

Synthesis of linear alkyl benzenes over zirconia-supported 12-molybdophosphoric acid catalysts

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Abstract

The liquid-phase alkylation of benzene with 1-octene and 1-dodecene was investigated using zirconia-supported 12-molybdophosphoric acid (MPA) as catalyst. The catalysts with different MPA loading (5–25 wt.% calcined at 700 °C) and calcination temperature (15 wt.% calcined from 500 to 750 °C) were prepared by suspending zirconium oxyhydroxide in methanol solution of MPA followed by drying and calcination. These catalysts were characterized by X-ray diffraction, and ³¹P MAS NMR spectroscopy measurements. The XRD results indicated that MPA stabilizes the tetragonal phase of zirconia. ³¹P MAS NMR spectra show that the nature of phosphorous species depend on MPA loading and calcination temperature, and it show the existence of three types of phosphorous species, one is the Keggin unit and the other is the decomposition product of MPA and third one an unidentified species. FT-IR pyridine adsorption on 15% MPA catalyst calcined at 700 °C showed the presence both Brönsted and Lewis acidity. Under the reaction conditions of 83 °C, benzene/1-olefin molar ratio of 10 (time, 1 h), the most active catalyst, 15% MPA calcined at 700 °C gave more than 90% olefin conversion with selectivity to 2-phenyl octane, 55% and 2-phenyl dodecane, 45%.

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1. Introduction

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry. Alkylation of benzene with C_{10–14} linear alkenes is used for the synthesis of linear alkyl benzenes (LAB), which are the primary raw material for the production of LAB sulfonates, a surfactant detergent intermediate [1]. Traditionally this reaction is catalyzed by a homogeneous Lewis acid such as AlCl₃ or a strong Brönsted acid such as HF, which are highly toxic, generate a substantial amount of waste and cause severe corrosion problems. At present, considerable efforts are being made to find efficient, sustainable, recyclable and eco-friendly solid

acid catalysts, which can successfully carry out above reaction [2,3]. Various catalysts such as zeolites, clays, heteropoly acids, sulfated zirconia and immobilized ionic liquids were tested for this reaction [4–8]. The Detal process developed by UOP uses solid acid catalyst for alkylation of benzene with heavy olefins, under liquid-phase conditions [1].

Heteropoly acids (HPAs) are a unique class of materials active both in redox and acid catalysis [9,10]. These are polyoxometallates made up of heteropoly anions having metal–oxygen octahedra as the basic structural unit. The Keggin type HPAs is the most important in catalysis, because of their high acidic strength and relatively high thermal stability. These are strong Brönsted acid catalysts and their strength of acidity is higher than that of the conventional solid acids like zeolites and mixed oxides.

HPAs can be used either directly as a bulk material or in supported form. The use in supported form is preferable

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because of its high surface area compared to the bulk material ($5\text{--}8\text{ m}^2\text{ g}^{-1}$) and better accessibility of reactants to the active sites. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports [11]. Serious problems associated with this type of materials are their susceptibility to deactivation during organic reactions due to the formation of carbonaceous deposit on the catalyst surface. The thermal stability of HPAs is not high enough to carry out conventional regeneration by burning coke at $500\text{--}550\text{ }^\circ\text{C}$, as routinely followed in the case of zeolites and aluminosilicates [12]. Thus, the preparation of an active and stable HPA in supported form is essential in order to utilize fully the potential of these materials as catalysts.

In recent years zirconia has attracted much attention both as a catalyst and catalyst support because of its high thermal stability, amphoteric character and oxidizing and reducing properties [13,14]. Recently, we have shown that zirconia-supported 12-tungstophosphoric acid acts as an efficient catalyst for alkylation and acylation of aromatics [15,16].

The present study reports the thermal stability of zirconia-supported 12-molybdophosphoric acid (MPA) by X-ray diffraction, and ^{31}P MAS NMR spectroscopy and the nature of acidic sites present on the most active catalyst by FT-IR pyridine adsorption spectroscopy. These catalysts were used in the synthesis of LAB by the acid catalyzed alkylation of benzene with higher linear alkenes such as 1-octene and 1-dodecene.

