Ion-exchanged ZSM-5 Zeolites As Catalysts for Toluene Disproportionation Reaction

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Production of benzene and p-xylene by disproportionation of toluene is carried out using ion-exchanged HZSM-5 catalysts in a downflow continuous fixed bed reactor at 1 atmos. The ion-exchange is done by replacing H⁺ ions of the ZSM-5 with Ni, Cr, Mg, Bi and Zn. The results indicate an increased toluene conversion as well as per cent p-xylene in the xylenes mixture much higher than its equilibrium value. The per cent p-xylene yield defined as mole p-xylene obtained per mole toluene fed, which takes into account both the conversion as well as p-xylene selectivity is found to be highest on Ni exchanged catalyst. Magnesium and chromium exchanged catalysts give much lower yields. At 550°C, Ni exchanged catalyst gives toluene conversion of 28.5 per cent and the p-xylene selectivity of 53 per cent. The reason for the poor performance of Cr may be attributed to its better oxidising property, which might have oxidised the coke particles formed on the surface of the catalyst which were responsible for the pore mouth size reduction to suit the molecular size of p-isomer only.

Introduction

Toluene disproportionation to produce benzene and xylenes is of considerable importance due to the increasing demand for xylenes and benzene in the chemical industries. Among benzene, toluene, and xylenes (the fraction obtained from reforming unit) the demand of toluene is always the lowest, whereas the p-isomer of xylenes is of greater significance for its use in polyester fibre and many petrochemicals industries. The commercial process involves the vapour phase disproportionation of toluene over various acid zeolites[1-4]. It has been proposed that toluene disproportionation yields benzene and a mixture of xylenes as initial product inside the zeolite pores. This product subsequently diffuses out of the pore system with p-xylene diffusing faster than the other two isomers owing to its smaller size. The o- and m-components undergo isomerization reaction within the zeolite crystal. Enhanced p-selectivity was further obtained by the use of modifier agents such as Si, B, P, and Mg (ref. 5). The deposition of modifier agents by suitable techniques, such as, chemical vapour deposition have been reported to: (i) Partially block the pores, increase tortuosity and thereby delay the exit of larger molecules and (ii) Block the unselective active sites. Modification of the zeolites by ion exchange, on the other hand, has been reported to increase the acid strength when pretreated by La³⁺ ion (ref. 6) and thereby increasing the initial toluene conversion and also the hydrothermal stability.

Based on the fact that the ion exchange of a zeolite may lead to: (i) Selectivity of the reactions based on the nature of the cation, (ii) Blockage of the zeolite pore mouth in proportion to the size of the exchanged ion, thereby leading to shape selectivity for the desired product (p-xylene in the present case), and also (iii) Greater stability of the exchanged zeolite than the modified form. The present work, therefore, was undertaken to study the nature of ZSM-5 zeolite after exchange with certain transition metal/base metal cations for the disproportionation reaction. The cations selected for exchange were Ni, Cr, Mg, Bi, and Zn.
**Experimental Procedure**

The HZSM-5 zeolite powder (silica-alumina ratio 60) used in the present studies was supplied by Indian Oil Corporation (R&D), Faridabad. The ion-exchange was performed by mixing with the respective metal nitrate solutions having a metal content equivalent to 4 per cent by weight of the zeolite. The solution was heated at 50°C for about 3h with constant stirring on a magnetic stirrer. The contents were further heated at 95±5°C for 15 h under total reflux. The exchanged zeolite powder thus obtained was filtered, dried at 110°C overnight and calcined at 700°C for 10 h. The dried powder, in order to make it suitable for tests in the reactor, was pelletized at 10 tonne/cm² pressure, broken and sieved to get a specific size range of 0.33 to 0.52 mm.

The catalytic activity tests were carried out in a down flow vertical silica glass tubular reactor. The reactor tube with an inside 1 cm diam and length 50 cm was heated at ±1°C. The catalyst in the size range of 0.33 to 0.52 mm was mixed with quartz particles of similar size and packed in the middle of the reactor tube. The portion of the reactor tube above the catalyst bed was packed with quartz particles (in the size range 0.95 to 1.14 mm) which served the dual purpose of preheating as well as mixing the reactants. The catalyst was activated in a current of air at 500°C for 1 h before the start of the reaction tests. The catalyst bed was then cooled to the reaction temperature in the nitrogen atmosphere.

