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Preparation of bulk and supported heteropolyacid salts

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Abstract

We describe the preparation of bulk and supported cesium and ammonium heteropolyacid and acid salts of 12-tungstophosphoric acid. Novel synthetic schemes to prepare supported forms of insoluble cesium- and ammonium-acid salts are discussed, and their behavior in model compound isomerization and alkylation reactions is described. In particular, we discuss the egg-white morphology associated with Cs-acid salts supported on silica extrudates prepared by a novel in situ-reaction/precipitation route. We also describe hydrothermal techniques developed for directly preparing the ammonium-acid salts of 12-tungstophosphoric acid and the extension of that technique to other heteropolyacid salts.

Keywords: Heteropolyacid; Heteropolyacid salt

1. Introduction

Reducing halogens in the process stream remains an environmental goal of the petrochemical industry. One particular area that has attracted considerable research interest involves the replacement of liquid- or halide-containing acids by solid (oxide) acids [1–3]. Heteropolycompounds are one class of oxides that have stimulated some attention in this regard. Both synthetic and engineering challenges exist in applying these catalysts under industrially relevant conditions. In this work, we describe the preparation and reactivity of supported heteropolyacids and acid salts of 12-tungstophosphoric acid. Supporting the water-insoluble acid salts on large particle carriers has been a barrier in evaluating their properties under industrially relevant conditions.

Heteropolycompounds contain large polyanions separated by easily accessible and reactive protons, the source of the interesting acid properties. We focus on the most widely studied group of heteropolycompounds, namely those containing the Keggin anion, $AB_{12}O_{40}^{n-}$. This ion contains a tetrahedrally coordinated central cation A, surrounded by 12 octahedrally coordinated B cations. For the highest acid strength, one chooses A and B to minimize the charge on the Keggin anion. The lower charge produces a more stable anion which, in turn, increases the strength of the 'conjugate' acid. Consequently, the most commonly studied strongly acidic heteropolyacid has been 12-tungstophosphoric acid: $H_3PW_{12}O_{40}$ (HPW) [4–7].

Heteropolyacid salts, which are produced by partially exchanging protons of the parent heteropolyacid, often have different physical properties and solubilities than their parent acids, particularly when protons are exchanged with large cations. These large cation acid salts of HPW differ from those formed by exchanging small cations, such as Fe, Co, Ni, and Na. The latter resemble the parent acid in forming water-

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soluble phases crystallizing on solution evaporation with low surface areas (<5 $m^2 g^{-1}$). Partially exchanging Cs^+ cations for protons in 12-tungstophosphoric acid converts a water-soluble low-surface area (<5 $m^2 g^{-1}$) acid into a water-insoluble submicron particle-size acid salt with a surface area >100 $m^2 g^{-1}$. The large surface area results primarily from the small elementary particles that are formed. The unusual retention of strong acidity in these partially Cs-exchanged acid salts is strikingly different than the behavior that zeolites or amorphous acids exhibit when exchanged with alkali cations. This difference apparently results from the strong association of cesium with neighboring heteropolyanions so that residual protons are not 'poisoned.' The bulk protons of HPW have been shown to be accessible to polar reactants (pseudo-liquid behavior as described by Misono) [8].

Supported heteropolyacids are easily prepared by aqueous impregnation of the soluble acid [9–11]. On a noninteracting support, the heteropolyacid structure is retained but the acid particles are much smaller than in the bulk acid. Consequently, both bulk Cs–HPW- and NH_4–HPW-acid salts as well as supported HPW form small particles with an increased number of accessible protons. As we will show below, the bulk acid salts and the acids supported on noninteracting supports often have comparable reactivities; however, for high-temperature reactions in polar solvents, the supported acid may partially dissolve creating long-term stability and contamination problems. The acid salts do not present this problem, since they are insoluble even in liquids as polar as water.

The disadvantage of acid salts lies in their insolubility which makes conventional aqueous impregnation impossible. The small particles cannot be used in packed- or slurry-bed reactors because of pressure-drop or filtration problems. Consequently, a need exists to find practical ways of preparing acid salts on large (mm-sized) supports. We present here a simple in situ deposition technique that produces sharply defined internal thin rings (egg-white distribution) of the Cs-acid salt within a silica extrudate. We describe in detail both gas- and liquid-phase acid-catalyzed reactions over this catalyst. We also describe techniques to prepare supported ammonium-acid salts and extend the hydrothermal technique to the 12-tungstoboric acid system.

2. Experimental

X-ray diffraction spectra, collected on a Rigaku D-Max diffractometer using CuK_α radiation, identified the crystalline phases. The 12-tungstophosphoric acid (HPW) was either synthesized by acid condensation from sodium tungstate and sodium phosphate [12] or obtained from Baker. Bulk ammonium and cesium salts and acid salts of 12-tungstophosphoric acid were prepared by dropwise addition of ammonium and cesium carbonate solutions into an HPW solution, air-drying the resulting precipitate, and then calcining at 300°C.

