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Benzene transalkylation with C9+ aromatics over supported 12-tungstophosphoric acid on silica catalysts

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Abstract

Silica-supported $H_3PW_{12}O_{40}$ (H_3PW) catalysts (8, 15, 20 and 25 wt.% H_3PW) were prepared and their catalytic activities were evaluated in benzene transalkylation with C9+ aromatics, using an industrial stream. This reaction is a convenient way to upgrade the low value of the stream produced in naphtha reforming and gasoline pyrolysis, by improving the production of xylenes. It was found that the activity and selectivity to xylenes changed with the acid loading and this was related to optimum acid strength and dispersion as well as specific surface area of the solids. The most active catalyst was the sample with 15 wt.% H_3PW, which showed the adequate combination of the three parameters cited above. This solid was also the most stable, showing the lowest rate of deactivation under the reaction conditions, producing the least amount of coke. In addition, it presented the highest activity and selectivity to xylenes, even when compared to a mordenite commercial catalyst. Consequently, this catalyst represents a promising catalyst for industrial applications.

Keywords: Benzene transalkylation; 12-Tungstophosphoric acid; Silica; Supported heteropoly acid

1. Introduction

Polioxometalates (POMs) with the Keggin structure are important catalysts for a number of acid and redox reactions [1–6]. The possibility of controlling acidity and redox properties of these materials is one of the main features that allows their design at atomic-molecular level [7]. A convenient route to obtain these solids is to disperse the POM in matrixes such as silica, alumina, titania and carbon, which enhances their specific surface area and allows them to be used more efficiently for surface type catalysis [8,9].

Among the POMs, the 12-tungstophosphoric acid (H_3PW) has recently been pointed out as a versatile environmentally friendly catalyst for several reactions [10,11]. The heterogenization of H_3PW on silica significantly improves the access of the reactants to the acid sites of H_3PW [12] by increasing the specific surface area of the catalyst, which is essential for catalytic reactions involving non-polar substrates.

Aromatic compounds are important raw materials for many intermediates of valuable petrochemicals and fine chemicals, such as monomers for polyesters, engineering plastics, as well as intermediates for detergents, pharmaceuticals, agricultural-products and explosives [13]. Among them, benzene, toluene and xylenes (BTX) are by far the most important raw materials, extensively used for most intermediates of aromatic derivatives [14]. The major commercial sources of BTX, the reforming and gasoline pyrolysis, also produce appreciable contents of trimethylbenzene and toluene. A convenient way to upgrade the low value C7 and C9 aromatics consists of converting them to benzene and xylenes [15]. The recent market reduction of benzene as a consequence of environmental restrictions increased the importance of benzene transalkylation with C9+ aromatics as a potentially important reaction for commercial

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applications and its investigation has attracted increasing attention in recent years.

In this work, silica-supported $H_3PW_{12}O_{40}$ (H_3PW) catalysts, with different amounts of H_3PW, were evaluated in the benzene transalkylation with C9+ aromatics in order to produce xylenes.

2. Experimental

2.1. Catalyst preparation

H_3PW was purchased from Aldrich and the thermogravimetric analysis showed 21 moles of water per mole of acid. Silica (Aldrich, Davisil® silica gel grade 62, 60–200 mesh and $Sg = 260\ m^2\ g^{-1}$) was used as the support. H_3PW was supported on silica by the impregnation-evaporation technique. The method consisted of the dissolution of H_3PW (8, 15, 20 and 25 wt.%) in HCl solution ($0.1\ mol\ L^{-1}$), followed by evaporation at 80 °C and calcination at 200 °C for 6 h under vacuum. Other details concerning the preparation of the catalysts can be found elsewhere [12].

2.2. Catalyst characterization

The calcined samples were characterized by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and magic angle spinning nuclear magnetic resonance of phosphorous (^{31}P MAS-NMR).

Fourier transform infrared spectra were obtained with a Bruker-Equinox 55 spectrophotometer with a DTGS detector. The samples were pressed with dried potassium bromide (Merck), producing discs that were analyzed in the range of $4000–400\ cm^{-1}$, with $4\ cm^{-1}$ resolution and 256 scans.

