

Synthesis of monoallyl guaiacol via allylation using HY zeolite

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Abstract

Monoallyl guaiacol such as eugenol, *o*-eugenol and chavibetol are industrially important compounds, which were synthesized by the allylation of guaiacol using zeolite HY. The reaction was performed in an autoclave in the temperature range 140–200 °C and allyl alcohol to guaiacol mole ratio 1:4, under nitrogen pressure. Among zeolites, HY gave maximum guaiacol conversion (46%) compared to H-beta (28%), H-mordenite (15%) and HZSM-5 (4%) when compared under identical reaction conditions. Zeolites showed better selectivity (>85%) for monoallyl guaiacol than K-10 montmorillonite clay (47%). The pore architecture and acidic sites of the zeolites seems to influence the product selectivity.

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1. Introduction

Friedel-Crafts reaction has been recognized as a versatile tool for substituting aromatic rings. Lewis acid catalysts such as AlCl₃, FeCl₃, ZnCl₂ and H₂SO₄ are widely used in various alkylation reactions to get substituted aromatics. But these homogeneous catalysts suffer from drawbacks such as environmental pollution, equipment corrosion and tedious work up [1]. So it is advantageous to use heterogeneous catalysts (solid acids) with halide free process to overcome the above problems.

Studies in the preparation of allyl aromatics have proven to be quite attractive because of the extensive use of these compounds in the dyestuff, perfume, flavor, agriculture and pharmaceutical industries. There are numerous reports in the literature on the use of homogeneous catalysts in the allylation reaction such as ZnCl₂ catalyzed allylation of 2,6-dimethyl anisole with allyl chloride to *meta* allylated product [2]. Pd catalysts in the presence of molecular sieve 4A for the allylation of naphthols with allylic alcohols [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]. Very recently phase transfer catalyst is used for allylation of *p*-methoxyphenol with allylbromide as a allylating agent [7]. Heterogeneous catalysts such as zeolites have been used for the allylation of alkyl aromatics [8]. There are very few reports on allylation of guaiacol using homogeneous catalyst [9–11] and no information is available on the use of heterogeneous catalyst for this reaction. In our earlier studies, we have reported zeolite H-beta, lead halo composite (Pb₃BrF₅) and supported heteropolyacid catalysts for the allylation of aromatic compounds [12–14].

Zeolites are used as catalysts for wide range of processes, from simple drying to complicated catalytic reactions [15,16]. Acidic zeolites such as HZSM-5, HY, and H-beta have been shown to be effective catalysts for alkylation of aromatic compounds. The main advantage of zeolites as an alkylating catalyst, in comparison with a non-zeolite catalyst, is that it can significantly influence the product selectivity due to its uniform microporous structure. It is well established that acid forms of zeolites are the most active in these reactions and the excellent catalytic abilities are due to the presence of Brønsted and Lewis acid centers in the zeolite structure. Zeolite HY contains a framework system of supercages [17], which are connected by a three-dimensional array of large diameter channels and this array enables a much easier diffusion of reactants and products.

Allylation of guaiacol is commercially important reaction, which gives products such as eugenol, *o*-eugenol and chavibetol used in perfumeries, flavorings, and essential oils and in

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medicine (local antiseptic and analgesic) [18]. They are used in formulating insect attractants and UV absorbers, analgesics, biocides and antiseptics. These chemicals occur naturally mainly in clove oil (eugenol) and betel nut (chavibetol). The aim of the present work is to study the allylation of guaiacol with allyl alcohol using zeolites as the catalyst and to optimize the reaction parameters to obtain high selectivity for monoallylated products. The effect of pore size and acidity on the activity and selectivity of catalysts in allylation of guaiacol is elucidated.

2. Experimental

2.1. Materials

Zeolite HY was purchased from Dow chemicals USA. Guaiacol was procured from Loba Chemie Ltd., Mumbai. Allyl alcohol (hereafter AA) was purchased from s.d.fine Chemicals Ltd., Mumbai. Montmorillonite K-10 (mont. K-10) obtained from Aldrich chemicals. Zeolites H-beta, HZSM-5 and HY recovered by calcining NH₄Y were obtained from Catalyst Pilot Plant (CPP-NCL, Pune). H-Mordenite was obtained from PQ Zeolites BV, Netherlands. All catalysts used in the reactions were in the powder form and were activated prior to their use in the reaction.

