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The Acidity and Catalytic Activity of Supported Acidic Cesium Dodecatungstophosphates Studied by MAS NMR, FTIR, and Catalytic Test Reactions

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Acidic cesium salts of dodecatungstophosphoric acid (H_3PW) supported on silica and MCM-41 were characterized by multinuclear MAS NMR, FTIR, and catalytic test reactions. ^{31}P-NMR data indicate that the supported samples contain salts of various stoichiometries (Cs_3PW and Cs_2HPW) and even H_3PO_4. According to ^{29}Si-NMR data, deposition of the Cs salt does not change the relative amount of various SiOH groups in the case of the silica support. In contrast, when the support is MCM-41, the relative amount of the SiOH groups increases significantly, indicating the breaking of the siloxane bonds resulting from their interaction with H_3PW. The ^{133}Cs MAS-NMR spectra also suggest that the CsPW salt interacts more strongly with the MCM-41 support than with SiO_2. The results of catalytic studies show that cesium salts of dodecatungstophosphoric acid with low Cs content supported on silica or MCM-41 ($Cs_{1.7}H_{1.3}[PW_{12}O_{40}]$-on-$SiO_2$ and $Cs_{1.8}H_{1.2}[PW_{12}O_{40}]$-on-MCM41) are active, selective, and recyclable catalysts in Friedel–Crafts alkylations (isopropylation, transalkylation), the aromatic *ortho*-Claisen rearrangement, and the dehydration of pinacol. The specific activity of these catalyst preparations are comparable with that of neat $Cs_{2.6}H_{0.4}[PW_{12}O_{40}]$. This indicates that the active species are in a well-dispersed form. © 2001 Academic Press

Key Words: **heteropoly acids; cesium salts; MCM-41; multinuclear ^{29}Si, ^{31}P, and ^{133}Cs MAS NMR; solid acid catalysis.**

INTRODUCTION

The heterogenization of homogeneous catalysts has been an important tendency in catalysis research in recent years. The ease of handling, easy recovery, reuse, and possible regeneration are the most significant advantages of heterogeneous catalysts as compared to their homogeneous counterparts. Similar research efforts have yielded interesting and important results in the application of heteropoly acids (HPAs) with Keggin anion structure as well. The unique structural properties of these compounds allow us to use them as electrophilic catalysts (1–9), and they also promote oxidation reactions. They work as heterogeneous catalysts in apolar solvents, but their high solubility in many polar solvents renders them into their homogeneous phase. In the latter case, therefore, heterogenization is necessary. The application of supported HPAs may be a possible solution. It is known, however, that most common supports can accommodate only a limited amount of HPAs in the range of 7–14 wt% (3). Moreover, supporting HPAs in low loading often results in the decomposition of the Keggin structure. One notable exception is activated carbon, which is able to retain substantial amounts of HPAs without significant losses even in polar media. The encapsulation of HPAs into zeolites, carried out successfully with dodecamolybdophosphoric acid ($H_3[PMo_{12}O_{40}]$) (10) and dodecatungstophosphoric acid ($H_3[PW_{12}O_{40}]$, denoted H_3PW) (11), is a viable solution to this problem.

Another possibility pursued recently is the immobilization of HPAs into a silica matrix by means of a sol-gel technique. Promising results have been published with respect to the application of such catalysts in esterification (12) and ester hydrolysis (13–15), hydration of isobutylene (12), the alkylation of phenol (12), the Friedel–Crafts alkylation (16) and transalkylation (16), and the synthesis of methyl *tert*-butyl ether (16).

An important development associated with this field was the discovery and development of acidic salts of HPAs. Of these $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, a water-tolerant, insoluble, acidic, nonstoichiometric salt of dodecatungstophosphoric acid has been found to exhibit excellent catalytic activities in electrophilic transformations of various organic compounds in liquid-phase heterogeneous systems. Thorough and wide-ranging studies in recent years have revealed that it can be used in skeletal isomerization (17–20), alkane–alkene alkylation (21, 22), Friedel–Crafts alkylation (16, 17, 23–27) and acylation (25, 26), and hydration of alkenes (28, 29). In addition, $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is also

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highly active in the transformation of oxygen-containing compounds including alcohol dehydration (19, 24) and the pinacol rearrangement (30, 31), formation of esters (29, 31–33), hydrolysis (25, 29, 32, 34, 35) and decomposition (17, 24, 31) of esters, and the transformation of methanol and dimethyl ether to lower hydrocarbons (36).

This outstanding performance of $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is attributed to its surprisingly high surface area and its micro- and mesoporous structure (17–19, 24–26, 37). The BET surface area of cesium dodecatungstophosphates—and, in fact, that of other salts of heteropoly acids with a substantially large cation, such as Rb^+ and NH_4^+—was shown to decrease with increasing cesium content until the composition of $Cs_2H[PW_{12}O_{40}]$ (17–19, 24–26). Further increase in cesium content brings about a marked increase in surface area, reaching a value of about 150 m^2 g^{-1} for $Cs_3[PW_{12}O_{40}]$. The highest specific surface acidity and, consequently, the highest activities are achieved when the stoichiometry of Cs equals 2.5.

