Liquid phase allylation of anisole using TPA/ZrO$_2$ catalyst

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Abstract

The allylation of anisole with allyl alcohol was investigated in liquid phase using 12-tungstophosphoric acid supported on zirconia (TPA/ZrO$_2$) calcined at 750 °C as the catalyst. The catalytic activity of 15% TPA/ZrO$_2$ has been compared with zeolite catalysts under the optimized reaction conditions. The reaction was performed in the temperature range 140–200 °C and allyl alcohol to anisole molar ratio 0.5–3, under nitrogen pressure. Higher molar ratio of allyl alcohol to anisole under optimum reaction conditions resulted in the formation of *ortho-* and *para*-allylanisole as the major products, while at lower molar ratio (excess of anisole), more of 1,1-bis(methoxyphenyl)propane was formed. The reaction was heterogeneously catalyzed, and no contribution from homogeneous (leached) TPA into reacting medium was observed.
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1. Introduction

Friedel–Crafts reaction using alkyl halides and Lewis acid catalysts such as AlCl$_3$, FeCl$_3$, ZnCl$_2$ has been widely used for large number of alkylation reactions to get substituted aromatics. But, these homogeneous catalyst systems suffer from drawbacks such as environmental pollution, equipment corrosion and tedious work up for the separation of the catalyst from the reaction mixture. So it is desirable to use heterogeneous catalysts (solid acids) with halide free process in the above catalytic reactions.

Allylation of aromatic compounds is industrially important as the allylated aromatics find application in polymer synthesis and in perfume industry. *p*-Allylanisole (or estragole), the main product of allylation of anisole is used in perfumes and flavoring agent in food and liquors [1]. There are several reports in the literature on the uses of homogeneous catalysts in the allylation reaction, such as, ZnCl$_2$ catalyzed allylation of 2,6-dimethyl anisole with allyl chloride to *meta* allylated product [2]. Allylation of naphthols with allylic alcohols using Pd catalysts in the presence of molecular sieve 4 Å [3] and Mo(II) complexes catalyzed allylation of anisole [4] have also been reported. Allylic carbonates

have been employed as allylating agents for toluene, xylene and 1,2-dimethoxy benzene using Mo and W catalysts [5]. *o*-Allylphenol has been selectively obtained using a mixture of anhydrous Cu(II) perchlorate and Cu metal powder catalyst [6]. Heterogeneous catalyst systems have also been used in the allylation reactions and among these zeolites, H-beta has been used for the allylation of phenol [7] and toluene [8]. In addition to zeolites, lead halo composite (Pb$_3$BrF$_5$) has been used for the allylation of diphenyl ether using ally bromide as allylating agent [9] in our earlier report. There is a scope to design new heterogeneous catalyst recipes for good number of reactions including allylation of aromatic substrates and improve their performances with respect to higher substrate conversions and selectivities for the desired allylated products.

Keeping in view of the above facts concerning the importance of allylation reactions and the newer catalyst recipes, it was decided to use heteropoly acid supported on solid metal oxide as a catalyst for the allylation of anisole using allyl alcohol as the allylating agent under liquid phase conditions. The present paper reports the evaluation of reaction parameters on the allylation of anisole by allyl alcohol using TPA/ZrO$_2$ catalyst, which has been established to provide high acidity and stability in our earlier report [10]. The activity of TPA/ZrO$_2$ catalyst has been compared with zeolites, TPA/SiO$_2$ and homogeneous TPA.

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2. Experimental

2.1. Materials

12-Tungstophosphoric acid (TPA), anisole and allyl alcohol were purchased from s.d. fine Chemicals Ltd., Mumbai. Zirconium oxychloride was procured from Loba Chemie Ltd., Mumbai. Methanol was purchased from E. Merck India Ltd., Mumbai. Zeolites H-beta, H-ZSM-5 and H-Y (recovered by calcining NH_4-Y in air at 550 °C for 8 h) were obtained from our Catalyst Pilot Plant (CPP-NCL). H-Mordenite was obtained from PQ Zeolites BV, Netherlands. All the above materials were used as-received in the catalyst preparation and allylation experiments.

