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Synthesis and characterization of HPW/MCM-41 (Si) and HPW/MCM-41 (Si/Al) catalysts: Activity for toluene alkylation with 1-dodecene

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Abstract

Solids of the MCM-41 type (BET specific surface area around 600 m^2/g), with only Si and with Si/Al (atomic ratio) = 25, were synthesized and employed as supports of dodecatungstophosphoric acid (HPW)-based catalysts. Catalysts were prepared by impregnation of HPW, in amounts of 20, 40 and 60 wt%. Characterization by DTA, TGA, XRD, FT-IR and NH_3-TPD suggest an interaction of HPW with the supports. This interaction in the HPW/MCM-41 (Si) catalysts leads to a higher thermal stability of the Keggin structure of HPW and thus a preservation of its acidic protons. This effect is reflected in a higher density of acid sites upon increasing HPW loading. Powder XRD patterns of catalysts and the steady loss of specific surface area in both supports are consistent with a uniform distribution of the supported HPW. Analysis by FT-IR of the supported catalysts shows a displacement of the W–O–W band of supported HPW as compared with pure HPW. This displacement decreases with increasing loading, being higher for 20% HPW/(Si/Al). The catalytic activity in the alkylation of toluene with 1-dodecene increases in the following sequence: 20% HPW/(Si/Al) < 40% HPW/(Si/Al) < 20% HPW/(Si) < 60% HPW/(Si/Al) < 40% HPW/(Si) < 60% HPW/(Si), which is directly related to the acid site density. The conversions and selectivities towards monoalkylated products for HPW/MCM-41 (Si) catalysts are higher than those for HPW/MCM-41 (Si/Al). The 60% HPW/MCM-41 (Si) catalysts presents the higher selectivity to monoalkylated products and the higher thermal stability, while for 20% HPW/MCM-41 (Si/Al) no catalytic activity was observed.

Keywords: Catalysts HPW/MCM-41; DTA; TGA; XRD; FT-IR; NH3-TPD characterization; Toluene alkylation

1. Introduction

Monoalkylbenzenes are employed in the formulation of detergents; basically, there are two types of alkylates with interesting characteristics for the formation of anionic surfactants. The first type is that called ''hard alkylate'', which are branched, and after sulfonated receive several commercial names, such as ABS (sulfonated alkyl benzene). The second type are the linear alkyl benzenes (LABs), ''soft alkylate'', synthesized by alkylation of benzene with long chain olefins, between C10 and C13, or with chloroparaffins or paraffins [1]; their sulfonation permits to obtain linear alkyl benzenes sulfonated (LAS).

Nowadays, the world consumption of detergents is constantly increasing and the total production of tensoactive agents is about 8 million tonnes. From this total, a fourth part corresponds to sulfonated linear alkyl benzenes, which are eco-friendly as they are more biodegradable than other surfactants. For the industrial synthesis of linear alkyl benzenes liquid protonic acids are employed as catalysts to induce the protonation of the alkylating agent, forming a carbenium ion or, in the case of Lewis acid catalysts (e.g., $AlCl_3$), formation of a polarized complex. One or the other is necessary for the electrophilic attack on the aromatic ring.

Catalysts employed for industrial synthesis of LABs are fluorhydric or sulfuric acids or aluminium trichloride (Friedel–Kraft catalyst) [2]; the use of such reagents in large scale processes pose a serious environmental risk, due to their high

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corrosive, pollutant, and toxic potential. For those reasons, in the last decade replacement for solid acid catalysts, more environmentally friendly but with appropriate catalytic activity and selectivity has been attempted. Zeolites and sulfated metallic oxides both have been employed in laboratory studies [2]. However, in the year 2000 the UOP Detal technology was released. This industrial process employs an undisclosed acid catalyst, around which in the latter years fundamental studies have been carried out on the reaction mechanism and catalytic properties, aiming to improve selectivity and stability of these acid solids under commercial operation conditions [3,4].

Heteropolyacids (HPAs) constitute a new alternative for the alkylation reactions, as they are characterized by a strong acidity, fundamentally of the Brönsted type, comparable to that of fluorhydric and sulfuric acids; some of the more interesting shows the Keggin structure and have been used as catalysts in other alkylation reactions either in homogeneous or heterogeneous systems. Advantages include easy preparation, high acidity and acceptable stability. Disadvantages are their low porosity and specific surface area ($\sim$5 m^2/g) [5], thus a high-surface area structure is required as a support.

Several solid supports have been employed for HPA, which, together with pre-treatment conditions, determine the activity of the resulting catalyst. Acid or neutral supports, such as silica, silica–alumina, ionic exchange acid resins, alumina, activated carbon, and also basic solids as magnesia have been tried [5]. It has been reported that the HPAs show a high catalytic activity if supported on silica or carbon, but not on alumina, that apparently causes decomposition and destruction of the Keggin structure of the heteropolyacid [6]. Also, a higher stability of dodecatungstophosphoric acid (HPW) has been observed on supports like MCM-41 (Si) as compared with mesoporous silica–alumina (MSA), in the alkylation of isobutene with 2-butene [7].