A problem associated with the use of this salt as catalyst material is its easy solubilization in water and in many organic solvents to form a colloidal solution. However, immobilizing $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ into a silica matrix (1, 12–15, 25) may eliminate the difficulty of the separation and work-up procedures. The resulting material exhibits strong acidity and effectively catalyzes the hydrolysis of ethyl acetate (13) and is active and selective in the synthesis of methyl *tert*-butyl ether (15). We reasoned that a viable alternative could be the use of high-surface-area support materials that can accommodate cesium salts. This method may even allow us to increase the effective surface of other cesium salts of low surface area, thereby transforming them into more effective catalysts. This can be of great significance in developing environmentally friendly practical applications. Similar approaches have recently been described (38, 39).

A comparative study, therefore, has been carried out using the well-studied $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ and two sets of newly prepared supported samples containing low and high amounts of cesium. Following a preliminary report about the first results of this study (40) herein we disclose our observations with respect to the MAS-NMR and FTIR characterization of these new supported cesium salts of dodecatungstophosphoric acid. New examples of catalytic reactions are also presented to widen the scope of applications. These new data further testify to the excellent performance of these catalytic materials.

EXPERIMENTAL

Materials

Benzene, toluene, *o*-xylene, and 1,3,5-tri-*tert*-butylbenzene were purchased from Aldrich whereas 2,3-dimethylbutane-2,3-diol was a Fluka product. They had a purity of at least 99%. The aromatic reagents (benzene, toluene, *o*-xylene) were stored over sodium wire. Isopropyl mesylate (41), 5-*tert*-butyl-1,2,3-trimethylbenzene (42), and allyl phenyl ether (43) were prepared according to the literature.

Catalyst Preparation

Davisil silica gel (Aldrich, grade 363, 35–60 mesh) and the mesoporous molecular sieve MCM-41 (synthesized according to the method by Kim *et al.* (44)) were used to prepare the supported cesium salts applying a literature method (45). The supports were pretreated at 573 K for 24 h before use. First, $CsNO_3$ (Aldrich) was deposited on 5 g of the support by impregnation with an aqueous solution. After drying (393 K, 12 h) and calcination (773 K, 2 h) $H_3[PW_{12}O_{40}]$ (SERVA, 1.6 g) was impregnated followed by drying (373 K for 2 h and 393 K for 12 h). The quantity of $CsNO_3$ was chosen to have less than monolayer loadings and nominal compositions $Cs_1H_2[PW_{12}O_{40}]$ and $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$.

For comparative studies unsupported salts with nominal compositions $Cs_{1.5}H_{1.5}[PW_{12}O_{40}]$ and $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ were prepared by adding dropwise an appropriate amount of aqueous $CsNO_3$ to aqueous $H_3[PW_{12}O_{40}]$ under continuous stirring. The resulting precipitate was aged for 24 h at room temperature, separated by centrifugation, and washed with distilled water.

Catalyst Characterization

Elemental analysis of the samples was performed by IPC and X-ray fluorescence (XRF) analysis. Instrumental methods of characterization included X-ray diffraction (XRD; DRON 2, operating under computer control), differential scanning calorimetry (DSC; Perkin Elmer DSC 2 equipment), and FTIR spectroscopy (Mattson Genesis 1) in the framework vibration range using the KBr pellet technique. Prior to measurements the samples were pretreated at 573 K for 2 h in vacuo (better than 10^{-5} torr) or in flowing helium.

The ^{29}Si, ^{31}P, and ^{133}Cs MAS-NMR spectra were recorded either on a Bruker MSL 400 or on a CXP 200 spectrometer. For ^{29}Si (79.468 MHz), a 4 μs ($\theta = \pi/6$) pulse was used with a repetition time of 6.0 s. For ^{31}P (161.924 MHz), a 6 μs ($\theta = \pi/6$) pulse was used with a repetition time of 10.0 s. For ^{133}Cs (52.464 MHz), a 2.0 μs ($\theta = \pi/12$) pulse was used with a repetition time of 0.5 s.

BET measurements were carried out in a conventional volumetric adsorption apparatus at liquid-N_2 temperature (77 K). IR spectroscopy was applied to determine the acidity of the samples by monitoring the adsorption of pyridine. Self-supporting wafers of the samples were pretreated in an IR cell and then cooled to room temperature and treated with 10 torr (1 torr = 133 Pa) of pyridine for 1 h. After evacuation (1 h), spectra were recorded at 293 K, 373 K, 473 K, and 573 K.

Chemical methods for characterization included the isomerization of 1-butene in a recirculatory batch reactor. After pretreatment (573 K, 2 h), the samples (50 mg) were cooled to reaction temperature (423 K), and then 1-butene (520 torr) was loaded. Sampling was carried out at regular time intervals and conversions and product distributions were determined by GC (HP-5710, 4.5-m dimethylsulfolane column, 293 K).