2.2. Preparation and characterization of the catalysts

The catalyst was prepared by wet impregnation method, following the procedure described in our earlier publication [10]. Zirconium hydroxide obtained by the hydrolysis of zirconium oxychloride was added to a methanolic solution of TPA. It was stirred well and evaporated to dryness and calcined in air at 750 °C. Catalysts with different TPA loading from 5 to 25 wt.% were prepared and calcined at 750 °C. Similarly, 15% TPA/SiO_2 was prepared as above using silica gel and calcined at 750 °C. Silica gel support was prepared by following the procedure described elsewhere [11].

The surface area of the catalysts was measured by the nitrogen BET method using an area meter. The acidities of TPA/ZrO_2 with different TPA loading measured by TPD of ammonia and their surface area are listed in Table 1. It is seen that acidity ($mmol\,g^{-1}$) increased with TPA loading up to 15% and then decreased with further increase in loading. The same trend was observed in case of surface area. High acidity of 15% catalyst among different loading is due to monolayer coverage of TPA on zirconia [10].

Table 1
Characteristics of TPA/ZrO_2 catalysts

TPA (wt.%)	Surface area ($m^2\,g^{-1}$)	Acidity ($mmol\,g^{-1}$)
5	40.2	0.23
10	46.3	0.36
15	53.2	0.46
20	52.3	0.23
25	48.6	0.19

2.3. Experimental

Experiments on allylation of anisole were carried out in a 50 ml Parr autoclave under nitrogen pressure. The catalysts were activated at 500 °C for 4 h and cooled to room temperature prior to their use in the reaction. In a typical run, a weighed amount of 15% TPA/ZrO_2 catalyst mixed with known amounts of anisole and allyl alcohol was placed in the reactor. The reactor was pressurized with nitrogen (20 bar) and heated to the desired temperature with stirring at 500 rpm. After a desired interval of time, the reactor was cooled to room temperature and a sample of the reaction mixture was withdrawn and centrifuged to get a clear solution and analyzed for products. The products of allylation of anisole were analyzed by Shimadzu 14B gas chromatograph fitted with a SE-52 packed column, coupled with FID detector. The identity of the products was confirmed by GC-MS (Shimadzu QP-5000). Conversion is given as the conversion of anisole to allylated products.

3. Results and discussion

The allylation of anisole by allyl alcohol catalyzed by TPA/ZrO_2 catalyst is shown in Scheme 1. The reaction of anisole with allyl cation formed from allyl alcohol in the presence of catalyst results in the formation of *ortho-* and *para*-allylanisole, 1,1-bis(methoxyphenyl)propane (hereafter referred as mpp) and diallyl ether as products. Attack
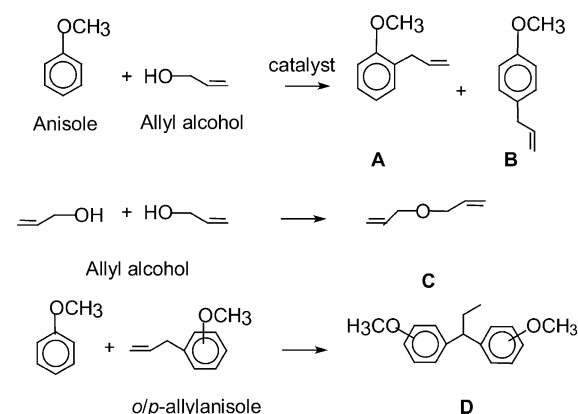

A = *o*-allylanisole, B= *p*-allylanisole, C= diallylether, D= 1,1-bis(methoxyphenyl)propane

Scheme 1.