2. Experimental

2.1. Chemicals

Zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) and ammonia (25%) were obtained from S.D. Fine Chemicals Ltd., Mumbai. 1-Octene (98%), 1-dodecene (95%), 12-MPA ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$), and methanol (99.9%) was purchased from Aldrich. Benzene (99.7%) was obtained from E. Merck India Ltd., Mumbai. All the chemicals were used as received without further purification.

2.2. Catalyst preparation

The catalysts were prepared by suspending a known amount of dried zirconium oxyhydroxide powder in a methanol solution of MPA. Zirconium oxyhydroxide was prepared by hydrolysis of 0.5 M zirconyl chloride solution by the drop wise addition of aqueous NH_3 (10 M) to a final pH of 10. The precipitate was filtered and washed with ammoniacal water (pH 8) until free from chloride ions by the silver nitrate test. The zirconium oxyhydroxide thus obtained was dried at $120\text{ }^\circ\text{C}$ for 12 h, powdered well and continued drying for another 12 h. Each time, 4 ml of methanol per gram of solid support was used and the mixture was stirred in a rotary evap-

orator for 8–10 h. After stirring, the excess of methanol was removed at ca. $50\text{ }^\circ\text{C}$ under vacuum. The resulting solid materials were dried at $120\text{ }^\circ\text{C}$ for 24 h and ground well. A series of catalysts with different MPA loading (5–25 wt.%) were prepared by changing the MPA concentration in methanol. The dried samples were then calcined in air at $700\text{ }^\circ\text{C}$. Samples with 15% MPA were calcined between 400 and $750\text{ }^\circ\text{C}$ to understand the role of the calcination temperature on the activity of the catalysts. The samples were heated at a rate of $5\text{ }^\circ\text{C min}^{-1}$ to the final temperature and held for 4 h under static conditions, and cooled at a rate of $5\text{ }^\circ\text{C min}^{-1}$ to room temperature and stored in desiccator. The catalysts are represented by $x\text{ MZ } t$, where x represents wt.%, M represents MPA, Z represents zirconia and t denotes calcination temperature ($^\circ\text{C}$).

For comparison, a catalyst with 15% $\text{MoO}_3/\text{ZrO}_2$ (15 Mo 700) was prepared by wet impregnation of zirconium oxyhydroxide with an aqueous solution of ammonium heptamolybdate, dried and calcined at $700\text{ }^\circ\text{C}$.

2.3. Characterization

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$).

^{31}P MAS NMR spectra (Bruker DSX-300 spectrometer) were recorded at 121.5 MHz with high power decoupling with a Bruker 4 mm probe head. The spinning rate was 10 kHz and the delay between two pulses was varied between 1 and 30 s to ensure that complete relaxation of the ^{31}P nuclei occurred. The chemical shifts are given relative to external 85% H_3PO_4 .

The nature of the acid sites (Brønsted and Lewis) of the catalyst sample (15 MZ 700) was characterized by in situ FT-IR spectroscopy with chemisorbed pyridine. The FT-IR (Shimadzu SSU 8000) pyridine adsorption studies were carried out in the DRIFT (diffuse reflectance infrared Fourier transform) mode. A calcined powder sample in a sample holder was placed in a specially designed cell. The samples were then heated in situ from room temperature to $400\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in a flowing stream (40 ml min^{-1}) of pure N_2 . The samples were kept at $400\text{ }^\circ\text{C}$ for 3 h and then cooled to $100\text{ }^\circ\text{C}$ and then pyridine vapor ($20\text{ }\mu\text{l}$) was introduced under N_2 flow and the IR spectra were recorded at different temperatures up to $400\text{ }^\circ\text{C}$. A resolution of 4 cm^{-1} was attained after averaging over 500 scans for the IR spectra reported here.

