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Preparation of highly dispersed Cs-tungstophosphoric acid salt on MCM-41 silica

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This paper describes a grafting technique that we developed for preparing highly dispersed Cs-tungstophosphoric acid (Cs-TPA) salt on a mesoporous silica carrier (MCM-41) using alcohols as solvents during impregnation. It is shown that this procedure leads to a novel class of catalysts with high dispersion of Cs-TPA salts which exhibit significantly improved catalytic performances for the alkylation of 1,3,5-trimethylbenzene with cyclohexene than those prepared using water as the solvent. Catalyst activity demonstrated to have a clear correlation with the type of alcohol used during impregnation which decreased in the following order: 1-butanol $>$ 1-propanol $\approx$ ethanol $>$ water. Adsorption data using molecules of various sizes suggest that our novel catalysts maintained open pore structures after the impregnation with tungstophosphoric acid (TPA). For comparison purposes, we also used a prior published method to prepare Cs-TPA on MCM-41, which seemed to have suffered unfavorable structural changes such as partial pore clogging leading to significant transport limitations for the reactants examined here.

KEY WORDS: alkylation; cesium salt of tungstophosphoric acid; MCM-41 silica; supported catalyst

1. Introduction

The first principle out of 12 outlined for “green chemistry” [1], states that it is better to prevent waste than to treat or clean up after it is formed. To this end, one of many environmentally-benign catalytic technologies that are likely to be commercialized in the near future involves replacing mineral acids with solid acid catalysts, specifically for alkylation processes [2–4]. Its potential industrial impact is well advocated by the vast attention it has received over this past decade [5–7].

Among the many solid acid candidates, systems that consist of a Keggin-type, 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, TPA) have been extensively studied since TPA possesses attractive features such as strong Brønsted acidity and relatively simple preparation procedures [8–10]. However, bulk TPA generally exhibits poor catalytic performances due to its low surface area, and thus, has very limited practical applications. For this reason, research has geared toward maximizing the efficiency of TPA with respect to utilizing its acidic features either by (1) incorporation of large cations in bulk TPA [6,11–13] to form high surface area TPA salts or by (2) supporting the active components onto a high surface area carrier [14–19]. In the former method, however, bulk TPA salts with large cations are formed in significantly small sized particles (μm) which restrict their use in commercial fixed-bed or slurry type reactors. In addition, preparation of this type TPA salts on engineered supports *via* conventional impregnation methods is difficult since they are not soluble in any solvent. With respect to the latter approach, majority of efforts, up to date, has been made to achieve high dispersion of these active TPA clusters without decomposing their Keggin structure. However, not much attention has been given to keeping the supported TPA properly anchored to the surface. As a result, the TPA clusters can migrate on the support material which potentially leads to catalyst deactivation, especially when polar solvents are used as the reaction medium.

Recently, Soled *et al*. [20] have combined both elements of a strategy to obtain high surface areas of TPA described above by developing a two-step impregnation method to support Cs-TPA salt on amorphous silica extrudates. A major benefit of their method is that it enables impregnation of insoluble Cs-TPA salts on high surface area carriers. Still, the resulting catalysts were not uniform in dispersion. Because of this, we have been investigating an approach to the preparation of these materials that maximizes the efficiency of the catalysts by enhancing dispersion of the active TPA clusters.

Very recently, we reported the development of supported Cs-TPA salts uniformly dispersed with intact Keggin anions on a mesoporous silica carrier (MCM-41) [21]. This published report was focused on structural characterizations in order to clearly show the enhanced dispersion of the Cs-TPA clusters as is also positively reflected in their catalytic performance for the alkylation of 1,3,5-trimethylbenzene with cyclohexene. In this paper, we describe the novel grafting technique used for the preparation of these materials and relate the effect of preparation conditions during synthesis on their catalytic properties.

2. Experimental

2.1. Catalyst preparation

TPA solutions were prepared using the Keggin type $H_3PW_{12}O_{40}\cdot nH_2O$ (Aldrich). MCM-41 type mesoporous