The toluene feed was pumped into the reactor at a regulated rate of 0.4 ml/min using a metering pump. The nitrogen gas was simultaneously introduced at the top of the reactor tube through a Y-junction and the weight hourly space velocity (WHSV) of the toluene feed was maintained at 10.4/h.

The product from the reactor was passed through a set of glass condensers fitted in series and cooled by ice-cold water. The liquid and gaseous products at each reaction temperature were collected in sampling bottles for further analysis. The flow rate of both the components was also recorded for overall mass balance. The analysis of the liquid product was carried out using a gas-liquid chromatograph fitted with FID detector. The column used was a SS column 1/8 in OD x 4 m length packed with 7 per cent Bentone-34 ± 5 per cent Dinonyl phthalate on Celite 545, 60-80 mesh.

The GC was operated under the following conditions: Oven temperature 90°C, flow rate of nitrogen carrier 30 ml/min. The nitrogen to toluene molar ratio was maintained at 5.9 in all the runs.

**Results and Discussion**

The zeolites were characterized by XRD for phase formation and per cent crystallinity, SEM for particle size, atomic absorption and ICP for elemental analysis. IR spectra of the samples were also taken to estimate the relative strengths of Bronsted acid sites (strong, weak and medium) and Lewis acid sites.

The XRD pattern of HZSM-5 compares well with the standards showing the crystalline nature of the zeolite. However the per cent crystallinity calculated after ion-exchange was found to decrease with respect to the parent ZSM-5 to the level 95.6, 69, and 68.3 per cent, respectively, for Cr, Bi and Ni. However, Mg exchanged ZSM-5 showed negligible decrease in its crystallinity. The reason for this decrease may be attributed to the partial dealumination due to heating in the presence of water.

The extent of ion exchange is a function of valency and nature of the ion, concentration of the solution as well as the time of contact. The atomic absorption data show that the actual level of ion exchange in the cases of Ni, Cr, and Zn were 3.35, 3.5 and 2.4 per cent, respectively, instead of a 4 per cent solution used for ion exchange in each case.

The results on the toluene disproportionation are presented as the variations of toluene conversion, xylene yield, per cent p-xylene in the xylenes product, benzene to xylene ratio, and p-xylene yield as a function of reaction temperature.

Figure 1 presents toluene conversion as a function of reaction temperature. It has been found that the catalytic activity for all the catalysts starts at around 400°C and increases continuously up to 550°C with an exception at 500°C with nickel loaded catalysts. The activities show declining trend hereafter. The reason for the decline may be attributed to the formation and deposition of coke on the active sites and pore blockage. It has also been suggested that during thermal treatment (above 550°C) the Bronsted acid sites of ZSM-5 zeolite undergo dehydroxylation, and thereby change to Lewis acid sites leading to a decrease in the conversion. The decline in activity of Ni exchanged catalyst after 500°C may be due to its
lower oxidising capability (Ni is a reducing catalyst) in comparison to all other catalysts leading to the lowest conversion (just 5 per cent at 600°C). It may be noted that at temperatures higher than 550°C, lot of coke is formed and in order to eliminate the coke a good oxidising catalyst is helpful. With Ni exchanged catalyst a maximum conversion of around 35 per cent is obtained at 500°C.

The per cent conversion at 550°C for all the catalysts were in the order: Ni (28.5) > Zn (25.5) > Cr (24) > Bi (15) > Mg (10.5). Coke formation in the case of Ni was found to be the maximum, whereas, Zn and Cr showed the least coke formation and thereby little decrease in activity at 600°C.

Though the decline in activity is more pronounced with the use of nitrogen as carrier gas (in comparison to hydrogen), most researchers have recommended the use of nitrogen. It has been suggested that the nitrogen as carrier gas is responsible for: (a) Less loss of hydrocarbons in the gaseous product (mainly methane, as the hydrogen helps in the formation of methane), i.e., more liquid product, (b) Nitrogen giving greater toluene conversion at a given reaction temperature in comparison to hydrogen, and (c) Nitrogen is less expensive in comparison to hydrogen.

