

Alkylation of *o*-toluidine with methanol over acidic zeolites

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Abstract

The catalytic property of H-beta zeolite in the methylation of *o*-toluidine was compared to that of other acidic zeolites, viz. HY, H-MOR, H-ZSM-5 and H-FER. The H-beta catalyst showed higher conversion of *o*-toluidine, the main product being 2,4-xylidine. The selectivity towards 2,4-dimethylaniline (2,4-xylidine) was about 69% (at 400 °C) over H-beta zeolite and was selective than the other zeolites under study. However, the other isomer (2,6-xylidine), over all zeolites, was formed in very less quantities (>4%). All the reaction parameters, viz. reaction temperature, weight hourly space velocity (WHSV), molar ratio of the reactants and time on stream was found to be profound effect on the conversion and selectivity of the product distribution. A detailed study of these reaction parameters was carried out over H-beta zeolite.

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1. Introduction

Alkylanilines are valuable intermediates for the manufacture of pharmaceuticals, drugs, dyes and agrochemicals. The alkylation of aniline with methanol is industrially important reaction as it gives toluidine, *N*-methylaniline (NMA) and *N,N*-dimethylaniline (NNDMA) as major compounds which are important intermediates in the manufacture of dyes, plastics and explosives. The alkylation of aniline has been well studied so far over various metal oxides, mixed oxides, clays and zeolites where in both methanol or dimethylcarbonate has been used as methylating agent [1–6]. A review on the aniline alkylation over solid acid catalysts also appeared recently [7].

Despite many studies on the aniline methylation, there are not many reports in the literature describing alkylation of *o*-toluidine (OTD). Choi et al. [8] has studied *N*-alkylation of *o*-toluidine with ether on HX zeolite catalysts modified with K, Cs, K-Mg and MgO and reported that HX zeolite gives maximum conversion at 300 °C, while the catalysts, modified catalysts with less acidity exhibit maximum conversions at higher temperatures. Synthesis of 2,6-dimethylaniline (2,6-DMA) is also an important industrial process and a potential route to 2,6-DMA might involve the direct *o*-methylation of aniline similar to the commercially used process to make 2,6-dimethylphenol [9] and the selective catalysts for this reaction have been reported [10]. Catalytic *o*-ethylation of aniline is a well-established process [11]. Zhang et al. [12] has studied synthesis of 2,6-DMA from *o*-toluidine and methanol by vapor phase alkylation over solid V₂O₅ catalyst. They reported that the optimum co-catalyst is Cr₂O₃ and the optimum ratio is V₂O₅/Cr₂O₃ = 10/1

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(mol/mol), *o*-toluidine/MeOH molar ratio 1/3, and liquid velocity 0.5 h^{-1} for the synthesis of 2,6-DMA and its selectivity can be improved by addition of water in the feed. Chen et al. [13–15] studied the alkylation of *o*-toluidine with methanol over $\text{V}_2\text{O}_5\text{-Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixture and $\gamma\text{-Al}_2\text{O}_3\text{-V}_2\text{O}_5$ mixture separately. However, there are no reports on the methylation of *o*-toluidine with methanol over zeolite catalysts. It was therefore intended to study the methylation of *o*-toluidine with methanol over both medium and large pore zeolites and the distribution of product selectivities was discussed with structural differences of the zeolites and their acidity.

2. Experimental

2.1. Materials, catalysts preparation and characterization

Methanol (E-Merck) and *o*-toluidine (Aldrich) were used as such without further purification. Commercially available zeolites such as HY, and H-MOR and H-beta were procured from Union Carbide and PQ Corporation, respectively. H-ZSM-5 and H-FER were prepared according to the literature procedure [16,17], and was crystalline as verified by XRD. All the materials were characterized by XRD (Rigaku, D-Max/III-VC model using the Cu $\text{K}\alpha$ radiation) for its phase purity and the Si/Al ratio of various zeolites were estimated by EDAX (Cambridge Stereoscan 400) and XRF (Rigaku). The surface areas of the catalysts were estimated by the BET method using nitrogen as adsorbed at liquid nitrogen temperature (Nova, Quantachrome, USA). The particle size and morphology of the zeolite catalysts were

estimated by scanning electron microscopy (SEM, Cambridge Stereoscan 400). The characteristics of the zeolites studied in this work are summarized in Table 1.

2.2. Acidity measurement

Pyridine adsorption–desorption was monitored by Fourier transform infrared (FT-IR) spectroscopy. Self-supported wafers of $15\text{--}20 \text{ mg cm}^{-2}$ thickness were evacuated in situ (400°C , 3 h, 10 Pa) in a Pyrex cell with KBr windows, contacted with probe (pyridine) at 100°C and desorbed at increasing temperature ($100\text{--}400^\circ\text{C}$) in dynamic vacuum and the spectra were recorded using Nicolet 60 SXB spectrometer with a resolution of 2 cm^{-1} averaging over 500 scans. Brönsted and Lewis acid sites were determined on the area of adsorbances on the PyB band near 1540 cm^{-1} and the PyL band near 1450 cm^{-1} .