Table 2
Comparison of the catalysts

Catalyst	Si/Al	Surface area ($m^2 g^{-1}$)	Acidity ($mmol\, g^{-1}$)	Anisole conversion (wt.%)	Selectivity (%, *ortho* + *para*)
15% TPA/ZrO$_2$-750 °C	–	53.2	0.46	25.9	86.3
15% TPA/SiO$_2$-750 °C	–	16	Nil	0.5	50.0
H-beta	15	540	0.94	34.0	67.6
H-Y	3	530	2.25	22.0	93.7
H-mordenite	10	490	0.72	24.7	80.8
H-ZSM-5	50	364	0.82	2.3	92.0
TPA	–	–	–	45.7	17.6

Conditions: catalyst wt. = 1.25 g, wt. of the reaction mixture = 25 g, temperature = 180 °C, allyl alcohol to anisole molar ratio = 1, time = 2 h.

on the *meta*-position of anisole by allyl cation is least favored since electron density at this position is less compared to *ortho*- and *para*-positions. Hence *meta*-allylated anisole was not formed in the above reaction.

3.1. Catalytic activity of different catalysts

To know the catalytic activities of zeolite-based solid acid catalysts and to compare their performances with zirconia and silica supported heteropoly acid, the allylation of anisole was conducted under similar reaction conditions. The characteristic data and catalytic activities of different catalysts viz. 15% TPA/ZrO$_2$, 15% TPA/SiO$_2$, H-beta, H-Y, H-mordenite, H-ZSM-5 and conventional catalyst, TPA for comparison are presented in Table 2 along with reaction conditions. It is seen from the results presented in Table 2 that TPA (homogeneous) gave the highest anisole conversion (45.7%) among the catalysts tested for their catalytic activities in allylation of anisole followed by H-beta, 15% TPA/ZrO$_2$, H-mordenite, H-Y and the rest. While H-Y gave the highest *ortho*- and *para*-product selectivity (93.7%) followed by H-ZSM-5, 15% TPA/ZrO$_2$, H-mordenite and the rest. Interestingly, 15% TPA/SiO$_2$ catalyst showed least activity in allylation of anisole, which is due to the absence of acidity required for acid catalyzed reactions. The absence of acidity in 15% TPA/SiO$_2$ calcined at 750 °C confirm that TPA is not stable and decompose on SiO$_2$. Similarly, among the zeolite catalysts, H-ZSM-5 having Si/Al = 50 having smaller pore size gave poor catalytic activity (2.3%). In general, it appears that the performance of the catalysts in allylation of anisole depends upon the compound effect of acidity and surface area among the zeolite catalysts, while, with TPA supported catalysts, the catalytic activity depends strongly on the stability (Keggin structure intact) of TPA over the support and their acidities. In addition to this, it is found that zirconia supported heteropoly acid (15% TPA/ZrO$_2$) calcined at 750 °C showed comparable activity (25.9%), with that of H-mordenite (24.7%).

If we look at the *ortho*- and *para*-product selectivities, which depends on the morphological features (cage structure, pore size, etc.) of the zeolite catalysts have shown marginally higher selectivities than zirconia supported TPA catalyst (86.4%). The overall conclusion is that zirconia supported TPA catalyst performed well in comparison with

zeolite-based catalysts keeping in view of their cost, easy method of preparation and our objective to develop heteropoly acid supported catalysts for alkylation reactions.

Allylation experiments were conducted using different TPA loaded (5–25 wt.%) catalysts and the results are presented in Fig. 1. It is seen that the anisole conversion increased with increase in TPA loading up to 15% and then decreased with further increase in loading. Since, 15% catalyst is more acidic than others (Table 1), it showed highest anisole conversion (25.9%) under the reaction conditions. It is interesting to note that the selectivities for the *ortho*- and *para*-allylated products were marginally affected with increase in TPA loading. Though, the conversion of anisole depended on TPA loading, it is seen from Fig. 1 that at all conversions of anisole, the selectivities for *p*-allylanisole on an average higher by 12% than *o*-allylanisole. The selectivity for mpp was maximum for 15% catalyst. This is expected since the formation of mpp depends on the built up concentrations of monoallylated products in the reaction.

