Chapter 5

Zirconia-supported phosphomolybdic acid

5.1. Introduction

This section deals with the characterization of zirconia-supported phosphomolybdic acid (PMA) catalysts by X-ray diffraction, and $^{31}$P MAS NMR spectroscopy and the nature of acidic sites present in the most active catalyst by FTIR pyridine adsorption spectroscopy. These catalysts were used in the synthesis of linear alkyl benzenes by alkylation of benzene with higher linear alkenes such as 1-octene and 1-dodecene and alkylation of phenol with tert-butanol.

5.2. Preparation

The zirconia-supported phosphomolybdic acid catalysts were prepared by the procedure given in Section 2.2. These catalysts were represented by x MZ-T, where x represents wt. %, M represents PMA, Z represents zirconia and T denotes calcination temperature (°C).

For comparison, a catalyst with 15 % MoO$_3$ on ZrO$_2$ calcined at 700 °C (15 Mo-700) was prepared by wet impregnation of zirconium oxyhydroxide with an aqueous solution of ammonium heptamolybdate (s.d. fine chemicals), followed by drying and calcination.

5.3. Catalyst characterization - Results and discussion

5.3.1. X-ray diffraction

The XRD pattern of the catalysts with different PMA loading calcined at 700 °C (Fig. 5.1A) showed the presence of PMA 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 PMA loading calcined at 700 °C, the XRD pattern could be described as the sum of the monoclinic and tetragonal phases of zirconia, this latter phase becoming dominant for
catalyst with 15 % PMA. This can be explained as the strong interaction of PMA with the support reduces the surface diffusion of zirconia, inhibits sintering and stabilizes the tetragonal phase of zirconia. It could be seen that up to a 15 % PMA loading, no diffraction lines, which could be attributed to the polyacid or to its decomposition products, were observed. The 20 MZ-700 catalyst showed the presence of new diffraction lines characteristic of MoO₃ and for 25 % catalyst, formation of ZrMo₂O₈ was observed. This indicated that, PMA decomposed to molybdenum oxide, forming relatively large particles and also reacting with the support forms ZrMo₂O₈.

![Fig. 5.1: X-ray diffractograms (A) a) ZrO₂, b) 5, c) 10, d) 15, e) 20, f) 25 MZ-700 catalysts; (B) 15 MZ catalyst calcined at a) 400, b) 500, c) 600, d) 700, e) 750 °C and f) 15 Mo-700 catalyst. T = tetragonal ZrO₂, M = monoclinic ZrO₂, I = MoO₃, H = ZrMo₂O₈.](image)

As shown in Fig. 5.1B, 15 % catalyst was amorphous, when it was calcined below 400 °C and the crystalline nature of zirconia increased with calcination temperature. As the calcination temperature increased from 500 to 700 °C, zirconia crystallized to tetragonal phase and at 750 °C, the formation of monoclinic phase was indicated. Such stabilization of tetragonal ZrO₂ in presence of other heteropoly acids has been known in literature [1, 2]. For comparison, the XRD of 15 % molybdenum oxide supported on
zirconia calcined at 700 °C (15 Mo-700) was recorded and it showed the stabilization of ZrO$_2$ in tetragonal phase together with the formation of small amount of ZrMo$_2$O$_8$ [3].

