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Cs-substituted tungstophosphoric acid salt supported on smesoporous silica

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Abstract

In this paper, we describe the characterization and catalytic properties of mesoporous silica supported Cs-substituted tungstophosphoric acid salt (Cs-TPA/MS) with improved dispersion of the active clusters compared to materials described previously in the literature. In particular, transmission electron micrographs and the activity results for a model alkylation reaction are presented as evidence for the enhanced dispersion and performance. In addition, we demonstrate improvements in the physical and thermal stability of these materials with Cs-substitution using various characterization techniques. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Tungstophosphoric acid (TPA); Heteropoly acid (HPA); Mesoporous silica; Cs-TPA

1. Introduction

Demands for a cleaner environment have continuously stimulated the chemical and petrochemical industries to develop alternative catalyst systems and/or processes to meet more stringent regulations. One particular area that has attracted considerable attention, recently involves the replacement of HF and H_2SO_4 liquid acids in the commercial alkylation units by more environmentally benign heterogeneous solid acids [1–3]. Although current homogeneous catalysts are efficient, their corrosive and toxic nature provides potential environmental hazards and present operational problems, including difficulty in separation, recovery and reutilization, that results in higher capital costs. Among many solid acid systems, heteropoly acids (HPA) with Keggin anion structures have received the most attention due to their simple preparation and strong acidity [4,5]. Specifically, 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$), denoted as TPA, hereafter, is among the most extensively studied [6–8], since it possesses the highest Brönsted acidity [9], stronger than that of 100% sulfuric acid, which results from minimized charge on the anion surface. However, to date, low efficiency due to low surface area, rapid deactivation and relatively poor stability are some of the major problems associated with these TPAs in conventional bulk acid forms.

Attempts to improve the efficiency of these materials have been made by supporting tungstophosphoric acid (TPA) on various high surface area supports [10,11] and, more recently, on mesoporous silica with ordered pore structures [12–15]. Kapustin et al. [10] reported that acidity of the supported TPA decreased in the following order: $SiO_2 > \alpha\text{-}Al_2O_3 >$ carbon. They concluded that the strong interaction between TPA and carbon might have resulted in the decomposition of the Keggin structure. Likewise, several reports in the literature have identified silica as a suitable support

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due to its intrinsic inertness [16–18]. Recently, mesoporous silica known as MCM-41, first developed by researchers at Mobil [19–20], has been used to support TPA clusters to take advantage of its uniform pore size and highly ordered structures. More recently, we have reported that acid neutralization of the mesoporous silica support assisted in preserving the Keggin structure even at TPA loadings as low as 10 wt.% [21]. Although, we have observed an enhancement in resistance to leaching of TPA by water when mesoporous silica was used as the support instead of amorphous silica, this was likely due to steric constraints rather than a direct improvement in the grafting of the TPA clusters on the surface.

Another method that could possibly enhance stability of the active clusters in solution is to prepare catalysts in the form of tungstophosphoric acid (TPA) salts [8,22,23]. Heteropolyacid (HPA) salts, as a result of partially exchanging protons with large cations, typically demonstrate different physiochemical properties than those of their precursor acids. For example, partial substitution of Cs^+ for protons render bulk TPAs with higher surface area (up to 150 m^2/g compared to 5 m^2/g) and improved thermal stability than their parent acids [8]. In addition, TPA salts are known to be insoluble even in liquids as polar as water. Consequently, TPA salts should be better suited for practical applications that might involve polar reagents in harsh operating conditions. However, their small particle size (μm) limit their application for use as catalysts in commercial fixed bed or slurry type reactors. An obvious solution as often applied in industrial practice is to support these TPA salts on a larger particle size (mm) carrier. Unfortunately, preparation of these catalysts in an engineered form is challenging since direct aqueous impregnation is not feasible. For example, Soled, et al. [23] first reported using a two-step impregnation in order to disperse TPA salts on to a silica support. However, they observed thin internal rings of Cs-substituted TPA salt, known as an egg-white distribution, within the silica extrudate suggesting nonuniform dispersion of the active clusters on silica.

The premise of our work, some of which is described in this paper is that, dispersion of TPA can be manipulated by adopting appropriate grafting techniques. In essence, we are attempting to highly disperse the active Cs-TPA salt species uniformly on a high surface area mesoporous silica with ordered structure for improved activity and/or added shape-selectivity. Our primary objective here is to prepare a series of mesoporous silica supported Cs-TPA salts with highly dispersed and intact Keggin anions, and compare their structural and catalytic properties to a conventionally prepared supported catalyst and their bulk counterparts. Alkylation of 1,3,5-trimethylbenzene by cyclohexene was used as a model reaction to evaluate the reactivities of these catalysts.