Supported HPW was prepared by conventional incipient wetness impregnation onto silica powder (300 $m^2 g^{-1}$), and γ-Al_2O_3 (reforming grade, 195 $m^2 g^{-1}$). The samples were dried at 110°C overnight and then calcined at 300°C for 4 h. The silica-supported Cs-acid salt was prepared by sequential impregnation and in situ reaction on the support. First, cesium carbonate was impregnated by aqueous incipient wetness onto silica powder (Davison 62) or extrudates (1/16″ diameter, 260 $m^2 g^{-1}$), dried at 110°C and calcined at 300°C. Following this, the 12-tungstophosphoric acid was impregnated by a similar aqueous impregnation route, dried at 110°C and calcined at 300°C.

Silica-supported ammonium salts were prepared by three techniques: gas-phase reaction with ammonia, hydrothermal precursor synthesis, and urea co-impregnation. In the first route, a 40% HPW/SiO_2 sample (Davison 62 SiO_2 powder, surface area 270 $m^2 g^{-1}$), prepared by incipient wetness, was heated in a 5% NH_3/N_2 mixture at 150°C with a space velocity and for a time sufficient to titrate the HPW protons with NH_3. The sample was purged in nitrogen and heated to 300°C. In the hydrothermal route, a water-soluble precursor was prepared by reacting ammonium *meta*-tungstate $[(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O]$ with ammonium phosphate dibasic ($NH_4H_2PO_4$) in a 12/1::W/P molar ratio. Both starting materials were dissolved in water and heated in an autoclave at 150°C overnight. A solution was produced, which on drying at 120°C, formed an amorphous solid product. Calcination to 300°C yielded a crystalline salt, crystallographically identical to the conventionally prepared ion-exchanged ammonium salt. This soluble precursor, when impregnated onto silica powder, and calcined at 300°C produced a supported ammonium-acid salt catalyst. In the third technique, urea (H_2NCONH_2) was incorporated into an HPW solution in a molar ratio of urea/HPW::0.5–2/1 and impregnated onto silica. The resulting samples were dried and calcined at 300°C.

An analogous hydrothermal technique was extended to the synthesis of the ammonium salt of 12-tungstoboric acid by reacting ammonium borate with ammonium tungstate hydrothermally at 150°C. The synthesis was also done by solid-state reaction between ammonium fluoroborate and ammonium tungstate at 300°C.

Ammonia temperature programmed desorption (TPD) experiments were carried out in a unit containing a quartz reaction tube, a programable furnace, and a Balzer's quadrupole mass spectrometer. A gas containing 4010 ppm of NH_3 in N_2 served as a calibration standard. Approximately 0.5 g of catalyst was weighed and loaded into the reaction cell, heated in helium to 300°C, and then cooled to 110°C. A flow of 50 cm^3 min^{-1} of 5% NH_3 in N_2 was passed through the catalyst for 30 min to insure sufficient NH_3 to titrate all acid sites. A 100% N_2 flow (80 cm^3 min^{-1}) at 100°C for 150 min stripped off most physisorbed NH_3. The furnace was heated to 700°C at 10°C min^{-1} and the gaseous effluent was analyzed quantitatively.

All catalysts were evaluated by a 2-methylpent-2-ene (2MP2) probe reaction, as described previously [13]. The formation rates and rate ratios of the product-hexene isomers of this test reaction reflect the relative acid-site concentration and strength, respectively. The product-hexene isomers formed include both *cis*- and *trans*-4-methylpent-2-ene (4MP2), *trans*-3-methylpent-2-ene (*t*-3MP2), and 2,3 dimethylbut-2-ene (2,3 DMB2). 4MP2 requires only a double-bond shift, a reaction occurring at weak acid sites. 3MP2 requires a methyl group shift (i.e. stronger acidity requirement than double-bond shift), whereas the double-branched 2,3 DMB2 product requires even stronger acidity. For a homologous series of solid acids, differences in *t*-3MP2 rates normalized with respect to surface area reflect changes in the density of acid sites possessing strengths sufficient to catalyze the skeletal isomerization. Since skeletal isomerization rates generally increase with increasing acid strength, the ratio of methyl-group-migration rate to double-bond-shift rate should increase with increasing acid strength. The use of rate ratios, in lieu of individual conversion rates is preferable, since differences in acid site populations are normalized. Fig. 1 outlines the reaction pathways for this model compound test.