In this work, the activity for the alkylation of toluene with 1-dodecene and the selectivity to monoalkylates, of *x*% HPW/MCM-41 (Si) and *x*% HPW/MCM-41 (Si/Al) catalysts with variable *x*, has been studied. The mesoporous MCM-41 (Si) and MCM-41 (Si/Al) were first synthesized and characterized, and afterwards they were impregnated with different amounts (20–60 wt%) of dodecatungstophosphoric acid. The supports and catalysts were characterized by means of several physicochemical techniques. The effect of the support composition was examined, as well as the effect of the loading of supported HPW phase, on the activity and selectivity to the desired product in the indicated reaction.

2. Experimental

2.1. Synthesis of MCM-41 (Si) and MCM-41 (Si/Al)

For the synthesis of the solid mesoporous supports, the procedure reported by Hu et al. [8] was employed. The molar composition of reactants for the synthesis was:

- *MCM-41 (Si)*: 1 SiO_2:0.21 tetraethyl ammonium hydroxide (TEAOH):0.28 cetyltrimethyl ammonium bromide (C16TAB):24H_2O.
- *MCM-41 (Si/Al)*: 1 SiO_2:0.21 TEAOH:0.28 C16TAB:0.02 $Al_2(SO_4)_3 \cdot 18H_2O$:23.6$H_2O$.

The resulting solids were fired up to 340 °C under N_2 flow and then up to 500 °C under dry airflow. Afterwards, they were characterized by several techniques as described below.

2.2. Preparation of catalysts

Catalysts containing 20, 40, and 60 wt% of HPW were prepared by impregnation of either calcined support with HPW solutions in concentrations appropriate to keep a ratio of 10 ml of solution per gram of support. The mixtures were heated at 60 °C with stirring until dryness. Then, the solids were heated in a stove for an additional 14 h at 100 °C to insure elimination of excess moisture.

2.3. Characterization of solid samples

To carry out the characterization of supports and catalysts, the following techniques and equipment were employed

Chemical analysis by atomic absorption in a PerkinElmer 3100 instrument. Powder X-ray diffraction (XRD) with a Philips 1730 apparatus, employing Cu Kα radiation, 2θ between 1° and 35° at a step velocity of 0.01°/s. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a TA Instruments model DSC 910/1600 DTA equipment. BET specific surface area (SSA) by N_2 physisorption at −196 °C, employing a Micromeritics Flowsorb II 2300 instrument. FT-IR spectroscopy with a PerkinElmer model Spectrum One, using wafers of a mixture sample/anhydrous KBr in 1/10 weight ratio, in order to make quantitative comparisons between spectra. Scanning electron microscopy (SEM) and EDX analysis was carried out with a XL 30 Philips equipment using a BSE detector and base pressure of 10^{-5} Torr. For analysis, samples were dispersed in ethanol and covered by sputtered gold. Acidity measurements by TPD of ammonia was performed in a Micromeritics Auto Chem instrument, model 2910, using a thermal conductivity detector and high purity He as carrier gas. Before runs, samples were degassed at 500 °C. Ammonia was adsorbed at room temperature and afterwards desorbed in the 150–500 °C range. Integration of the TPD traces and comparison with the area given by a known amount of NH_3 allows to quantify the amount of acid sites per gram of solid.

2.4. Alkylation of toluene with 1-dodecene

Reaction was carried out in the liquid phase in a batch reactor for 6 h at 90 °C and atmospheric pressure, using 0.5 g of catalyst and a molar ratio toluene/1-dodecene = 3. Activation of the catalysts was carried out at 130 °C for 12 h under N_2 flow. Effluents of the reactor were analysed at varying times, between 10 min and 1 h, using a HP 5890 GC with FID detection and a CP sil SCB column of 50-m length.

Activity is reported in terms of percent of olefin transformed (conversion), employing the following equation:

$$X\,(\%) = \frac{\sum \text{area}_{\text{products}}}{\sum(\text{area}_{\text{products}}) + (\text{area}_{\text{olefin-not-transformed}})} \times 100$$

3. Results and discussion

3.1. Structural characterization by XRD

Fig. 1a shows the X-ray diffractogram of the MCM-51 (Si) calcined support in the 2θ range between 1° and 5°. It can be seen that this diffractogram is typical of this type of solids, presenting the characteristic reflections 1 0 0, 1 1 0 and 2 0 0. From the 100 line a pore size of approximately 70 Å could be estimated, corresponding to the cell parameter $a_0 = 2d_{1\,0\,0}/\sqrt{3}$. In Fig. 1b a SEM micrograph of this solid is presented; the observed morphology is consistent with this kind of molecular sieve materials [9,10].

For the MCM-41 (Si/Al) solid, the XRD trace shows broader bands, less intense and defined (Fig. 1c), suggesting either a higher degree of structure disorder or that most of the particles are very small. Morphology of this solid, Fig. 1d, shows particles similar to those of MCM-41 (Si) (Fig. 1b), however, most of the observed particles are smaller than 5 μm, consistent with the XRD data. Chemical analysis by atomic absorption for this solid showed a Si/Al ratio of 25, while EDX analysis shows a ratio of 23, close to the value for the bulk analysis; although EDX is not a true surface analysis technique, this small discrepancy could suggest slightly higher concentration of aluminium at the surface, probably amorphous aluminium oxide.