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 silica with monodimensional pores of 50 Å was synthesized using a protocol reported elsewhere [19,20]. Mesoporous silica was first treated with a 0.1 M HNO_3 solution (10 ml of solution per gram 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 using as the support material. Preparation of highly dispersed Cs-TPA on mesoporous silica, denoted as Cs_x-TPA/MS (x = Cs stoichiometry, MS = mesoporous silica), hereafter, is explained in detail elsewhere [24]. For comparison, supported Cs-TPA samples using the two-step impregnation method reported by Soled et al. [23] were also prepared. In their first step, Cs_2CO_3 (Aldrich, 99.9%) was impregnated by aqueous incipient wetness onto mesoporous silica, dried at 110°C overnight and calcined at 300°C for 2 h. Following this, TPA was impregnated using a similar aqueous incipient wetness technique, dried at 110°C overnight and calcined at 300°C for 2 h. Supported TPA (without Cs-substitution) catalysts were prepared by aqueous incipient wetness impregnation onto mesoporous silica, dried at 110°C overnight and calcined at 300°C for 2 h. Bulk Cs-TPA materials were prepared by adding the Cs_2CO_3 solution dropwise to the TPA solution while stirring [22]. The resulting precipitate was dried at 110°C overnight in vacuum and calcined at 300°C for 2 h.

2.2. Characterization

Keggin structures of bulk and supported samples were examined using a Vector 22 (Bruker) FT-IR spectrometer equipped with a DTGS detector. The spectra were collected at room temperature under continuous N_2 purge with a spectral resolution of $1\,cm^{-1}$. For sample preparation, ca 5% sample material was mixed in KBr and then pressed into a 5 mm OD disc waffle using a hand press. A plain KBr spectrum was used as background.

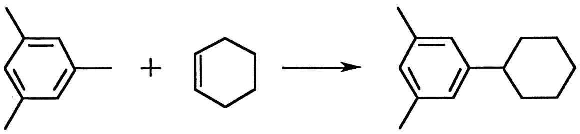
The TGA/DTA experiments were performed using a Netzsch STA 409C. Transmission electron microscopy (TEM) was performed on a JEOL 1200 microscope at 120 kV. The TEM samples were prepared by grounding the powder and dispersing it on a TEM copper grid with suspended carbon films. The composition was also analyzed using the energy dispersive spectroscopy technique (EDS).

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.

Selected samples were examined for leaching of TPA by water after stirring vigorously for 2 h at 50°C in a water bath. A Hewlett-Packard 8453 UV spectrometer equipped with an auto sampler was used to collect the absorbance spectra at 267 nm.

2.3. Catalytic properties

The catalytic properties were evaluated using a probe reaction, the liquid phase alkylation of 1,3,5-trimethylbenzene (mesitylene, Aldrich, 98%) with cyclohexene (Aldrich, 99%), as reported in the literature [23,25]:



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 withdrawn to an ice bath for cooling and centrifuged for further sampling. 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

3.1. Characterization of supported Cs-TPA catalysts

Primary structures of the supported catalysts were identified by comparing their FT-IR absorbance bands to those of bulk TPA, tungstophosphoric acid salt (Cs-TPA), and mesoporous silica (Fig. 1).