The acid properties of the catalysts were also determined by the temperature-programmed desorption method, using ammonia as a probe molecule (TPDA) using an AutoChem 2910 (Micromeritics, USA) instrument. Each sample was pre-treated in a flow of helium at 500°C for 3 h (50 ml min^{-1}). Adsorption of ammonia was performed by passing a He stream with ammonia vapor over the catalyst for 30 min at 80°C . The sample was flushed with the carrier gas at 105°C for another 1 h to remove physisorbed ammonia. The TPD profile of ammonia was obtained from 50 to 700°C at a heating rate of $10^\circ\text{C min}^{-1}$. The ammonia concentration in the effluent stream was monitored with the thermal conductivity detector and the areas under the peaks were integrated using GRAMS/32 software to determine the amount of ammonia desorbed during TPD.

Table 1
Characteristics of zeolites studied for *o*-toluidine methylation

| Sample | H-ZSM-5 | H-FER | H-beta | H-MOR | HY |
|--|---------|-------|--------|-------|-------|
| $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio | 200 | 34 | 30 | 25 | 4.76 |
| Surface area ($\text{m}^2 \text{ g}^{-1}$) | 372.6 | 335.5 | 706.1 | 421.5 | 836.9 |
| LT (mmol g^{-1}) | 0.12 | 0.53 | 0.69 | 0.8 | 1.34 |
| HT (mmol g^{-1}) | 0.15 | 0.39 | 0.95 | 0.96 | 3.2 |
| B/L ratio at 100°C | 6 | 2 | 0.7 | 1.0 | 0.98 |
| B/L ratio at 200°C | 10.7 | 6.66 | 1 | 1.87 | 1.56 |
| B/L ratio at 300°C | – | 6 | 2.7 | 2.2 | 1.85 |

2.3. Catalytic runs

The catalytic alkylation of *o*-toluidine with methanol at temperatures 250–450 °C was carried out at atmospheric pressure using a fixed-bed down flow reactor containing 3 g of previously calcined zeolite catalyst and activated under a stream of nitrogen for 30 min prior to the experiment. A mixture of *o*-toluidine and methanol with the required molar ratio was introduced into the reactor by means of a syringe pump (ISCO, 500D, USA). The liquid products were collected every hour, and quantified by gas chromatograph (GC) using a flame ionization detector and HP-1 capillary column. Reaction products were identified by GC–MS (Shimadzu QP 5000) and GC–FT-IR (Perkin-Elmer Spectrum 2000).

3. Results and discussion

The crystallinity and phase purity of the zeolite samples were checked by XRD. The X-ray pattern of all zeolites matched with those in the literature. The surface areas and scanning electron micrographs showed the absence of amorphous matter inside the channels as well as on the external surface of the zeolites. The

zeolites used in this study and their physicochemical properties are presented in Table 1.

FT-IR spectra of adsorbed pyridine on H-zeolite samples at 100, 200, 300 and 400 °C were and the spectra were normalized with respect to 5 mg cm⁻² of the wafer and the relative concentration of Brønsted and Lewis acid sites corresponding to the bands at 1540 and 1450 cm⁻¹ are presented in the Table 1.

TPD spectra of NH₃ on various H-zeolites (H-ZSM-5, H-FER, H-MOR, H-beta and HY) are shown in Fig. 1. Spectra exhibited a fairly good resolution of two peaks, low temperature (LT < 300 °C) and high temperature (HT > 300 °C) peaks. The peaks are further resolved by Gaussian function and the acid site densities (total acidity) of the different zeolites under study are shown in Table 1. The TPD profile of large pore zeolites (HY, H-mordenite and H-beta) exhibited peaks having two maxima corresponding to low and high acid strength whereas H-ZSM-5 and H-FER showed three peaks corresponding to weak, medium and strong acid sites. It has already been reported that three peaks are observed in the TPD of NH₃ from ZSM-5 zeolite [18]. In the HT region of H-ZSM-5 and H-FER, the peak seems to consist of at least two components: a dominating large peak and a smaller peak with