5.3.2. $^{31}$P MAS NMR spectroscopy

This is one of the most important characterization techniques to study the state of phosphorous in heteropoly acids. The bulk PMA showed a sharp intense peak at -3.5 ppm in the $^{31}$P MAS NMR spectrum, due to the uniform phosphorous environment in highly hydrated structure of the PMA. The small peak observed nearer to the main peak at 6.3 ppm might be due to the part of the sample containing different degrees of hydration [4]. The $^{31}$P MAS NMR spectra of catalysts with 5 to 25 % PMA calcined at 700 °C and 15 % PMA calcined between 600 to 750 °C shows that the state of phosphorous in catalysts depend on PMA loading and calcination temperatures. The spectra of catalysts with different PMA loading are shown in Fig. 5.2A. For 5 % PMA catalyst, NMR showed a peak at -8.6 ppm assigned to the presence of phosphomolybdate, which is in interaction with zirconia [5, 6]. However, when the PMA loading increased to 10 %, NMR showed peaks at -3.5 ppm, -8.2 ppm and 18 ppm, respectively. The peak at -3.5 ppm is assigned to microcrystalline PMA, similar to the unsupported PMA [6, 7] and the chemical shift at -8.2 ppm is due to PMA interacting strongly with the zirconia surface. The origin of the peak at 18 ppm is not clear at present. For catalysts with 15 % PMA loading and above, an additional peak at -30 ppm was observed, which is attributed to phosphorous oxide (P-O=P) resulting from the decomposition of the polyoxometalate [8]. However, 15 MZ-700 catalyst gave the highest conversion of octene and the $^{31}$P CPMAS NMR spectrum of this catalyst showed the peak at -8.5 ppm due to the presence of PMA strongly interacting with zirconia surface (Fig. 5.2C).

The $^{31}$P MAS NMR spectra of 15 MZ catalyst calcined between 500-750 °C are shown in Fig. 5.2B. At a calcination temperature of 500 °C, NMR spectrum showed two peaks, one at -8 ppm and the other at 17.2 ppm. As the calcination temperature was increased to 600 °C, NMR spectrum showed peaks at -3.5 ppm, -8.2 ppm and 18 ppm,
similar to the NMR spectrum of 10 MZ-700 catalyst and 15 MZ-750 catalyst showed a sharp peak at −30 ppm.

Fig. 5.2: $^{31}$P MAS NMR spectra of (A) catalysts with different PMA loading a) pure PMA, b) 5 MZ-700, c) 10 MZ-700, d) 15 MZ-700, e) 20 MZ-700, f) 25 MZ-700; (B) 15 MZ catalyst calcined at different temperature a) 500, b) 600, c) 700, d) 750 °C; (C) $^{31}$P CP MAS NMR spectrum of 15 MZ-700 catalyst.
5.3.3. FTIR pyridine adsorption

FTIR spectra of pyridine adsorbed on 15 MZ-700 catalyst recorded from 100 to 400 °C are shown in Fig. 5.3A. At 100 °C, important pyridine ring modes occur at approximately 1609, 1579, 1487 and 1443 cm\(^{-1}\) termed 8a, 8b, 19a and 19b, respectively [9, 10]. In addition to these modes of vibrations, spectra showed two peaks at 1637 and 1535 cm\(^{-1}\). The peak at 1579 cm\(^{-1}\) was found to be very labile and its stability on the surface was temperature dependant. When the temperature was increased to 200 °C, this peak almost disappeared, 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) showed absorbance at 1535 cm\(^{-1}\) and at 1637 cm\(^{-1}\) [11]. The band at 1487 cm\(^{-1}\) (19a-ring mode of pyridine) is a combined band originating from pyridine bonded to both Brønsted and Lewis acid sites. The Brønsted/Lewis (B/L) site ratio was calculated from the IR absorbance intensities of bands at 1536 and 1442 cm\(^{-1}\) [12], respectively and is shown in Fig. 5.3B. The results indicated that an increase of activation temperature decreased 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.

![Fig. 5.3: The IR spectra of pyridine adsorbed on 15 % catalyst after in-situ activation at a) 100, b) 200, c) 300, and d) 400 °C.](image)
5.4. Alkylation of benzene

General introduction to linear alkyl benzenes (LAB) and the procedure to carry out alkylation of benzene with higher linear olefins are given in section 4.4.1, 4.4.2 respectively and the formation of different reaction products are shown in Scheme 4.1.