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silica with monodimensional pores of 50 Å was synthesized using a protocol reported elsewhere [22,23]. Mesoporous silica was first treated with a 0.1 M HNO_3 solution (10 ml of solution per g of silica) and stirred for 15 min at 80 °C before drying in vacuum at 110 °C overnight. Then, it was calcined at 540 °C for 1 h before use as the support material. Preparation of highly dispersed Cs-TPA on mesoporous silica, denoted as Cs_x-TPA/MS (x = Cs stoichiometry, MS = MCM-41 mesoporous silica) hereafter, is as follows. First, Cs_2CO_3 (Aldrich, 99.9%) was impregnated by aqueous incipient wetness onto mesoporous silica, dried at 110 °C overnight and calcined at various temperatures between 300 and 700 °C for 2 h. Following this, TPA, with desired stoichiometry ratio to Cs, was impregnated using a similar incipient wetness technique with various organic solvents including ethanol, 1-propanol and 1-butanol. For comparison purposes, we also prepared samples using the method published by Soled *et al.* [20], *i.e.*, with aqueous TPA solutions. These samples were then dried at 110 °C overnight and calcined at 300 °C for 2 h.

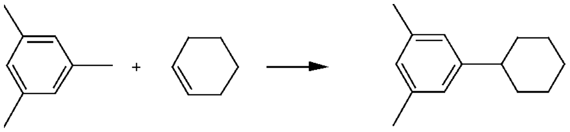
2.2. Characterization

BET surface area and pore size distributions were determined from BJH and multi-point BET methods, respectively, using a Quantachrome Autosorb 6-B gas sorption system.

Sorption capacities of the supported catalysts were obtained using a Netzsch STA-409C thermal gravimetric analysis (TGA) system. Samples were degassed at 300 °C for 1 h in flowing dry air and subsequently cooled down to 28 °C prior to being exposed to a stream of air saturated with an adsorbate gas using a set of bubblers placed in an ice water bath. Equilibrium uptake, as indicated by no further weight gain, was measured at least after 2 h at 28 °C in the flowing gas mixture. Benzene (Aldrich, 99.9+%) and 1,3,5-trimethylbenzene (mesitylene, Aldrich, 98%) were used as the adsorbate molecules without further purification.

2.3. Reactivity testing

The catalytic properties of the materials were evaluated using a probe reaction, the liquid phase alkylation of 1,3,5-trimethylbenzene with cyclohexene (Aldrich, 99%), as reported [20,21,24]:



Approximately 50 mg of bulk or supported catalyst was loaded into a 7 mm OD vial and calcined at 300 °C under N_2 for 2 h. Under an inert environment (argon), 2 g of premixed 5 wt% cyclohexene in 1,3,5-trimethylbenzene solution was added and then reacted in an 80 °C water bath while being vigorously stirred. After a certain period of time, the reaction vial was quenched in an ice bath and centrifuged to separate the reactant/product mixture from the catalyst. The products were separated using a J&W DB-5 capillary column and analyzed using a HP 5890A GC equipped with a flame ionization detector.

3. Results and discussion

As aforementioned, a two-step impregnation technique has been attempted by Soled *et al.* [20] to disperse Cs-TPA on silica supports: (1) impregnation of aqueous Cs_2CO_3 solution, followed by (2) impregnation of aqueous TPA solution on silica supports. Using this approach, it has been reported that an egg-shell type distribution of Cs-TPA was formed within silica pellets when water was used as a solvent. One hypothesis is that during the second impregnation, Cs cations were re-dissolved in the aqueous TPA solution *via* hydrolysis of Si–O–Cs, and migrated within the support to precipitate out forming a layer of Cs-TPA.

Our primary aim was to minimize the Cs mobility during the second impregnation with TPA so that Cs-TPA is highly dispersed on the support surface. This was achieved by using non-hydrolyzing solvents such as ethanol, propanol, and butanol, to inhibit the hydrolysis of Si–O–Cs bonds and the subsequent dissolution of CsOH [25]. An additional advantage with non-hydrolyzing solvents is that it avoids the decomposition of the TPA Keggin structure since water is known to hydrolyze TPA at a pH higher than 1 [26]. Consequently, the Keggin structure is preserved during catalyst synthesis and, at the same time, dispersion is maintained during and/or after the TPA impregnation.