The ^{31}P MAS-NMR spectra were acquired in a MAS probe of 7 mm (silicon nitride rotor with torlon cap) with a Varian 7.05 T Mercury Plus spectrometer at room temperature. The following conditions were used: operation at 121.469 MHz for ^{31}P, single pulse excitation with 8.0 μs duration ($\pi/2$), acquisition time of 0.1 ms, recycle delay of 10 s, no ^{1}H decoupling, MAS rate at 5 kHz and minimum of 128 acquisitions. Signals were external referenced to 85 wt.% H_3PO_4 (0 ppm).

Thermal analysis was performed in a simultaneous TG-DSC model SDT 2960 (TA Instruments) with a heating rate of $10\ °C\ min^{-1}$, from room temperature to 600 °C under air (99.999%) flow of $100\ mL\ min^{-1}$.

The XRD patterns were obtained using a Rigaku D/Max-2A/C with Cu Kα radiation (40 kV and 20 mA) varying the 2θ angle from 2 to 40° at $2°\ min^{-1}$. The specific surface area (BET method) was measured by a Micromeritics model TPD/TPO 2900 equipment on both fresh and spent catalysts previously heated under nitrogen (150 °C for 2 h). The amount of carbon on spent catalysts was determined by Leco model CS-200 equipment, using Lecocel and the iron chip accelerator.

The transalkylation reaction of benzene with trimethylbenzene was carried out in a tubular reactor at 1 atm and several temperatures (350, 380, 410, 440 and 470 °C), with 0.5 g of catalyst, using a H_2/hydrocarbon (molar) = 4, $WHSV = 1\ h^{-1}$ and a feed obtained by mixing benzene (99.8% purity) and a C9+ stream in a benzene/C9+ (weight) = 70:30. The C9+ stream was collected in an industrial unit as a by-product of the naphtha catalytic reforming and had the following mass composition: 2% C10+ aromatics, 9% propylbenzene, 43% ethyltoluene, 45% trimethylbenzene and 0.6% indane. The gaseous effluent was analyzed by on-line gas chromatography. A commercial mordenite sample was also evaluated as a reference. After the tests, the catalysts were characterized by specific surface area measurements, carbon elemental analysis, ^{31}P MAS-NMR and FT-IR.

3. Results and discussion

3.1. Characterization of the catalysts before reaction

As previously reported [12], the general fingerprint for the Keggin anion is partially obscured by the strong silica absorptions in the range $1200–400\ cm^{-1}$. However, a subtraction spectrum, i.e., supported H_3PW minus SiO_2 reveals the loading effect in the Keggin bands (Fig. 1). As the H_3PW content increases from 8 to 25%, the characteristic bands emerge. Initially, only one peak is visible ($983\ cm^{-1}$ related to W=O) and then the others appear (W–Oc–W at $898\ cm^{-1}$ and W–Oe–W at $797\ cm^{-1}$. These results confirmed the presence of the intact polyanion under the preparation conditions.

The ^{31}P NMR spectra for all samples showed a single peak centered at −15.0 ppm (Fig. 2). This indicates that the Keggin structure was kept after the impregnation and calcination processes and no decomposition was observed, in agreement with FT-IR results. As reported earlier, the main position of the single peak for pure H_3PW depends on the hydration degree [16], even though the peak is around −15 ppm [17] for the supported polyacid in different matrices.

XRD provided the same pattern reported earlier [12]. As the concentration of H_3PW increases, the peaks became narrower, indicating the formation of the H_3PW crystalline phase. This pattern is better resolved for the 25% supported H_3PW.

3.2. Thermal stability of the catalysts

The stability of silica-supported H_3PW was examined by thermal analysis (TG/DTG and DTA curves) under air flow. For

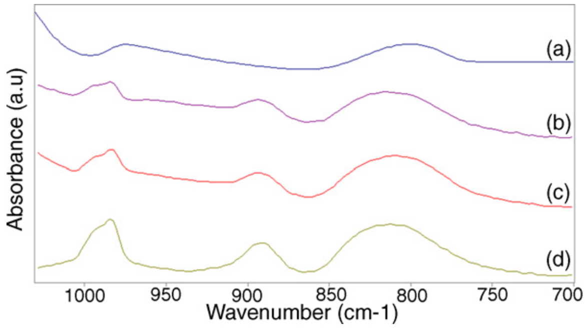

Fig. 1. FT-IR spectra obtained by subtraction (i.e., supported H_3PW/SiO_2 minus SiO_2) for the samples with: (a) 8 wt.% H_3PW, (b) 15 wt.% H_3PW, (c) 20 wt.% H_3PW, and (d) 25 wt.% H_3PW.

