

## MFI metallosilicates catalyzed *ortho*- and *para*-toluidine conversion

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### Abstract

Conversion of *ortho*- and *para*-toluidine to industrially important *meta* isomer has been studied over metallosilicates of ZSM-5 type. The effect of reaction temperature, WHSV on the catalytic performance is discussed. A good correlation exists between the acidity of the metallosilicates and their conversion activity.

**Keywords:** MFI metallosilicates; Toluidine; Isomerization; Acidity

### 1. Introduction

The conversion of *ortho*- and *para*-toluidine to *meta*-toluidine is important from the point that the *meta* isomer is used as an intermediate for dyestuffs and agrochemicals. This conversion is catalyzed by acidic zeolites like H-ZSM-5 [1]. Weigert has reported that zeolite H-ZSM-5 catalyzes equilibrium of toluidines and ethylanilines by an intermolecular 1,2-shift mechanism [2]. Hardy et al. proposed that toluidine isomerization occurs by migration of  $\text{NH}_3^+$  rather than by a  $2^+$  species [3]. It may be noted that the equilibrium mixture is obtained and not as with the xylenes, a mixture in which the *para* isomer dominates. Apparently diffusion rate differences do not prevail in toluidine isomerization, factors are the higher reaction temperature and the fact that amines diffuse slower

presumably more jumpy due to protonation/deprotonation through H-ZSM-5 channels than hydrocarbons of the same size [4].

As the isomerization mechanism involves protonation/deprotonation it will be of interest to look into the aspect of zeolite acidity and its effect on toluidine isomer conversion. In case of zeolite the acidity can be modified by changing Si/Al ratio, by isomorphous substitution or by controlling extent of cation exchange. The present work was attempted with the objective of studying the role of acidity of isomorphous substituted MFI metallosilicates on the conversion *ortho*- and *para*- to *meta*-toluidine.

### 2. Experimental

The isomorphous substituted ZSM-5 zeolites viz. Al-ZSM-5, Ga-ZSM-5 and Fe-ZSM-5 used in our study were synthesized following

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the reported procedure [5–8]. These metallosilicates were characterized by XRD for phase purity, SEM for crystal size, TPD of ammonia for acidity and a combination of atomic absorption spectrometry and wet chemical analysis for determining  $\text{SiO}_2/\text{M}_2\text{O}_3$  ratio. The metallosilicates were calcined at  $540^\circ\text{C}$  in the presence of air for 7 h to burn off the organic template, and then ion-exchanged with 1 M ammonium nitrate solution four times. Further they were converted to proton form by calcining at  $540^\circ\text{C}$  for 5 h in presence of air.

The conversion of *ortho*- and *para*-toluidine was carried out in a tubular, fixed-bed, down flow, integral reactor at atmospheric pressure. The reactant toluidine was fed by a syringe pump (Sage Instruments, Model 362), vaporized in a preheater assembly and passed through the catalyst bed maintained at the desired reaction temperature. Ultra high pure nitrogen was used as carrier gas. The products were condensed in a chilled water cooled condenser at the reactor outlet and analyzed in a Varian Vista 6000 gas chromatograph equipped with a Carbowax 20 M capillary column of length 30 m and i.d. 0.32 mm.

### 3. Results and discussion

The characterization data of the metallosilicates determined by different physico-chemical techniques is presented in Table 1. The metallosilicates were of same morphology with a slight variation in  $\text{SiO}_2/\text{M}_2\text{O}_3$  and crystallite size. The acidity of the metallosilicate was high-

Table 1  
Characterization data of MFI metallosilicates

Metallosilicate	Crystal size $\mu\text{m}$	Morphology	$\text{SiO}_2/\text{M}_2\text{O}_3$	Acidity (mmol $\text{NH}_3$ per g zeol.)
Al-ZSM-5	0.5–2.0	spheroidal	37	0.49
Ga-ZSM-5	1.0–3.0	spheroidal	39	0.42
Fe-ZSM-5	0.5–1.5	spheroidal	40	0.24

Table 2  
*Para*-toluidine conversion over Al-ZSM-5

Composition (wt%)	Feed	Product
Aniline	82.03	81.92
<i>Para</i> -toluidine	17.97	3.14
<i>Ortho</i> -toluidine	0.00	6.21
<i>Meta</i> -toluidine	0.00	8.55
Unidentified	0.00	0.18
Toluidine distribution		
<i>Para</i> -	100.00	17.54
<i>Ortho</i> -	0.00	34.69
<i>Meta</i> -	0.00	47.77

Temperature:  $400^\circ\text{C}$ , WHSV:  $0.8\text{ h}^{-1}$ ,  $\text{N}_2$  flow rate = 20 ml/min. Thermodynamic equilibrium composition of toluidine isomers (Hardy et al.) at  $400^\circ\text{C}$ : 16.1 *para*-, +33.7 *ortho*-, +50.2 *meta*-.

est for Al-ZSM-5 followed by Ga-ZSM-5 and Fe-ZSM-5.