Figure 2 presents the effect of reaction temperature on per cent p-xylene formation in the xylene product. The thermodynamic equilibrium proportions for the formation of the three isomers are 24, 54 and 22 per cent for p-, m- and o- respectively. In an attempt to cross the thermodynamic barrier for the greater p- isomer production the zeolite has been modified by the deposition of suitable materials, such as Si, B, Mg, and P. The depositions, in turn, were found to reduce the pore size to an extent that it was just favourable to the production of p-component only. In the present work, we have tried to achieve similar effect by exchanging ZSM-5 with different atomic size ions, and thereby controlling the effective pore mouth size. From Figure 2, it can be seen that in general, the p- isomer formation is above its equilibrium level. At 550°C the per cent p- in the xylene mixture were achieved to be in the order Ni (53 per cent) > Bi (42 per cent) > Mg (35 per cent) > Zn (32 per cent) > Cr (30 per cent). The p-selectivity was noticed to increase further by more than 10 per cent in each case at 600°C. This phenomenon may be attributed to the reduction in pore size due to coke deposition at 600°C. Enhanced p-selectivity due to coke deposition has been reported by many investigators. But, in fact, this technique of increasing p-selectivity due to coke deposition may not be a reliable and reproducible process in comparison to the more stable ion exchange process. The p-selectivity...
results at 550°C reported above may also be well correlated with the ionic radius: Ni (0.74), Bi (1.07), Mg (0.72), Zn (0.74) and Cr (0.62). The values in the parenthesis show the ionic radius in Å. It can be seen that the larger ions have the greater effect on pore mouth blockage leading to higher p-selectivity except in the case of Ni. Nickel is supposed to be responsible for isomerising p-component back to o- and m- on the surface of the catalyst.

Another advantage of ion exchange over the modification processes using vapour deposition techniques is the higher toluene conversion obtained in the former case. The silon, boron, and phosphorous modified catalysts are reported to increase the selectivity at the cost of reducing total toluene conversion on account of the coverage of some of the active sites by these atoms. The results obtained with magnesium and silicon modified ZSM-5 show up to 80 per cent selectivities for p-xylene against the lower per cent toluene conversions of the order of 6.5 and 15 per cent respectively. In order to achieve better overall performance of a catalyst towards maximizing p-xylene yield, both the factors, toluene conversion as well as per cent p-xylene must be high.

In the present work, therefore, we have calculated per cent p-xylene yield by defining as:

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\text{Per cent p-xylene yield} = \frac{\text{Mole p-xylene formed}}{\text{Mole toluene fed}} \times 100.
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Figure 3 depicts per cent p-xylene yield as a function of reaction temperature. Nickel exchanged catalysts are shown to be best among the catalysts studied, whereas magnesium exchanged one gives the lowest yield. At 550°C the per cent p-xylene yield for all the catalysts was in the order Ni (3.9 per cent) > Zn (3.4 per cent) > Cr (3.1 per cent) > Bi (2.6 per cent) > Mg (1.1 per cent). The lower yield in the case of magnesium is the result of its lower conversion as well as lower selectivity.

While judging the performance of a catalyst the activity towards byproduct formation must also be taken into consideration. The disproportionation of xylenes to form toluene and trimethyl benzene (TMB) is one such reaction noticed. The catalysts having greater tendency to form TMB shows greater B/X ratio. The results indicate the B/X ratios in the order Ni (2.9), Cr (1.3), Zn (1.44), Bi (1.38), and Mg (1.13) at 550°C which is in agreement with the extent of TMB formed during the reaction. The magnitude of TMB formed was in the order Ni > Cr > Zn > Bi > Mg.

It has been reported that ion exchange by certain ions leads to greater thermal stability, adsorption behaviour and selectivity, catalytic activity and other physical properties of zeolites\(^1\). The hydrothermal stability of Y zeolite was improved by La\(^{3+}\) ion exchange, especially for the calcined La HY with further \(\text{NH}_4^+\) ion-exchange\(^2\). The hydrothermal treatment caused the dealumination of zeolite more significantly than calcination and the presence of La\(^{3+}\) ion in the zeolite could inhibit the dealumination process. Further studies in the direction of testing the thermal stabilities with exchanged ions other than La\(^{3+}\) are yet to be done.

References

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