2.4. Catalyst testing

The liquid-phase alkylation reaction is carried out in a 50 ml glass batch-slurry reactor with anhydrous CaCl_2 guard tube. The temperature is maintained by silicon oil bath equipped with a thermostat and magnetic stirrer and measured at the reaction mixture. The catalyst freshly activated

at 400 °C for 2 h, is weighed in the reactor and then benzene is then added. Finally, 1-alkene is added in order to obtain the molar ratio of benzene/1-alkene of 10 (with benzene to alkene molar ratio of 10 well within the industrial process range). For example, a typical reaction mixture consists of 21.86 g (280 mmol) of benzene, 3.14 g of 1-octene (28 mmol) together with 0.125 g of catalyst. After 1 h, the reaction is stopped and the catalyst separated. The filtrate is analyzed using a Shimadzu 14B gas chromatograph using HP-5 capillary column (cross-linked 5% ME silicone, 30 m × 0.53 μm × 1.5 μm film thickness), coupled with FID. The product identification is carried out using GC–MS.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. X-ray diffraction

The XRD pattern of the catalysts with different MPA loading calcined at 700 °C (Fig. 1A) shows that, the presence of MPA strongly influences the crystallization of zirconium oxyhydroxide into zirconia. Pure zirconia calcined at 700 °C is mainly monoclinic with small amount of the tetragonal phase. For catalysts with low MPA loading calcined at 700 °C, the XRD pattern can be described as the sum of the monoclinic and tetragonal phases of zirconia, this latter phase becoming dominant for catalyst with 15% MPA. It can also be seen that up to a 15% MPA loading, no XRD peaks, which could be attributed to the polyacid or to its decomposition products, are observed. The 20 MP 700 catalyst shows the presence of new peaks characteristic of MoO₃ and for 25% catalyst formation of ZrMo₂O₈ is observed. This indicates that, MPA gets decomposed to molybdenum oxide, which is present

as large particles and also reacts with the support forms ZrMo₂O₈.

As shown in Fig. 1B, 15% catalyst was amorphous, when it was calcined below 400 °C and the crystalline nature of zirconia increases with calcination temperature. As the calcination temperature increases from 500 to 700 °C, zirconia crystallizes to tetragonal phase and at 750 °C, the formation of monoclinic phase is indicated. Thus, the added MPA stabilizes the tetragonal phase of zirconia and such stabilization of tetragonal ZrO₂ in presence of other heteropoly acid is reported earlier [15,16]. For comparison, the XRD of 15% molybdenum oxide supported on zirconia calcined at 700 °C (15 Mo 700) was recorded and it shows the stabilization of ZrO₂ in tetragonal phase together with the formation of small amount of ZrMo₂O₈ [17].

3.1.2. ³¹P MAS NMR

This is one of the most important characterization techniques to study the state of phosphorous in heteropoly acids. The chemical shift depends upon the phosphorous environment, which in turn depends upon factors like hydration number, addenda metal ion, support, etc. [18–22]. The bulk MPA shows a sharp intense peak at –3.5 ppm in the ³¹P MAS NMR spectrum, due to the uniform phosphorous environment in highly hydrated structure of the MPA, while the small peak observed near to the main peak at 6.3 ppm may be due to the part of the sample containing different degrees of hydration [23]. The ³¹P MAS NMR spectra of catalysts with 5–25% MPA calcined at 700 °C, and 15% MPA calcined from 600 to 750 °C shows that the state of phosphorous in catalysts depend on MPA loading and calcination temperatures. The spectra of catalysts with different MPA loading (5–25 MZ 700) are shown in Fig. 2A. For 5% MPA catalyst, NMR shows a peak at –8.6 ppm assigned to the phosphorous in the Keggin unit of MPA [24,25]. The up field shift compared to pure MPA may be due to the strong interaction of MPA with zirconia [25]. However, when the MPA loading increased to 10%, NMR shows peaks at –3.5, –8.2, and 18 ppm, respectively. The peak at –3.5 ppm is assigned to microcrystalline MPA, similar to unsupported MPA [26] or MPA without interaction with the surface of zirconia [25] and the chemical shift at –8.2 ppm is due to MPA interacting strongly with the zirconia surface. The origin of the peak at 18 ppm is not clear at present. For catalysts with 15% MPA loading and above, an additional peak at –30 ppm is observed, which is attributed to phosphorous oxide (P–O–P) resulting from the decomposition of the polyoxometalate [27]. However, the catalyst 15 MZ 700 gave the highest octene conversion and hence we recorded the ³¹P CPMAS NMR spectrum of this catalyst and interestingly it shows the peak at –8.5 ppm due phosphorous in the Keggin unit of MPA (Fig. 2C). To the best of our knowledge, this is the highest thermal stability reported so far for supported MPA catalysts.