#### 3.1. *Para*-toluidine conversion

A solution of *para*-toluidine (18 wt%) in aniline was used in the runs. The results its conversion over Al-ZSM-5 are given in Table 2. This data clearly indicates that *para*-toluidine is converting to *ortho* and *meta* isomers in proportion close to thermodynamic equilibrium composition reported by Hardy et al.

The effect of temperature on the conversion of *para*-toluidine over Al-ZSM-5 was studied in the temperature range 300 to  $450^\circ\text{C}$ . The distribution of three toluidine isomers in the product mixture is depicted in Fig. 1. *Para*-toluidine conversion increased with enhancement in reaction temperature from 300 to  $400^\circ\text{C}$ , above this temperature it remained nearly same as it is getting converted to thermodynamic equilibrium composition. At  $300^\circ\text{C}$ , there was not any *ortho*-toluidine formation; around 10% *para*-toluidine got converted only to *meta* isomer, there was not any *ortho*-toluidine formation. With increase in temperature to  $350^\circ\text{C}$  *para*-toluidine conversion went up to 36% and *ortho*-toluidine started appearing in the product. This means *para*-toluidine conversion follows 1,2-shift mechanism. This is in line with the

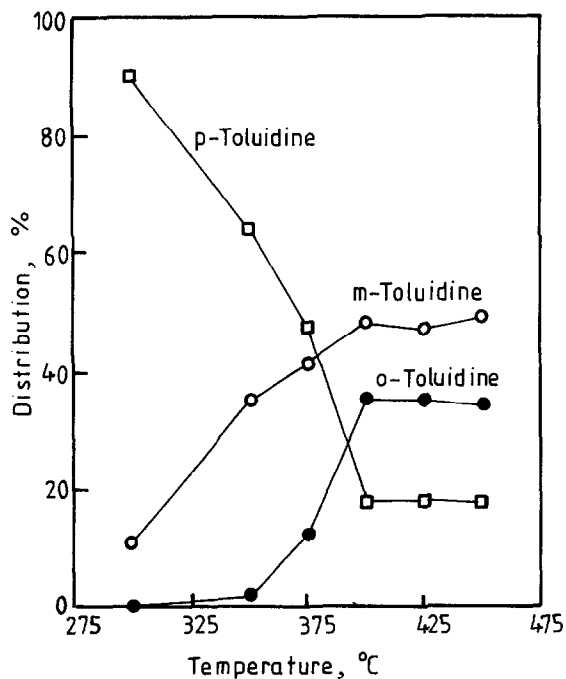


Fig. 1. Effect of temperature on the conversion of *para*-toluidine to isomeric toluidines over Al-ZSM-5.

mechanism adopted by Weigert [2] to explain the isomerization of alkyylanilines. He has estimated the constants for rate equations by least square techniques. The fits were not improved by adding two additional equations for the direct interconversion of *ortho* and *para* isomers.

Table 3 presents the results of the run in which WHSV was varied over Al-ZSM-5. The increase in WHSV from 0.4 to 1.3 h<sup>-1</sup> resulted in decrease in *para*-toluidine conversion and at higher WHSV of 1.3 h<sup>-1</sup>, *ortho*-toluidine was not present in the product mixture. In other words when WHSV is higher the contact time

Table 3  
Influence of WHSV on the isomerization activity of Al-ZSM-5

	WHSV (h <sup>-1</sup> )		
	0.4	0.8	1.3
<i>Ortho</i> -toluidine	2.59	1.55	0.00
<i>Para</i> -toluidine	55.13	63.79	82.05
<i>Meta</i> -toluidine	57.72	34.66	17.95

Feed: 17.97% *para*-toluidine + 82.03% aniline; temperature: 350°C, N<sub>2</sub> flow rate: 20 ml/min.

Table 4  
Effect of *para*-toluidine concentration in aniline on the isomeric product distribution over Al-ZSM-5

	<i>Para</i> -toluidine in aniline (wt%)		
	18.00	12.62	2.89
<i>Ortho</i> -toluidine	1.55	8.27	14.54
<i>Para</i> -toluidine	63.79	31.13	26.46
<i>Meta</i> -toluidine	34.66	60.60	58.94

Temperature: 350°C; WHSV: 0.8 h<sup>-1</sup>; N<sub>2</sub> flow rate: 20 ml/min.

between *para*-toluidine and Al-ZSM-5 is less and *meta*-toluidine concentration is not sufficient for further conversion to *ortho*-toluidine.

It is also of interest to study the role of *para*-toluidine concentration in aniline. The results of the runs in which *para*-toluidine concentration in aniline was varied from 2.89 to 18 wt% is summarized in Table 4. As *para*-toluidine concentration enhanced its conversion to other two isomers decreased. This may be ascribed to lesser accessibility of active site for *para*-toluidine at higher concentration.