In Fig. 2 XRD traces for 2θ between 5° and 35° are shown for the following solids: the pure support MCM-41 (Si); the *x*% HPW/MCM-41 (Si) catalysts with $x = 20$, 40, and 60; the 60% HPW/MCM-41 (Si/Al) sample; and pure HPW. By comparing the diffractograms of the three *x*% HPW/MCM-41 (Si) samples with that of HPW it can be seen that neither of the catalysts show peaks that can be assigned to this active phase, which shows that the supported HPW is well dispersed on the surface of the MCM-41 (Si) support, even at contents as high as 60 wt%. Results reported by Kozhevnikov et al. [11] for the synthesis and XRD characterization of similar HPW/MCM-41 (Si) catalysts with HPW contents between 10 and 70 wt% show the peaks characteristic of HPW in the catalysts at contents as low as 20 wt%. The main difference between the solids employed in that work and the present report is the mean pore diameter, which is nominally 41 Å (measured 32 Å) for Kozhevnikov's and about 70 Å for the present work. This large difference in the pore diameter can allow a more uniform distribution of HPW on the support surface, minimizing the possibility of agglomerations of HPW which could induce crystallization.

In the XRD patterns of 20% and 40% HPM/MCM-41 (Si/Al) no peaks which could be assigned to HPW are observed, only for the 60% HPM/MCM-41 (Si/Al) catalyst (Fig. 2e) several wide and low-intensity signals could be assigned to HPW.

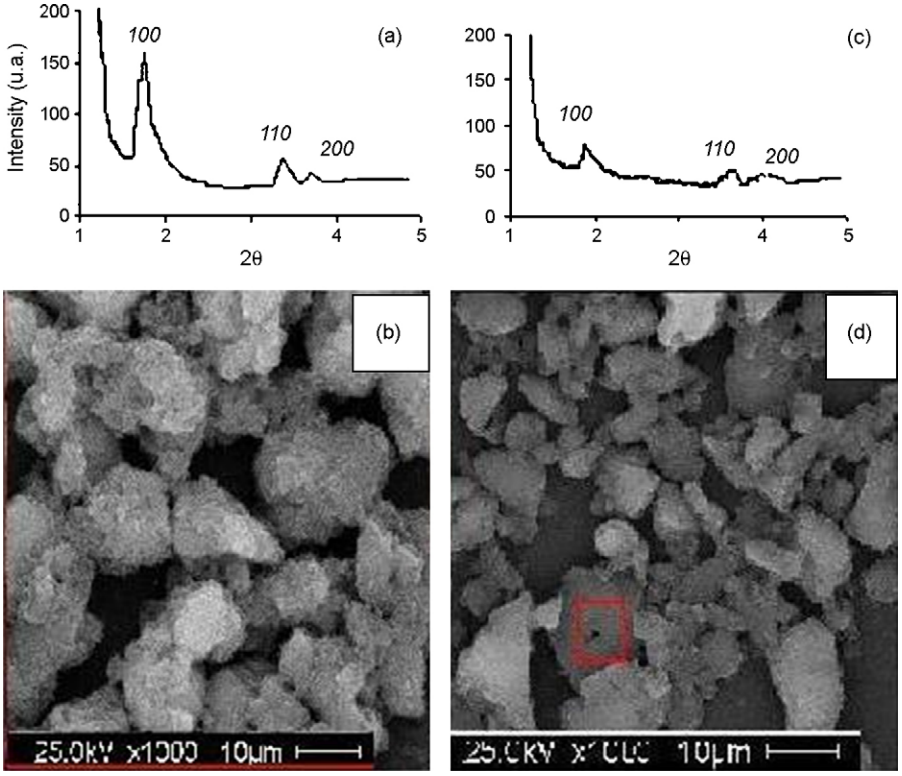


Fig. 1. (a) Powder diffractogram of the calcined MCM-41 (Si) support. (b) SEM micrograph of MCM-41 (Si). (c) Powder diffractogram of the calcined MCM-41 (Si/Al) support. (d) SEM micrograph of MCM-41 (Si/Al).

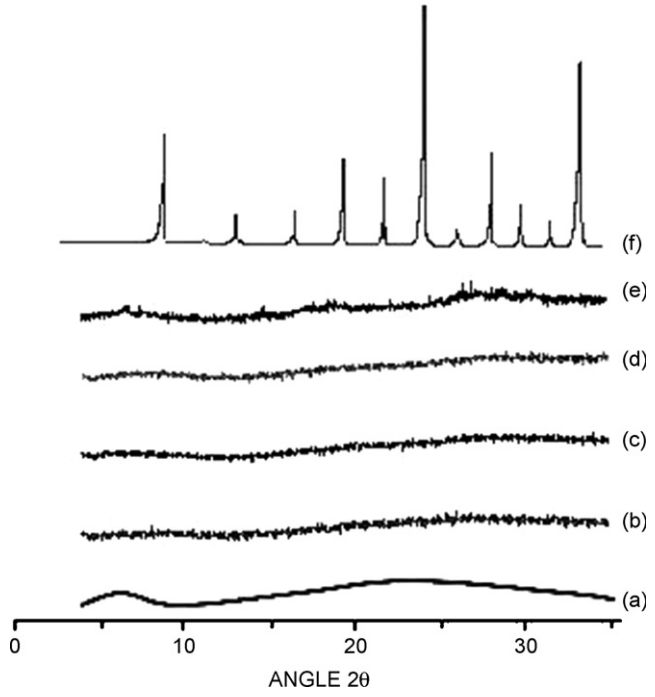


Fig. 2. Powder diffractograms of: (a) MCM-41 (Si), (b) 20 wt% HPW/MCM-41 (Si), (c) 40 wt% HPW/MCM-41 (Si), (d) 60 wt% HPW/MCM-41 (Si), (e) 60 wt% HPW/MCM-41 (Si/Al) and (f) dodecatungstophosphoric acid, HPW.