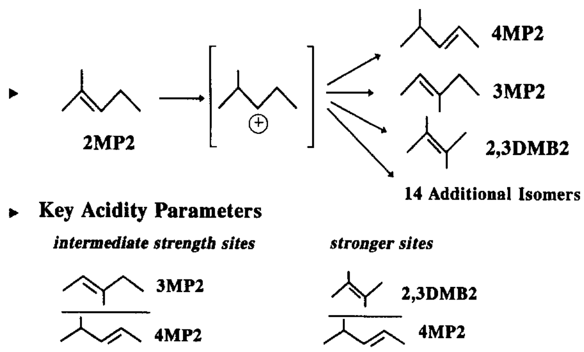

Fig. 1. Reaction scheme for 2MP2 isomerization acidity probe reaction.

Some catalysts were also evaluated for the liquid-phase aromatic alkylation of 1,3,5-trimethylbenzene (mesitylene) with cyclohexene as described earlier [14]. A catalyst of 0.5 g or the equivalent weight of supported catalyst (freshly calcined at 300°C) was loaded with 160 cm^3 of a premixed 5% cyclohexene in mesitylene solution into a 300 cm^3 Parr autoclave, heated to 100°C under N_2 at 15 psi and mixed at 600 rpm. The heat and stirrer were turned off 2 h after the temperature reached 100°C; the sample was then withdrawn and analyzed by GC.

3. Results and discussion

3.1. Bulk acid salts

The conventional preparation for alkali or ammonium-acid salts involves adding aqueous alkali or ammonium solutions to the acid [4,5]. The insoluble precipitates are too small to filter, so they are isolated by solvent evaporation. Misono has shown that the Cs-acid salt precipitates require calcination at 300°C to become compositionally uniform [15]. We tracked the formation of the Cs and NH_4^+ acid salts by pH and conductometric titrations, as seen in Fig. 2. As Cs_2CO_3 is added to HPW, the pH remains low until the $Cs/PW_{12}O_{40}^{3-}$ molar ratio approaches 3 and then rises rapidly, as the capacity of the acid to accept

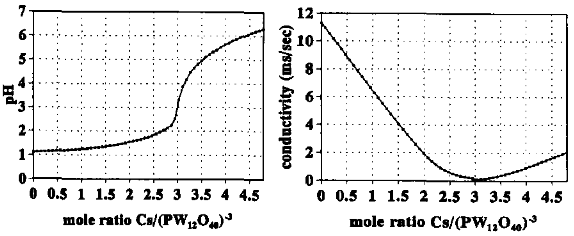

Fig. 2. pH and conductometric titration of HPW with cesium carbonate.

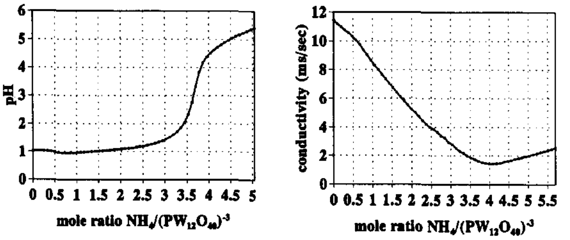

Fig. 3. pH and conductometric titration of HPW with ammonium carbonate.

additional Cs ions is exceeded. The corresponding conductometric curve also passes through a minimum at 3 Cs atoms per each Keggin ion. As the number of Cs atoms approaches 3 per Keggin anion, one would expect that the Bronsted acidity of the phase would disappear since no protons remain.

The ammonium-acid salts behave differently. As Fig. 3 shows, titration of HPW with ammonium carbonate goes to completion only when the nominal $NH_4^+/PW_{12}O_{40}^{3-}$ molar ratio exceeds 3. To verify our results, we checked the normality of the titrating ammonium carbonate solution with a standardized 0.1 M HCl solution. Consequently, formation of $(NH_4)_3PW_{12}O_{40}$ requires more than 3 ammonium ions in solution per Keggin ion. A nominal preparation of $(NH_4)_3PW_{12}O_{40}$ formed by stoichiometric ion exchange produces a solid with an actual composition close to $(NH_4)_{2.2}H_{0.8}PW_{12}O_{40}$.

We evaluated samples from the solid-solution series, $H_{3-x}M_xPW_{12}O_{40}$ (M = Cs, NH_4, calcined at 300°) by the 2MP2 isomerization test. For the Cs-acid salts, the 2,3-DMB2/4MP2 rate ratio (i.e. the marker for stronger acid sites) passes through a maximum at $x = 2.5$. This is consistent with prior results that show a maximum activity at $x = 2.5$ for isopropanol dehydration [15]. Recent studies suggest that this maximum represents a compromise between increasing pore size (accessibility) of reactants as x increases from 2.0 to 2.5, and decreasing proton concentration as x increases from 2.5 to 3 [16]. Fig. 4 also suggests that between $x = 2.5$ and 3.0, the sites strong enough to catalyze the more difficult acid reactions are replaced by ones capable of catalyzing facile reactions (like double-bond migration).