In order to check the dissolution of TPA into solution during the reaction, the allylation reaction was stopped after 2 h and the catalyst was filtered. The reaction was continued with the filtrate for another 2 h and from the anal-
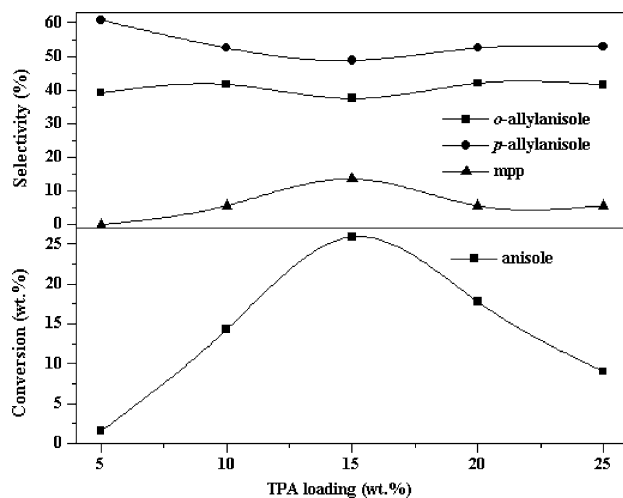

Fig. 1. Effect of different TPA loading (wt.%) on ZrO$_2$. Conditions: catalyst wt. = 1.25 g, wt. of the reaction mixture = 25 g, temperature = 180 °C, allyl alcohol to anisole molar ratio = 1, time = 2 h.

ysis it was found to be no change in the conversion of anisole and it remained at the previous level. This ensured that the reaction was catalyzed heterogeneously. In addition to this, leaching of TPA (dissolution of P or W) in the filtrate was tested by inductively coupled plasma-optical emission spectroscopy (ICP-OES). This showed the absence of P or W in solution after reaction and supported the fact that the allylation reaction occurs by surface mechanism heterogeneously.

3.2. Effect of temperature

The allylation of anisole was carried out in the range 140–200 °C to know the effect of temperature on the conversion of anisole and the product selectivities. The results obtained are presented in Fig. 2. Conversion of anisole was poor at lower temperature (<140 °C) and enhanced with increase in temperature. The selectivity for *ortho-* and *para*-allylanisole decreased marginally with increase in temperature. However, increase in reaction temperature increased the amount of mpp and hence reduced the selectivities for the major products. The anisole conversion increased by 14%, when the temperature was increased from 160 to 180 °C but allylation selectivity was decreased by 7%. When the temperature was increased from 180 to 200 °C, conversion of anisole increased by 6% only, but selectivities for the allylated products decreased by 10%. At 180 °C, anisole conversion was 25.9%, *ortho-*, *para-* and mpp selectivities were 37.6, 48.8 and 13.6%, respectively. Hence, 180 °C was selected for further optimization of the reaction conditions. In addition to the above major products, diallyl ether and others (unidentified products) were also formed (Table 3).

Table 3
Product distribution

Distribution	wt.%
Allyl alcohol	23.1
Anisole	44.9
o-Allylanisole	5.9
p-Allylanisole	7.7
Diallyl ether	8.1
mpp	2.2
Others	8.1
Anisole conversion (wt.%)	25.9
Selectivity (%)	
o-Allylanisole	37.6
p-Allylanisole	48.8
mpp	13.6

Conditions: catalyst = 15% TPA/ZrO$_2$, catalyst wt. = 1.25 g, temperature = 180 °C, wt. of the reaction mixture = 25 g, allyl alcohol to anisole molar ratio = 1, time = 2 h.