2.2. Characterization

BET surface area of catalysts was determined by Omnisorb 100 CX (Coulter USA). The acidity of the catalysts were measured by temperature programmed desorption (TPD) of NH₃ using micromeritics AutoChem-2910 instrument. For this, ~0.3 g of the sample was dehydrated at 500 °C (for mont. K-10 200 °C) in He (30 cm³ min⁻¹) for 1 h. The temperature was decreased to 100 °C and NH₃ was adsorbed by exposing samples treated in this manner to a stream containing 10% NH₃ in He for 1 h at 100 °C. It was then flushed with He for another 1 h to remove physisorbed NH₃. The desorption of NH₃ was carried out in He flow (30 cm³ min⁻¹) by increasing the temperature to 650 °C (300 °C for mont. K-10) at 10 °C min⁻¹ measuring NH₃ desorption using TCD detector. Both Surface area (630 m²/g) and total acidity (2.25 mmol/g) were highest for zeolite HY compared to other zeolites and mont. K-10 (Table 1).

2.3. Activity measurement

All reactions were carried out in a 50 ml Parr autoclave under nitrogen atmosphere. The catalysts were activated at 500 °C for

4 h (200 °C for mont. K-10) and cooled to room temperature just prior to the reaction. In a typical experiment, powder form of zeolite HY catalyst (0.85 g) was mixed with guaiacol (8.79 g) and allyl alcohol (8.21 g) and placed in the reactor. The reactor was pressurized with nitrogen (100 psig) and heated to desired temperature with stirring at 500 rpm. At a desired interval of time, the reactor was cooled to room temperature, sample was withdrawn and centrifuged to get a clear solution and analyzed for products. The products of allylation of guaiacol were analyzed by Shimadzu 14B gas chromatograph fitted with a SE-52 capillary column, coupled with FID detector. The identity of the products was confirmed by GC-MS (Shimadzu QP-5000) and GC-IR (Perkin-Elmer, System 2000). Conversion is given as the conversion of guaiacol to allylated products.

3. Results and discussion

The allylation of guaiacol with AA yields isomers of monoallylated products viz. eugenol (4-allyl-2-methoxyphenol), *o*-eugenol (2-allyl-6-methoxyphenol), chavibetol (5-allyl-2-methoxyphenol), 3-allyl-2-methoxyphenol, allyl-2-methoxyphenylether and small amount of diallyl guaiacol (Scheme 1). Diallyl ether also formed as a byproduct during the reaction. The *O*-allylated product, i.e. allyl-2-methoxyphenylether undergoes Claisen Rearrangement to give *C*-allylated guaiacol. This reaction is mainly facilitated at high temperatures with enhanced rates by acid catalyst. The selectivity of monoallyl guaiacol represents the mixture of five isomers of monoallyl guaiacol as shown in Scheme 1.