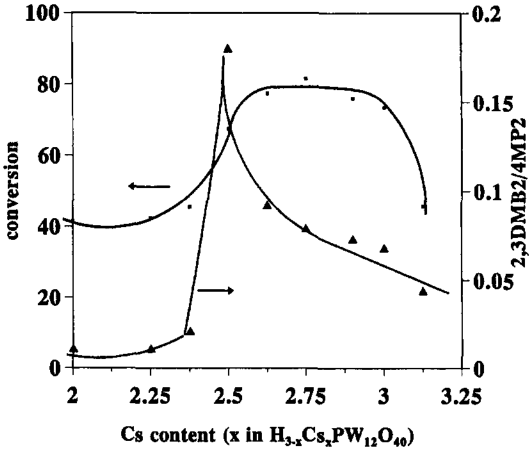

Fig. 4. 2MP2 acidity test for $Cs_{3-x}H_xPW_{12}O_{40}$ ($2 < x < 3.1$).

For the ammonium-acid salts, the actual ammonium content is lower than the nominal content. Fig. 5 clearly shows this effect during the conversion of 2MP2, where the formation rate of 2,3 DMB2 increases for $(NH_4)_{3-x}H_xPW_{12}O_{40}(0 < x < 3)$ as x varies from a nominal value of 0 to 3. As with the Cs-acid salt, there is a complex interplay of surface area,

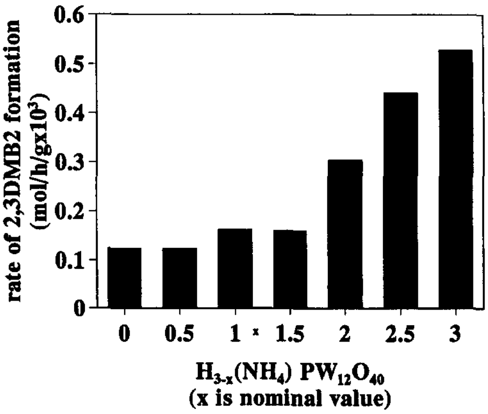

Fig. 5. 2MP2 acidity test for $(NH_4)_{3-x}H_xPW_{12}O_{40}(0 < x < 3)$.

Table 1
Comparison of alkylation of 1,3,5 trimethylbenzene with cyclohexene at 100°C after 2 h

Catalyst	Catalyst (g)	Calcination temperature (°C)	% Cyclohexene conversion at (2 h)
Amorphous SiO_2–Al_2O_3 (75% SiO_2; 25% Al_2O_3)	0.5	500	0.8
H-Mordenite	0.5	450	1.2
Bulk 12-tungstophosphoric acid $H_3PW_{12}O_{40}\cdot 6H_2O$ (HPW)	0.5	120	1.1
Bulk ammonium salt of 12-tungstophosphoric acid $(NH_4)_3PW_{12}O_{40}$	0.5	300	28.0
ZrO_2/SO_4	0.5	575	1.2
24% HPW/SiO_2	2.06 (0.5 g HPW)	300	98.0
Bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.5	300	90.0

pore-size and proton-concentration determining activity that has not been completely unraveled. However, since the isomerization rate should decrease as full proton occupancy is achieved ($x = 3$ if stoichiometric exchange is occurring), this behavior is consistent with an NH_4 content lower than the nominal value.

We examined several catalysts for the alkylation of mesitylene (1,3,5-trimethyl benzene) with cyclohexene at 100°C, similar to the procedure described by Okuhara et al. [17]. The results in Table 1 show that both the bulk Cs-acid salt of HPW and HPW-supported on silica are active catalysts for mesitylene alkylation. Independent of the NH_4^+ level, we found the bulk ammonium-acid salts less active than the optimum Cs-acid salt. Since the reactants are nonpolar, the reactivity for bulk HPW is low.

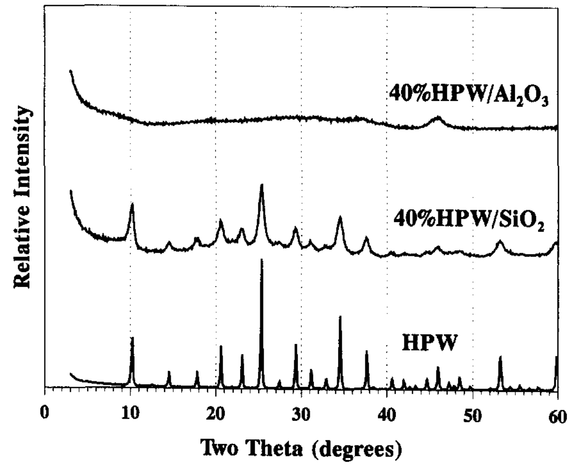

Fig. 6. X-ray diffraction scan of bulk, silica- and alumina-supported HPW.