Catalytic Studies

The Friedel–Crafts reactions were carried out in a two-necked flask (10 ml) with vigorous stirring (magnetic stirrer) under reflux conditions with catalyst samples heat treated before use (573 K, 2 h, flowing He). Isopropylation of benzene was studied by reacting isopropyl mesylate (0.138 g, 0.001 mol) with 5 ml of benzene in the presence of 0.1 g of catalyst at 363 K. Transalkylation was carried out by reacting a mixture of 4.24 ml (0.04 mol) of toluene and 0.495 ml (0.001 mol) of 5-*tert*-butyl-1,2,3-trimethylbenzene in the presence of 0.1 g of catalyst at 383 K. Samples periodically withdrawn were analyzed by gas chromatography (GC).

The aromatic *ortho*-Claisen rearrangement was carried out by refluxing a continuously stirred mixture of 2.01 g (0.015 mol) of allyl phenyl ether, 0.05 g of 1,3,5-tri-*tert*-butylbenzene (internal standard), and 0.1 g of catalyst in *o*-xylene (5 ml) for 3 h.

The pinacol rearrangement was studied by heating 1 g (0.085 mol) of pinacol (2,3-dimethylbutane-2,3-diol) and 0.1 g of catalyst. The product was continuously distilled off from the reaction flask and collected at 250 K. For further details see Table 7.

Product compositions were determined by means of gas chromatography (Carlo Erba Fractovap 2350, TCD, 1.2-m SE 52 or Reoplex 400 column, and HP-5890, FID, 30-m DB-5 column). Compounds formed were identified via the GC retentions of authentic samples and GC-MS spectroscopy (HP 5890 GC coupled with a HP 5970 MSD). None of the supports was found to exhibit any activity under the experimental conditions applied.

RESULTS AND DISCUSSION

Preparation and Characterization of Supported Cesium Salts

Data collected in Table 1 with respect to elemental analysis of the samples performed with IPC and XRF show that the actual Cs/H ratios are substantially higher than the nominal values. The loadings calculated considering the actual compositions of salts are 16 wt% for samples with lower Cs content and 12 wt% for samples with higher Cs content. These observations may be explained by the specific method of preparation as opposed to the usual synthesis found in the literature. Salts of heteropoly acids are prepared, in general, by titrating the aqueous solution of the acid with Cs_2CO_3, followed by evaporation of the resulting slurry. In our case, due to the specific requirements of the method applied, the solution of $H_3[PW_{12}O_{40}]$ was added to $CsNO_3$ adsorbed on various supports. It appears that such modifications result in the formation of cesium salts with stoichiometries higher than expected.

Further data of the supports and supported cesium salts are also collected in Table 1. It is seen that loading the salts to the supports brings about a certain decrease in the BET surface areas. The resulting supported samples, nevertheless, still have high enough surface area to ensure the formation of well-dispersed catalytic materials. Data acquired by DSC (not shown) indicate that the supported samples are stable up to about 800 K and they show full crystallinity similar to that of neat $Cs_{2.5}PW$ (XRD). No change in the structure of MCM-41 was found after pretreatment at 573 K.

All samples display both Brønsted and Lewis acidity. The acidity of the samples was determined by calculating the integral absorption of bands at 1560 cm^{-1} characteristic of Brønsted acidity and that at 1450 cm^{-1} assigned as pyridine bonded to Lewis acid sites. These values were divided by the

TABLE 1

Characteristic Data of the Supports and Cesium Salts

Cs content		Sample denomination	BET (m^2 g^{-1})	Acidity (m^{-3})		Surface acidity (μmol g^{-1})
Nominal	Measured			Brønsted	Lewis	
2.5	2.6	$Cs_{2.6}PW$	113			30
1.5	1.7	$Cs_{1.7}PW$	13			11.2
		SiO_2	555	0.02	1.27	
2.5	2.9	$Cs_{2.9}/SiO_2$	326	0.04	2.58	3.5
1	1.7	$Cs_{1.7}/SiO_2$	312	0.27	1.95	33.4
		MCM-41	773	0.07	0.83	
2.5	2.8	$Cs_{2.8}$/MCM41	609	0.07	1.71	7.1
1	1.8	$Cs_{1.8}$/MCM41	544	0.22	2.34	30.8