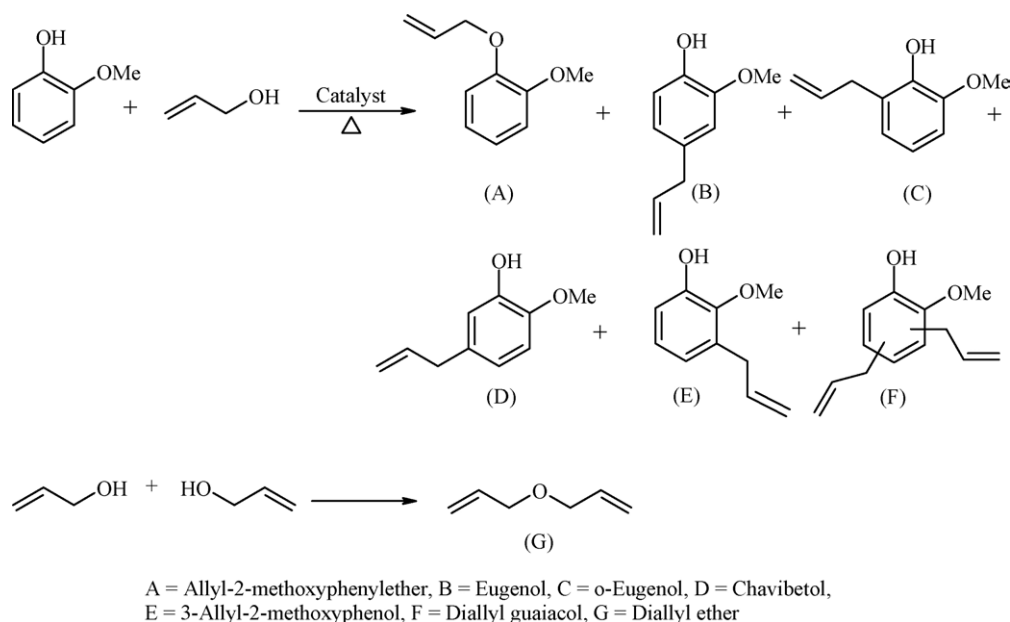
3.1. Catalytic activity of different catalysts

The initial investigations of allylation of guaiacol with AA using different zeolites and mont. K-10 yielded some interesting results. The characteristic data and catalytic activities of catalysts are presented in Table 1 along with reaction conditions. The reaction was carried out at 180 °C for 2 h with AA to guaiacol mole ratio 2. The conversion of guaiacol was in the range 6–61% and the selectivities of monoallylated products varied from 47 to 94%. The large pore zeolites such as HY, H-beta and H-mordenite gave 46, 28 and 15% guaiacol conversions with comparable monoallyl guaiacol selectivities 85, 90 and 92%, respectively. Total acidity of HY (2.25 mmol/g NH₃) is greater than H-beta (0.94 mmol/g NH₃) and H-mordenite (0.72 mmol/g NH₃) while these contain three-dimensional (one dimensional for H-mordenite) array of large diameter channels,

Table 1
Comparison of the catalysts

Catalyst	Si/Al	Surface area (m ² g ⁻¹)	Pore size (Å) [17]	Acidity (mmol g ⁻¹)	Guaiacol Convn. (wt.%)	Selectivity (%) monoallyl guaiacol
HY	6.7	630	7.4	2.25	46	85
H-beta	15	540	5.7 × 7.5 (linear) 6.5 × 5.6 (tortuous)	0.94	28	90
H-mordenite	10	490	6.5 × 7.0 2.6 × 5.7	0.72	15	92
HZSM-5	50	364	0.54 × 0.56 (straight) 0.55 × 0.51 (sinusoidal)	0.82	4	94
Mont. K-10	–	230	–	0.4	61	47

Conditions: catalyst wt. = 0.85 g, total reaction mixture = 17 g, temperature = 180 °C, AA/guaiacol mole ratio = 2, time = 2 h.



Scheme 1.

which might allow easier diffusion of reactants to form mainly monoallylated products. It is suggested that small amount of diallylated products and others were formed due to surface acidity of these zeolites. The low activity (6% conversion of AA) of H-ZSM-5 could be because of smaller pore size (5.4×5.6 and $5.1 \times 5.5 \text{ \AA}$) and hence bulkier sizes of the allylated products do not have easy access. Mont. K-10 gave maximum conversion (61%) but suffered from poor selectivity of monoallylated products. Due to the spatial restriction arising from the controlled pore size, guaiacol conversion was lower in zeolites than in mont. K-10.

