INTRODUCTION

Aromatic nitro compounds are important starting materials for the manufacture of various industrial products such as pharmaceuticals, dyes and plastics. Industrially nitration is mainly carried out by a mixed-acid process. In this process a mixture of conc. nitric acid and sulfuric acid is used for nitration of toluene. However, this traditional process suffers serious disadvantages, including low selectivity for the desired product and the requirement for large quantities of mineral or lewis acids as activators. Such conditions lead to excessive acid waste which is environmentally unfriendly and expensive to treat. These disadvantages have encouraged extensive efforts to develop alternative methodologies to replace conventional nitration process. A lot of efforts have been directed to search for reusable and environmentally friendly catalysts and many progresses have been achieved.

Recently many reagents and catalysts such as acetyl nitrate, trimethylsilyl nitrate, benzoyl nitrate, nitrogen oxide, sulfuric acid supported on silica, clay-supported metal nitrates have been introduced for the nitration of aromatic compounds. Three isomers of nitrotoluene can be formed in the toluene mononitration process. p-Nitrotoluene isomer is highly desirable over the ortho- and meta- isomers because of its high commercial value. In the present paper, we wish to report the nitration of toluene with nitric acid and acetic anhydride in organic solvent over zeolite catalyst, where the regio-selection of nitration can be improved and in certain cases the isomer ratio of nitration products can be reversed.

EXPERIMENTAL

1H NMR spectra were determined in CDCl₃ on a Bruker 400 MHz spectrometer. GC 2041-C (WONDACAP-1 df = 1.5 µm 0.53 mm I.D. × 30 m) was utilized to determine product isomer composition. IR measurements were made on a Hitachi IR meter 260-10 for KBr pellets and only characteristic peaks were recorded. Melting points were determined on a WRS-2 apparatus and uncorrected.

Typical experimental procedure for the zeolite cation-exchange: The standard procedure for cation-exchange involved stirring a supplied commercial zeolite (5 g) in a refluxing aqueous solution of the corresponding metal chloride (2 mol/L, 100 mL) for 24 h. The solid was filtrated, washed with deionized water until halide-free and dried at 110 °C for 3 h and then calcined in air at 550 °C for 6 h.

General procedure for the nitration with nitric acid and acetic anhydride: Quantities are recorded in the footnotes to the appropriate tables. All reactions were carried out in a 100 mL three-necked round bottomed flask equipped with a water condenser and a magnetic stirrer. In a typical experiment, a mixture of zeolite Hβ-25 (Si/Al = 25, 0.03 g), toluene (0.2 mL, 1.89 mmol), acetic anhydride (0.53 mL, 5.6 mmol), nitric acid (95 %, 0.23 mL, 5.6 mmol) in acetonitrile (5 mL) was heated under reflux for 12 h. When the reaction was over, the zeolite was removed by filtration and the filter liquor was washed with NaHCO₃ (10 mL × 3) and water (10 mL × 3).
The organic layer was separated, nitrobenzene (0.0580 g) was added as a GC standard. The mixture was analyzed by gas chromatography and the yields of mononitration product was calculated. The zeolite was recovered by washing and calcination.

RESULTS AND DISCUSSION

Toluene can form three isomers of nitrotoluene in the mononitration process (Scheme-1). 2-Nitrotoluene 2 and 4-nitrotoluene 4 are useful intermediates in the manufacture of pigments, pesticides and dyestuffs. The latter compound is greater solven used, acetonitrile with a high dielectric constant exhibited the best yield, while n-hexane gave highest selectivity of p-nitrotoluene for its low polarity.

Table-1 shows the effect of various solvent on the nitration reaction of toluene. The solvents influence is an important parameter for the determination of yield of the product. The yield of various solvents are in the following order: acetonitrile > dichloromethane > hexane. Among the four different polarity solvent used, acetonitrile with a high dielectric constant exhibited the best yield, while n-hexane gave highest selectivity of p-nitrotoluene for its low polarity.

To further improve the selectivity of p-nitrotoluene, zeolite was used as catalyst for it was very attractive to make the positive contributions to the positional selectivity in the novel nitration process. Zeolite BEA was used as catalyst because preliminary screening suggested that it was quite active. And ZSM-5, a medium-pore zeolite, was included for comparison. Additionally, cation-exchanged zeolites were undertaken in order to find a best catalyst to improve p-selectivity. The result was shown in Table-2.