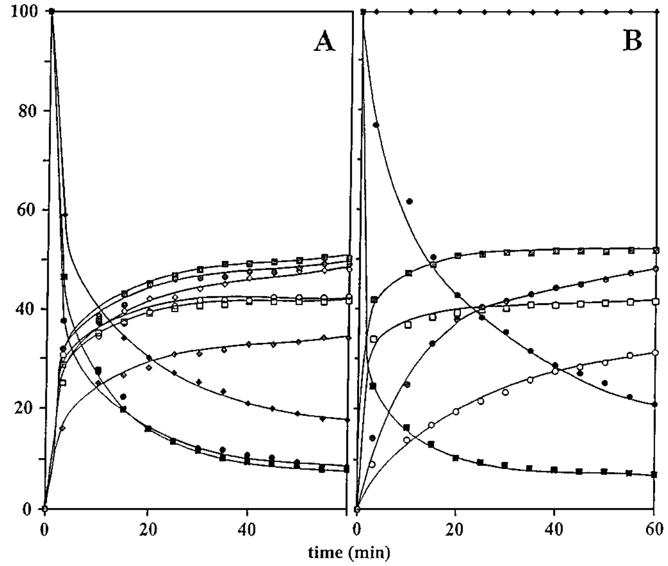


FIG. 1. Changes in the composition of the reaction mixture vs time in the isomerization of 1-butene: (A) MCM-41 (diamonds), $Cs_{1.8}$/MCM41 (squares), and $Cs_{2.8}$/MCM41 (circles); (B) SiO_2 (diamonds), $Cs_{1.7}/SiO_2$ (squares), and $Cs_{2.9}/SiO_2$ (circles). Black symbols: 1-butene, open symbols: *cis*-2-butene, shaded symbols: *trans*-2-butene.

mass of the samples and the corresponding BET areas and provide the acidity data given in columns 5 and 6. It is clearly seen that the deposition of cesium salts with low Cs content ($Cs_{1.7}/SiO_2$ and $Cs_{1.8}$/MCM41) on the supports results in a significant increase in Brønsted acidity, which is in harmony with the NMR results. Significant increases in Lewis acidity, in contrast, are measured for all supported samples.

Data for the isomerization of 1-butene are shown in Fig. 1. Of the two supports MCM-41 exhibited an activity comparable to that of the Cs-containing samples, whereas SiO_2 was completely inactive. Cs salts supported MCM-41 ($Cs_{1.8}$/MCM41 and $Cs_{2.8}$/MCM41) showed practically the same activity. This is in sharp contrast to the behavior of the silica-supported samples. Here the activity of $Cs_{1.7}/SiO_2$ was much higher than that of $Cs_{2.9}/SiO_2$. The ratio of the isomeric 2-butenes is approximately unity what is usually observed in acid-catalyzed double bond migrations.

Multinuclear MAS-NMR Characterization

The ^{31}P-NMR chemical shifts of pure $Cs_{2.6}$PW heteropoly acid salt and its supported samples are reported in Table 2. The spectra were recorded both with and without ^{1}H–^{31}P cross-polarization. The −14.6 ppm line characterizes the Cs_3PW salt, the −13.4 ppm line the Cs_2PW salt, and the −10.6 ppm line the H_3PW acid form (19, 23, 46). Note that the CP spectra only show the −14.6 ppm line. This underlines unambiguously the fact that in the other forms the proton exchanges quite quickly, thereby destroying the cross-polarized signal. The small NMR lines at ca. 0.4 and 1.6 ppm stem from PO_4^{3-} and $H_2PO_4^-$ impurities. They are only detected on SiO_2-supported samples and the low cesium content initial $Cs_{1.7}$PW salt.

TABLE 2

^{31}P-NMR Data of the Pure and Supported Cesium Salts without Cross Polarization

	δ (ppm vs aq H_3PO_4) (I%)			
Sample	Cs_3PW	CsH_2PW	H_3PW	PO_4^{3-}, $H_2PO_4^-$
$Cs_{2.6}$PW	−14.6 (88)		−10.5 (12)	
$Cs_{1.7}$PW	−15.5 (40)	−13.6 (16)	−12.0 (8)	−4.9 (33), −0.3 (3)
$Cs_{2.9}/SiO_2$	−14.5 (77)			0.4 (23)
$Cs_{1.7}/SiO_2$	−14.5 (60)	−13.4 (18)	−10.8 (18)	1.6 (4)
$Cs_{2.8}$/MCM41	−14.5 (100)			
$Cs_{1.8}$/MCM41	−14.5 (75)	−13.4 (12)	−11.1 (13)	

The pure $Cs_{2.6}$PW salt contains some 88% Cs_3PW and 12% H_3PW acid forms. This high content Cs salt, when deposited on MCM-41, conserves only the Cs_3PW form. When deposited on SiO_2, a rather large amount of PO_4^{3-} impurities (ca. 23%) is also detected. The low Cs loading leads to the coexistence of Cs_3PW, Cs_2HPW, and H_3PW forms in various amounts as shown in Table 2.

