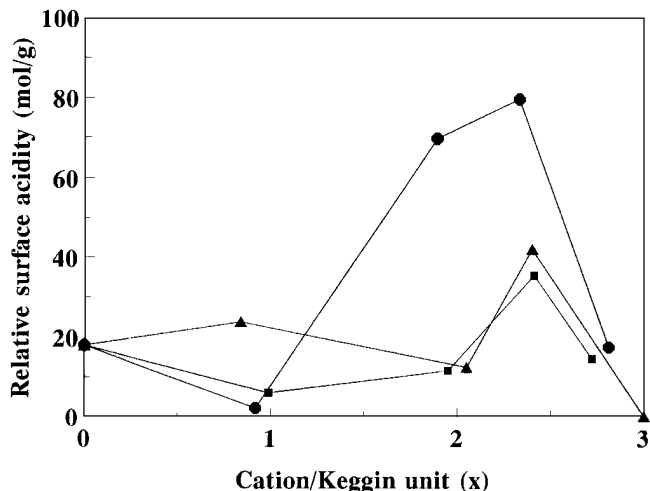


FIG. 4. Relative surface acidity as a function of cation content per Keggin unit (x). Same symbols as those found in the legend for Fig. 3.

HPW is given in Fig. 3 as a function of cation content per Keggin unit (x). The conversion obtained with the pure HPW acid under the same reaction conditions is also included in Fig. 3 as $x = 0$. It can be observed that the conversion does not follow a straight relationship with the total concentration of protons ($3 - x$) in the heteropoly compound, but it goes through a maximum for a cation content per Keggin unit of $x = 2$ or 2.5 depending on the particular cation. Reactions involving nonpolar molecules have been shown to occur on the surface acid sites of the heteropoly acids and their acidic salts, and in this sense they are classified as “surface-type” reactions. Examples of surface-type reactions on heteropoly compounds are butene isomerization, butane cracking, and propene oligomerization (34), *n*-butane isomerization (40–42), cracking of C₆–C₈ alkenes (43), and aromatics alkylation (21, 22). In these cases the activity does not correlate with the total proton content of the catalyst, but with the concentration of protons on the catalyst surface. Results of Fig. 3 show that alkylation of isobutane with 2-butene belongs to the surface-type class reactions on heteropoly compounds, and therefore, the catalyst activity is expected to increase with the surface acidity. Indeed, the relative surface acidity (Fig. 4), calculated as the product of the bulk acidity, $3 - x$, of the salt (and assuming a uniform composition throughout the surface and the bulk) and the specific surface area, varies similarly to the initial 2-butene conversion (Fig. 3) with the cation content, x , for each heteropoly salt. Figure 3 also shows that for the NH₄⁺ and K⁺ salts, the maximum in 2-butene conversion occurs for a cation content (theoretical) of $x = 2.5$, whereas for the Cs⁺ series it was in the range $2 < x < 2.5$. In this case, and in agreement with the expected surface acidity (Fig. 4), Cs₂PW and Cs_{2.5}PW give similar initial activities. This result is in contrast with the higher catalytic activity usually

reported for the Cs_{2.5}PW compound (36, 40, 44). Recently, Essayem *et al.* (41) have also found a maximum of activity for Cs₂PW in *n*-butane isomerization, which is known to be catalyzed by strong acid sites, whereas the maximum activity in methanol dehydration, which can be carried out on weaker acid sites, occurred for Cs_{2.5}PW. Our Cs₂PW sample possesses a relatively high surface area (63 m² g⁻¹), which is comparable to the 71 m² g⁻¹ reported by Essayem *et al.* (42). These results contrast with the low surface area previously reported for the Cs₂PW salt (45, 46). These differences in surface area may be caused by differences in the Cs content of the catalysts. Moreover, the preparation and activation conditions of the final precipitates, e.g. relative amounts of preparative reagents and calcination temperature, do also have a clear effect on the final textural characteristics of the solids (20, 47). This would also explain the differences in surface area observed for samples having similar composition.

It can also be observed in Fig. 3 that the parent acid, HPW, is more active than the partially exchanged salts with a theoretical composition of $x = 1$. This is explained by the very low surface area of the salts with $x = 1$, which in the case of Cs₁PW and K₁PW is even lower than that of HPW (Table 1), and also by their lower proton concentration, which determined a lower surface acidity. It should be noted that, despite its low surface area, HPW gives a relatively high initial conversion (ca. 57 wt%) when compared to the high surface area salts.