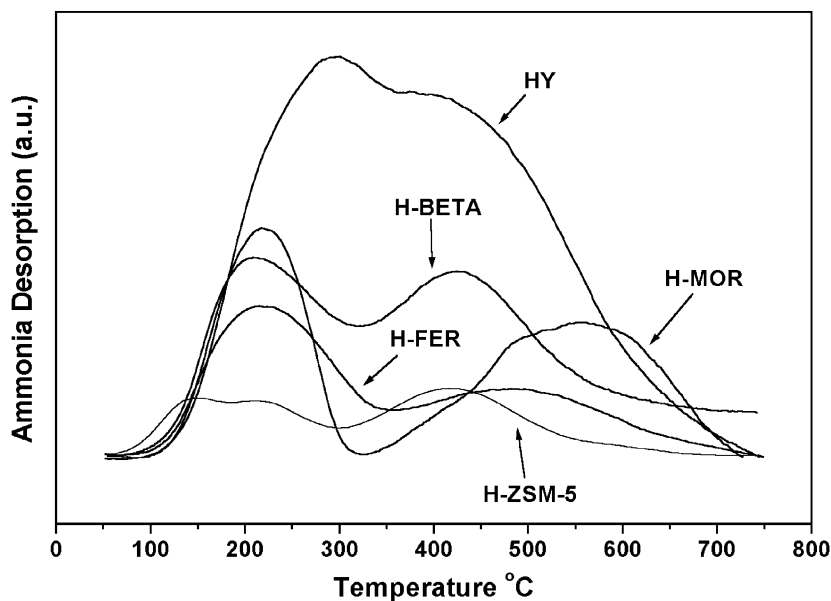


Fig. 1. NH₃-TPD profiles of H-zeolites under study.

maximum at somewhat higher temperature. Out of these resolved peaks, the peak having larger area can be assigned to desorption from strong B (Brönsted) sites, while the smaller peak at higher temperature is assigned to desorption from strong L (Lewis) sites. These B and L sites were related to framework Al atoms charge compensated by acidic protons and to extra-framework Al atoms, respectively [19]. The HT B acid peak of H-ZSM-5 and H-FER appeared at 417 and 401 °C, respectively whereas HT L acid peak appeared at 593 and 566 °C, respectively. The total amount of ammonia desorbed from these zeolites was respectively 0.27 and 0.92 mmol g⁻¹. In the case of large pore zeolites (H-MOR, H-beta and HY) first peak corresponds to weak + medium acid sites and second one is for stronger B and L acid sites as only two peaks were resolved for these zeolites. HY had a long tailing and showed broad unresolved spectra. Improper resolution indicates the overlap of various components desorbing in relatively broad temperature range. Such a complexity in the TPD spectra of NH₃ taken from faujasite-type zeolites has already been reported by Cattanach et al. [20]. The HT component of TPD spectra of HY is most likely to be associated with the water desorption as a result of dehydroxylation of surface hydroxyl groups. The HT B peak of H-beta and HY appeared at temperatures 413 and 425 °C, respectively, whereas that of H-mordenite appeared at a temperature (547 °C) about 100 °C higher

than the corresponding peak of other zeolites under study.

The major products of the reaction of *o*-toluidine (OTD) methylation were *N*-methyl-*o*-toluidine (NM-OTD), *N,N*-dimethyl-*o*-toluidine (NNDM-OTD), 2,4-dimethylaniline (2,4-DMA), *N*-methylxylydines (NM-Xy) and 2,4,6-trimethylaniline (2,4,6-TMA), and minor amounts of 2,6-dimethylaniline (2,6-DMA), *N,N*-dimethyl xylydines (NNDM-Xy) and other unidentified compounds on all the zeolites under study.

3.1. Effect of catalyst type and temperature

Tables 2 and 3 shows the activity and selectivity of various catalysts for the methylation of *o*-toluidine at different reaction temperatures (250–450 °C) for a time on stream of 2 h. The main products of the reaction are both NM-OTD and 2,4-DMA. The medium pore zeolites H-ZSM-5 and H-FER showed very less conversion (>30%, even at 400 °C) and are selective to *N*-mono-methylation of *o*-toluidine. However, the large pore zeolite, H-beta showed more selectivity towards *C*-alkylated product, 2,4-DMA. Due to pore restrictions in H-MOR, both NM-OTD and 2,4-DMA are formed in equal amounts at higher temperatures. HY showed very low activity than other two large pore zeolites H-beta and H-MOR. Even at higher temperature, 400 °C, the selectivity of NM-OTD is higher

Table 2
Catalytic properties of medium pore zeolites studied in *o*-toluidine methylation