3.3. Effect of molar ratio

The reaction was carried out with different molar ratio of allyl alcohol to anisole (0.5–3) and the results are presented in Fig. 3. The conversion of anisole decreased with increase in allyl alcohol to anisole molar ratio up to 2 and then there was no appreciable change in the conversion with further increase. At higher molar ratio, allyl alcohol is converted into diallyl ether (Scheme 1) and hence its availability for the main reaction is limited. Maximum conversion was obtained at higher molar ratio (>1) but mpp was the major product. This indicates that the reaction between allylated products and anisole to form mpp is more probable at higher anisole concentrations. The selectivities for both *ortho-* and *para*-products increased as the allyl alcohol concentration
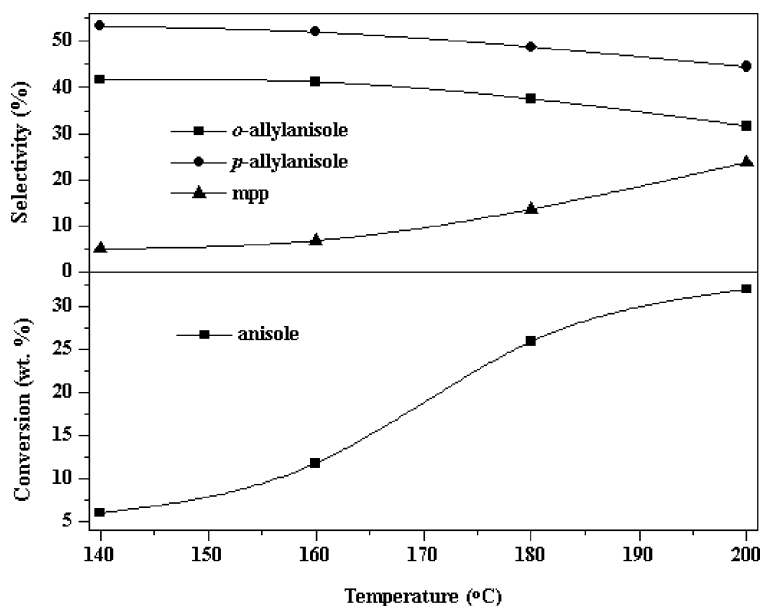

Fig. 2. Effect of reaction temperature. Conditions: catalyst = 15% TPA/ZrO$_2$, catalyst wt. = 1.25 g, wt. of the reaction mixture = 25 g, allyl alcohol to anisole molar ratio = 1, time = 2 h.
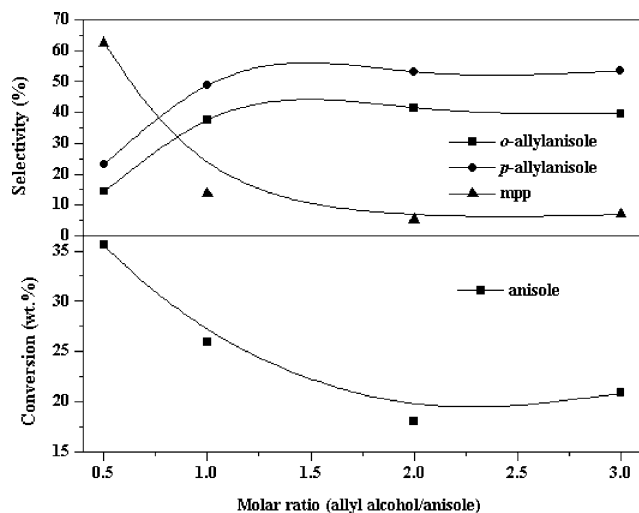
Fig. 3. Effect of allyl alcohol to anisole molar ratio. Conditions: catalyst = 15% TPA/ZrO$_2$, catalyst wt. = 1.25 g, wt. of the reaction mixture = 25 g, temperature = 180 °C, time = 2 h.

Fig. 5. Effect of reaction time. Conditions: catalyst = 15% TPA/ZrO$_2$, catalyst wt. = 1.25 g, wt. of the reaction mixture = 25 g, temperature = 180 °C, allyl alcohol to anisole molar ratio = 1.

increased (molar ratio 1) and then remained almost the same with further increase. Hence, equimolar ratio of allyl alcohol to anisole was found to be appropriate to get reasonably good conversion of anisole and selectivities for *ortho-* and *para-*allylated products.