The supports were characterized by ^{29}Si-NMR both with and without ^{1}H–^{29}Si cross-polarization. The spectra are composed of three lines: the −111 ppm line stems from the $Si(OSi)_4$ groups, the −101 ppm line from the SiOH defect groups, and the −92 ppm line from the $Si(OH)_2$ defect groups (Table 3) (47). The relative amount of the SiOH groups does not change when the CsPW salt is deposited on SiO_2. Only a slight decrease of the $Si(OH)_2$ groups can

TABLE 3

^{29}Si-NMR Data of the Pure and Supported Cesium Salts

(A) Without cross polarization

	δ (ppm vs TMS) (I%)		
Sample	$Si(OSi)_4$	SiOH	$Si(OH)_2$
SiO_2	−111.0 (64)	−101.3 (30)	−92.0 (6)
$Cs_{2.9}/SiO_2$	−111.3 (66)	−101.7 (30)	−91.8 (4)
$Cs_{1.7}/SiO_2$	−111.4 (67)	−101.8 (29)	−92.3 (4)
MCM41	−109.0 (70)	−100.2 (25)	−91.8 (5)
$Cs_{2.8}$/MCM41	−110.8 (58)	−101.2 (36)	−91.8 (6)
$Cs_{1.8}$/MCM41	−110.8 (60)	−101.5 (36)	−91.9 (4)

(B) With cross polarization

	δ (ppm vs TMS) (I%)		
Sample	$Si(OSi)_4$	SiOH	$Si(OH)_2$
SiO_2	−110.8 (32)	−101.2 (57)	−92.0 (11)
$Cs_{2.9}/SiO_2$	−111.1 (31)	−101.4 (61)	−91.8 (8)
$Cs_{1.7}/SiO_2$	−111.2 (39)	−101.3 (53)	−92.0 (8)
MCM41	−108.9 (37)	−100.2 (53)	−91.8 (10)
$Cs_{2.8}$/MCM41	−110.8 (17)	−101.0 (70)	−91.7 (13)
$Cs_{1.8}$/MCM41	−110.9 (21)	−101.1 (69)	−91.9 (10)

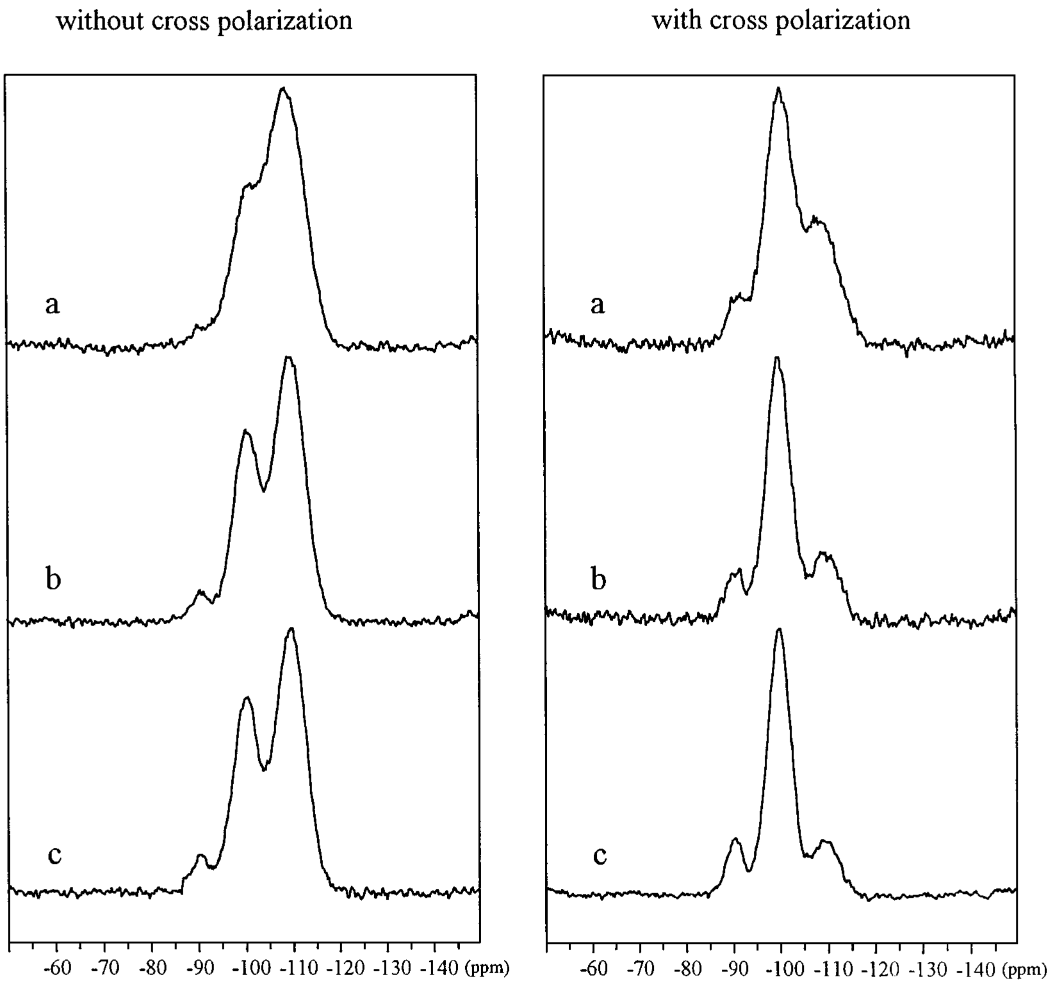
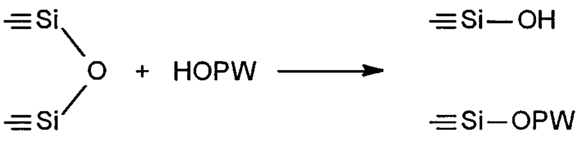