A set of 10 wt% Cs-TPA supported on 50 Å MS catalysts was prepared with various organic solvents and also with water for comparison. The effect of solvent type on the alkylation activity of 1,3,5-trimethylbenzene with cyclohexene on these catalysts is illustrated in figure 1 as a function of Cs stoichiometry. We have previously reported that the Keggin structures remain intact at loadings as low as 10 wt% as confirmed using ^{31}P NMR [21]. As expected, catalysts prepared with organic solvents showed significantly improved performance than those prepared using water where the activity decreased in the following order: 1-butanol $>$ 1-propanol $\approx$ ethanol $>$ water. Similar trends have been observed for catalysts with TPA loadings as high as 50 wt% on mesoporous silica. This difference in activity from using different solvents is almost certainly due to differing dispersions of Cs-TPA on MS as we have previously evidenced by TEM for samples prepared using 1-butanol and water [21]. For a given solvent, conversion decreases with increasing Cs stoichiometry, which is likely due to a decrease in the total number of catalytically active protons. The aforementioned activity relationship with the type of alcohols is not surprising since alcohols exhibit polarity that decreases with chain length. For example, the dielectric constants for ethanol, 1-propanol and 1-butanol are 24.3, 20.1 and 17.1, respectively. However, these values are all much lower than that of water (78.6) at 25 °C. Using solvents of lower dielectric

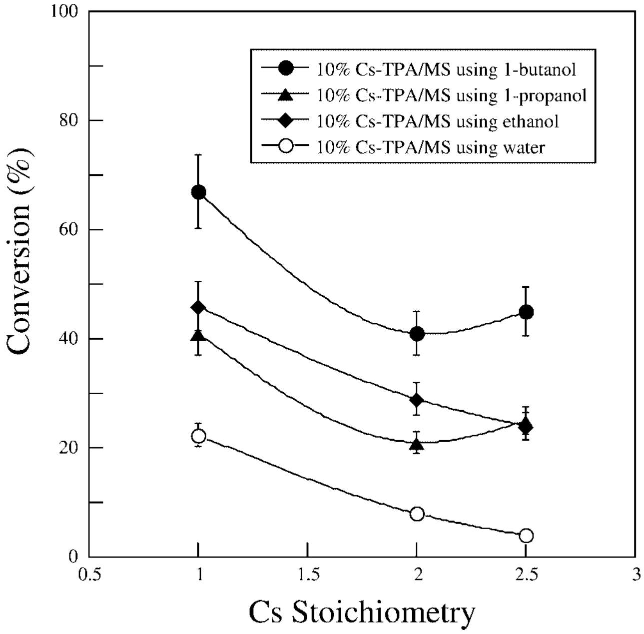


Figure 1. Alkylation of 1,3,5-trimethylbenzene by cyclohexene at 80 °C on 10 wt% Cs-TPA/MS prepared using various solvents as a function of Cs stoichiometry. The reaction was carried out for 2 h.

constant also provides a higher probability for TPA anions to diffuse further into the pores with lessened restriction due to reduced electrostatic interactions with the silica support. In addition, CsOH solubility also decreases as the hydrocarbon chain length of the alcohol increases, which could also affect the Cs-TPA dispersion. Accordingly, 1-butanol was selected as our primary solvent for further investigation.

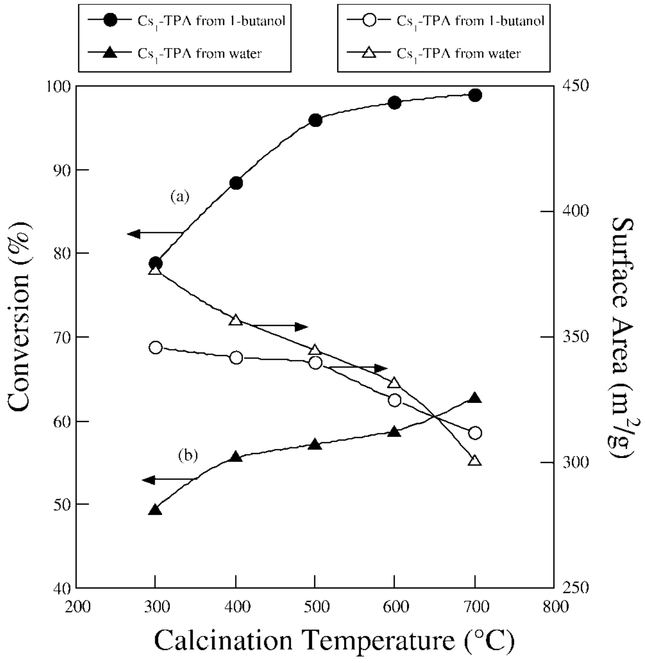


Figure 2. Effects of calcination temperature on BET surface area and the alkylation of 1,3,5-trimethylbenzene by cyclohexene at 80 °C for (a) improved 50 wt% Cs_1-TPA/MS (1-butanol as solvent) and (b) "conventional" 50 wt% Cs_1-TPA/MS (water as solvent). The reaction was carried out for 2 h.