The acidity of heteropoly acids and some of the related acidic salts has been frequently determined by common characterization techniques such as Hammett indicators (22, 48, 49), IR spectroscopy with adsorbed bases (e.g., NH₃, pyridine) (34, 50, 51), TPD of NH₃ or pyridine (34, 38), NMR spectroscopy (52), and microcalorimetry of adsorbed ammonia (35). Among these techniques, microcalorimetry of adsorbed NH₃ is claimed to be the most reliable method to measure the acidity of these compounds (35). However, in all cases the total acidity of the catalyst (bulk and surface) is determined (the polar ammonia and pyridine molecules are capable of penetrating the bulk structure of the heteropoly compounds), and therefore, no correlation between the acidity measured by these techniques and the catalytic activity for surface-type reactions is often found (34). Then, determination of the catalytic activity of HPAs and related acidic salts for different surface-type reactions requiring different acidities is probably the best way to study the surface acidic characteristics of these catalysts. In this sense, our results obtained for isobutane/2-butene alkylation, a reaction requiring strong acid sites (24), showed that the activity can be correlated with the surface acidity of the heteropoly salts, giving a maximum for Cs₂PW, (NH₄)_{2.5}PW, and K_{2.5}PW salts.

On the other hand, the initial (1 min TOS) composition of the alkylate product formed on the different salts and the acid HPW is given in Tables 2–4. For each series of

TABLE 2

Composition of the Alkylate Product Obtained at 1 min TOS on the Cs_xH_{3-x}PW Compounds and the Parent Acid

Sample	HPW	Cs _x H _{3-x} PW			
		$x = 1$	$x = 2$	$x = 2.5$	$x = 3$
2-Butene conversion (wt%)	56.9	6.5	82.1	73.1	6.5
Initial rate (mmol/h g)	10.2	1.2	14.7	13.1	1.2
Relative yields (wt%)					
C ₅ -C ₇	36.5	1.1	43.8	21.0	0
TMP	35.4	0.3	29.9	38.5	0
DMH	7.8	3.7	10.8	13.8	0
Octenes	13.2	92.6	2.9	15.2	100
Total C ₈ 's	56.4	96.6	43.6	67.5	100
C ₉₊	7.1	2.3	12.6	11.5	0
TMP/DMH	4.5	0.1	2.8	2.8	—
TMP's distribution (%)					
2,2,4-	47.4	0	45.7	21.4	—
2,2,3-	16.8	31.6	20.3	11.9	—
2,3,4-	17.1	68.4	14.3	41.5	—
2,3,3-	18.7	0	19.7	25.2	—

salts the amount of light components (C₅-C₇ products), which are formed by the cracking of large oligomers on the strongest acid sites of the catalyst, increases as the activity of the salt increases, and is maximum for the salts showing maximum olefin conversion. On the contrary, the heteropoly compounds with $x = 1$ and $x = 3$ show a product distribution shifted toward the formation of octenes, which are mainly formed by dimerization of the butenes on acid sites of weaker acidity. However, and with the exception of the Cs⁺ salts, the NH₄⁺ and K⁺ compounds with $x = 1$ present a product distribution significantly different

TABLE 3

Composition of the Alkylate Product Obtained at 1 min TOS on the (NH₄)_xH_{3-x}PW Compounds

Sample	(NH ₄) _x H _{3-x} PW			
	$x = 1$	$x = 2$	$x = 2.5$	$x = 3$
2-Butene conversion (wt%)	28.7	45.3	88.9	28.3
Initial rate (mmol/h g)	5.1	8.1	15.9	5.1
Relative yields (wt%)				
C ₅ -C ₇	30.4	30.2	72.0	26.0
TMP	25.4	34.4	18.5	11.8
DMH	7.3	9.3	5.4	23.6
Octenes	28.2	19.5	1.0	36.1
Total C ₈ 's	60.9	63.2	24.9	71.5
C ₉₊	8.7	6.8	3.1	2.5
TMP/DMH	3.5	3.7	3.4	0.5
TMP's distribution (%)				
2,2,4-	39.2	41.2	49.9	16.1
2,2,3-	16.6	17.9	23.5	14.3
2,3,4-	21.1	18.7	10.3	37.5
2,3,3-	23.1	22.2	16.3	32.1