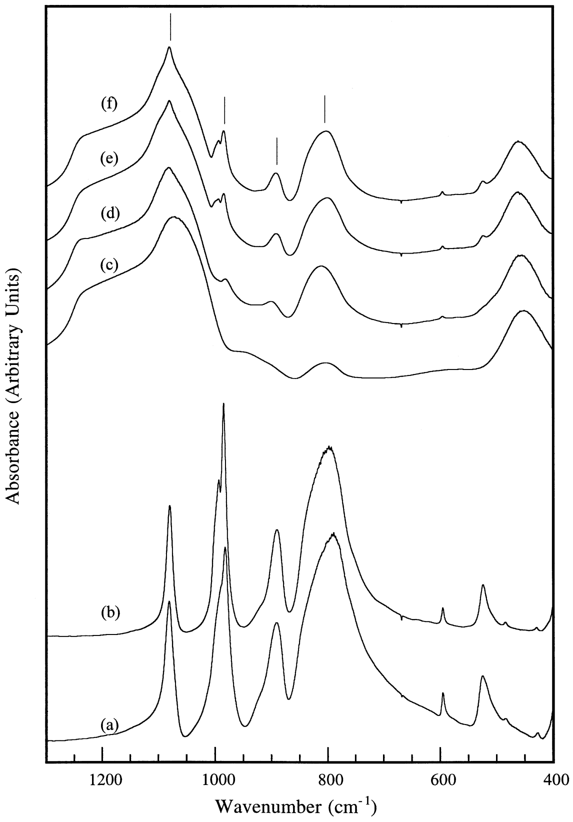


Fig. 1. Infrared spectra of (a) tungstophosphoric acid (TPA); (b) bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$-TPA); (c) 50 Å mesoporous silica; (d) 'conventional' [23] 50 wt.% TPA/MS; (e) 'conventional' 50 wt.% $Cs_{2.5}$-TPA/MS, and (f) improved 50 wt.% $Cs_{2.5}$-TPA/MS.

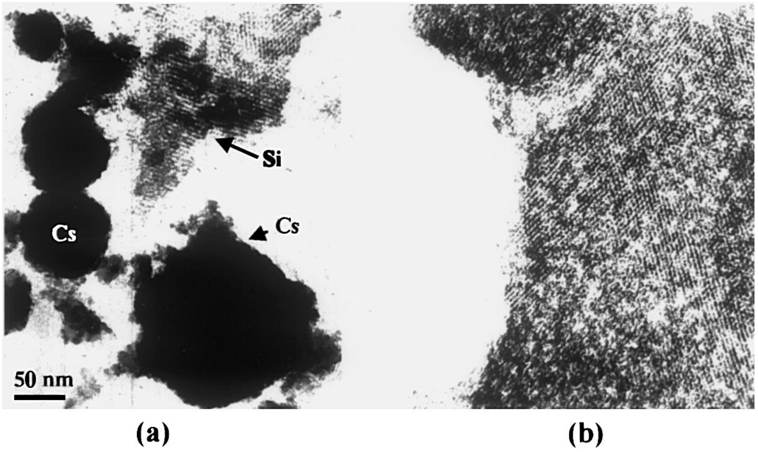


Fig. 2. Transmission electron micrographs of (a) $Cs_{2.5}$-TPA/MS prepared from a published method [23] and (b) our improved, newly synthesized $Cs_{2.5}$-TPA/MS material.

Bulk tungstophosphoric acid ($H_3PW_{12}O_{40}$) and tungstophosphoric salt ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) show the characteristic IR bands at ca 1080 cm^{-1}(P–O in the central tetrahedra), 984 cm^{-1} (terminal W=O), 897 cm^{-1} and 812 cm^{-1} (W–O–W) associated with the asymmetric vibrations in the Keggin polyanion (Fig. 1a and b); however, the Cs-TPA catalysts are distinctively characterized by a split in the W=O band. This doublet becomes more prominent as the Cs stoichiometry in the catalyst increases (not shown here), suggesting a direct interaction between the polyanion and Cs^+ exists. Similar observations have been reported for the case of W=O vibrations in $Cu_{1.5}PW_{12}O_{40}$ anions [26]. The same distinguishable features were observed for the 50 wt.% TPA/MS (Fig. 1d) and Cs-TPA/MS catalysts (Fig. 1e and f), indicating that the primary Keggin structure is preserved after supporting it onto mesoporous silica. Thus, the new materials prepared in this study had intact polyanion structures and/or species on the silica surface. Similar results (not shown) were obtained even for the supported materials with lower HPA loadings (10 wt.%) and different Cs stoichiometry ($Cs_xH_{3-x}PW_{12}O_{40}$, $x=1$). Furthermore, ^{31}P NMR results have confirmed that $[PW_{12}O_{40}]^{3-}$ were the only species present on the support as evidenced by a single ^{31}P NMR peak at a chemical shift of ca -15 ppm referenced to a 0 ppm response from 85% H_3PO_4. This was the case for both the novel 50 wt.% Cs-TPA materials newly prepared in this study as well as those we prepared using published [23] methods. We have previously reported that the Keggin structure remains intact on mesoporous silica even at TPA loadings as low as 10 wt.% [21]. In particular, no additional ^{31}P MR peaks, for example, at ca -13 ppm, generally attributed to a defect ($P_2W_{21}O_{71}{}^{6-}$) Keggin structure [27,28], was evident.