FIG. 2. ^{29}Si-NMR spectra of MCM-41, $Cs_{1.8}$/MCM41, and $Cs_{2.8}$/MCM41.

be found. In contrast, when the CsPW salt is formed on MCM-41, the relative amount of SiOH increases from 25% to 36%. The relative amount of $Si(OH)_2$ remains about the same within experimental errors. Figure 2 illustrates the ^{29}Si-NMR spectra of the initial MCM-41 and the two CsPW/MCM41 samples. The presence of SiOH groups is clearly shown by the increased intensity of the −101 ppm line in cross-polarized conditions.

The increase in the relative intensities of the SiOH lines on MCM-41 during the formation and deposition of CsPW suggests the reaction depicted in [1], where siloxane bonds interacting with dodecatungstophosphoric acid are broken to yield the silanol group. At the same time, the Keggin anion strongly interacts with the MCM-41 surface.



[1]

Similar conclusions have been arrived at when organic moieties were deposited on MCM-41 (48, 49). Indeed, it was shown by both ^{29}Si-NMR and IR results that owing to the high strain in the MCM-41 walls this reaction readily occurs, while on the relaxed structure of SiO_2 this reaction does not take place. This result also emphasizes the fact that the Keggin units are certainly incorporated in the interior of MCM-41 channels.

The ^{133}Cs MAS-NMR spectra also show a difference between the influence of the two supports (Table 4). SiO_2 does not significantly perturb the environment of the Cs ion in $Cs_{2.6}$PW, as both the chemical shift (−58.7 ppm in 1 M aqueous CsCl solution) and the linewidth (500 Hz) remain the same as for the pure $Cs_{2.6}$PW salt. In contrast, the supported MCM-41 shows an influence on the chemical shift, which becomes equal to ca. −56.5 ppm. This result also suggests that the $Cs_{2.6}$PW salt interacts more strongly with the MCM-41 support, as explained above.

However, the ^{133}Cs MAS-NMR spectra of the $Cs_{1.7}$PW sample show greater changes. Indeed, the chemical shift is

TABLE 4

^{133}Cs-NMR Data of the Pure and Supported Cesium Salts

Sample	δ (ppm vs 1 M aq CsCl)[a]
$Cs_{2.6}PW$	−58.7
$Cs_{1.7}PW$	−63.5[b]
$Cs_{2.9}/SiO_2$	−58.5
$Cs_{1.7}/SiO_2$	−59.1
$Cs_{2.8}$/MCM41	−56.2
$Cs_{1.8}$/MCM41	−56.9

[a] $\Delta H = 500$ Hz at $\nu_{rot} = 2100$ Hz.

[b] $\Delta H = 1000$ Hz at $\nu_{rot} = 3500$ Hz.

equal to −63.5 ppm in the initial sample and the linewidth is double that of the $Cs_{2.6}PW$ sample. When the $Cs_{1.7}PW$ is deposited on SiO_2, a great change occurs in the chemical shift, which becomes equal to −59.1 ppm. Finally, as Cs^+ ions are adsorbed on MCM-41 the interaction between them and the support increases, and the chemical shift is now close to that of the $Cs_{2.8}$/MCM41 sample.

CATALYTIC STUDIES

The results of catalytic studies with the supported samples are shown in Tables 5–7. Also shown are data for comparison obtained with the unsupported cesium salts.

Data for the Friedel–Crafts reactions indicate that in the isopropylation of benzene the supported samples with low Cs content are more active than the corresponding samples with high Cs content (Table 5). In the transalkylation of toluene [2], in turn, the latter samples proved to be completely inactive (Table 5).

TABLE 5

Activity of the Catalysts in Friedel–Crafts Alkylations

Catalyst samples	Isopropylation[a] Conversion	Transalkylation Conversion	TOF (min^{-1})
$Cs_{2.6}PW$	100[b] (85)[c]	54[d] (70)[e]	1
$Cs_{1.7}PW$	100[b] (75)[c]	0	
$Cs_{2.9}/SiO_2$	47	0	
$Cs_{1.7}/SiO_2$	93	73[d] (90)[e]	1.4
$Cs_{2.8}$/MCM41	44	0	
$Cs_{1.8}$/MCM41	100	69[d] (81)[e]	1.3

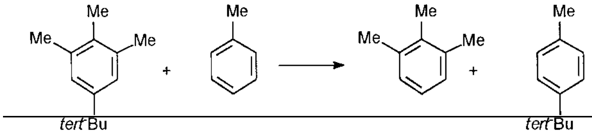
[a] Reaction time = 1.5 h.