3.2. Effect of temperature

The allylation of guaiacol was carried out in the range 140–200 °C and the results are presented in Fig. 1. Conversion of guaiacol was poor at lower temperature (<140 °C) and

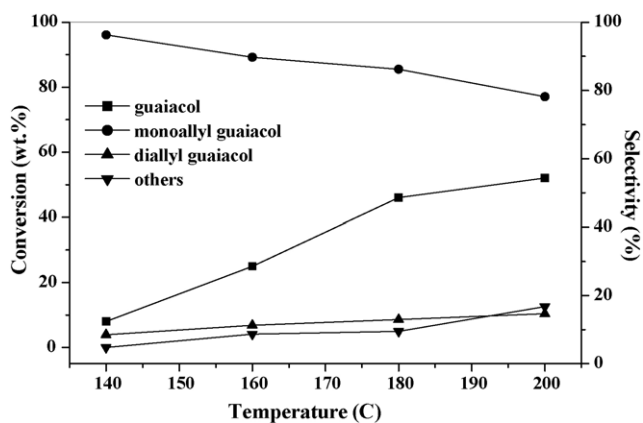


Fig. 1. Effect of reaction temperature. Conditions: catalyst = zeolite HY, catalyst wt. = 0.85 g, weight of the reaction mixture = 17 g, AA/guaiacol mole ratio = 2, time = 2 h.

enhanced with increase in temperature. Amount of side products also increased with increase in reaction temperature and there by reducing the major product selectivities. Polymerization seems to dominate at high temperatures, which decreases the selectivity of monoallyl guaiacol. At 180 °C, 46% of guaiacol was converted to products while monoallyl guaiacol and diallyl guaiacol selectivities were 85, 9%, 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) also formed during the reaction (Table 2).

3.3. Effect of mole ratio

The reaction was carried out with different mole ratio of AA to guaiacol (1–4) keeping the total reaction mass constant and the results are depicted in Fig. 2. It was observed that the conversion of guaiacol decreased with increase in

Table 2
Product distribution

Product distribution	wt.%
AA	27
Guaiacol	37
Monoallyl guaiacol	29
Diallyl guaiacol	3
Diallyl ether	2
Others	2
Guaiacol conversion (wt.%)	46
Selectivity (%)	
Monoallyl guaiacol	85
Diallyl guaiacol	9
Others	6

Conditions: catalyst = zeolite HY, catalyst wt. = 0.85 g, temperature = 180 °C, total reaction mixture = 17 g, AA/guaiacol mole ratio = 2, time = 2 h.

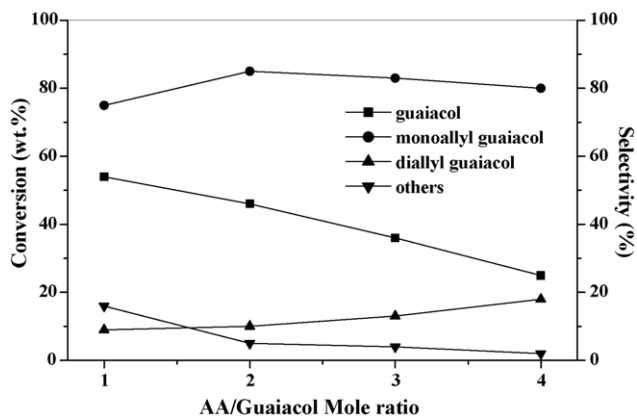


Fig. 2. Effect of AA to guaiacol mole ratio. Conditions: catalyst = zeolite HY, catalyst wt. = 0.85 g, weight of the reaction mixture = 17 g, temperature = 180 °C, time = 2 h.

mole ratio. The conversion of AA was highest at equimolar ratio (54%) but suffered with lower selectivity of monoallyl guaiacol. As the AA concentration increased, the selectivity to diallyl alcohol increased from 9 to 18%. At higher mole ratio, AA is being utilized in forming diallyl ether limiting its availability for the main reaction. Hence, AA to guaiacol mole ratio of 2 was found to be appropriate to get reasonably good conversion of guaiacol and selectivities for monoallyl guaiacol.

3.4. Effect of catalyst concentration

The reaction was carried out with the catalyst concentration in the range 2.5–10% of the total reaction mixture weight (17 g) and the results are presented in Fig. 3. It was found that the conversion of guaiacol increased with increase in catalyst concentration (15–60%), due to the proportional increase in the number of active sites. As it was observed in the effects of the other parameters, at higher conversion of guaiacol more of side products were formed, which ultimately decreased the selectivities for monoallyl guaiacol.