TABLE 4

Composition of the Alkylate Product Obtained at 1 min TOS on the $K_xH_{3-x}PW$ Compounds

Sample	$K_xH_{3-x}PW$			
	$x=1$	$x=2$	$x=2.5$	$x=3$
2-Butene conversion (wt%)	24.5	69.4	85.7	13.9
Initial rate (mmol/h g)	4.4	12.4	15.3	2.5
Relative yields (wt%)				
C_5-C_7	27.3	22.8	30.5	0
TMP	21.6	35.6	41.1	0
DMH	6.0	10.8	12.1	0
Octenes	20.0	11.5	2.3	100
Total C_8 's	47.6	57.9	55.5	100
C_{9+}	25.1	19.3	14.0	0
TMP/DMH	3.6	3.3	3.4	—
TMP's distribution (%)				
2,2,4-	39.3	38.9	43.8	—
2,2,3-	17.2	17.7	17.2	—
2,3,4-	21.1	18.8	16.5	—
2,3,3-	22.4	24.6	22.5	—

from that observed for compounds with $x=3$, despite both salts have a similar initial 2-butene conversion. The parent acid (Table 2) gives a higher concentration of cracked products (ca. 37 wt% C_5-C_7) than the Cs_2PW , K_2PW , and $K_{2.5}PW$ catalysts, despite the initial 2-butene conversion of the former catalyst was lower. Since the acid strength required to perform the different reactions occurring during isobutane/butene alkylation decreases in the order cracking > alkylation > dimerization (oligomerization) (24, 28), these results suggest a higher acid strength of the surface protons in HPW. Furthermore, HPW also gives a high selectivity toward the desired trimethylpentanes (TMPs) within the C_8 fraction, in accordance with the above hypothesis.

When the product distribution obtained is compared for the most active salts, that is Cs_2PW , $(NH_4)_{2.5}PW$, and $K_{2.5}PW$, all three catalysts giving similar initial 2-butene conversions (82–89 wt%), it can be observed that $(NH_4)_{2.5}PW$ gives a much higher initial cracking activity (72 wt% of C_5-C_7) than Cs_2PW (ca. 44 wt%) and $K_{2.5}PW$ (ca. 31 wt%). This leads to a lower concentration of the desired TMPs in the C_{5+} alkylate product in the case of $(NH_4)_{2.5}PW$. These results are in full agreement with those reported in the patent literature (53) claiming the use of the acidic monovalent salts of HPW for isobutane alkylation. Since all the three salts have comparable surface areas and micropore volumes (Table 1), the significantly greater cracking activity of the ammonium salt might be related with a higher strength of its surface acid sites, as compared to the caesium and potassium compounds. Indeed, the ammonium salts of HPW have shown a high catalytic activity for cracking C_6-C_8 alkenes (43). As a consequence of the lower cracking activity, $K_{2.5}PW$ gives the highest initial con-

centration of TMPs (41 wt%) in the C_{5+} alkylate. As seen in Tables 2–4, the relative distribution of the different C_8 compounds and that of TMPs in the initial alkylate product is very similar for the most active compositions of each heteropoly salt. Thus, TMPs are the predominant products (70–75 wt%) in the C_8 fraction, indicating that isobutane/2-butene alkylation is the favored process in the initial reaction stages on these catalysts. Furthermore, the thermodynamically favored 2,2,4-TMP is the most abundant isomer initially formed in the three active heteropoly salts.

Evolution with time on stream (TOS). The change in 2-butene conversion with TOS for the solid 12-tungstophosphoric acid and the most active Cs_2PW , $(NH_4)_{2.5}PW$, and $K_{2.5}PW$ salts is presented in Fig. 5. It can be seen that, under our reaction conditions, the 2-butene conversion rapidly declines with time during the first 5 min on stream for all samples, and then tends to reach a steady-state value at higher TOS. Despite the fact that the three salts gave similar initial (1 min) conversions, the rate of deactivation was clearly higher for $(NH_4)_{2.5}PW$, whereas it was similar for Cs_2PW and $K_{2.5}PW$. Moreover, the parent HPW deactivates faster than the latter two catalysts, but it stabilizes at a similar conversion level (about 30 wt%) at larger TOS. The fact that no correlation is found between the initial 2-butene conversion (Fig. 3) and the steady-state activity achieved by the different samples might be related to differences in the concentration of surface acid sites (which depended on the textural characteristics) and also with differences in acid strength distribution of the surface acid sites.