| | Catalyst | | | | | | | | | |
|-------------------------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| | ZSM-5 | | | | | H-FER | | | | |
| | 250 °C | 300 °C | 350 °C | 400 °C | 450 °C | 300 °C | 350 °C | 400 °C | 450 °C | |
| Conversion of OTD | 5.5 | 26.8 | 34.9 | 42.5 | 55.7 | 10.8 | 17.1 | 24.3 | 33.4 | |
| Product selectivity (%) | | | | | | | | | | |
| Lower boilers | 0 | 0 | 0.3 | 0.4 | 0.4 | 0 | 0.7 | 0.8 | 0.5 | |
| NNDM-OTD | 8.7 | 6.5 | 3.9 | 1.4 | 1.3 | 9.5 | 6.6 | 4.8 | 2.5 | |
| NNDM-Xy | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| NM-OTD | 80.7 | 72.6 | 65.4 | 56.5 | 47.1 | 83.1 | 78.5 | 73.7 | 62.8 | |
| 2,6-DMA | 0.3 | 0.7 | 0.7 | 1.5 | 2.1 | 0.2 | 0.5 | 0.5 | 1.2 | |
| 2,4-DMA | 10.3 | 19.1 | 25.6 | 34.4 | 40 | 6.9 | 11.6 | 16.6 | 27.1 | |
| NM-Xy | 0 | 0 | 1.1 | 1.7 | 2 | 0 | 0 | 0.5 | 0.9 | |
| 2,4,6-TMA | 0 | 1 | 2.7 | 3.7 | 6.6 | 0.2 | 1.7 | 2.6 | 4.5 | |
| Others | 0 | 0.1 | 0.3 | 0.4 | 0.5 | 0.1 | 0.4 | 0.5 | 0.5 | |

Reaction conditions: methanol:*o*-toluidine = 2:1 (mol/mol), WHSV = 1 h⁻¹, TOS = 2 h.

Table 3
Catalytic properties of large pore zeolites studied in *o*-toluidine methylation

| | Catalyst | | | | | | | | | | | | | | |
|-------------------------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| | H-beta | | | | MOR | | | | | HY | | | | | |
| | 300 °C | 350 °C | 400 °C | 450 °C | 250 °C | 300 °C | 350 °C | 400 °C | 450 °C | 250 °C | 300 °C | 350 °C | 400 °C | 450 °C | |
| Conversion of OTD | 24.5 | 61.1 | 77.1 | 83.5 | 22.2 | 37.3 | 41 | 51 | 65.2 | 19 | 28.8 | 36.7 | 45.7 | 56.2 | |
| Product selectivity (%) | | | | | | | | | | | | | | | |
| Lower boilers | 0.4 | 0.3 | 0.6 | 3.1 | 0.9 | 0.5 | 0.8 | 1.5 | 1.7 | 0 | 3 | 1 | 1.6 | 0.6 | |
| NNDM-OTD | 9.1 | 3.1 | 1 | 0.4 | 3.9 | 4.2 | 4.1 | 3.8 | 3.6 | 4.7 | 4.4 | 2.6 | 1.4 | 0.7 | |
| NNDM-Xy | 0 | 0.2 | 0.4 | 0.2 | 0 | 0 | 0 | 0.2 | 0.2 | 0 | 0.1 | 0.2 | 0.4 | 0.4 | |
| NM-OTD | 69.7 | 43.7 | 3.8 | 1.1 | 81.8 | 68 | 44.8 | 35.9 | 23.5 | 79.4 | 60.6 | 48.7 | 41.4 | 23.6 | |
| 2,6-DMA | 1.2 | 1.8 | 2.4 | 1.9 | 0.2 | 1.5 | 2.9 | 3.1 | 3.5 | 0.5 | 0.9 | 1.4 | 1.5 | 1 | |
| 2,4-DMA | 14.3 | 32 | 69.1 | 57.8 | 8.9 | 17.9 | 35.8 | 37.8 | 43.3 | 13.7 | 21.1 | 30.2 | 31 | 44.8 | |
| NM-Xy | 2.7 | 7.8 | 8.3 | 6.8 | 0 | 2.4 | 2.3 | 2.1 | 2 | 1.2 | 2.7 | 2.7 | 3.5 | 2.9 | |
| 2,4,6-TMA | 2.4 | 10.9 | 12.9 | 26.4 | 3.6 | 5.1 | 8.7 | 14.5 | 20.5 | 0.5 | 4.2 | 6.5 | 8.5 | 16.6 | |
| Others | 0.2 | 0.2 | 1.5 | 2.3 | 0.7 | 0.4 | 0.6 | 1.1 | 1.7 | 0 | 3 | 6.7 | 10.7 | 9.4 | |

Reaction conditions: methanol:*o*-toluidine = 2:1 (mol/mol), WHSV = 1 h⁻¹, TOS = 2 h.

than 2,4-DMA. Similar effect is also observed for aniline methylation and is reported that for a given structure the N-alkylation is favored on basic zeolites ZSM-5 or faujasite [21,22] while protonic ZSM-5 gives C-alkylation [4].

The activity of the catalyst follows the order (at 350 °C):

H-beta > H-MOR > HY > H-ZSM-5 > H-FER
(based on OTD conversion)

H-beta > H-ZSM-5 > H-MOR > HY > H-FER
(based on NM-OTD yield)

H-beta > H-MOR > HY > H-ZSM-5 > H-FER
(based on 2, 4-DMA yield)

Comparing the catalytic activity at similar conversion levels of OTD (26.8, 24.3, 24.5, 22.2 and 28.8%) for zeolites H-ZSM-5, H-FER, H-beta, H-MOR and HY, respectively, one can find that all these zeolites invariably produced N-alkylates ~79–85% except HY zeolites (~65%). However, it can be generalized with respect to the reaction temperature that in the reaction of *o*-toluidine with methanol, the medium pore zeolite favors the formation of N-alkylates and large pore zeolites has a bias towards C-alkylation based on acidity and the structural features.