Those results suggest that there is a good dispersion of HPW in the MCM-41 (Si/Al) solid at contents of active phase lower than 60 wt%, in agreement with the less uniform and ordered structure of this support.

3.2. Specific surface area (SSA)

In Table 1 the BET SSA for supports and catalysts is reported. In the case of the catalysts, the area normalized per gram of support was calculated and is shown as SSA*. This parameter neglects any contribution to the area by the HPW supported phase. As an example, the 40% HPW/MCM-41 (Si) catalyst has 40% of active phase and 60% of support, thus, SSA* = 234 m^2/g_{cat} × 100/60 = 390 m^2/g_{sup}. The loss of surface area for each catalyst was calculated from SSA* with respect to SSA of the pure support. The following observations can be made:

(a) The SSA of the MCM-41 (Si/Al) support is lower than that of the MCM-41 (Si) one, which could be a consequence of the isomorphic substitution of Al for Si [12].
(b) Upon increasing HPW loading on either support, SSA and SSA* both decrease, which seems logical as the impregnated HPW is dispersed and deposited on the support surface, decreasing the effective pore diameter and thus diminishing the surface area.
(c) The area loss is very similar for both supports. It is somewhat higher, however, for the 20% HPW/MCM-41 (Si/Al) than for 20% HPW/MCM-41 (Si), 21% vs. 18%. This difference could be indicating an interaction at the lower active phase loading between HPW and Al of the (Si/Al) support.

Results by Nowinska et al. [13] for HPW/γ-alumina solids show a diminution of SSA in comparison with HPW/silica solids, which was assigned to the formation of aluminium compounds with HPW that erode the pore system of the alumina support. A similar phenomenon is probably occurring in the 20% MCM-41 (Si/Al) catalyst, but this effect decreases upon increasing active phase loading, which should be deposited regularly in layers that block the original surface of the solids. Thus, at the higher loadings, the area loss is similar independently of the type of support.

3.3. Thermal stability of supports and catalysts

DTA and TGA results in the temperature range between 40 and 700 °C for the calcined supports render information on the thermal stability of these solids. For both MCM-41 (Si) and MCM-41 (Si/Al), loss of physisorbed H_2O is reflected by an endothermal peak centered near 100 °C and extending up to 150 °C. At higher temperatures no new inflexions are observed, but there is a constant drift over 250 °C which can be assigned to loss of water due to dehydroxilation (Fig. 3a).

The DTA traces of 60% HPW/MCM-41 (Si) and 60% HPW/MCM-41 (Si/Al) catalysts are shown in Fig. 3b. The signals around 100 °C are much less pronounced than in the case of the supports. Exothermic signals can be observed at 602 °C (Si) and 548 °C (Si/Al). For unsupported HPW a similar signal has been reported in the temperature range 474–545 °C and is assigned to total destruction of the Keggin structure to form the corresponding oxides [5,10,13,14]. The increase in the characteristic temperature upon incorporation to the support reflect a thermal stabilization of the HPW structure on the MCM-41 (Si) support. Similar results were reported by Blasco et al. [7], who observed a peak at 590–600 °C for HPW supported on MCM-41 (Si) and peaks at 552 and 564 °C for HPW supported on a mesoporous aluminosilicate (MSA). The

Table 1
Specific surface areas of supports and catalysts, and area loss of catalysts

HPW loading (wt%)	MCM-41 (Si)			MCM-41 (Si/Al)		
	SSA (m^2/g_{cat})	SSA* (m^2/g_{supp})	Area loss (%)	SSA (m^2/g_{cat})	SSA* (m^2/g_{supp})	Area loss (%)
0	635	635	–	592	592	–
20	417	521	17.9	373	466	21.3
40	234	390	38.6	213	355	40.0
60	133	332	47.6	123	308	48.1

SSA* = specific surface area normalized per gram of support present in the catalyst.