The ³¹P MAS NMR spectra of 15 MZ catalyst calcined from 500–750 °C are shown in Fig. 2B. At a calcination temperature of 500 °C, NMR spectrum shows two peaks, one at

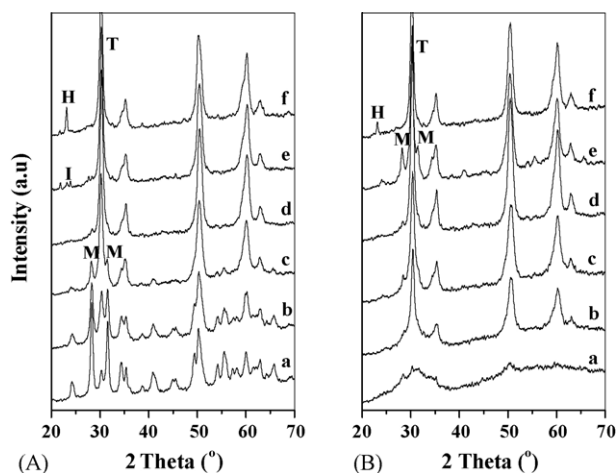


Fig. 1. (A) X-ray diffraction patterns of (a) Zr 700, (b) 5 MZ 700, (c) 10 MZ 700, (d) 15 MZ 700, (e) 20 MZ 700, and (f) 25 MZ 700 catalysts; (B) X-ray diffraction patterns of 15 MZ catalyst calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 750 °C, and (f) 15 Mo 700 catalyst. T = tetragonal ZrO₂, M = monoclinic ZrO₂, I = MoO₃, H = ZrMo₂O₈.

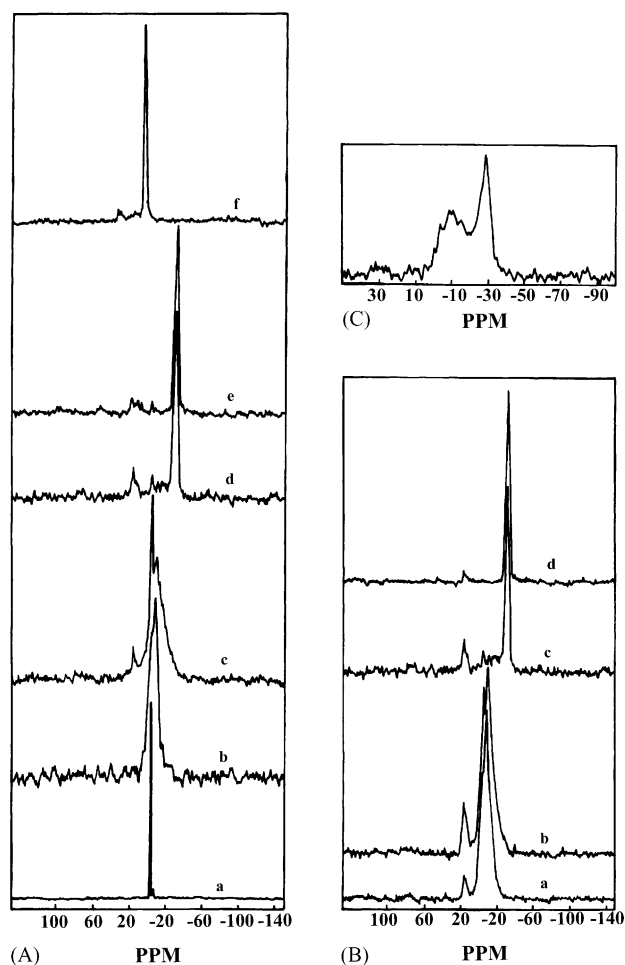


Fig. 2. ^{31}P MAS NMR spectra of (A) catalysts with different MPA loading (a) pure MPA, (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 25%; (B) 15% catalyst calcined at different temperature (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 750 °C and (C) CP MAS NMR spectra of 15 MZ 700 catalyst.