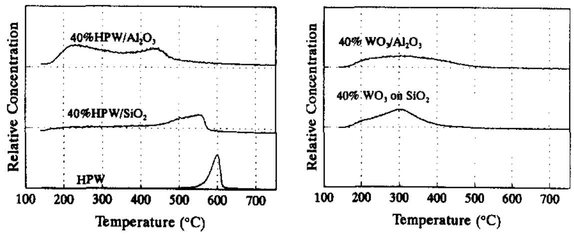

Fig. 7. NH_3 TPD of bulk HPW, HPW and WO_3 supported on Al_2O_3 and SiO_2.

3.2. Supported acids

We monitored the behavior of 12-tungstophosphoric supported on silica and alumina prepared by simple aqueous impregnation, drying, and low-temperature (300°C) calcination. HPW retains its crystallinity and forms small particles on silica, whereas on alumina, an amorphous X-ray pattern is found, similar to that observed with a WO_3 precursor (ammonium metatungstate, AMT) (Fig. 6). This result suggests that HPW either forms small crystallites (< 40 Å) on Al_2O_3 or it decomposes substantially. Acidity probe reactions and NH_3 TPD suggest the latter. In Fig. 7, the temperature-desorption spectra of silica and alumina-supported HPW and WO_3 are shown. NH_3 desorbs from a bulk HPW sample (with a molar ratio of NH_3 to total protons near unity) at temperatures near 575°C. The desorption pattern of HPW on silica resembles that of bulk HPW and the number of

Table 2
NH_3 adsorption titers on HPW, and silica and alumina-supported HPW and WO_3

Catalyst	µmol of NH_3 per g	µmol of H^+ per g	µmol of WO_3 per g
Bulk HPW	860	1042	
40% HPW/Al_2O_3	672	436	
40% HPW/SiO_2	441	436	
40% WO_3/Al_2O_3	790		1725
40% WO_3/SiO_2	791		1725

micromoles of ammonia desorbed correspond closely to the number of protons (Table 2).

The supported WO_3 catalysts adsorb about 1 NH_3 molecule for two tungsten-oxide groups. The desorption spectrum of HPW supported on alumina behaves similar to WO_3 supported on alumina both in the temperature of desorption and in the number of ammonia molecules adsorbed per tungstate group. These results suggest that HPW has substantially decomposed to WO_3 on the alumina support. This instability may relate to the surface acidity of the support in aqueous suspension. Silica is more acidic in aqueous suspension than alumina (isoelectric point of 2 vs. 8), so that in the presence of the basic sites on alumina, the acid is probably not stable and decomposed predominantly to WO_3. Consequently, we choose silica as the support for heteropolyacid salts.

The rate ratio for the acid on silica and alumina was compared for 2MP2 isomerization. As seen in Table 3, the acid strength of HPW/SiO_2 is substantially higher than for a catalyst prepared with tungsten oxide (ammonium metatungstate precursor). Calcining the SiO_2-supported HPW to 500°C lowers the activity close to the value observed with WO_3/SiO_2. On alumina, catalysts prepared with either WO_3 or HPW show similar acid strengths. These data support the X-ray and TPD results showing that HPW supported on silica maintains the unique HPW structure whereas, on alumina, HPW decomposes and resembles a WO_3 catalyst. The apparent higher value of the rate ratio for the catalysts on alumina vs. silica appears to result from more rapid deactivation of the stronger acid sites initially present on SiO_2, an effect we have seen earlier with the 2MP2 reaction test on zeolites. Catalytic results for aromatic alkylation [18] and paraffin isomerization [19] clearly show the stronger acid sites on the HPW/SiO_2 catalysts.

3.3. *Supported acid salts*

We have found a novel in situ reactive deposition technique to prepare supported Cs-acid salts. A soluble cesium salt is first impregnated onto silica, dried and calcined, and the support is then impregnated with the soluble (HPW) acid, dried and calcined. The X-ray diffraction spectrum of the Cs-acid salt supported on silica extrudates clearly shows the presence of the Cs-acid salt (Fig. 8). As an analogy to the bulk Cs-acid

Table 3
Rate ratios for 2MP2 isomerization at 250°C for 1 h for supported acids

	40% HPW (300°C)	40% HPW (500°C)	40% WO_3(AMT) (300°C)	40% WO_3(AMT) (500°C)
Support	SiO_2	SiO_2	SiO_2	SiO_2
Phases present in X-ray	HPW	WO_3	Amorphous	WO_3
Surface area	134	155	172	181
3MP2/4MP2; 2,3DMBD2/4MP2	1.75; 0.21	0.77; 0.12	0.59; 0.048	0.55; 0.044
Support	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3
Phases present in X-ray	γ-Al_2O_3	WO_3	γ-Al_2O_3	WO_3
Surface area	102	115	89	103
3MP2/4MP2; 2,3DMB2/4MP2	2.04; 0.27	1.27; 0.16	1.75; 0.20	1.62; 0.22