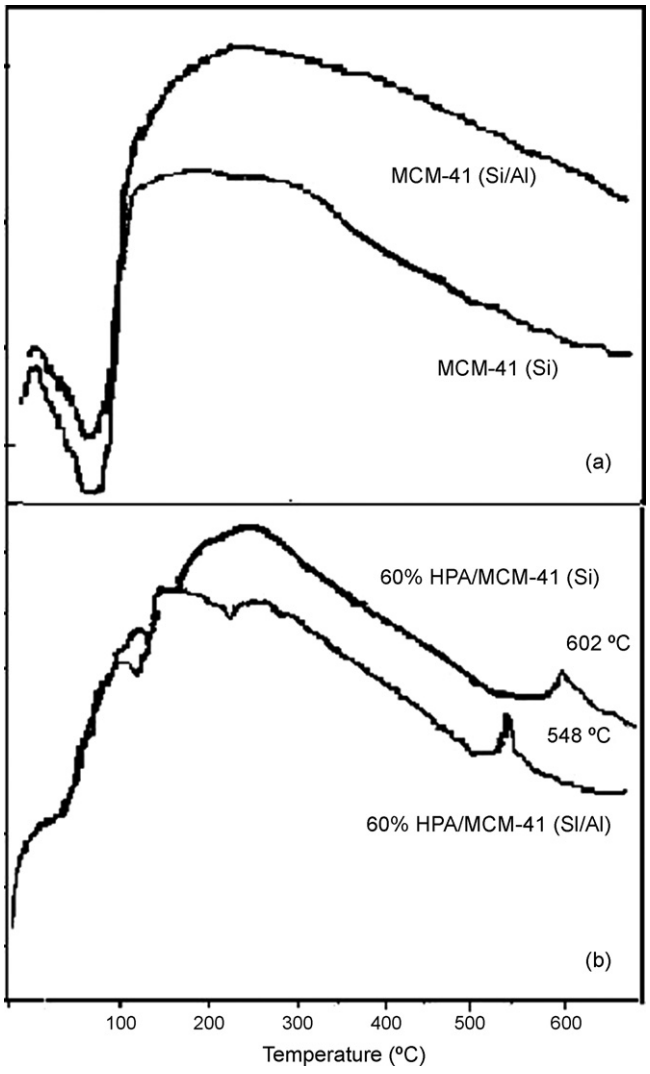


Fig. 3. DTA traces of: (a) MCM-41 (Si) and MCM-41 (Si/Al) supports and (b) 60 wt% HPW/MCM-41 (Si) and 60 wt% HPW/MCM-41 (Si/Al) catalysts.

lower stability of HPW on MSA is explained in terms of a strong interaction of the heteropolyacid with the Si–(OH)–Al bridges in supports that contain tetrahedrally coordinated Al. On the other hand, the nature of the HPW interaction with silica is not well understood. It has been reported that a proton of HPW reacts with silanol OH groups forming a complex of the type $(SiOH_2)^+(H_2PW_{12}O_{40})^-$ [15].

For 40% HPW/MCM-41 (Si) and 40% HPW/MCM-41 (Si/Al) catalysts similar exothermic signals at 602 and 548 °C are observed, with lower intensity, which can be associated to the lower weight ratio HPW/support. In the same sense, the signals are not observed for 20% HPW/MCM-41 (Si). Curiously, the 20% HPW/MCM-41 (Si/Al) solid shows an exothermic peak at 402 °C, suggesting an even lower stability of HPW on this support at this low loading. This would be in agreement with the above commented decreasing direct interaction of the supported phase with the (Si/Al) support upon increasing HPW loading. It has been reported that the interaction of this heteropolyacid with SiO_2 supports decreases upon increasing loading, being relatively inert for loadings higher than 20 wt% [5,14,15].

Thermogravimetric analysis results for supports and hydrated catalysts (not shown) present weight losses between 8 and 16% up to 250 °C, depending on the initial state of hydration of the solids. These losses can be assigned to physisorbed and hydration water. Between 250 and 550 °C, the percent weight loss for supports MCM-41 (Si) and MCM-41 (Si/Al) is 2.3 and 2.5%, respectively, that correspond to further dehydroxilation water loss. For pure HPW in the same range, a 0.93% weight loss was observed, corresponding to 1.5 water molecules per Keggin unit, with the corresponding loss of three acidic protons and decomposition of the heteropolyacid [10,14]:

$$H_3PW_{12}O_{40} \rightarrow 1.5H_2O + PW_{12}O_{38.5}$$

However, for the supported *x*% HPW/MCM-41 (Si) and *x*% HPW/MCM-41 (Si/Al), the losses of weight in the same temperature range are between 2.3 and 3.1%. Subtracting the weight losses associated to the supports, the weight change due to the HPW phase is obtained, which is between 0 and 0.6%, lower than the 0.93% of the pure HPW. This could mean that there is a partial preservation of the Keggin structure, and thus of its acidic protons, in supported HPW. Nevertheless, the higher weight losses in this range of temperature belong to solids whose support is MCM-41 (Si/Al), demonstrating a lower stability of HPW on this support.

To sum up, from DTA and TGA results obtained in the present work it can be inferred that the Keggin (primary) structure of the heteropolyacid is thermally more stabilized by interaction with the MCM-41 (Si) than with MCM-41 (Si/Al); the stability increases for both supports with HPW content; the acidic protons in 60% HPW/MCM-41 (Si) are totally preserved up to 600 °C, while in 20% HPW/MCM-41 (Si/Al) they are destabilized, as decomposition occurs at 402 °C. Thus, the former catalyst should present the best catalytic activity, and the worst should be observed for the latter one.