5.4.1. Results and discussion

Zirconia-supported PMA catalysts were used in alkylation of benzene with 1-octene. The main reactions occurred with these catalysts were double bond shift isomerization of alkene and alkylation of benzene. Monooctyl benzene (MOB) was the major product of alkylation, whereas dioctyl benzene (DOB) appeared as minor product. The conversion is expressed as the percentage of alkene converted into alkylated products. The effect of PMA loading on conversion of octene and product selectivity is shown in Fig. 5.4A. The 5 MZ-700 catalyst showed 3 % conversion and the conversion increased to a maximum of 53 % with 15 MZ-700 catalyst under the reaction conditions studied.

![Graph A](image)

![Graph B](image)

**Fig. 5.4:** The conversion of octene 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).
To study the effect of calcination temperature on conversion of octene and product selectivity, 15 MZ catalyst calcined between 500 and 750 °C were used. The catalyst calcined at 500 °C showed 3 % conversion of octene and conversion increased to 52 % at a calcination temperature of 700 °C (Fig. 5.4B). The selectivity to mono and dialkylated products was found to be independent on PMA loading and calcination temperature and all the catalysts gave more than 95 % mono-alkylation selectivity. For comparison, alkylation of benzene with 1-octene was also carried out using 15 Mo-700 catalyst and it showed an octene conversion of 30 % with 96 % MOB selectivity and 4 % DOB selectivity under the same reaction conditions. Thus, 15 MZ-700 catalyst was nearly two times more active than 15 Mo-700 catalyst. This clearly indicates that the higher activity of 15 MP-700 catalyst compared to 15 Mo-700 is due to the presence of PMA in the catalyst.

Therefore, the catalyst with optimum PMA loading (15 %) and calcination temperature (700 °C) was taken to study the influence of different reaction parameters on
the conversion of octene of and products selectivity. The influence of temperature was studied in the range 60 to 83 °C, keeping other conditions similar. The results indicated that the temperature has a profound effect on the conversion of octene (Fig. 5.5A). At 60 °C, the conversion was 4 % and it increased to 16 % at 70 °C. An increase of 37 % conversion of octene was observed when the temperature was increased from 70 to 83 °C (boiling point of the reaction mixture, 83-84 °C).

The effect of catalyst concentration on the conversion of octene showed that 0.5 wt. % (of the total mass of the reactants) of catalyst gave 53 % conversion of octene and increased to 93 % with 2 wt. % catalyst, with similar MOB selectivity (Fig. 5.5B). The increase in conversion with increasing catalyst concentration is due to the proportional increase in the number of active sites.

Thus, under the reaction conditions of 83 °C, 1 h and benzene/olefin molar ratio of 10, alkylation of benzene with 1-octene gave 93 % conversion of octene 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 was carried under the reaction conditions of 83 °C, 1 h and benzene/olefin molar ratio of 10. The 5 wt. % catalyst of the total reaction mixture gave 91 % conversion of dodecene, with the MDB isomer distribution of 45 % 2-PD, 20 % 3-PD, 12 % 4-PD and 23 % 5+6 PD.

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 was refluxed with dichloromethane to remove adsorbed products and alkene oligomers [2] and dried in air at 120 °C for 4 h. This catalyst was reused with fresh reaction mixture and was found to be completely inactive after first use. The loss in catalytic activity is due the reduction of PMA during reaction as indicated by the color change of the catalyst from light yellow to dark blue after reaction [13]. However, the deactivated catalyst could be regenerated by thermal methods and the regeneration was achieved by calcination of the separated catalyst at 500 °C for 3 h in air. After the first use, the regenerated catalyst was reused twice without appreciable loss in activity.
5.5. Phenol tert-butylation

General introduction to phenol tert-butylation and the procedure to carry out alkylation of phenol with tert-butanol are given in section 3.5.1, 3.5.2 respectively and the formation of different reaction products are shown in Scheme 3.2.

5.5.1. Results and discussion

The main products of the tert-butylation of phenol were 2-tert-butyl phenol (2-TBP), 4-tert-butyl phenol (4-TBP), 2,4-di-tert-butyl phenol (2,4-DTBP) and tert-butyl phenyl ether (TBPE). The products like 2,6-di-tert-butyl phenol and 2,4,6-tri-tert-butyl phenol (TTBP) were formed in small amount. C8 and C12 olefins, formed by the oligomerization of isobutene were also observed in the reaction, where isobutene was formed by the acid catalyzed dehydration of tert-butanol.