The dispersion of Cs-TPA on mesoporous silica can be inferred from the TEM results illustrated in Fig. 2, and from EDS analysis (not shown). The material we prepared using a previously published method [23] resulted in a segregated phase, where Cs-TPA is not uniformly dispersed (Fig. 2a), whereas our novel material consists of uniformly dispersed Cs-TPA salt on mesoporous silica (Fig. 2b). As aforementioned, direct impregnation using a Cs-TPA solution was not possible, since Cs-TPA is not soluble in any solvent. The previous synthetic approach used by Soled and coworkers [23] consists of a two-step impregnation, where the support was first impregnated with aqueous Cs_2CO_3 solution prior to aqueous TPA impregnation. However, as indicated in Fig. 2a, the previously published two-step impregnation resulted in poor dispersion of the active species, due likely to the high mobility of Cs during TPA impregnation, and hence poor activity. In contrast, our synthetic approach [24] leads to enhanced dispersion as evidenced in Fig. 2b.

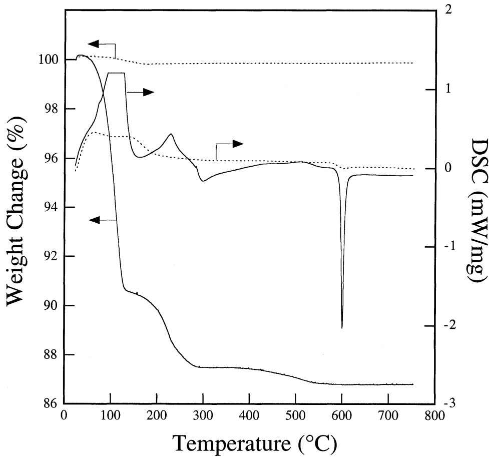


Fig. 3. Thermal gravimetric and differential thermal analysis of tungstophosphoric acid (TPA, solid lines) and bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$-TPA, dashed lines).

3.2. Catalyst stability

An important potential benefit of supporting TPA on oxide supports (including MS) is enhanced thermal stability for the TPA salts. As such, the thermal stability of bulk TPA and Cs-TPA was investigated using TGA/DTA and FT-IR techniques and the results are shown in Figs. 3 and 4. At about 600°C (Fig. 3), bulk TPA seemed to undergo an exothermic decomposition [4],

$$H_3PW_{12}O_{40} \rightarrow \tfrac{1}{2}P_2O_5 + 12WO_3 + \tfrac{3}{2}H_2O$$

resulting in a weight loss of <2% above 300°C while the bulk $Cs_{2.5}$-TPA did not show any significant weight change. Initial weight loss of ∼11% (below 300°C) for the bulk TPA was probably due to dehydration of the sample. Unfortunately, TGA/DTA techniques were not suitable to accurately analyze the supported materials. Therefore, FT-IR was used to examine the stability of bulk and supported materials after a thermal treatment at 600°C (Fig. 4). In agreement with the TGA/DTA results just described, the infrared spectrum of bulk $Cs_{2.5}$-TPA (Fig. 4b) shows the characteristic bands of the Keggin structure, while that of bulk TPA (Fig. 4a) clearly indicates that decomposition occurred above 600°C as evidenced by the disappearance and shift of characteristic IR bands. After annealing to 600°C for 10 min, even the supported Cs-TPA (Fig. 4c and d) show the characteristic IR bands of the Keggin structure. Previously, we have reported that the thermal stability of HPA is enhanced by 75°C (to 585°C), when TPA is supported on mesoporous silica [21]. It is worth noting that the thermal stability of the supported TPA is enhanced further even with a single Cs-substitution. However, the enhancement in thermal stability for these catalysts should be correlated with the loss of acidic groups and/or protons for proper evaluation of changes in their catalytic properties (see below).

The stability of the active species in solution has also been of concern for solid acids, specifically for the supported materials [8,21]. Silica has been identified as one of the most suitable carrier materials for supporting TPA [16]. However, silica was also pointed out to have a relatively weak interaction with TPA species due to its inert surface. This can result in significant leaching of TPA in presence of a polar solvent. We have previously reported that the ordered structure of mesoporous silica with the proper pore size mitigated leaching of TPA from silica in water likely due to steric constraints [21]. In other words, pore size relative to the size of a TPA cluster was crucial in mitigating leaching. In order to examine the effect of Cs, we have tested the leach resistance of both bulk and supported Cs-TPA materials with varying Cs content (Fig. 5). Supported materials show the same trend as the bulk material where resistance to leaching improved significantly with increasing Cs stoichiometry. Considering the fact that one of our purposes in using Cs was to anchor the TPA species to the silica support material, it is worth noting that a small amount of Cs readily enhances its stability in aqueous solution.