3.4. FT-IR spectroscopy

FT-IR spectra of the supports, MCM-41 (Si) (Fig. 4) and MCM-41 (Si/Al) (not shown), show adsorption bands at 3458 and 3447 cm^{-1}, respectively, assigned to stretching of Si–OH and Al–OH groups. For these supports, transmittance of this band is of 70%, suggesting that the OH groups are not too many. The most intense and representative signal for MCM-41 (Si) is that at 1086 cm^{-1}, assigned to Si–O–Si flexions; for MCM-41 (Si/Al) it is at 1089 cm^{-1}, and corresponds to the flexions of both Si–O–Si and Si–O–Al [16]. FT-IR of the *x*% HPW/MCM-41 (Si) and (Si/Al) catalysts show similar bands, characteristic of the supports.

In Fig. 4 the FT-IR spectra of MCM-41 (Si) and 60% HPW/MCM-41 (Si) can be compared. The latter one shows three bands which are present in all supported catalysts, but whose positions and intensities depend on the type of support and amount of HPW. These bands are between 960 and 980 cm^{-1}, 890 and 900 cm^{-1}, and around 800 cm^{-1}; the first one is

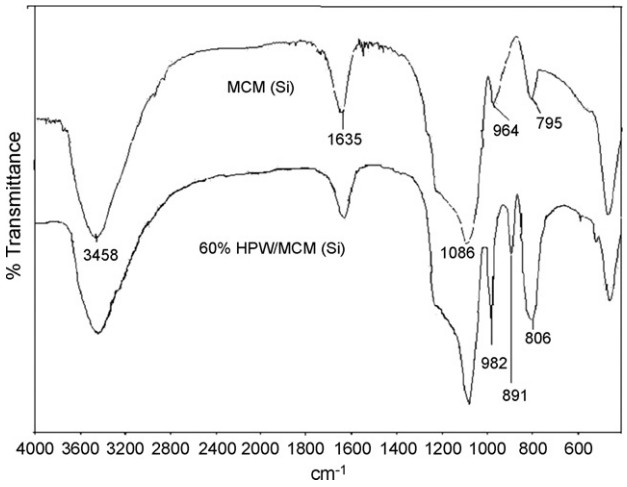


Fig. 4. FT-IR spectra of the MCM-41 (Si) support and 60 wt% HPW/MCM-41 (Si) catalyst.

assigned to stretching of W = O groups, and the other two to asymmetric vibrations of the W–O–W bridge [7,10,17]. These bands are slightly displaced with respect to pure HPW, where they appear at 985, 887 and 807 cm^{-1}, respectively [18]. This displacement is probably due to a perturbation of the Keggin structure. Interaction between the Keggin unit of HPW and silica has been confirmed by IR studies for the 14% HPW/SiO_2, where the characteristic bands were at 978, 910 and 805 cm^{-1}, respectively [19].

Table 2 shows the position of the IR band around 890 cm^{-1} for the *x*% HPW/MCM-41 (Si) and *x*% HPW/MCM-41 (Si/Al) catalysts. It can be seen that upon increasing HPW content in either support, the displacement of the band decreases with respect to the position of pure HPW (887 cm^{-1}). It also can be appreciated that the higher displacement is that of 20% HPW/MCM-41 (Si/Al), due to the pronounced interaction of HPW with the support. This confirms, again, the destabilization of HPW in this catalyst sample.

From the observations on the IR spectra, it can be said that the perturbation of the Keggin structure on MCM-41 (Si) is not as important as that given by the MCM-41 (Si/Al) support. In both cases, this perturbation decreases upon increasing HPW loading (Table 2). This is consistent with the view that for increasing loadings of HPW this compound is regularly deposited and the interaction with the support decreases, allowing a higher stability of the Keggin structure and thus a higher acid strength of the catalyst.

Table 2
Position of the W–O–W vibration FT-IR band and displacement respect the unsupported HPW compound

Sample	υ (cm^{-1})	$\Delta = \upsilon - 887$ (cm^{-1})
20% HPW/MCM-41 (Si)	894	+7
40% HPW/MCM-41 (Si)	893	+6
60% HPW/MCM-41 (Si)	891	+4
20% HPW/MCM-41 (Si/Al)	898	+11
40% HPW/MCM-41 (Si/Al)	894	+6
60% HPW/MCM-41 (Si/Al)	890	+3

3.5. Ammonia TPD

Results for the catalysts containing 60 wt% of active phase are shown in Fig. 5. It can be seen that both solids show a similar density of acid sites, but the 60% HPW/MCM-41 (Si) catalyst show a higher amount of the stronger acid sites ($T > 400$ °C). This could be related to a higher interaction of HPW with the Al sites of the MCM-41 (Si/Al) support. Quantitative results of the amount of acid sites per gram of catalyst are presented in Table 3. One can see that while the MCM-41 (Si/Al) support shows a much larger amount on acid sites than the support with only Si, the acidities of the catalysts supported in the latter are higher for all loadings of HPW. Again, this fact must reflect the stronger interaction of the supported active species with the (Si/Al) solid, which renders supported HPW less acidic.

3.6. Catalytic test: reaction of alkylation of toluene with 1-dodecene

The control of water content in heteropolyacids is of paramount importance for their efficiency as acid catalysts, thus, their activation is generally carried out between 110 and 200 °C [5,7,10,11,13]. In the present work, the supports and catalysts were activated at 130 °C and evaluated by means of the alkylation of toluene with 1-dodecene.