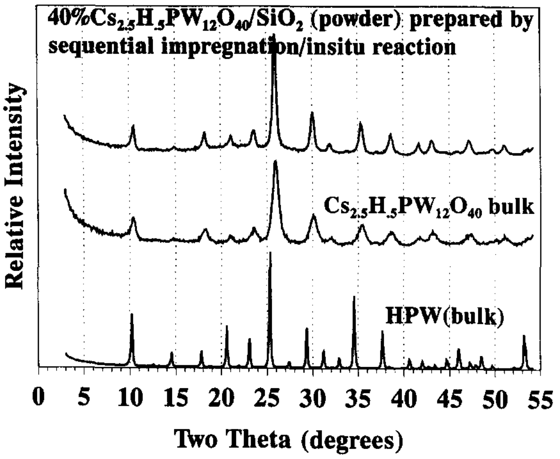

Fig. 8. X-ray diffraction scan of 40% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported in SiO_2 extrudate prepared by in situ reactive deposition procedure.

salt, the reflections shift slightly to higher 2θ values relative to $H_3PW_{12}O_{40}{\cdot}6H_2O$ (i.e. HPW dried at 110°C), indicating contraction of the unit cell as $H_5O_2^+$ ions are replaced by the smaller Cs^{+1} ions. In Fig. 9, the unusual egg-white rings of the Cs-acid salt are clearly seen within the 1/16″ diameter silica extrudates (surface area: 260 m^2 g^{-1}, pore volume: 1.1 cm^3 g^{-1}, and median pore diameter: 180 Å) by backscattered electron imaging. The bright white areas contain the large Cs and W scatterers, and EDS measurements indicate that Cs and W are always present in the same locations. Nearly 80–90% of the Cs-acid salt is present in a ring ~10 μm thick located more than half way into the 1/16″ diameter extrudates.

During the initial impregnation, at high pH, Cs ions apparently exchange with the protons of the surface