The novel grafting technique described in this paper also involves pretreating Cs_2CO_3 impregnated MS samples at higher temperatures (300–700 °C) prior to a second TPA impregnation step. This approach was adopted to help anchor the Cs cations by promoting interactions between silanols and Cs_2CO_3. The effect of the precalcination temperature used in this synthesis step on the catalytic properties and BET surface area for 50 wt% Cs_1-TPA/MS, prepared using 1-butanol and water as solvents, are shown in figure 2. In both cases, catalytic activities increased even though BET surface area slightly decreased with precalcination temperature, which is probably due to enhanced dispersion of Cs_1-TPA resulting from improved anchoring of the Cs species on mesoporous silica prior to TPA impregnation. As also shown in this figure, catalysts prepared using 1-butanol were almost twice as active as those prepared using water under the conditions studied. In fact, figure 3(a) demonstrates that the supported catalysts prepared using 1-butanol (both Cs_1-TPA and $Cs_{2.5}$-TPA) were as much as 4–5 times more active than those prepared using water at lower conversions. At higher conversions (figure 3(b)), as much as 2–3 times enhancement in activity was observed with the catalysts prepared using 1-butanol. In addition, the Cs_1-TPA materials were typically more active than the $Cs_{2.5}$-TPA catalysts partly due to more available proton (Brønsted) sites. It is noteworthy that the primary role of Cs here is to anchor the active TPA species for improved dispersion and stability while minimizing proton substitution, which can be achieved at much lower Cs content to retain higher proton density in the catalysts; whereas in bulk forms, Cs = 2.5 is specifically required for optimum textural and structural properties as associated with surface area, porosity and number of proton sites [6].

Variations in the alkylation activities with different preparation methods and synthesis conditions appear to be, in part, associated with the textural properties of the catalysts. For example, 50 wt% Cs_1-TPA/MS prepared in 1-butanol and water have similar surface areas (figure 2); however, their activities can vary by as much as a factor of two or more. Recall that N_2 adsorption/desorption is used to estimate the surface area whereas the reactants used to evaluate the activity such as cyclohexene and 1,3,5-trimethylbenzene are significantly larger than a N_2 molecule. Hence, activity compared in terms of surface area will be served as a meaningful metric provided no limitation in diffusion exists for the reactant molecules. Typically, larger molecules such as benzene have been utilized to assess the sorption properties for various mesoporous molecular sieve systems with variable pore sizes and structures [27,28]. In general, the diffusion characteristics in the bulk structures cannot be adequately represented by an average radius when the pores vary substantially in size and hence it is required to determine the pore size distribution that depends on the model assumed for interpretation. Fortunately, however, for mesoporous silica systems having cylindrical pores fairly close in size, one can easily assess the average pore diameter (d_{pore}) from the equation, $d_{\text{pore}} = 4V/S_g$, where V is the total pore volume