The alkylation of toluene with 1-dodecene under the studied experimental conditions and at a molar ratio toluene/1-dodecene = 3 for the catalysts containing 60 wt% HPW throws the results shown in Fig. 6. It can be appreciated that the 60% HPW/MCM-41 (Si) catalyst shows a higher activity, which is probably related to the higher dispersion of HPW on this particular support and to its larger amount of strong acid sites (Fig. 5). As shown by the DTA, IR, and NH_3-TPD characterization results there is a stronger interaction of the supported phase with MCM-41 (Si/Al) which could explain the decreased activity of the HPW in the latter case.

Fig. 7 presents the conversion at 3 h of reaction time against the content of supported HPW. It shows that neither support presents activity in the conversion of the olefin. However,

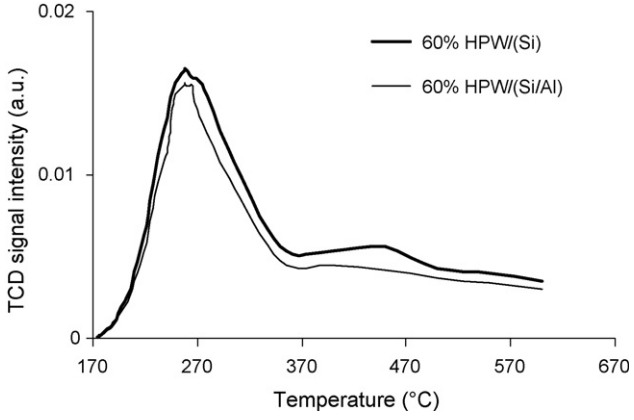


Fig. 5. Ammonia TPD profiles for catalysts with 60 wt% HPW.

Table 3
Distribution of reaction products in the alkylation of toluene with 1-dodecene at 3 h of reaction and density of acid sites of catalysts samples

Catalysts	(Acid sites/g × 10^{20})[a]	SSA (m^2/g)[b]	% Monoalkylate	% Dimer
0% HPW/MCM-41 (Si)	0.70	635	0	0
20% HPW/MCM-41 (Si)	1.80	417	95	5
40% HPW/MCM-41 (Si)	2.00	234	100	0
60% HPW/MCM-41 (Si)	2.20	133	100	0
0% HPW/MCM-41 (Si/Al)	1.30	592	0	0
20% HPW/MCM-41 (S/Al)	1.70	373	0	0
40% HPW/MCM-41 (S/Al)	1.80	213	87	13
60% HPW/MCM-41 (Si/Al)	2.00	123	93	7

[a] Density of acid sites.
[b] Specific surface area.

supported catalysts *x*% HPW/MCM-41 (Si) and *x*% HPW/MCM-41 (Si/Al) show increasing activities upon increasing HPW loadings. A natural conclusion is that the supports do not have acid sites with the required strength to catalyze the reaction, but that supported HPW does.

Although the catalytic activity augments upon increasing concentration of supported HPW, there is no linear relationship between both parameters. This could be a consequence of the higher interaction of HPW with the support at low concentrations, as seen for 20% HPW/MCM-41 (Si/Al), which does not show catalytic activity. However, 20% HPW/MCM-41 (Si) shows activity, confirming that in the case of 20% HPW/MCM-41 (Si/Al) there is a stronger interaction between HPW and the support, which decrease the strength of the acid sites or eliminates them. Several of the characterization techniques employed in this work demonstrate the interaction between active phase and support, which destabilizes the Keggin structure and results in loss of active acid protons. The NH_3-TPD results shown in Table 3 are consistent with this interpretation, as there is an almost perfect match between the order of increasing conversions at 3 h (Fig. 7) and the order of increasing amounts of acid sites, as reflected in Table 3.

Table 3 also shows the selectivity of the catalysts (at 3 h) in the reaction. Mostly monoalkylated products were observed; the absence of bialkylated ones can be explained in terms of steric restrictions if two alkyl groups coexist in the toluene molecule. In Table 3 it can be seen that the production of olefin dimers decreases with increasing HPW loading on either support, which could be assigned to an increment in the number of strong acid sites, that favours selectivity towards monoalkylates.

Table 4
Distribution of reaction products in the alkylation of toluene with 1-dodecene at isoconversion for catalysts with 60 wt% HPW

Conversion (%)	Selectivity			
	60 wt% HPW/MCM-41 (Si)		60 wt% HPW/MCM-41 (Si/Al)	
	% Monoalkylate	% Dimer	% Monoalkylate	% Dimer
8	94	6	93	7
14	98	2	97	3
28	100	0	[a]	–

[a] This catalyst does not reach this conversion level.

In Table 3, for similar loadings of HPW, the MCM-41 (Si/Al) systems show higher amounts of dimers than the MCM-41 (Si) supported ones. However, this data was taken at different levels of conversion. Table 4 compares the selectivity to monoalkylates and dimers at isoconversion (three different levels of conversion) for both 60% HPW/MCM-41 (Si) and 60% HPW/MCM-41 (Si/Al). In general, at lower conversion the both catalysts tend to produce similar amounts of dimers, while at higher conversion the amount of dimers decreases rapidly for the 60% HPW/MCM-41 (Si) catalyst.