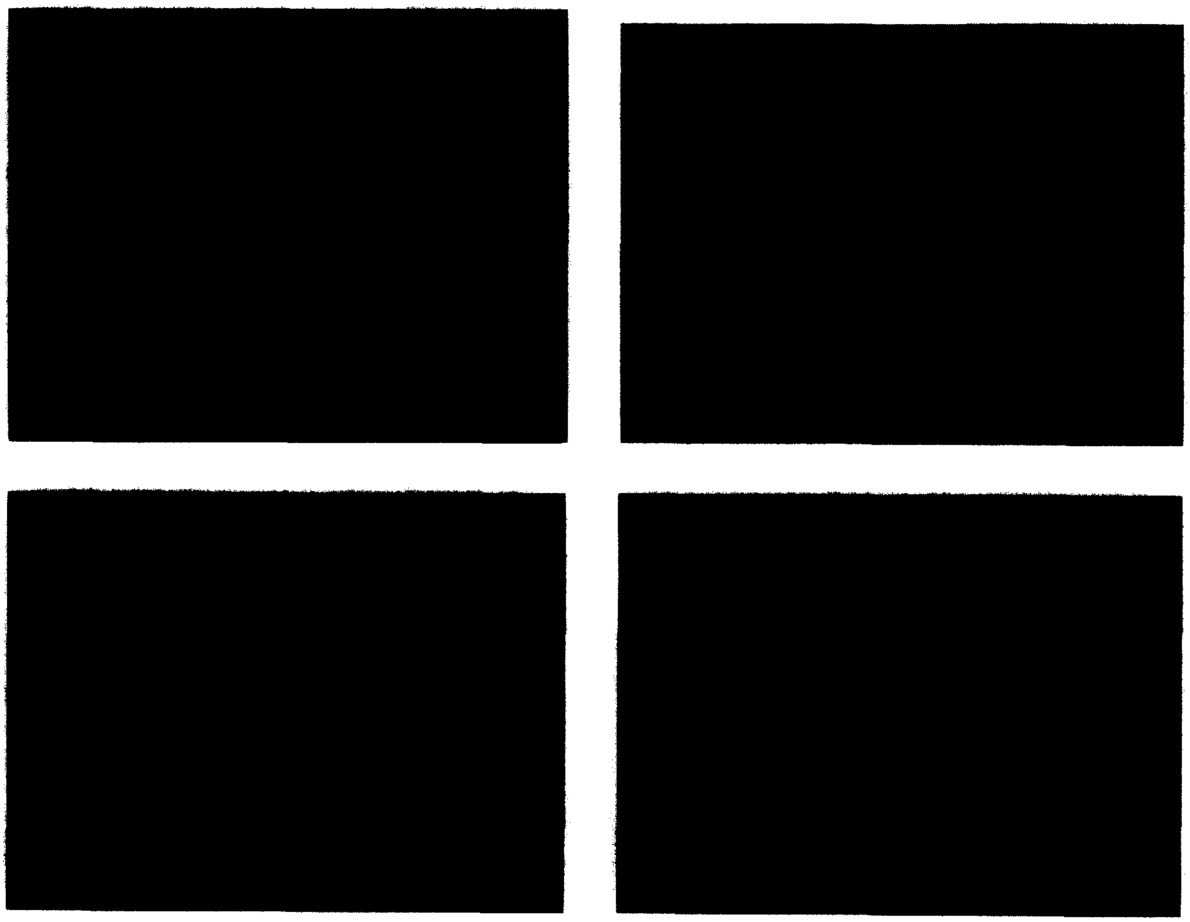

Fig. 9. Backscattered electron image of 40% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported in SiO_2 extrudate showing unusual egg-white distribution of acid salt.

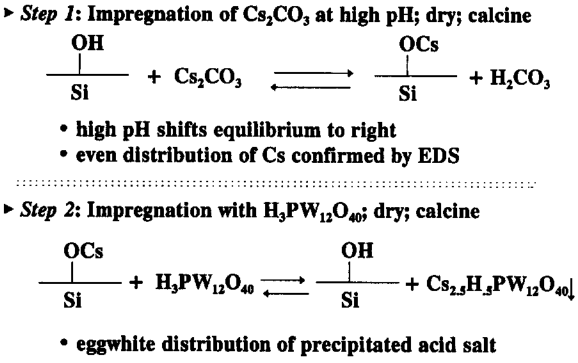

Fig. 10. Proposed mechanism for egg-white ring formation.

hydroxyls, creating an even distribution of surface Si–O–Cs groups. EDS confirms an even Cs distribution following impregnation and calcination, but before acid addition. During the subsequent impregnation with 12-tungstophosphoric acid, protons from the acid exchange with and release Cs ions attached to the surface, so that a homogeneous, rapidly moving front of composition, $H_{3-x}Cs_xPW_{12}O_{40}$, passes into the extrudate. As the front progresses further into the extrudate, x increases. When a critical content of Cs is reached, the acid-salt precipitates, creating a well-defined egg-white pattern within the extrudate. The proposed mechanism is illustrated in Fig. 10.

Not surprisingly, transport limitations affect catalysis over the egg-white catalyst, particularly for liquid-phase reactions. Table 4 compares a catalyst of 40% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on SiO_2 powder (0.17 mm diameter) on silica extrudates (1.4 mm diameter) for both the vapor-phase reaction of 2MP2 and the liquid-phase aromatic alkylation of 1,3,5-trimethylbenzene (mesitylene) with cyclohexene. For the Cs-acid salt inside the extrudate, particle transport limitations substantially decrease conversions during the liquid-phase alkylation reaction relative to the ground catalyst. For the gas-phase reaction of 2MP2 over these catalysts, activity over the powder and extrudate silica supports does not differ substantially. We discuss in more detail, aromatic alkylation data and issues regarding deactivation and regeneration elsewhere [18].

In Section 2, we described three techniques for preparing supported ammonium salt catalysts: (1) gaseous NH_3 reaction on supported HPW; (2) hydrothermal synthesis of soluble precursors; and (3) co-impregnation of an HPW solution with urea. Fig. 11 shows the clearly distinguishable X-ray spectrum (i.e. smaller unit cell) of bulk $(NH_4)_{3-x}H_xPW_{12}O_{40}$ made by ion exchange compared with the starting acid. The figure also shows that 24% HPW/SiO_2 converts easily to the supported ammonium salt by treatment in NH_3. Fig. 12 show the X-ray spectrum of the bulk and supported phase formed by hydrothermal preparation. The dry reaction of ammonium *meta*-tungstate and ammonium phosphate dibasic does not form this phase, nor does a simple solution reaction at 80°C in water. The hydrothermal synthesis at 150°C is necessary to produce the acid-salt precursor. Fig. 13 shows diffraction spectrum of the sample of the supported ammonium salt on silica using the urea-addition technique. This procedure is the simplest since it merely involves adding urea to an HPW

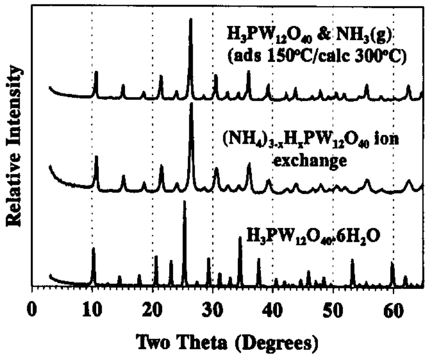

Fig. 11. Preparation of $(NH_4)_{3-x}H_xPW_{12}O_{40}$ by reaction with NH_3.