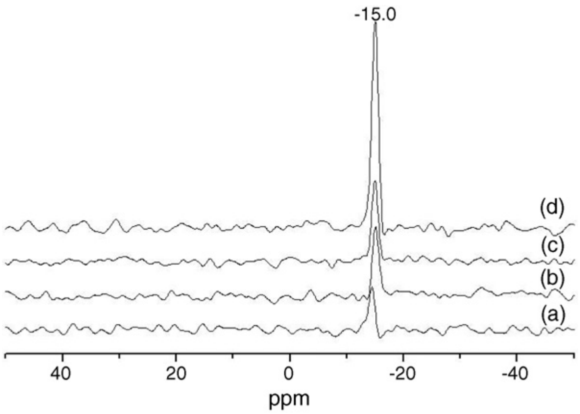

Fig. 2. ^{31}P MAS-NMR spectra of H_3PW/SiO_2 with (a) 8 wt.% H_3PW, (b) 15 wt.% H_3PW, (c) 20 wt.% H_3PW, and (d) 25 wt.% H_3PW.

all catalysts, the curves are similar. An illustrative curve is presented in Fig. 3 for 15% H_3PW/SiO_2. The TG/DTG curves show three thermal events, analogous to the pure polyacid [18]. The first weight loss is related to the release of physically adsorbed water and part of the hydrated water (usually forming the hexahydrate H_3PW for the pure compound). This water release ranges from room temperature up to 120 °C with the maximum at about 37 °C. The temperature range, as well as the maximum, may vary according to the amount of water contained initially in the material, since heteropoly acids are known to adsorb different amounts of water depending on the preparation method and on the storage conditions [19,20]. A second weight loss occurs from 120 to 230 °C, with a maximum at about 174 °C, which is associated with the formation of the anhydrous catalyst. The third step takes place in a very wide range of temperatures (at about 350–580 °C) with a maximum at 430–450 °C. Pure H_3PW shows a close behavior for starting decomposition (maximum about 400–430 °C) [20]. The wide range of the third mass loss is related to more than one event under that condition. The global event is attributed to the decomposition of the Keggin structure as well as the silica dehydroxylation [19–22].

Another source of concern is the stability of H_3PW under hydrogen atmosphere. It is known the effect of hydrogen over the reduction of heteropolyacids in the solid state forming the heteropolyblues [7]. The reduction easily occurs for Mo than W heteropoly compounds and depends on the presence of water if the process is reversible or not. According to the literature reports, the temperature of the reduction process strongly depends on the heating rate and on the hydrogen concentration in the stream, and ranges, for instance, from 400 to 452 °C [23,24]. In addition, this reduction temperature also depends if H_3PW is supported or not. For example, it has been reported for silica support that H_3PW (10%) showed a TPR profile with only one reduction peak in the maximum range of 870–950 °C, which depends on the kind of silica [11]. On the other hand, another report showed two peaks with the maximum temperature at 532 °C (weak peak) and 852 °C (strong peak) [24]. The difference might be explained by the unlike preparation method, type of silica used and hydrogen concentration on the flow.

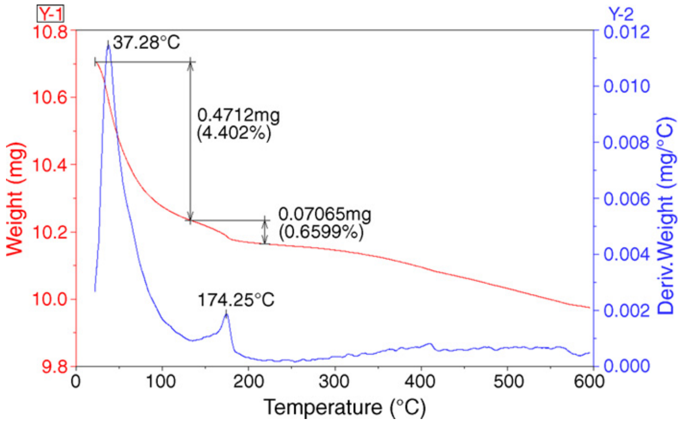

Fig. 3. TG and DTG curves (under air flow) for 15 wt.% H_3PW/SiO_2 catalyst.