5.5.1.1. Effect of PMA loading

In order to investigate the effect of PMA loading, catalysts with 5-25 % PMA on zirconia calcined at 700 °C were used in alkylation of phenol with tert-butanol at 120 °C with a space velocity of 4 h⁻¹ (Fig. 5.6). The 5 MZ-700 catalyst showed the lowest conversion of phenol 41.9 %, while 15 MZ-700 catalyst gave the highest conversion 64.6 %. Further increase in PMA loading decreased the conversion of phenol and for 25 % catalyst it was 60.8 %.

The selectivity to different alkylated products also depended on PMA loading. The 5 MZ-700 catalyst showed the highest selectivity to TBPE. As the conversion of phenol increased from 51.9 % for 5 % catalyst to 64.6 % for 15 % catalyst, the selectivity to TBPE decreased from 10.3 to 1.6 %. The 5 % catalyst showed 2-TBP selectivity of 25 % and 4-TBP selectivity of 21.1 %. When PMA content was increased to 10 %, the selectivity to 2-TBP was decreased to 20.2 %, while selectivity to 4-TBP was similar to that of 5 % catalyst. The catalysts with higher PMA content gave products with similar selectivity to 2-TBP and 4-TBP as that of 10 % catalyst. The selectivity to 2,4-DTBP increased up to 15 % PMA loading (52.2 %) and further increases in PMA loading decreased its selectivity.
5.5.1.2. Effect of calcination temperature

The 15 MZ catalyst calcined between 500 °C to 750 °C were used to study the change in catalytic activity with calcination temperature (Fig. 5.7). It is clear from Fig. 5.7, that calcination temperature has a profound effect on catalytic activity. The catalyst calcined at 500 °C, gave 40 % conversion of phenol and increased to 64.6 % at a calcination temperature of 700 °C. Further increase in calcination temperature decreased the conversion of phenol.

The selectivity to different alkylated products also varied with catalyst calcination temperature. As the conversion of phenol increased from 40 % for the catalyst calcined at 500 °C to 64.6 % for the one calcined at 700 °C, the selectivity to TBPE decreased from 12.5 to 1.6 %, 2-TBP from 26.5 to 19 % and 4-TBP from 25.8 to 20.5 %. However, the selectivity to 2,4-DTBP was increased with calcination temperature up to 700 °C (52.2 %) and further increase in calcination temperature decreased its selectivity.
Fig. 5.7: Effect of calcination temperature on the conversion of phenol and product selectivity. (conditions: temperature = 120 °C, tert-butanol/phenol molar ratio = 2, LHSV = 4 h⁻¹, time = 2 h).

5.5.1.3. Effect of reaction temperature

The reaction was studied in the temperature range of 80 to 180 °C using 15 MZ-700 catalyst. The changes in the conversion of phenol and selectivity to different products as a function of temperature are shown in Fig. 5.8. At 80 °C, the conversion of phenol was 21.3 % and increased to 76.5 % at 140 °C. An increase in temperature above 140 °C decreased the conversion of phenol. The decrease in conversion of phenol could be due to the dealkylation of tert-butyl phenol to phenol at high temperature and also the diminishing availability of tert-butanol as it undergoes oligomerization rather than alkylation [14, 15].

At 80 °C, TBPE obtained as the major product (53.5 %) and as the conversion of phenol increased, TBPE selectivity decreased and it was completely absent at 140 °C. The decrease in TBPE selectivity with temperature might be due to its rearrangement to C-alkylated product. Indeed, it has been shown that such rearrangement occurred on heating by contact with an acid catalyst [16]. The highest selectivity to 2-TBP was found to be at 100-120 °C (21 %), while, selectivity to 2,4-DTBP (45 %) was highest at 140 °C. The higher selectivity of 2,4-DTBP at this temperature might be due to the higher stability and the availability of tert-butyl cation at this reaction temperature. The
formation of 4-TBP is favored at high temperature as it is the thermodynamically stable product and hence an increase in temperature always increased its selectivity.