Regarding the selectivity results, it seems that these obey to the fact that the reactant with lower molecular proportion (the

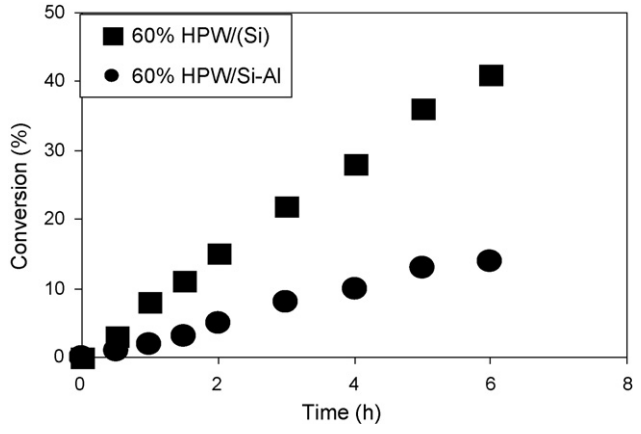


Fig. 6. Olefin conversion in the alkylation of toluene with 1-dodecene for the catalysts containing 60 wt% of HPW, as a function of time.

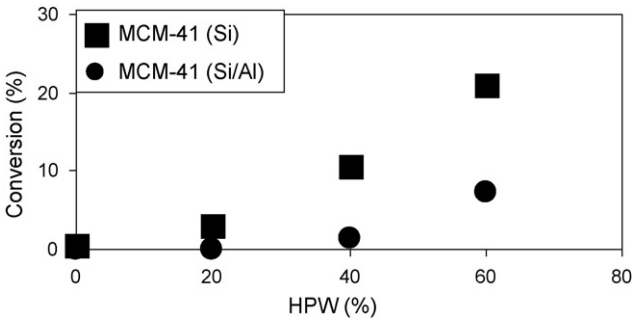
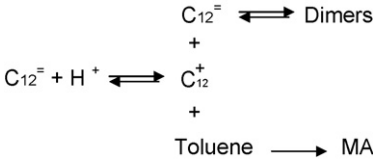


Fig. 7. Olefin conversion at 3 h of reaction of alkylation of toluene with 1-dodecene for the two series of catalysts, as a function of the amount of supported active phase.

olefin) would be interacting with the medium and strong acid sites to form the C_{12}^{+} carbocation; this species could react with toluene to produce the monoalkylated product or either it could react with a second olefin molecule to form the products named ''dimers''. The latter could suffer further additions to carbocationic species forming heavy oligomer products, which would be favoured in the case of the 60% HPW/MCM-41 (Si/Al) catalyst, explaining the eventual deactivation of these solids (see, e.g., Fig. 6), as the surface becomes covered by the produced oligomeric or polymeric deposits. The 60% HPW/MCM-41 (Si) catalyst possess the necessary strong acid sites to catalyze the formation of monoalkylates at the expense of the dimerization products, reversing the latter to the olefin, as suggested in the following scheme:



Thus, the dimer formation would be the result of an equilibrium, favoured at low conversion and for the solids with lower surface acidities. Similar results have been reported in the case of HY zeolites [2].

Comparing the results obtained in this work with those reported employing Faujasite-type zeolites [2], it can be seen that the zeolites in general are more active than and similarly selective toward monoalkylated products as the present catalysts. This could be due to the higher acid strength showed by these zeolites. Although the present solids showed a lower activity in this study, nevertheless, they could be promising for the reaction studied.

4. Conclusions

Mesoporous solids of the MCM-41 (Si) and MCM-41 (Si/Al = 25) types were synthesized, showing BET surface areas close to 600 m^2/g. These solids showed low acid site strengths and are unable to catalyze the alkylation of toluene with 1-dodecene.

Variable amounts (between 20 and 60 wt%) of HPW (dodecatungstophosphoric acid) were incorporated on MCM-41 (Si) and MCM-41 (Si/Al). Characterization of these solids using DTA, TGA, powder XRD, and FT-IR produces results consistent with an interaction of the supports with HPW.

Interaction of HPW with MCM-41 (Si) leads to a higher thermal stability of the Keggin structure of the heteropolyacid, and thus a preservation of the active acidic protons of HPW, leading to a higher density of acid sites on increasing HPW loading and in consequence a higher catalytic activity and selectivity to the desired products.

Interaction of MCM-41 (Si/Al) with HPW causes a diminution in the strength of acid sites to the extreme that the 20% HPW/MCM-41 (Si/Al) solid does not show catalytic activity for the studied reaction.

Powder XRD data for all the catalysts does not show signals due to HPW, demonstrating that this active phase is completely dispersed on the supports. The steady loss of surface area upon increasing loading may also reflect a uniform distribution of HPW in superimposed layers.

Acid site density of the catalysts, as determined by NH_3-TPD, follows the sequence:

20% HPW/MCM-41 (Si/Al) < 40% HPW/MCM-41 (Si/Al) < 20% HPW/MCM-41 (Si) < 60% HPW/MCM-41 (Si/Al) < 40% HPW/MCM-41 (Si) < 60% HPW/MCM-41 (Si).

The catalytic activity in the alkylation of toluene with 1-dodecene is directly correlated with the density and strength of acid sites.

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