In addition, the nature of the support demonstrates that the maximum temperature is related to the strength of the interaction. For instance, supported on alumina H_3PW displayed a peak at about 680 °C with a second peak around 1000 °C. This behavior indicates that the interaction is stronger in the alumina-supported samples than in the silica-supported catalysts. This has also been observed by calorimetric measurements of acidity of H_3PW supported on these carriers, separately [12,17].

Based on those results, it can be concluded that pure H_3PW is stable under hydrogen atmosphere up to 450 °C and, when supported on silica, it does not decompose before 532 °C.

The maximum temperature of the transalkylation reaction was 470 °C, thus the occurance of negligible decomposition of the catalyst because of the the presence of hydrogen in the reactional medium can be antecipated. It is believed that the main effect of hydrogen is to increase the catalyst performance because it decreases the high levels of coke precursors (polyaromatic compounds) that are prevalent in industrial feedstocks. Because isolated hydrogen at low levels does not affect the H_3PW extensively, its consequence is mainly to hydrogenate coke precursors and thereby minimize the steady-state coke levels on the catalyst, which would otherwise suppress its activity faster. No specific interactions of H_3PW, which could lead to any decomposition, were observed.

3.3. Activity and analysis of the catalysts after reaction

All catalysts were active in the transalkylation of trimethylbenzene with benzene at 470 °C, as shown in Fig. 4. The sample with 8% of H_3PW presented the lowest activity while the catalyst with 15% H_3PW was the most active one. The samples with 20 and 25% H_3PW showed close activity values. The low activity of the 8% H_3PW sample can be assigned to the low number of acidic sites, as previously stated [12]. The catalysts with 20 and 25% H_3PW showed similar behaviors, probably due to their comparable number of acidic sites, as shown by the close values of dispersion, related to the mean size of the particles (Table 1). They showed high activities in the beginning of reaction, which decreased relatively fast up to steady values, reached after 4 h of reaction. This may be related to a partial decomposition of H_3PW, followed by a decrease of specific surface area. According to the specific surface area measure-

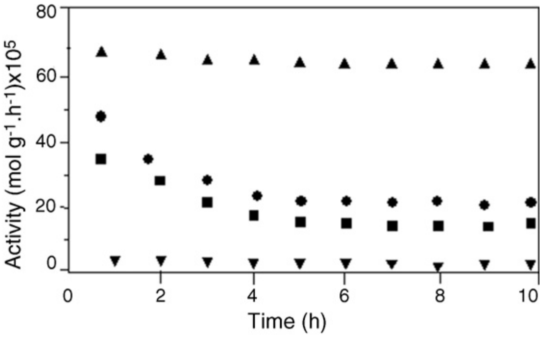

Fig. 4. Activity of the catalysts as a function of reaction time in the benzene transalkylation with C9+ at 1 atm and 470 °C. (▼) HPW8, (▲) HPW15, (●) HPW20, and (■) HPW25, with 8, 15, 20 and 25 wt.% loading on silica, respectively.

Table 1
Specific surface areas of fresh (Sg) and spent (Sg*) catalysts and mean crystallite sizes (*D*) of fresh catalysts

Sample	Sg ($m^2 g^{-1}$), fresh	Sg* ($m^2 g^{-1}$), spent	*D* (nm)[a]
HPW8	74	23	12
HPW15	63	60	15
HPW20	57	43	17
HPW25	40	20	18

HPW8, HPW15, HPW20 and HPW25 are 8, 15, 20 and 25 wt.% of acid loading on silica gel, respectively.

[a] The crystallite size was calculated from the XRD patterns of the fresh catalysts using Scherrer equation to the H_3PW plane (1 1 0), equivalent to $2\theta = 10.2°$.

ments of the catalyst samples, taken before and after the reaction (Table 1), there is a high decrease on the area of 8% H_3PW followed by the sample with 25% and with 20%. On the other hand, the sample with 15% H_3PW displayed a quite different behavior, showing high and relatively stable values of activity during all of the reaction time. This can be attributed to its high dispersion as well as to its high specific surface area, which remained practically constant during the reaction (decreased from 63 to 60 $m^2 g^{-1}$, see Table 1).