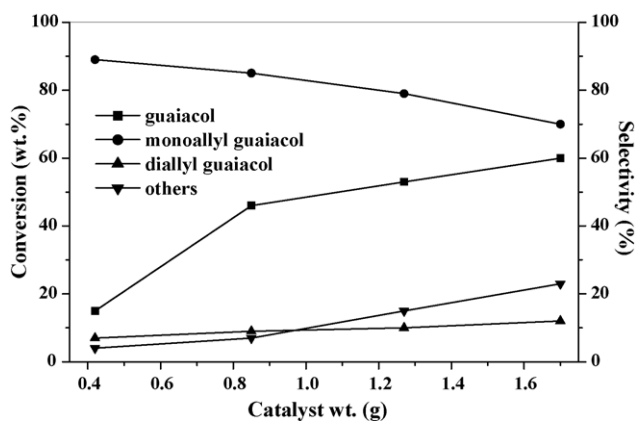


Fig. 3. Effect of catalyst concentration. Conditions: catalyst = zeolite HY, weight of the reaction mixture = 17 g, temperature = 180 °C, AA/guaiacol mole ratio = 2, time = 2 h.

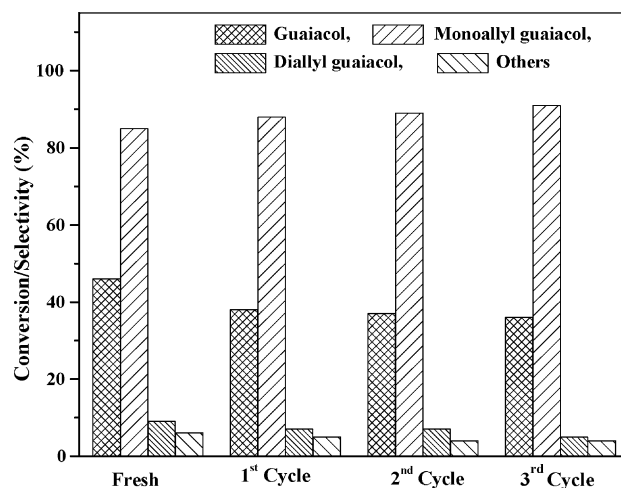


Fig. 4. Recyclability of the catalyst. Conditions: catalyst = zeolite HY, catalyst wt. = 0.85 g, weight of the reaction mixture = 17 g, temperature = 180 °C, AA/guaiacol mole ratio = 2, time = 2 h.

3.5. Effect of reaction time

The reaction was studied as a function of time over a period of 4 h, at 180 °C with AA to guaiacol mole ratio 2, in order to know the effect of time on the activity and selectivity of zeolites HY for allylation of guaiacol. The conversion of guaiacol increased with time up to 2 h (46%) and then remained constant, which could be due to product inhibition after 2 h. There was no appreciable change in the product selectivities.

3.6. Recyclability of the catalyst

The recyclability HY zeolite was carried out by conducting three runs (Fig. 4). After each run, the catalyst (brown in color) was repeatedly washed with methanol, dried at 120 °C for 2 h and calcined at 500 °C in air for 4 h (turned white). It was then used in the allylation reaction with a fresh reaction mixture. Only small decrease in guaiacol conversion after 3 cycles was noticed while the selectivity of monoallyl guaiacol increased marginally.

4. Conclusions

Allylation of guaiacol with AA was studied in detail using HY zeolite and the reaction conditions were optimized. Under the optimized reaction conditions (temperature = 180 °C; mole ratio (AA/guaiacol) = 2; time = 2) conversion of guaiacol was 46% with selectivity to monoallyl guaiacol 85%, diallyl guaiacol 9% and rest others. HY zeolite showed better activity than the other zeolites because of its higher acidity. H-ZSM-5 is less active, which could be attributed to its small pore size. K-10 clay was more active (61%), however the selectivity for monoallyl guaiacol was poor (47%). Zeolites showed higher selectivity to monoallyl guaiacol due to the steric restriction imposed by the pore structure, suppressing consecutive reactions of the allyl aromatics.

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