With the increase of temperature (Tables 2 and 3), in general, the conversion of *o*-toluidine increases over all the catalysts. At low temperature formation of N-mono-methylation is favored over all the zeolites. At high temperature formation of 2,4-DMA is favored over large pore zeolites. The selectivity of NM-OTD decreases with temperature with concomitant increase in that of 2,4-DMA.

The higher conversion obtained on large pore zeolites than on medium pore zeolites can be attributed to the number and nature of acid sites. Nitrogenous bases are known to poison the acid sites on zeolites by strong adsorption and hence the available Brønsted acid sites on medium pore zeolites are quickly poisoned where as the number of Brønsted acid sites available in large pore zeolites are higher and are not poisoned to the same degree. It is also seen from Table 3 that the zeolite H-beta catalyzes the reaction efficiently towards C-alkylation more than the other zeolites under study.

The selectivity to 2,4-DMA and 2,4,6-TMA increased while that of NNDM-OTD and NM-OTD decreased at higher reaction temperatures. The selectivity towards NM-OTD decreased steadily with reaction temperature from 79.8% to a mere 1.1% at 250 and 450 °C, respectively. At lower temperature (250 °C), there is no formation of NM-Xy and NNDM-Xy, however, with increase of temperature, these products also are formed which are due to the methylation of DMA and NM-Xy, respectively.

A moderate reaction temperature (400 °C) was helpful to enhance the product selectivity to 2,4-DMA. Considering the *o*-toluidine conversion and product distribution, the optimum reaction temperature is 400 °C. At this reaction temperature, the selectivity to 2,4-DMA is the highest (69.1% and yield 53.3%) at high *o*-toluidine conversions (77.1%).

3.2. Influence of acidity

Woo and coworkers [23,24] investigated the selective alkylation of aniline with methanol over several metallosilicates. They suggested that strong acid sites, medium acid sites, and weak acid sites, are all active sites that yield C-alkylate and coke, NNDMA and *N*-methyltoluidine (NMT), and NMA, respectively. It has been observed by various authors for aniline alkylation over different solid acid catalysts that weak and moderate acid sites are sufficient for the N-alkylation, whereas strong acid sites are prerequisite for C-alkylation [22,25,26]. From the TPD profiles, it can be seen that both the number and strength of acid sites are less in the medium pore zeolites and this is reflected in the alkylation activity. The higher selectivity of NM-OTD even at low temperature suggest that a weak or medium acid sites are sufficient for its formation. Even though both beta and MOR possessed the same acidity in the HT region, the acid strength of MOR is higher than that of beta. The lesser conversion observed with H-MOR may be due to the fact some of the acid sites are present in the narrow pore which are accessible for ammonia and not to OTD.

In the alkylation of aromatic amines, the studies show that the reaction is acid catalyzed and the product distribution primarily depends up on the nature and strength of acid sites. Narayanan and Deshpande proposed a mechanism of aniline alkylation involving

Brönsted and Lewis acid sites [27]. The activation of alcohol is initiated by hydrogen bonding between Brönsted hydroxyl proton of the zeolite and oxygen of alcohol, followed by alcohol protonation and dehydration, releasing the carbocation. The preponderance of the interaction of zeolite with the lone pair of electrons on “N” in amine group or with the π electrons of aromatic ring dictates the product distribution in favor of side chain alkylation or ring alkylation respectively. Hence, the product distribution also seems to depend on the relative amount of Brönsted and Lewis acid sites on the zeolite surface. Tables 2 and 3 shows that the product distribution not only depends on the pore structure of the catalysts but also on acid site distribution. It is widely accepted that Lewis acid sites form N-methylated products in the methylation reaction of alkylaromatic amines. Comparing the Lewis acid site distribution over the temperature range of our study (B/L ratio given in Table 1) and product distribution in Tables 2 and 3, similar trends can be noted. C-alkylation is found to follow the concentration of Brönsted acid sites except H-beta zeolite, which showed more Lewis acid sites at lower temperatures and Brönsted acid sites at higher temperature above 300 °C (as seen by B/L ratio) and this may be responsible for marked increase in the conversion of *o*-toluidine as compared with the other zeolite systems under study. Also a sudden drop in N-alkylation and an increase in C-alkylation from 350 to 400 °C is observed which can be attributed to the increase in Brönsted acidity of beta zeolite. Even though HY possess higher number of acid sites, the conversion is less than H-beta and H-MOR. Also the C-alkylation is less compared to H-beta. This can be due to the fact that HY possessed almost same B/L ratio above 200 °C and hence it produced both N- and C-alkylated products.