3.4. Effect of catalyst concentration

The reaction was carried out with the catalyst concentration in the range 2.5–10 wt.% of the total weight of the reactants (25 g) and the results are presented in Fig. 4. It was found that the conversion of anisole increased with increase in catalyst concentration. As observed previously, at higher conversion of anisole more mpp formed decreased the selectivities for *ortho-* and *para-*allylated products.
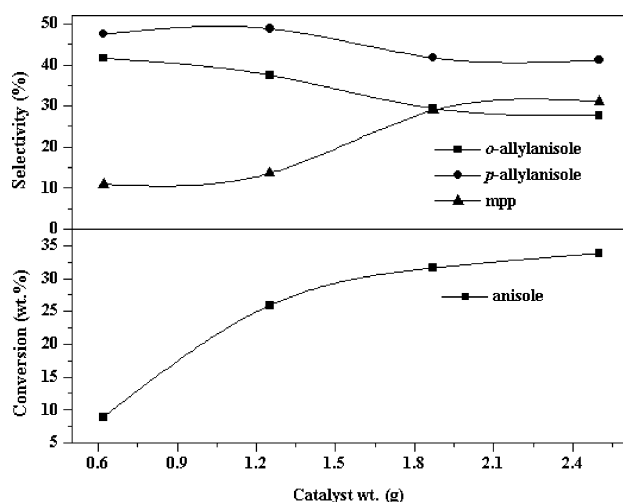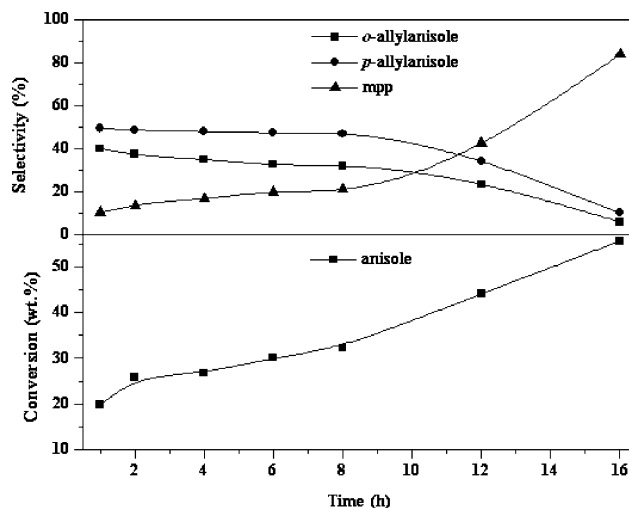

Fig. 4. Effect of catalyst concentration. Conditions: catalyst = 15% TPA/ZrO$_2$, wt. of the reaction mixture = 25 g, temperature = 180 °C, allyl alcohol to anisole molar ratio = 1, time = 2 h.

3.5. Effect of reaction time

In order to study the effect of time, reaction was carried out for 16 h and the results are shown in Fig. 5. Conversion of anisole linearly increased with increase in time. After 16 h the conversion of anisole was 55.6%. Interestingly, selectivities of allylated products decreased after 8 h, while mpp formation increased substantially. This is because the allyl alcohol was totally consumed till 8 h and anisole conversion increased further due to the reaction of anisole with either *ortho-* or *para-*allylanisole to form mpp.

3.6. Recyclability of the catalyst

The catalyst with 15% loading was used for recycling experiments. In order to recycle the catalyst after 2 h reaction, it was separated by filtration, washed with ether, dried and calcined in air at 500 °C and used in the allylation reaction with a fresh reaction mixture. The conversion of anisole after 2 h was found to be the same as that of the fresh catalyst. The catalyst recycling was performed thrice, and the conversion of anisole was found to be almost the same.

4. Conclusions

Allylation of anisole with allyl alcohol was carried out with TPA/ZrO$_2$ catalyst and reaction conditions have been optimized. The catalyst with 15% loading showed higher catalytic activity at 180 °C, equimolar ratio of allyl alcohol to anisole and 5% catalyst (total weight of reaction mixture). The selectivity of 86% for *ortho-* and *para-*(*ortho*:*para* = 37:49) allylated products was achieved at maximum anisole conversion (25.9%) under the optimized conditions. The catalytic activity of zirconia supported TPA system is close to that of H-beta and better than other zeolites. 15% TPA/ZrO$_2$

catalyst was thermally stable, recyclable, cost effective, environmental friendly and could be used in similar reactions.

Acknowledgements

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