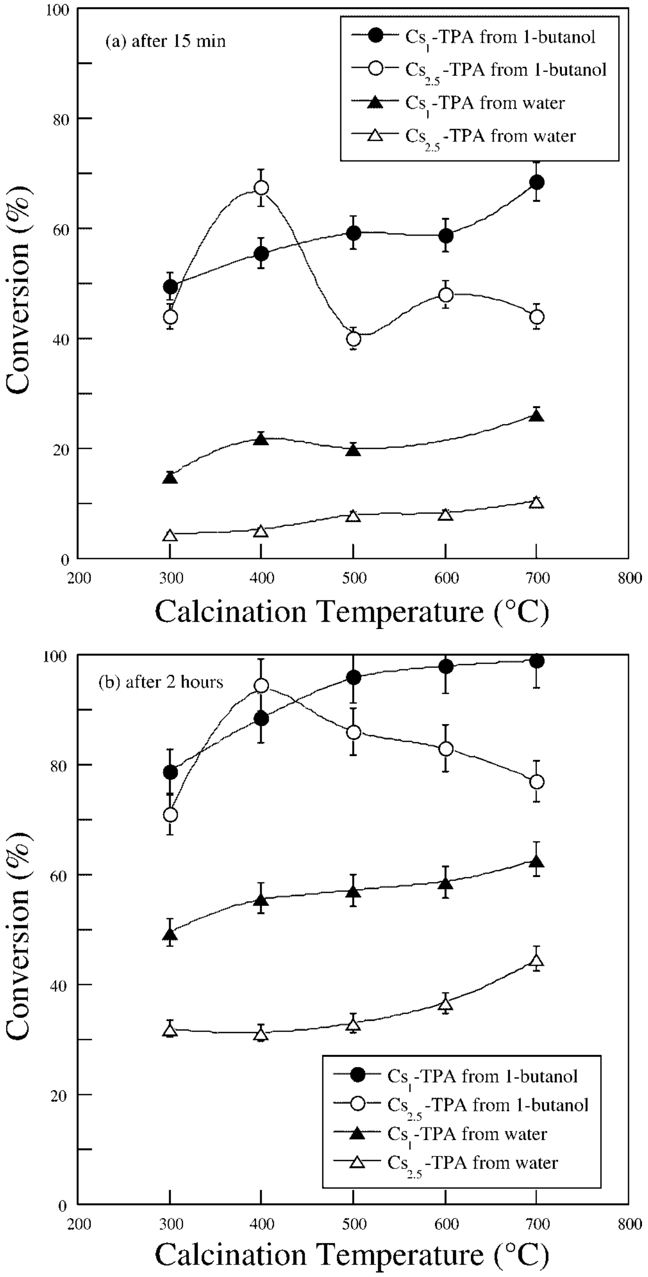


Figure 3. Alkylation of 1,3,5-trimethylbenzene by cyclohexene for 50 wt% Cs_1-TPA/MS and for 50 wt% $Cs_{2.5}$-TPA/MS prepared in 1-butanol and water after (a) 15 min and (b) 2 h at 80 °C.

and S_g is the surface area [29]. Provided that the surface areas are similar, one can assess any variation in the apparent pore diameter as seen by the reactant from estimating its total adsorption amount. Thus, changes in the adsorption amount of adsorbate molecules of varying size can be related to the degree of diffusional limitations expected for a reaction in a mesoporous material. Accordingly, we have conducted this type of equilibrium adsorption experiments for a selected set of materials and the results are summarized in table 1.

Table 1
Summary of adsorption data using molecules of various sizes.

Adsorbate	Size (nm)	Adsorption amount (μmol/g_{cat}) 50 wt% Cs_1 $(BuOH)^c$	 50 wt% Cs_1 $(H_2O)^c$	 50 wt% $Cs_{2.5}$ $(BuOH)^c$	 50 wt% $Cs_{2.5}$ $(H_2O)^c$
N_2[a]	0.36	3480	3530	3100	2770
Benzene[b]	0.59	970	960	910	720
1,3,5-TMB[b]	0.75	370	260	301	203

[a] Calculated from the surface area measurement data at −196 °C and $p/p_0 = 0.1$.
[b] Measured at 28 °C after 2 h.
[c] Precalcination prior to TPA impregnation was carried out at 500 °C.

For both benzene and 1,3,5-trimethylbenzene (1,3,5-TMB) adsorbates employed, the equilibrium adsorption was reached approximately after 2 h at 28 °C as evidenced by no additional uptake for up to an additional 4–5 h on stream. The supported Cs-TPA materials selected for these experiments were prepared under identical conditions except for the solvent type, 1-butanol and water, used during impregnation with TPA. These catalysts were chosen because they showed the largest difference in activity (figure 3) despite their similar BET surface areas as measured by N_2 adsorption. Comparing catalysts with a Cs stoichiometry of 1 (table 1), use of benzene, a molecule that is close to cyclohexene in size, gave similar benzene adsorption amount regardless of the solvent used, suggesting that the materials have similar pore structures as seen from the N_2 uptake. However, when a larger adsorbate such as 1,3,5-TMB is used, the total amount adsorbed on the 1-butanol prepared catalyst was 30% more than that on the water prepared sample. This might be due to partial clogging within the pore; an effect that cannot be distinguished from the adsorption isotherm of N_2 and only becoming apparent in the data with larger adsorbate molecules. For catalysts with a Cs stoichiometry of 2.5, higher surface Cs concentration likely increases the probability of TPA clustering. Therefore, it is not surprising to see in table 1 that the total adsorbate uptake on the 1-butanol prepared catalyst was higher than that on the water prepared sample regardless of adsorbate molecule size, and the difference increased with the adsorbate size. This, again, suggests that by using a much less polar solvent, 1-butanol, one can avoid any potential pore plugging that seems to be associated with the use of water during TPA impregnation. Clustering, resulting from poor diffusivity of the TPA anions and/or induced by mobile Cs species, could lead to narrow and non-uniform pore structures following impregnation. Consequently, heterogeneity resulting from varying dispersions and pore structures could account for the differences in the alkylation performance of these catalysts.

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