–8 ppm and the other at 17.2 ppm. As the calcination temperature is increased to 600 °C, NMR spectrum shows peaks at –3.5, –8.2, and 18 ppm, similar to the NMR spectrum of 10 MZ 700 catalyst. The 15 MZ 750 catalyst shows a sharp peak at –30 ppm.

Thus a combination of the XRD and ^{31}P MAS NMR results reveals that at low loadings (15%) and calcination temperature (700 °C), MPA retains its structure almost intact, while for higher loadings and at high calcination temperature it decomposes to its oxides.

3.1.3. FT-IR pyridine adsorption

Adsorption of pyridine as a base on the surface of solid acids is one of the most frequently applied methods for the characterization of surface acidity. The use of IR spectroscopy to detect the adsorbed pyridine enables us to distinguish among different acid sites. FT-IR spectra of pyridine adsorbed on 15 MZ 700 catalyst recorded from 100 to 400 °C and the results are shown in Fig. 3A. At 100 °C, important pyridine ring modes occur at approximately

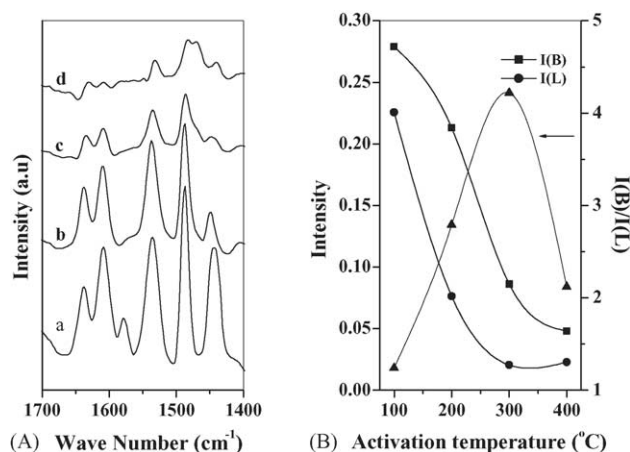


Fig. 3. The IR spectra of pyridine adsorbed on 15% catalyst after in situ activation at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C.

1609, 1579, 1487, and 1443 cm^{-1} termed 8a, 8b, 19a, and 19b, respectively [28,29]. In addition to these modes of vibrations, spectra shows two peaks, one at 1637 and another at 1535 cm^{-1} . The 8b vibration mode at 1579 cm^{-1} is found to be very labile and its stability on the surface is temperature dependant. When the temperature is increased to 200 °C, the 8b band almost disappears, confirming its labile nature and hence, it is concluded that these species are bound to the surface OH groups via H-bonding. Pyridine molecules bonded to Lewis acid sites absorbed at 1609, and 1443 cm^{-1} (ascribed to the 8a and 19b-ring mode of pyridine), while those responsible for Brønsted acid sites (pyridinium ion) show absorbance at 1535, and 1637 cm^{-1} [30]. The band at 1487 cm^{-1} (19a-ring mode of pyridine) is a combined band originating from pyridine that is bonded to both Brønsted and Lewis acid sites. It is interesting to note that pure zirconia after high temperature calcination shows only Lewis acidity, while MPA in solid state shows pure Brønsted acidity [31,32]. On the other hand, the catalyst with 15% MPA shows both Brønsted and Lewis acidity and the catalyst retains well-defined Brønsted acidity even after an in situ activation at 400 °C. The Brønsted/Lewis (B/L) site ratio was calculated from the IR absorbance intensities of bands at 1536, and 1442 cm^{-1} [31], respectively and is shown in Fig. 3B. The results indicate that an increase of activation temperature results in a decrease in both Brønsted and Lewis acidity but an overall increase in Brønsted character of the catalyst up to an activation temperature of 300 °C. This clearly indicates the presence of strong Brønsted acid sites in the catalyst.