On the other hand, it has to be considered that conversion of 2-butene includes not only the desired isobutane/butene alkylation products (TMPs), but other competing parallel and consecutive reactions, such as

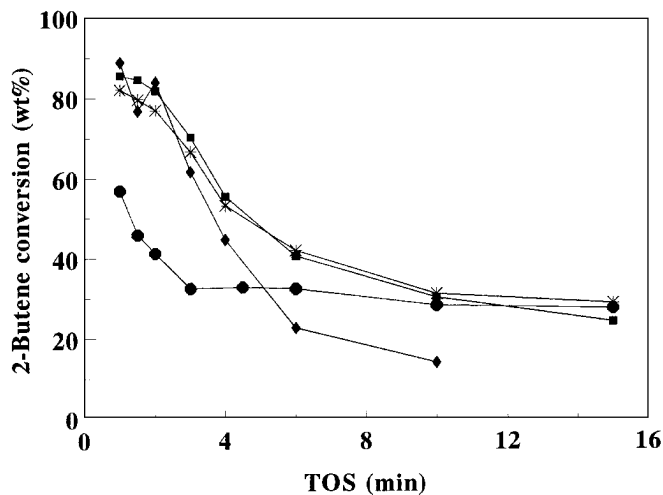


FIG. 5. Change in 2-butene conversion with time on stream (TOS) obtained during isobutane/2-butene alkylation on: (●) HPW, (*) Cs_2PW , (◆) $(NH_4)_{2.5}PW$, and (■) $K_{2.5}PW$ catalysts.