The amount of coke after the reaction was low in all catalysts and can be associated to the loss of activity in the beginning of the reaction. As one can see in Table 2, almost no coke was produced on the catalyst with 15% H_3PW, which was the most stable. From these results we can conclude that a low acid loading is unable to produce active catalysts to transalkylation of trimethylbenzene with benzene but acid loadings ranging from 15 to 25% produce active catalysts. The acid loading of 15% can be considered optimum and produces a very active catalyst with high acidic dispersion and high specific surface area. However, loadings of 20 and 25%, which are near saturation [12], lead to the formation of bigger crystallites of H_3PW, which are less active and more susceptible to coke deposition. More coke was deposited on the catalyst with 25% of H_3PW, as compared to that with 20% of H_3PW and this can be assigned to the stronger acidic sites of the HPW25 sample, as shown in Table 2.

All catalysts produced lower amounts of coke as compared to the commercial mordenite-based one. This can be related to the different ability of mordenite and of silica-supported H_3PW for producing coke. As found in previous work [25] the coke deposition largely depends on the catalyst structure. While mordenite is highly susceptible to coke deposition [14,26], silica is believed to suppress coke formation during the interconversion of alkylbenzenes and the catalyst surface modification by silica deposition is an applied industrial practice to improve the selectivity of zeolite-based catalysts for toluene disproportionation [14,27,28]. In the present work, it seems that H_3PW is not very active to coke formation, when supported on silica, mainly in a highly dispersed form.

The yield of xylenes also changed with the acid loading in the solids, as shown in Table 2. The catalysts with 8 and 25% H_3PW were not able to produce xylenes, while the sample with 15% H_3PW produced the highest amount, followed by the solid with 20% H_3PW. These values are higher than that produced by a mordenite-based commercial catalyst.

These results lead to the analysis of the role of the acid sites strength in the formation of xylenes. The strength of the strongest acidic sites (Brönsted) measured by calorimetric and adsorption of pyridine in liquid phase (Cal-Ad method) is listed in Table 2 [12,29]. Mordenite, which has similar acidity strength to 8% H_3PW/SiO_2, is active for xylenes formation, while the supported 8% H_3PW formed toluene as the main product. The main reason for this behavior may be the different distribution of acid sites as well as diffusion properties of the catalysts [30] for reactions of alkylaromatics in porous catalysts [31]. The higher density of Brönsted acid sites in mordenite and the presence of regular unidirectional pores may favor the xylenes formation. The absence of those pores to stabilize the dialkylbenzenes leads to formation of coke on 8% H_3PW/SiO_2. On the other hand, 15 and 20% H_3PW are stronger acids and

Table 2
Activity (*a*) of the catalysts, xylenes yield (Y_X) and coke deposited on the catalysts during the benzene transalkylation with C9+ aromatics at 470 °C

Sample	*a* ($\times 10^5$ mol g^{-1} h^{-1})	Y_X (%)	Coke content (%)	$-\Delta H_{AVG}$[a] (kJ mol^{-1})
HPW8	4.1	0.0	1.6	85.9
HPW15	67	3.9	0.3	100.4
HPW20	25	2.8	1.0	108.8
HPW25	18	0.0	2.4	116.7
Mordenite	42	2.1	14.1	82.9[b]

HPW8, HPW15, HPW20 and HPW25 are 8, 15, 20 and 25 wt.% of acid loading on silica gel, respectively.

[a] Average enthalpy interaction ($-\Delta H_{AVG}$) of the strongest sites of H_3PW/SiO_2 with pyridine in liquid phase, obtained from Ref. [12].

[b] Data obtained from Ref. [29].

produce more xylenes than 8% H_3PW. The decreased activity for the 20% sample suggests that acid sites over 100 kJ mol^{-1} are not favorable to produce xylenes, probably because they strongly adsorb the formed xylenes, which prevent desorption and produce coke instead. This effect is confirmed by the 25% H_3PW which does not produce any xylenes during reaction conditions studied. These results show that there is an optimum value of acidity for producing xylenes using these supported heteropolyacids. A similar conclusion was obtained in the study of transalkylation of diisopropylbenzene with benzene over a series of zeolites [31].