ZSM-5 gave lower para selectivity which probably reflect more restricted diffusion through the pores, allowing greater opportunity for competition from reaction at the external surface of the solid. With the Si/Al ratio increasing of HBEA, a high ratio of formation of p-nitrotoluene was favored. It may be due to the dealumination would modify the distribution of the size and shape of pores in the zeolite. Interestingly, the yield and selectivity were both significantly lower when the cation associated with zeolite. The highest yield was reached when LaZSM-5 was used. It may be that rare earth cation-exchanged zeolite would display both Lewis and Brønsted types of acidity due to high charge density which generated acidic hydroxyl groups inside the zeolite cavities.

The temperature effect on the nitration of toluene in the solvent of choice (acetonitrile) was also carefully investigated. The results are shown in Table-3. The effect of the amount of zeolite for the nitration reaction was then investigated at the optimal temperature discovered above. The results are shown in Table-4. Increasing the amount of catalyst favored the reaction further toward the 2:4 ratio up to 0.553, while the yield was decreased. More products may be adsorbed in the catalyst.

### Table 1

| Entry | Reaction condition | Solvent | Conversion (%) | Yield (%) | Temperature (°C) | Isomer proportion (%) | 2:4 Ratio |
|-------|--------------------|---------|----------------|-----------|------------------|----------------------|-----------|
| 1     | HNO₃ (65 %)        | -       | 18.3           | 8.81      | RT               | 58.7                 | 6.40      | 34.9 | 1.68 |
| 2     | HNO₃ (95 %)        | -       | 77.2           | 67.4      | RT               | 55.6                 | 3.70      | 40.7 | 1.37 |
| 3     | HNO₃ (95 %)        | Acetonitrile | 77.0           | 73.1      | Reflux           | 60.8                 | 4.80      | 34.4 | 1.77 |
| 4     | HNO₃ (95 %)        | Dichloromethane | 57.6           | 90.5      | Reflux           | 57.4                 | 2.60      | 40.0 | 1.44 |
| 5     | HNO₃ (95 %)        | Hexane   | 82.5           | 46.8      | Reflux           | 53.6                 | 4.10      | 42.3 | 1.27 |
| 6     | HNO₃ (95%)         | Acetic anhydride | 79.8           | 63.8      | Reflux           | 58.0                 | 3.80      | 38.2 | 1.45 |

*Reaction condition: n(nitric acid) : n(toluene) = 1 : 1, n(acetic anhydride) = 1 : 1, solvent (5 mL), reflux temperature. *Determined by GC, Nitrobenzene was used as an internal standard. *Combined yield of 2, 3 and 4 based on consumed 1. Nitrobenzene was used as an internal standard. *Proportion of products was determined by GC. *Acetic anhydride was used as solvent.

### Table 2

| Entry | Catalyst* | Reaction condition | Yield (%) | Isomer proportion (%) | 2:4 Ratio |
|-------|-----------|--------------------|-----------|----------------------|-----------|
| 1     | HZSM-5    | HNO₃               | 72.2      | 62.0                 | 4.30      | 33.7 | 1.84 |
| 2     | HBEA -25  | HNO₃               | 79.2      | 47.3                 | 4.80      | 47.9 | 0.987 |
| 3     | CuBEA-25  | HNO₃               | 54.5      | 37.8                 | 5.40      | 56.8 | 0.665 |
| 4     | HBEA-280  | HNO₃               | 68.8      | 41.5                 | 4.40      | 54.1 | 0.767 |
| 5     | FeBEA-25  | HNO₃               | 78.0      | 58.9                 | 4.50      | 36.6 | 1.61 |
| 6     | LaZSM-5   | HNO₃               | 67.2      | 62.6                 | 4.10      | 33.3 | 1.88 |
| 7     | LaZSM-5   | HNO₃               | 94.4      | 62.2                 | 4.30      | 33.5 | 1.86 |

*All reactions were carried out in acetonitrile (5 mL) with substrate 1 (0.2 mL, 1.89 mmol), nitric acid (0.23 mL, 5.67 mmol), acetic anhydride (0.53 mL, 5.67 mmol) and zeolite catalyst (0.03 g). Acetonitrile was dried over 4 Å molecular sieves before using. *Zeolites were calcined at 550 °C for 2 h in air prior to use. *Combined yield of 2, 3 and 4 based on consumed 1. Nitrobenzene was used as an internal standard. *Proportion of products was determined by GC.
Conclusion

To conclude, we have developed an efficient procedure for the nitration of toluene with nitric acid and acetic anhydride in HBEA-280 zeolite catalyst. Moreover, the solid catalysts could be recovered and reused with the avoidance of toxic waste generated.

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