[b] 25 mg of catalyst.

[c] 20 mg of catalyst.

[d] Reaction time = 3 h.

[e] Reaction time = 7 h.



[2]

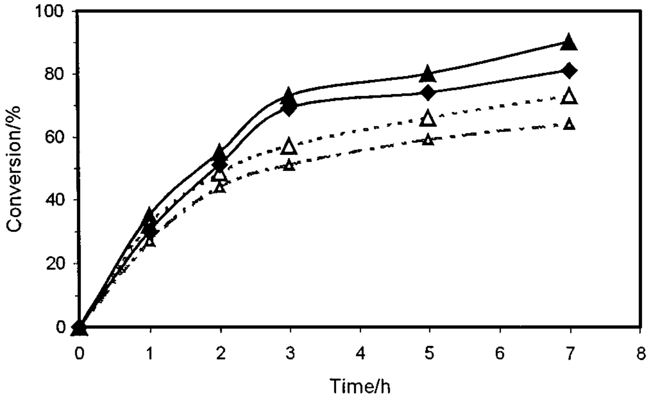


FIG. 3. Change in catalytic activity vs time in the trans-*tert*-butylation of toluene. ▲ $Cs_{1.7}/SiO_2$, 1st run, ··· △ ··· 2nd run, — · —△— · — 3rd run, ◆ $Cs_{1.8}$/MCM41.

This difference observed in the two reactions between the activities of the salts of high and low Cs contents is easy to explain. Isopropyl mesylate is a reagent that can quite readily yield the 2-propyl carbocation as the reactive intermediate participating in the electrophilic aromatic substitution to give the alkylated product. As a result, even the samples with high Cs content ($Cs_{2.9}/SiO_2$ and $Cs_{2.8}$/MCM41), i.e., those with low actual surface proton concentration, are able to generate the carbocation in an appropriate concentration ensuring certain low activities. Transalkylation, in contrast, where the reacting *tert*-butyl carbocation is formed by the dealkylation of the aromatic compound, is a more demanding reaction. In this case the samples with high Cs content, i.e., those with low concentration of acid sites, are unable to generate carbocations.

The catalysts were also employed in repeated experiments to learn about the stability and the possibility of recycling the samples. As data obtained for transalkylation illustrate (Fig. 3) the $Cs_{1.7}/SiO_2$ sample shows good stability in repeated use. Although a certain drop of activity is seen after each run, the conditions were not optimized and the possibility of reactivation was not pursued.

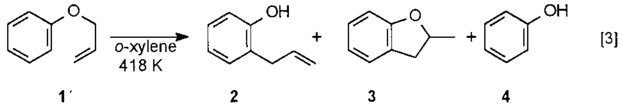
In the transformation of allyl phenyl ether (Table 6) the main product is always 2-methyldihydrobenzofurane (**3**) [3]. This compound is thought to be formed by the further transformation of the primary product *o*-allylphenol (**2**), the product of the aromatic *ortho*-Claisen rearrangement. By-products are phenol (the product of de-acetylation) formed in significant amounts and some oligomers. Similar selectivities, i.e., the formation of **3** as the major product, were observed by Sheldon *et al.* over H-beta and H-mordenite zeolites (50) and in our recent study applying various Nafion-based catalysts (51). The ring-closing transformation of compound **2** to compound **3** was shown to result from the highly acidic nature of the catalysts used.

In the dehydration of pinacol (**5**) carried out in the presence of the supported cesium salts, the main product is always 3,3-dimethylbutane-2-one (**6**) formed as a results

TABLE 6

Conversions and Selectivities of the *ortho*-Claisen Rearrangement of Allyl Phenyl Ether (1)

Catalyst samples	Conversion (%)	Selectivity (%)				
		2	**3**	**4**	Oligomers	TOF (min^{-1})
$Cs_{2.6}PW$	39	11	59	26	4	10.8
$Cs_{1.7}PW$	0					
$Cs_{2.9}/SiO_2$	0					
$Cs_{1.7}/SiO_2$	60	7	53	40	traces	15
$Cs_{2.8}/MCM41$	0					
$Cs_{1.8}/MCM41$	66	8	62	30	traces	17.8



[3]

of the pinacol rearrangement (Table 7) [4]. The unsaturated by-products (**7** and **8**) are formed through stepwise β-eliminations. The appearance of these compounds and especially that of the unsaturated alcohol (**7**) are indicative of decreased acidity as found and discussed earlier (52). Again, the activity of the samples with high Cs content (low surface acidity) is significantly and characteristically lower than that of the salts with low Cs content (high surface acidity) (note the increased reaction temperature necessary to achieve complete conversion in the case of $Cs_{2.9}/SiO_2$ and $Cs_{2.8}/MCM41$).