At higher temperatures (≥ 400) over H-beta, the selectivity to NM-OTD decreased to less than 4% and a marked increase in selectivities of 2,4-DMA. This may be due to isomerization of NM-OTD to 2,4-DMA at higher temperatures by Brönsted acid sites. Pyridine cannot access the internal acid sites of eight-membered ring of H-FER and hence some of the product (di-alkylated product) may be produced on the surface of the zeolite. The lower conversion than H-ZSM-5, even though the Si/Al ratio is lesser than that of H-ZSM-5, can be correlated to this.

Singh et al. [28] studied the interaction of aniline and *N*-methylaniline over large pore zeolites such as H-beta, HY and H-MOR. They found the interaction of both aromatic ring and amino group with the zeolite surface. They concluded that the interaction of aniline molecules is limited to external surface sites of H-MOR as they cannot enter easily inside the channels of H-MOR. They also concluded that *N*-methylaniline is strongly interacting with HY where as that with H-MOR is restricted to surface groups only, which are not strong.

3.3. Influence of molar ratio

The effect of varying molar ratio of methanol/*o*-toluidine on the activity and selectivity of zeolite H-beta at 400 °C and a space velocity (WHSV (h^{-1})) of 1 is depicted in Table 4. The results show that the conversion of *o*-toluidine and selectivity to 2,4,6-TMA increased with increasing molar ratios. The conversion of *o*-toluidine is almost complete at methanol/*o*-toluidine molar ratio of 7. Also it is interesting to note the formation of NNDM-2,4,6-TMA at molar ratios ≥ 5 . The product selectivity to 2,4-DMA reached 69.1% at 77.1% *o*-toluidine conversion at a molar ratio of 2:1 with very less side products. The

Table 4
Influence of reactant molar ratio (methanol:*o*-toluidine) on *o*-toluidine methylation over H-beta

| | MeOH/ <i>o</i> -toluidine molar ratio | | | | |
|-----------------------------------|---------------------------------------|------|------|------|------|
| | 7 | 5 | 2 | 1 | 0.5 |
| Conversion of <i>o</i> -toluidine | 100 | 92.9 | 77.1 | 51.7 | 29.3 |
| Product selectivity (%) | | | | | |
| Lower boilers | 0.9 | 0.6 | 0.6 | 0.5 | 0.5 |
| Aniline | 0 | 0 | 0 | 2.9 | 6.9 |
| NNDM-OTD | 7.2 | 3.9 | 1 | 1.2 | 0.5 |
| NNDM-Xy | 18.2 | 10.6 | 0.4 | 0 | 0 |
| NM-OTD | 15.3 | 9.5 | 3.8 | 3.4 | 2 |
| 2,6-DMA | 4.3 | 3.6 | 2.4 | 3.1 | 0.5 |
| 2,4-DMA | 20.4 | 45 | 69.1 | 78.3 | 83.1 |
| NNDM-2,4,6-TMA ^a | 3.9 | 2.1 | 0 | 0 | 0 |
| NM-Xy | 10.1 | 9.4 | 8.3 | 2.1 | 1 |
| 2,4,6-TMA | 19.3 | 14.8 | 12.9 | 7.2 | 4.5 |
| Others | 0.4 | 0.5 | 1.5 | 1.3 | 1 |

Reaction conditions: temperature, 400 °C; TOS = 2 h; WHSV = 1 h^{-1} .

^a *N,N*-Dimethyl-2,4,6-trimethylaniline.