Table 4
Reaction of bulk and supported Cs-acid salts for 2MP2 isomerization and cyclohexene alkylation

Catalyst	2MP2 Conversion (200°C, 5 m)	Cyclohexene conversion to alkylate (100°C, 2 h)
Bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$	67 (1.0 g, 10–20 mesh)	90 (0.50 g)
40% $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ powder	46 (1.0 g, 10–20 mesh)	91 (1.25 g)
40% $Cs_{2.5}H_{0.5}PW_{12}O_{40}/SiO_2$ extrudate	41 (1.0 g, 1/16″ extrudate)	38 (1.25 g)

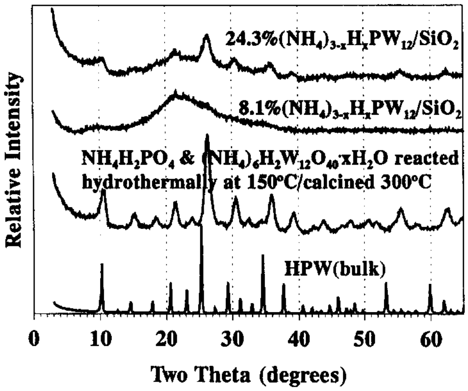

Fig. 12. Preparation of $(NH_4)_{3-x}H_xPW_{12}O_{40}$ by hydrothermal synthesis.

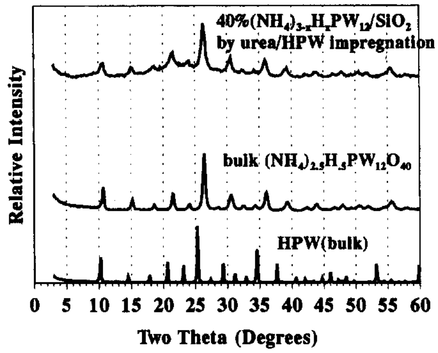

Fig. 13. Preparation of $(NH_4)_{3-x}H_xPW_{12}O_{40}$ by urea decomposition.

solution prior to impregnation. During the thermal decomposition of the urea, the generated NH_3 reacts with HPW to form the acid salt.

The interesting hydrothermal preparation technique was extended to the 12-tungstoboric acid system. When we hydrothermally reacted ammonium borate or ammonium tetrafluoroborate, NH_4BF_4, with ammonium metatungstate in a W/B::12/1 molar ratio at 150°C for 24 h, we produced a liquid product which on drying and calcination at 300°C yielded the ammonium heteropoly-acid salt. Misono et al. [20] recently reported some catalytic reactions over 12-tungstoboric acid. Surprisingly, we observed that solid-state reaction of a dry physical mixture of ammonium metatungstate with ammonium tetrafluoroborate (W/B::12/1) at 300°C in air yielded the ammonium acid salt. In Fig. 14, the X-ray spectrum from this preparation shows a phase isomorphous with $(NH_4)_3PW_{12}O_{40}$, but with peaks shifted to smaller 2θ values, as the unit cell contracts with boron substitution for phosphorus. We suspect that here the tetrafluoroborate may be acting as a flux. The surface area of this acid salt (4 $m^2\,g^{-1}$) is much lower than those formed with the corresponding tungstophosphoric acid.

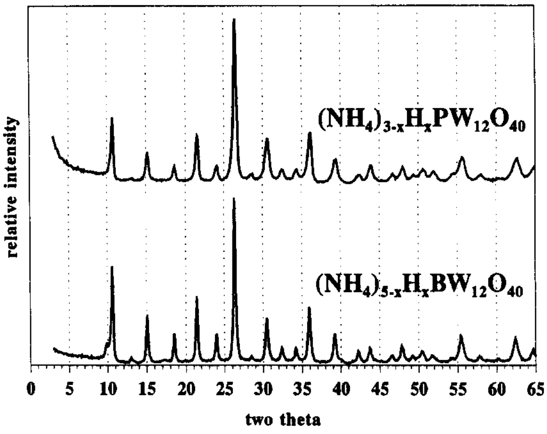

Fig. 14. Preparation of $(NH_4)_{5-x}H_xBW_{12}O_{40}$ by solid-state reaction.

4. Summary

Supported catalysts containing the water-insoluble ammonium and cesium heteropolyacid salts of 12-tungstophosphoric acid have been prepared by gas-phase reaction, hydrothermal synthesis, precursor decomposition, in situ reaction and precipitation. These supported versions of bulk insoluble acid salts provide an interesting set of new, strong acid catalysts.

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