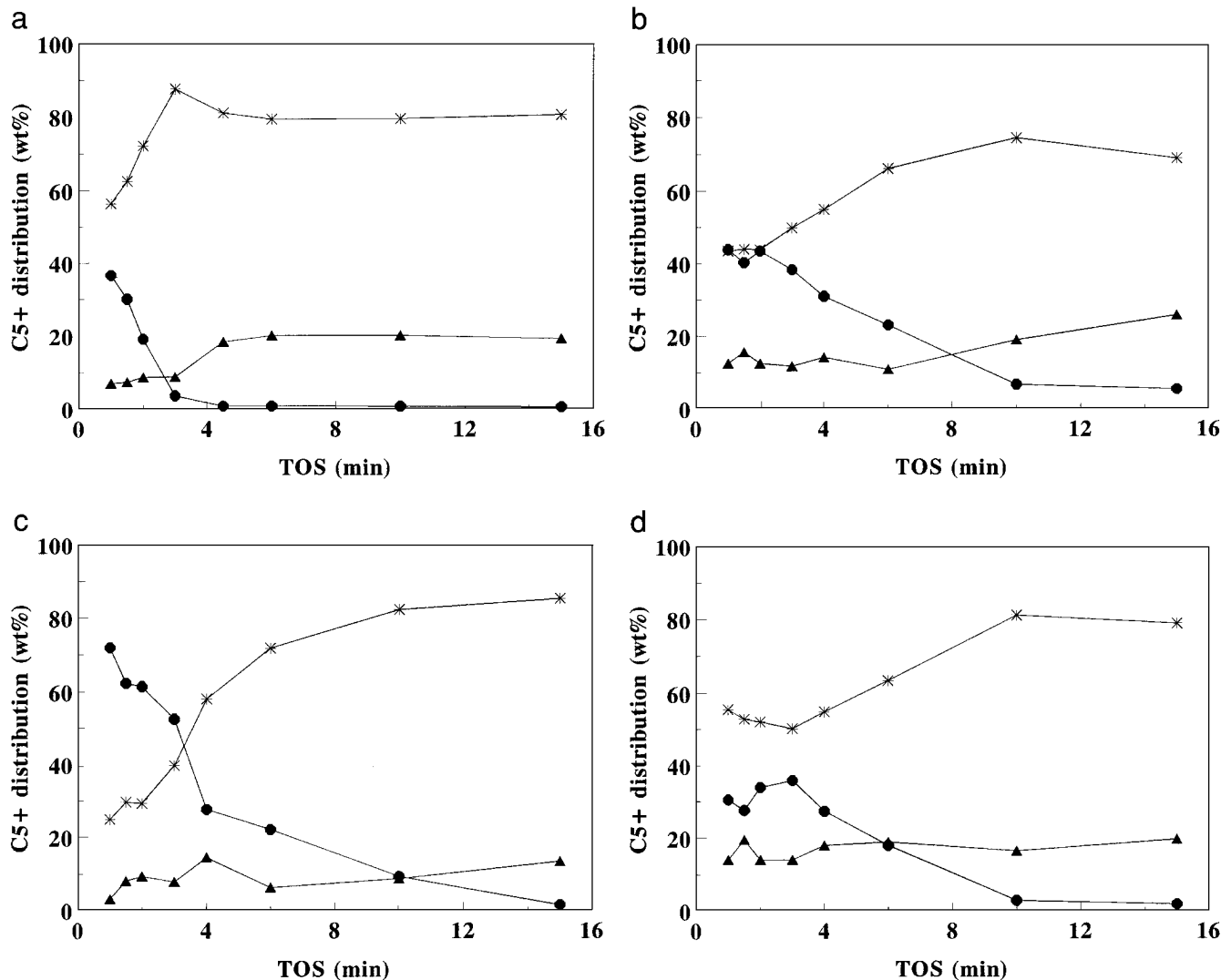


FIG. 6. Evolution with TOS of C₅-C₇ (●), C₈S (*), and C₉+ (▲) in the C₅+ alkylate product obtained on: (a) HPW, (b) Cs₂PW, (c) (NH₄)_{2.5}PW, and (d) K_{2.5}PW catalysts.

dimerization/oligomerization of the olefin, cracking of oligomers into light components, and hydrogen transfer reactions also take place during isobutane/butene alkylation (24). In order to further discuss the deactivation behavior of the catalysts it would be interesting to study the evolution of the different components of the product with catalyst aging. Thus, the change in the distribution of the different C₅+ products with TOS for the HPW and the most active salts of each cation is given in Figs. 6a-6d. In all cases, the concentration of cracked C₅-C₇ products rapidly decreases during the first minutes on stream and becomes negligible at larger TOS. This decrease is accompanied by a significant increase of C₈ products, which became the majority fraction in the reaction product after the rapid deactivation period, whereas the amount of C₉ and larger hydrocarbons changes little with time and generally slightly

increases in the latter stages of the reaction. In general, this is the same trend observed for other solid acid catalysts, e.g., zeolites (28, 54, 55) and sulfated metal oxides (25, 56, 57) during isobutane/2-butene alkylation. The strong decrease of C₅-C₇ products during the first stages of the reaction is ascribed to a rapid poisoning of the strongest acid sites of the catalysts, which are responsible for the cracking reactions. As seen in Figs. 6a-6d, the rate of decrease of cracked products is higher for the parent HPW and (NH₄)_{2.5}PW salt as compared to Cs₂PW and K_{2.5}PW, suggesting a faster poisoning of the strongest acid sites present in the former two catalysts, as discussed above. Due to the very low surface area of HPW as compared to their acidic salts, deposition of carbonaceous deposits on the solid surface, which is mostly responsible for catalyst deactivation, may account for the very rapid loss of catalyst activity and selectivity observed