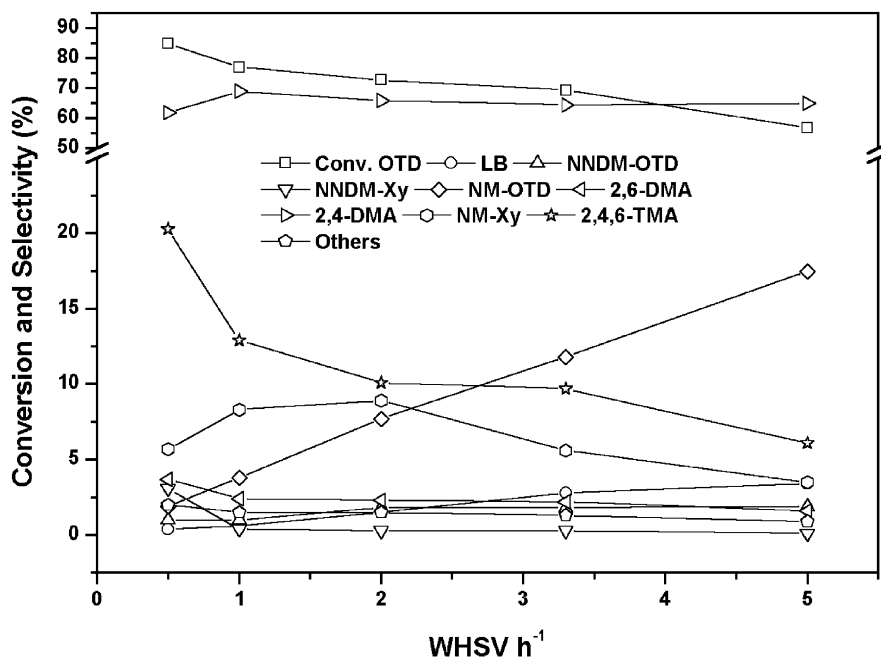


Fig. 2. Influence of WHSV on *o*-toluidine methylation and product selectivities over H-beta. Reaction conditions: temperature, 400 °C; catalyst, H-beta; methanol:*o*-toluidine = 2:1 (mol/mol); TOS = 2 h.

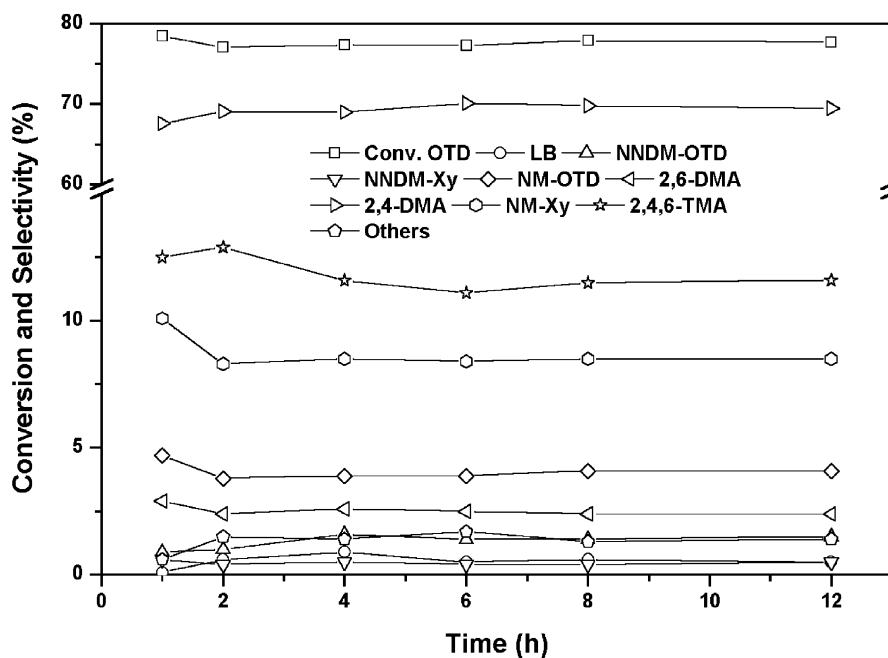


Fig. 3. Influence of time on stream on *o*-toluidine methylation and product selectivities over H-beta. Reaction conditions: temperature, 400 °C; methanol:*o*-toluidine = 2:1 (mol/mol); TOS = 2 h.

formation of side products (N-, N,N-, C-, C,N-alkylated products) was observed at higher concentration of methanol. It is noteworthy that at lower molar ratio (0.5), apart from the decrease in conversion, formation of aniline in considerable amount shows that the disproportionation of *o*-toluidine has taken place.

3.4. Influence of WHSV

The influence of space velocity on the activity and selectivity of zeolite H-beta catalyst was studied at

400 °C for a methanol/*o*-toluidine (molar ratio) of 2:1. Fig. 2 shows *o*-toluidine conversion and product distribution of the reaction at WHSV (h^{-1}) ranging from 5 to 0.5. It is clear from Fig. 2 that *o*-toluidine conversion decreases from 84.9 to 56.9% with increase in WHSV from 0.5 to 5 h^{-1} , respectively and product selectivity to 2,4-DMA remains almost unchanged. The linear increase in OTD conversion up to 84.9% with contact time indicates that there are no external mass transfer limitations. At longer contact times, the selectivity to 2,4,6-TMA increased approximately to 14%.