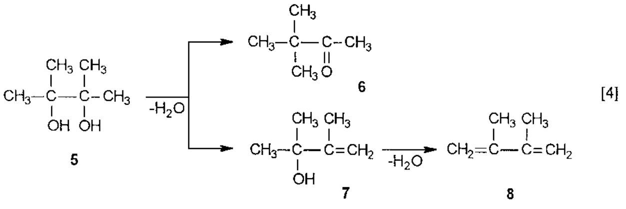
The activity pattern shown by the unsupported salts is quite the opposite to what was observed for the supported samples in the two demanding reactions, in transalkylation and the transformation of allyl phenyl ether: $Cs_{2.6}PW$ is highly active, whereas $Cs_{1.7}PW$ shows no activity at all. As discussed in the introduction, $Cs_{2.5}PW$ is known to have the highest specific surface acidity of the cesium salts of dodecatungstophosphoric acid. Although it contains only a relatively low number of protons, almost all are available for catalysis due to the high surface area of this sample. It is not surprising, therefore, that our $Cs_{2.6}PW$ sample shows good catalytic activities. $Cs_{1.7}PW$, in turn, has very low specific surface acidity although it possesses more protons. Because of the low surface area, however, most of the protons are unavailable for participating in a catalytic process. As a result, this sample is inferior to $Cs_{2.6}PW$. Isopropylation and the dehydration of pinacol are more facile processes and such differences are not observed in these reactions.

TABLE 7

Selectivities in the Dehydration of Pinacol (5)[a,b]

Catalyst samples	Selectivity (%)		
	6	**7**	**8**
$Cs_{2.6}PW$	79	0	21
$Cs_{1.7}PW$	81	0	19
$Cs_{2.9}/SiO_2$[c]	85	3	12
$Cs_{1.7}/SiO_2$	77	0	22
$Cs_{2.8}/MCM41$[c]	80	4	16
$Cs_{1.8}/MCM41$	80	0	20

[a] Conversion is 100% in each reaction.
[b] Reaction temperature = 438 K.
[c] Reaction temperature = 473 K.



[4]

A comparison of the results found for $Cs_{1.7}PW$, and for the two supported salts with low Cs content ($Cs_{1.7}/SiO_2$ and $Cs_{1.8}/MCM41$), shows that the catalytic performance of the supported samples significantly exceeds that of $Cs_{1.7}PW$. This observation clearly indicates that cesium salts of dodecatungstophosphoric acid with low Cs content and low surface area (and, therefore, low specific surface acidity) can be transformed into highly active catalytic materials. Activity data were calculated for transformations when reaction conditions were identical for the three catalysts samples using the surface acidity values collected in the last column in Table 1 (these values were calculated as described in Ref. 24). The corresponding activity data (TOF values) for transalkylation (Table 5), aromatic *ortho*-Claisen rearrangement (Table 6), and dehydration of pinacol (Table 7) clearly show that the specific activities of the two supported catalysts samples with low Cs content and those found for the unsupported $Cs_{2.6}PW$ sample are comparable. It follows that the method described here, i.e., supporting acidic cesium salts of heteropoly acids in submonolayer loading on suitable high-surface area carriers, is a viable process to produce catalytic materials of high efficiency. A further notable advantage of these samples containing the active phase in a finely dispersed form is that they can be recycled as discussed earlier.

It is also important to discuss the effect of phosphate impurities found in some of the samples. No significant difference is found in the activities of the two supported samples with low cesium content, although $Cs_{1.8}/MCM41$ is free of impurities. In addition, $Cs_{1.7}PW$ with the highest amount of PO_4^{3-} and $H_2PO_4^-$ exhibits no activity at all in transalkylation and the aromatic *ortho*-Claisen rearrangement, the two most demanding reactions, just as the pure $Cs_{2.8}/MCM41$. These impurities, therefore, do not appear to affect catalyst performance.

CONCLUSIONS

According to ^{31}P-NMR data, salts of various stoichiometries (Cs_3PW and Cs_2HPW) and even H_3PO_4 exist on the supported samples. No change in the relative amount of various SiOH groups of the silica support is detected by ^{29}Si-NMR. In contrast, when the support is MCM-41, the relative amount of the SiOH groups increases significantly, indicating the breaking of the siloxane bonds resulting from its interaction with H_3PW. A stronger interaction of the CsPW salt with the MCM-41 support than with SiO_2 is also suggested by ^{133}Cs MAS-NMR spectra.

Cesium salts of dodecatungstophosphoric acid with low Cs content supported on silica or MCM-41 ($Cs_{1.7}H_{1.3}[PW_{12}O_{40}]$-on-$SiO_2$ and $Cs_{1.8}H_{1.2}[PW_{12}O_{40}]$-on-MCM41) have been found to be active, selective, and recyclable catalysts in organic transformations requiring the use of electrophilic catalysts. The specific activity of these catalyst preparations are comparable with that of neat $Cs_{2.6}H_{0.4}[PW_{12}O_{40}]$. This indicates that the active species are in a well-dispersed form.

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