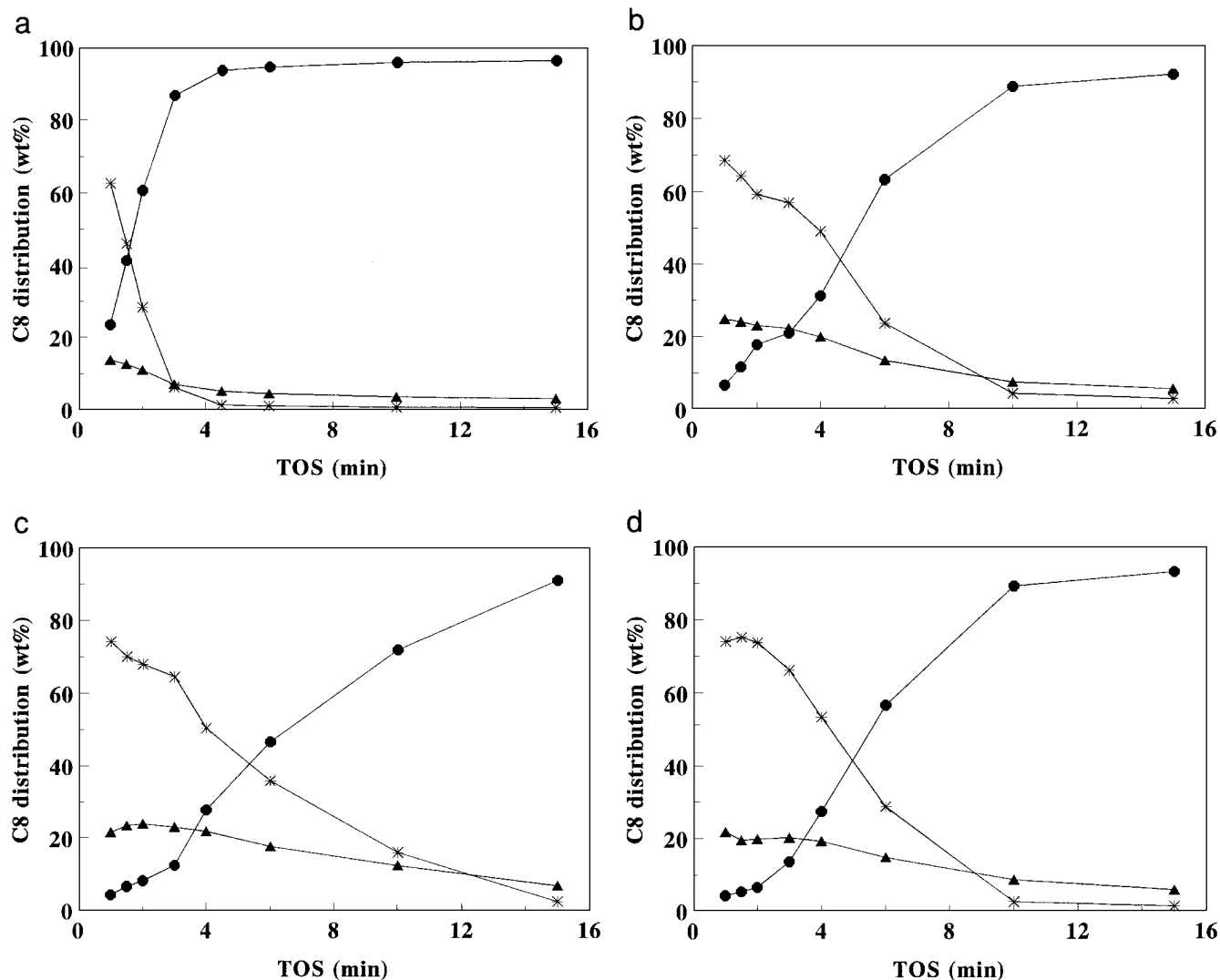


FIG. 7. Change in the concentration of TMPs (*), DMH (▲), and octenes (●) within the C₈ fraction with increasing TOS on: (a) HPW, (b) Cs₂PW, (c) (NH₄)_{2.5}PW, and (d) K_{2.5}PW catalysts.

for HPW. Indeed, no cracked products are formed on HPW after 4 min TOS, whereas the loss of cracking activity occurs at longer TOS for the high surface area salts.

Results in Figs. 6a–6d show that C₈'s are the majority compounds in the reaction product obtained on all samples after a given TOS. However, the distribution of the different compounds in this fraction also experiences dramatic changes as the catalyst deactivates. Figures 7a–7d show the evolution of the concentration of trimethylpentanes (TMPs), dimethylhexanes (DMHs), and octenes (mainly formed by 3,4-dimethylhexenes) within the C₈ fraction with increasing reaction time. Again, a general trend is observed for all catalysts; i.e., TMPs (which are the predominant compounds in this fraction in the initial reaction stages) decrease with TOS in favor of octenes, whereas the concentration of DMHs remains almost constant during the

first minutes TOS and then slightly decreases. It can be observed in Figs. 7a–7d that the rate of decrease of TMPs is much higher for HPW than for the monovalent salts, and that the loss of selectivity to TMPs occurs at higher TOS for the (NH₄)_{2.5}PW sample as compared to Cs₂PW and K_{2.5}PW, despite the 2-butene steady-state conversion was lower for the former salt (Fig. 5).