3.3. Catalytic properties

Catalyst activities were evaluated using the alkylation of trimethylbenzene (mesitylene) by cyclohexene as a model reaction. Catalytic properties of selected catalysts and their bulk counterpart are summarized in Table 1. The novel 50 wt.% $Cs_{2.5}$-TPA/MS material synthesized in this study was about five times as active as that made from a previously published method [23], and was also more active than the bulk $Cs_{2.5}$-TPA. The primary purpose for adopting the Cs = 2.5 for

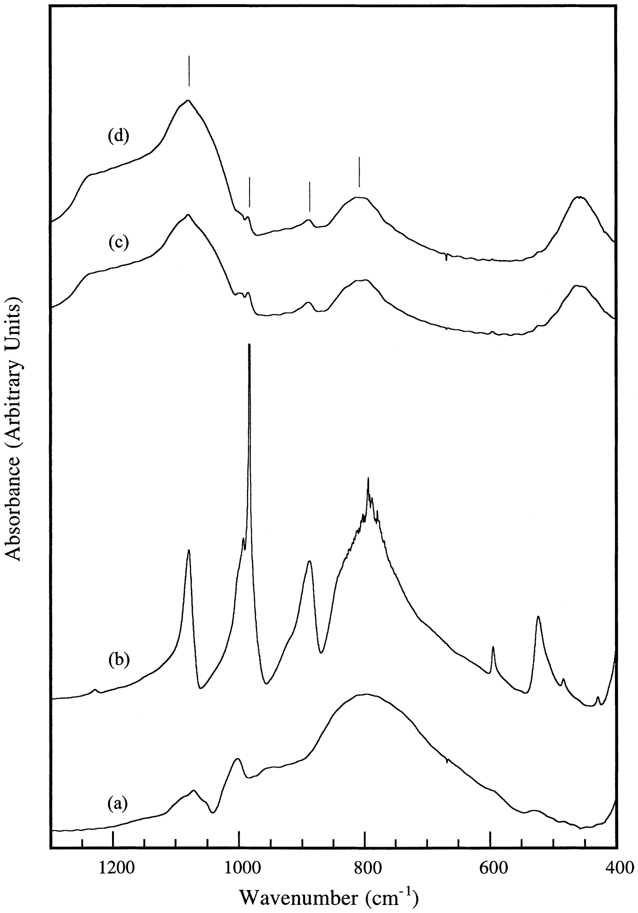


Fig. 4. Infrared spectra of (a) tungstophosphoric acid (TPA); (b) bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$-TPA); (c) improved 50 wt.% $Cs_{2.5}$-TPA/MS and (d) improved 50 wt.% Cs_1-TPA/MS, after heating at 600°C for 10 min.

Table 1
Catalytic properties of Cs-substituted tungstophosphoric acid (TPA) catalysts

Catalyst code[a]	Activity (mmol/g TPA/hr)[b]
50% $Cs_{2.5}$-TPA/MS/S	13.2
50% $Cs_{2.5}$-TPA/MS/I	64.8
Bulk $Cs_{2.5}$-TPA	39.8

[a] Catalyst code represents TPA loading, Cs stoichiometry, support material, and the synthetic procedure used (S: previously published [22] method; I: improved material newly synthesized in this study [24]).

[b] Alkylation of 1,3,5-trimethylbenzene by cyclohexene (5 wt.%) measured after 15 min at 80°C.

bulk materials is that this specific stoichiometry provides high surface area, and mesoporous porosity giving rise to optimized activity [8]. Considering the fact that a high surface area carrier with ordered structure is adopted here to support the TPA clusters and that more Cs-substitution leads to a reduction of acidic protons, we have prepared and examined supported Cs-TPA catalysts with a lower Cs stoichiometry. In this way, Cs-substitution levels that are optimized for catalytic activity and stability to solvent leaching can be determined.