3.2. Catalytic activity

3.2.1. Alkylation of benzene

Zirconia-supported MPA catalysts were used in alkylation of benzene with 1-octene. With these catalysts, the main reactions were double bond shift isomerization of alkene and alkylation of benzene. Monoctyl benzene (MOB) was the major product of alkylation, whereas dioctyl benzene (DOB)

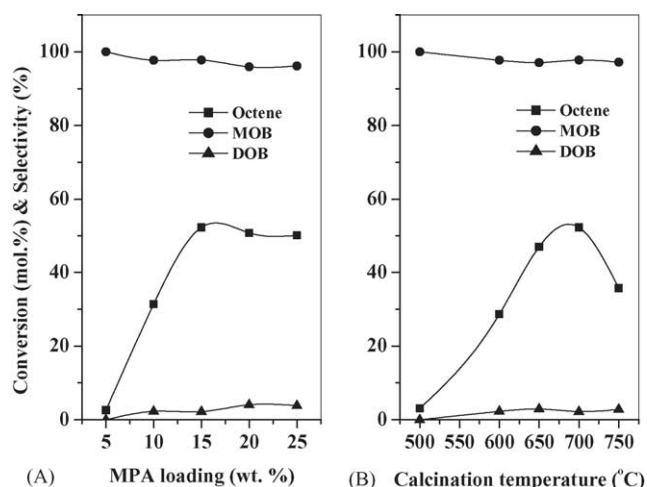


Fig. 4. Octene conversion and product selectivity over various catalysts (conditions: total weight = 25 g; catalyst weight = 0.125 g; temperature = 83 °C; benzene/1-octene (molar ratio) = 10; time = 1 h).

appears as minor product. The conversion is expressed as the percentage of alkene converted into alkylated products. The effect of MPA loading on octene conversion and product selectivity is shown in Fig. 4A. The 5 MZ catalyst showed 3% conversion and the conversion increased to a maximum of 52% at 15% loading under the reaction conditions studied.

To study the effect of calcination temperature, 15 MZ catalyst calcined between 500, and 750 °C were used. The catalyst calcined at 500 °C showed 3% octene conversion and conversion increased to 52% at a calcination temperature of 700 °C (Fig. 4B). The selectivity to mono and dialkylated products were found to independent on MPA loading and calcination temperature and all the catalysts shows more than 95% monoalkylation selectivity. For comparison, alkylation of benzene with 1-octene is also carried out over 15 Mo 700 catalyst and it shows an octene conversion of 30% with 96% MOB selectivity and 4% DOB selectivity. Thus, 15 MZ 700 catalyst is found to be around 1.8 times more active than 15 Mo 700 catalyst. This clearly indicates that the higher activity of 15 MZ 700 catalyst compared to 15 Mo 700 catalyst is due to the presence of MPA in Keggin form on this catalyst.

Therefore, the catalyst with optimum MPA loading (15%) and calcination temperature (700 °C) is taken to study the influence of different reaction parameters on octene conversion and products selectivity. The influence of temperature is studied in the range 60–83 °C. The results indicate that the temperature has a profound effect on conversion of octene (Fig. 5A). At 60 °C, the conversion is only 4% and it increases to 16% at 70 °C. An increase of 37% octene conversion is observed when the temperature is increased from 70 to 83 °C (boiling point of the reaction mixture, 83–84 °C).