Fig. 5.8: Effect of reaction temperature on the conversion of phenol and product selectivity. (conditions: tert-butanol/phenol molar ratio = 2, LHSV = 4 h⁻¹, time = 2 h).

5.5.1.4. Effect of molar ratio

The effect of molar ratio on the conversion of phenol and product selectivity was studied at 120 °C by varying tert-butanol/phenol molar ratio from 1 to 4 (Fig. 5.9). Generally, the conversion of phenol was increased with an increase in the amount of tert-butanol. At a molar ratio of 1, conversion of phenol was 58.1 %, which increased to 80.6 % at a molar ratio of 3. A further increase in molar ratio had no appreciable effect on the conversion of phenol. It was shown that the polar molecule, such as methanol and higher alcohols compete with phenol for adsorption sites and an increase in the molar excess of alkylating agent results in an increase in the conversion of phenol as observed in the present study [17].

The formation of TBPE was observed in small amounts under these conditions. The selectivity to 2-TBP was low and it decreased from 17.3 to 9.8 %, when the molar ratio increased from 1 to 4. With an increase in molar ratio from 1 to 4, the selectivity to 4-TBP decreased from 41.3 to 21.3 %, while 2,4-DTBP selectivity increased from 38 to
64.6 %. This could be due to the higher availability of tert-butanol, which leads to the formation of the dialkylated product.

![Graph showing the effect of molar ratio on the conversion of phenol and product selectivity.](image)

**Fig. 5.9:** Effect of molar ratio on the conversion of phenol and product selectivity. (conditions: temperature = 120 °C, LHSV = 4 h⁻¹, time = 2 h).

### 5.5.1.5. Effect of space velocity

The effect of space velocity was studied at 140 °C using tert-butanol/phenol molar ratio of 3 from LHSV of 2 to 10 h⁻¹ and the results are shown in Fig. 5.10. With an increase of space velocity from 2 to 10 h⁻¹, the conversion of phenol was changed from 82 to 62.4 %. The decrease in conversion with an increase in space velocity is due to the lower contact time available for the reactants to be in contact with the active sites of the catalyst. With decrease in the conversion of phenol, the selectivity to 2,4-DTBP decreased from 60.5 to 44.6 %. However, change in space velocity had no appreciable effect on the selectivity to other products.
5.5.1.6. Effect of time on stream

In order to study the deactivation behavior of the catalyst, the reaction was studied at 140 °C with LHSV of 4 h⁻¹ using tert-butanol/phenol molar ratio of 3, for 31 h (Fig. 5.11). The conversion of phenol was found to be 80.6 % after 2 h with selectivity to 2-TBP 11.5 %, 2,4-DTBP 55.2 %, and 4-TBP 25.7 %, and after 31 h, the conversion of phenol was decreased to be 58.5 % with selectivity to 2-TBP 15.2 %, 2,4-DTBP 41.6 %, and 4-TBP 38.4 %. However, the major drawback of PMA/ZrO₂ catalyst is its deactivation, which is in sharp contrast with the catalytic behavior of zirconia-supported silicotungstic acid catalyst, where the catalyst is found to be stable and regenerable [16]. The color of the product mixture obtained from 15 MZ-700 catalyst was found to be dark blue and it indicated the major reason for the catalyst deactivation is due to the reduction and leaching of PMA from the catalyst surface [14].

Fig. 5.10: Effect of space velocity on the conversion of phenol and product selectivity. (conditions: temperature = 140 °C, tert-butanol/phenol molar ratio = 3, time = 2 h).
Fig. 5.11: Effect of time on stream (TOS) on the conversion of phenol and product selectivity. (conditions: temperature = 140 °C, LHSV = 4 h⁻¹, tert-butanol/phenol molar ratio = 3).
5.6. References