In Fig. 6, activities of MS-supported 50 wt.% Cs-TPA are plotted as a function of Cs stoichiometry. Typically, the novel, improved Cs-TPA catalysts demonstrated superior catalytic properties than those prepared with the previously published method [23], regardless of the Cs stoichiometry. Even the supported

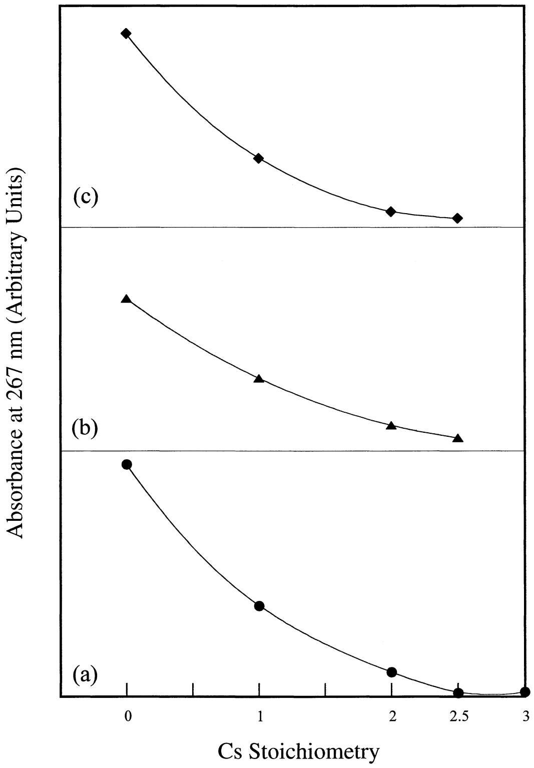


Fig. 5. Leaching of TPA from (a) bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$-TPA); (b) improved 10 wt.% Cs-TPA/MS and (c) 'conventional' [23] 10 wt.% Cs-TPA/MS, using water at 50°C. Leaching rates were evaluated by following the maximum UV absorption band, observed at 267 nm, for the $[PW_{12}O_{40}]^{3-}$ species.

TPA materials (without Cs-substitution) were more active and therefore, better dispersed than those prepared using the 'conventional' method. That is, the former materials were probably less susceptible to pore-clogging by poorly dispersed acid anion clusters. It is also worth noting that supported Cs_1-TPA catalysts are more active than their supported parent acids despite lower quantities of active acid proton sites. This result suggests that the dispersion of Cs-TPA clusters is improved regardless of the preparation method. It is important to note that these measurements may underestimate the enhanced activity of the novel, improved catalysts prepared in this study relative to those prepared by the 'conventional' method. This is because conversions for the most active materials were near 100% under the conditions tested here.

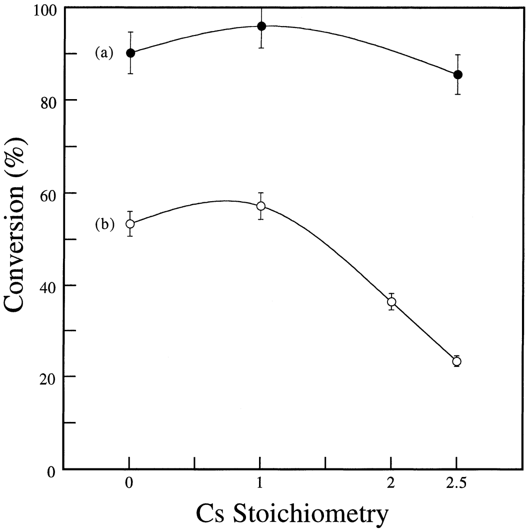


Fig. 6. Alkylation of 1,3,5-trimethylbenzene by cyclohexene at 80°C for (a) improved 50 wt.% Cs-TPA/MS and (b) 'conventional' [23] 50 wt.% Cs-TPA/MS as a function of Cs stoichiometry.

4. Conclusion

For the first time, we have described novel, improved supported Cs-TPA salts that are uniformly dispersed on a mesoporous silica carrier. This is confirmed by TEM results and from improved catalytic performance for a model alkylation reaction. Experiments assessing the stability of supported TPA catalysts indicate that resistance to leaching by solvents, and the thermal stability of these catalysts are significantly improved as well, even at low Cs-substitutions (Cs = 1). The availability of well-dispersed, supported TPA catalysts opens opportunities for producing TPA catalysts in an engineered form that takes advantage of the unique properties of bulk Cs-TPA while minimizing proton substitution for optimized catalytic performance. Finally, porosity of the carrier material can also be tailored to potentially add shape selectivity for specific reactions.

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