Studies of the most promising catalyst were carried out by FT-IR and ^{31}P MAS-NMR in order to characterize the supported species after the reaction. FT-IR spectrum (not shown) of the 15% H_3PW/SiO_2 spent catalyst showed bands related to fragmented structures of the original Keggin anion. The main peaks could be assigned to a defect Keggin structure ($PW_{11}O_{39}{}^{7-}$) [32,33]. In addition, the presence of aromatic coke is confirmed by the absorptions at 1266 and 1391 cm^{-1}. The presence of a decomposed Keggin species was better accessed by ^{31}P MAS-NMR (Fig. 5). The spent catalyst displayed the original Keggin anion peak (−15.0 ppm) and two new peaks at −11.9 ppm (attributed to α-$P_2W_{18}O_{62}{}^{6-}$) and at −10.7 ppm (assigned to α-$PW_{11}O_{39}{}^{7-}$) [34,35]. The decomposition of the Keggin structure may be associated with the small decrease in activity of this catalyst in the beginning of the reaction. The steady activity after 3 h is also related to this process, since the other forms of polyoxometalates are known to be active in transalkylation reactions [34].

The experiments carried out at lower temperatures (350, 380 and 410 °C) showed stable values of trimethylbenzene conversion since the beginning of reaction, except for the sample with 8% H_3PW, which was inactive at 350 and 380 °C. It means that no deactivation took place in these conditions. In all cases, the activity increased with temperature, as displayed in Table 3. The catalyst with 15 wt.% H_3PW showed an activity at 380 °C (3.8×10^5 mol g^{-1} h^{-1}) close to the activity of mordenite at 470 °C (4.2×10^5 mol g^{-1} h^{-1}), meaning that it can work at lower temperature with a similar conversion and higher catalyst half-life due to slower deactivation by thermal decomposition of the Keggin anion. This catalyst was more active than mordenite in the whole temperature range, as shown in Table 3. Therefore, this material is a promising candidate to replace mordenite in the transalkylation of ethylbenzene with benzene.

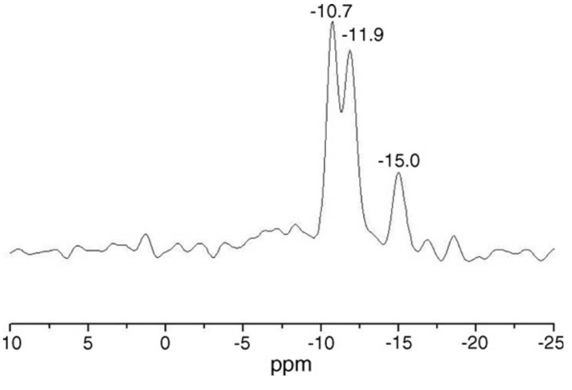

Fig. 5. ^{31}P MAS-NMR spectrum of 15 wt.% H_3PW/SiO_2 after reaction.

Table 3
Activity (a) of the catalysts as a function of temperature

Samples	a ($\times 10^5$ mol g^{-1} h^{-1})				
	350 °C	380 °C	410 °C	440 °C	470 °C
HPW8	0	0	1.2	2.0	4.1
HPW15	30	38	45	50	67
HPW20	5.1	9.6	13	17	25
HPW25	1.2	5.0	11	15	18
Mordenite	7.8	22	24	30	42

HPW8, HPW15, HPW20 and HPW25 are 8, 15, 20 and 25 wt.% of acid loading on silica gel, respectively.

4. Conclusions

The polyoxometalate 12-tungstophosphoric acid (H_3PW) supported on silica, with acid loading of 8, 15, 20 and 25 wt.%, was found to be an active catalyst in the transalkylation of trimethylbenzene with toluene in the range of 350–470 °C. The sample with 15% loading of H_3PW on silica was the most active, stable and selective catalyst to produce xylenes, which was related to its high specific surface area, adequate acid strength and high dispersion of acid sites. An acid loading of 8% H_3PW seems not to be able to produce an active catalyst while acid loadings of 20 and 25% produce large H_3PW particles less active and selective to xylenes and also more susceptible to deactivation by coke deposition. The solid with 15% H_3PW was more active and selective to xylenes than a commercial mordenite catalyst and thus presents promising characteristics to improve the xylene production in industrial streams from naphtha reforming and gasoline pyrolysis.

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