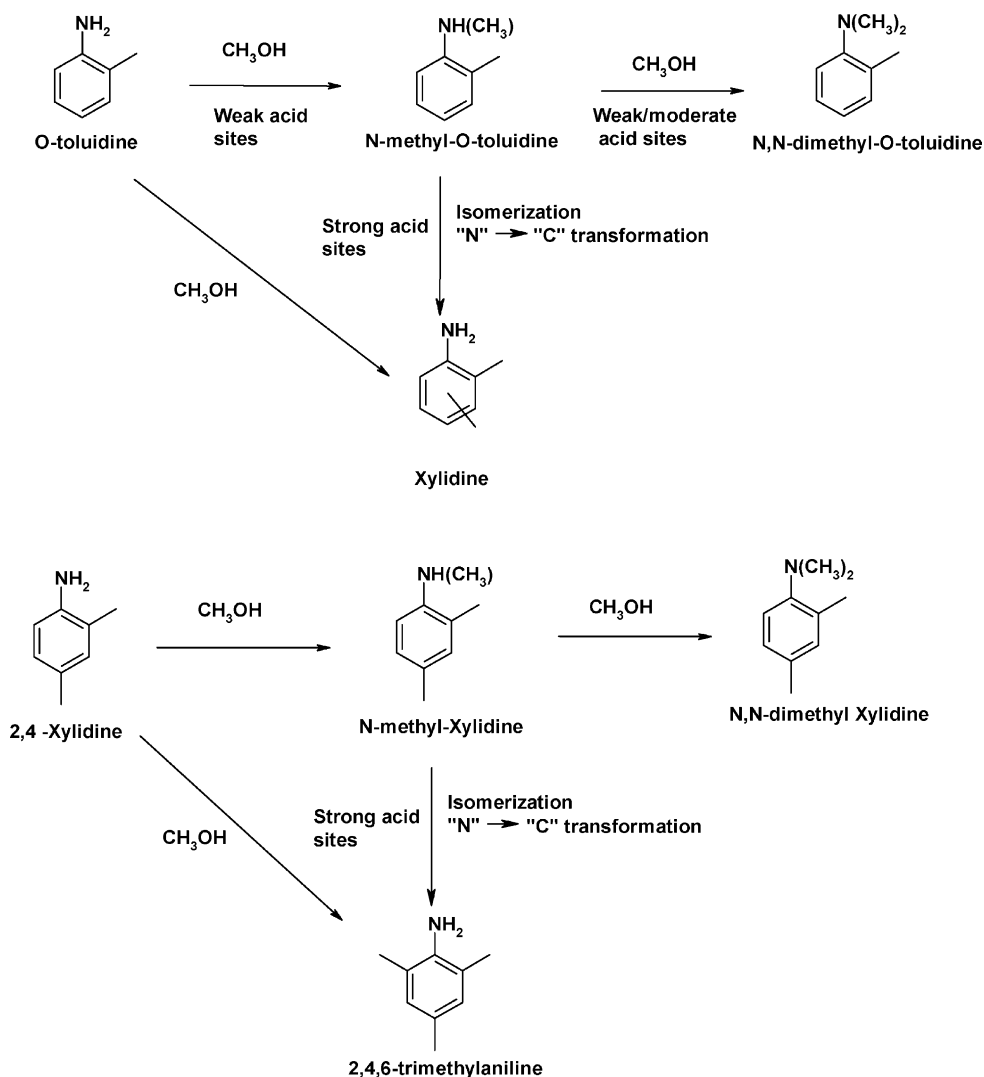


Fig. 4. Scheme of methylation of *o*-toluidine over acidic zeolites.

The selectivity towards NM-OTD decreased with increase in contact time, due to further methylation (secondary reactions) of NM-OTD to NNDM-OTD and NM-Xy. The increase in the selectivity for 2,4,6-TMA suggests that the formation of C-alkylated products by transalkylation of N-alkylated products at higher contact time by N → C-transformation. The increase in concentration of NM-Xy was up to 8.9% at WHSV (2 h^{-1}); a further increase in contact time resulted in a decrease in its selectivity with concomitant increase in the formation of NNDM-Xy. Also the selectivity towards NNDM-OTD was nearly same, suggesting that NNDM-Xy is produced by methylation of NM-Xy and not by NNDM-OTD.

3.5. Influence of time on stream

The activity and product selectivity of zeolite H-beta catalyst as a function of time for the reaction of *o*-toluidine alkylation with methanol at 400°C , WHSV of 1 h^{-1} and molar ratio of methanol to *o*-toluidine of 2:1 was depicted in Fig. 3 for a period of 12 h. The OTD conversion decreases slightly during initial 2 h on stream and thereafter remains stable up to 12 h. The catalytic activity and product selectivity remained almost same during the period of study.

From the above study, the scheme of methylation of *o*-toluidine may be presented as shown in Fig. 4.

4. Conclusions

The main products of the reaction of OTD methylation are both NM-OTD and 2,4-DMA. All the zeolites are selective for N-mono-methylation of *o*-toluidine at lower temperatures. C-alkylation is favored over large pore zeolites at higher temperatures. Weak acid sites are active for NM-OTD, whereas medium acid sites are active for formation of NNDM-OTD and NM-Xy and strong acid sites are responsible for 2,4-DMA, 2,6-DMA and 2,4,6-TMA. Lower molar ratios are beneficial to xylydines and higher ones are helpful to produce poly-methylated products. The catalytic activity and product selectivity remained almost same during the period of study of 12 h over H-beta zeolite.

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