Alkylation of 2-butene with the tertiary *t*-C₄⁺ cation would give 2,2,3-TMP⁺ as primary product (24). The low concentration of 2,2,3-TMP in the TMP fraction observed in the initial reaction stages (Tables 2–4) is explained by a rapid rearrangement of the 2,2,3-TMP⁺ carbocation into the other TMP⁺ isomers before it desorbs from the catalyst acid sites after hydride transfer from another isobutane molecule. In all cases, the thermodynamically favored 2,2,4-TMP is the predominant isomer initially formed on these

catalysts. On the other hand, DMHs are mainly formed by dimerization of 2-butene on weaker acid sites, although in a much lower extent they can also be formed by alkylation of isobutane with 1-butene (24), the latter formed by isomerization of 2-butene on the catalyst acid sites. When the hydride transfer capacity of the catalyst is high (initial reaction stages) both TMP⁺ and DMH⁺ cations are desorbed as paraffins, and the olefin content in the alkylate product is low. As soon as the hydride transfer activity is lost, the carbocations desorb as olefins by giving back a proton to the catalyst. The low concentration of octenes observed on the most active heteropoly salts during the first min on stream indicates a high initial hydrogen transfer capacity, which is being lost as the catalyst becomes deactivated. This explains the continuous increase of octenes in the reaction products observed in Figs. 7a–7d, which are by far the predominant compounds in the latter stages of the reaction. As seen in Figs. 7a–7d, the faster the rate of decrease of TMPs, the faster is the rate of increase of octenes on the different catalysts, that is, the loss of selectivity to the true alkylation products (TMP) runs parallel to the loss of hydrogen transfer capacity of the heteropoly compound. Obviously, a high hydrogen transfer capacity will also determine a high concentration of *t*-C₄⁺ cations, and consequently, a high selectivity to alkylation products (TMPs). According to these results, deactivation of the alkylation sites and loss of hydrogen transfer activity occurs much faster on HPW than on the monovalent salts. Moreover, (NH₄)_{2.5}PW maintains the alkylation and hydrogen transfer capacities at higher TOS as compared to Cs₂PW and K_{2.5}PW. The high hydrogen transfer capacity of (NH₄)_{2.5}PW observed during isobutane/butene alkylation seems to be in agreement with the unexpected high concentration of saturated C₄ products reported during the cracking of C₆–C₈ alkenes on (NH₄)₃PW salts prepared from different ammonium sources (43).

CONCLUSIONS

Considering the initial activity and selectivity results and the deactivation behavior of solid HPW and their Cs⁺, NH₄⁺, and K⁺ salts, it can be stated that the ion-exchange process induces, besides the known changes in textural properties (increase of surface area and creation of a defined microporosity), modifications in the acid strength and strength distribution of the surface acid sites of the catalysts. It has been shown that the catalytic activity for isobutane/2-butene alkylation can be correlated with the surface acidity (number and strength of surface acid sites) of the catalysts, which in turn depended not only on the degree of exchange in the different salts (*x*), but also on the nature of the cation exchanged. Thus, a maximum in the initial (1 min TOS) olefin conversion was found for a cation content around *x* = 2.5 in the case of the NH₄⁺ and K⁺ salts, whereas the maximum occurred in the range 2 < *x* < 2.5 for

the Cs⁺ compounds. The high catalytic activity of Cs₂PW was ascribed to its relatively high surface area (63 m² g⁻¹) determining a high surface acidity. Furthermore, our alkylation results suggest that HPW not only has a lower concentration of surface acid sites than their high surface area monovalent salts resulting in a lower initial activity, as expected from its much lower surface area, but it probably has surface Brønsted acid sites of a higher acid strength, as reflected by its relatively high initial cracking and alkylation selectivities. The lower concentration of surface acid sites and the faster poisoning of the strongest acid sites may account for the rapid deactivation observed for HPW. On the other hand, the very high initial cracking selectivity and the higher stability toward the formation of TMPs and hydrogen transfer reactions observed at longer TOS for the (NH₄)_{2.5}PW salt suggests a higher concentration of strong acid sites on the surface of this salt as compared to Cs₂PW and K_{2.5}PW, all three samples having similar surface areas. Taking into account that the stronger acid sites responsible for cracking and alkylation reactions are poisoned faster than those of a lower acid strength acting for butene dimerization, the lower steady-state 2-butene conversion obtained on (NH₄)_{2.5}PW is also in agreement with a higher concentration of strong Brønsted acid sites on the surface of this catalyst.

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