The effect of catalyst concentration on octene conversion shows that the catalyst concentration of 0.5 wt.% (of the total mass of the reactants) gives an octene conversion of 52% and increases to 93% with 2 wt.% catalyst, giving similar MOB selectivity (Fig. 5B). Thus, under the reaction conditions of

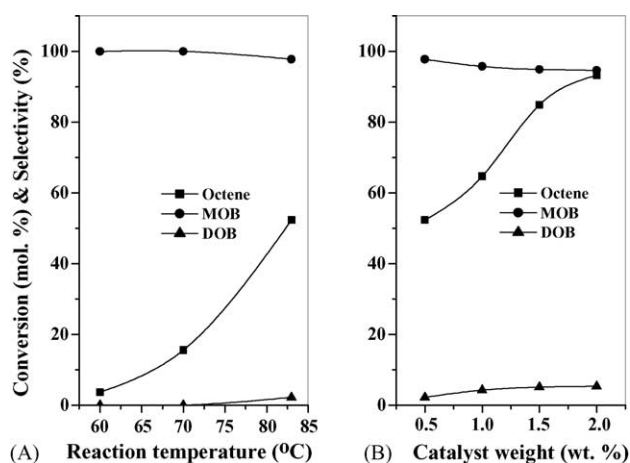


Fig. 5. Effect of reaction conditions on octene conversion and product selectivity. (A) Effect of temperature (conditions: total weight = 25 g; catalyst weight = 0.125 g; benzene/1-octene (molar ratio) = 10; time = 1 h); (B) effect of catalyst weight (conditions: total weight = 25 g; temperature = 83 °C; benzene/1-octene (molar ratio) = 10; time = 1 h).

83 °C, 1 h and benzene/olefin molar ratio of 10, alkylation of benzene with 1-octene gave 93% octene conversion with 95% MOB selectivity (isomer distribution 55% 2-PO, 25% 3-PO, and 20% 4-PO) and 5% DOB selectivity.

Similarly, alkylation of benzene with 1-dodecene is carried out under the reaction conditions of 83 °C, 1 h and benzene/olefin molar ratio of 10, as the desired product, monododecyl benzene (phenyl dodecane-PD) is the precursor to linear alkyl benzene sulfonate, which is the most widely used surfactant in the detergent industry. A 5 wt.% catalyst in the total reaction mixture gave dodecene conversion of 91%, with the MDB isomer distribution of 45% 2-PD, 20% 3-PD, 12% 4-PD, and 23% 5 + 6 PD. Zirconia-supported 12-tungstophosphoric acid also shows similar catalytic performance [16]. Sulfated zirconia is shown to be more active [7], and zeolites as more selective catalyst (to 2-isomer but at low activity) for this reaction [16].

For supported heteropoly acid catalysts, it is important to study recycling of the catalyst, since the limited thermal stability of heteropoly acids usually prevent regeneration of the deactivated catalyst by thermal methods. The recyclability of 15 MZ 700 catalyst was tested in the alkylation of benzene with 1-octene at 83 °C (2 wt.% catalyst, 1 h, and 10:1 molar reactants ratio). In order to study recycling, the separated catalyst after first cycle is refluxed with dichloromethane to remove adsorbed products and alkene oligomers [16] and dried in air at 120 °C for 4 h. This catalyst is reused with fresh reaction mixture and it is found that the catalyst is completely inactive after first use. The loss in catalytic activity is due the reduction of MPA during reaction as indicated by the color change of the catalyst from light yellow to dark blue after reaction [33]. However the deactivated catalyst can be regenerated by thermal methods and the regeneration is achieved by calcination of the separated catalyst at 500 °C for 3 h in air. After the first

use, the catalyst is reused twice without appreciable loss in activity.

4. Conclusions

Zirconia-supported 12-molybdosporic acid acts as an efficient solid acid catalyst for the synthesis of linear alkyl benzenes. The activity of the catalyst in alkylation of benzene with 1-octene is depends on MPA loading and calcination temperature. Under the reaction conditions of 83 °C, benzene/1-olefin molar ratio of 10 (time, 1 h), the most active catalyst 15% MPA supported on zirconia calcined at 700 °C gives more than 90% olefin conversion, and 55% selectivity to 2-phenyl octane, and 45% selectivity to 2-phenyl dodecane.

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