The conversion of *para*-toluidine over three isomorphous substituted zeolites viz. Al-ZSM-5, Ga-ZSM-5 and Fe-ZSM-5 is given in Fig. 2. It is quite indicative from this figure that under the same reaction conditions, *para*-toluidine conversion to *ortho* and *meta* isomers is least on Fe-ZSM-5 and highest on Al-ZSM-5. Ga-ZSM-5 showed a behaviour in between the two metallosilicates. It looks that there is a relationship between the intrinsic acidity of the metallosilicates and *para*-toluidine conversion pattern. Among the three, Al-ZSM-5 has got the highest acidity, followed by Ga-ZSM-5 and Fe-ZSM-5. This is quite evident from temperature programmed desorption (TPD) of ammonia profile of the metallosilicates (Fig. 3). The TPD profile consisted of two peaks, a low temperature corresponding to sites of lower acidity and a high temperature corresponding to sites of higher acidity. The area under each peak is proportional to concentration of the sites. In case of Al-ZSM-5 areas of both low and high temperature peak are greater than Ga-ZSM-5 and Fe-ZSM-5. Hence the acidity of the metal-

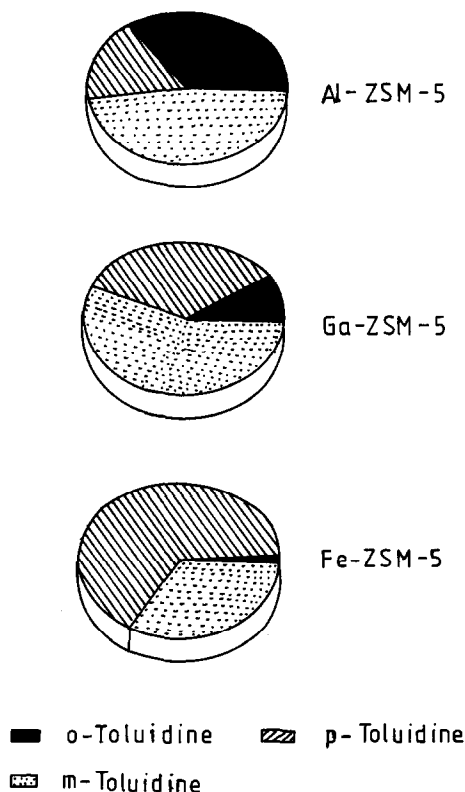


Fig. 2. Comparison of *para*-toluidine conversion to *meta*- and *ortho*-toluidine over the metallosilicates.

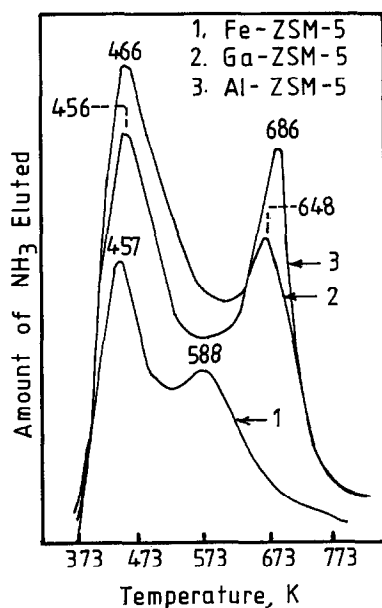


Fig. 3. Ammonia TPD profiles of the metallosilicates.

Table 5  
*Ortho*-toluidine conversion over Al-ZSM-5

Composition (wt%)	Feed	Product
Aniline	82.36	81.09
<i>Para</i> -toluidine	0.00	3.04
<i>Ortho</i> -toluidine	17.64	6.07
<i>Meta</i> -toluidine	0.00	8.49
Unidentified	0.00	0.28
Toluidine distribution		
<i>Para</i> -	0.00	17.27
<i>Ortho</i> -	100.00	34.49
<i>Meta</i> -	0.00	48.24

Temperature: 400°C; WHSV: 0.8 h<sup>-1</sup>; N<sub>2</sub> flow rate: 20 ml/min.

losilicates decreases in the order Al-ZSM-5, Ga-ZSM-5 and Fe-ZSM-5. The lower is the acidity of metallosilicate, lesser is *para*-toluidine conversion.

### 3.2. *Ortho*-toluidine conversion

The concentration of *ortho*-toluidine in aniline was also kept around 18% in these runs. Table 5 reports the results of the run in which *ortho*-toluidine was transformed over Al-ZSM-5. Like *para*-toluidine case *ortho*-toluidine got converted to other two isomers viz. *para* and *meta* isomers close to thermodynamic equilibrium composition.

The effect of reaction temperature on *ortho*-toluidine conversion is given in Fig. 4. The temperature of the reaction was varied from 325 to 450°C. At lower temperature of 325°C, no *para*-toluidine was formed, *ortho*-toluidine was selectively converted to *meta* isomer. At temperature above 325°C *para*-toluidine started appearing in the product, all three isomers are at equilibrium around 400°C. The formation of only *meta* isomer at lower temperature further confirmed that the reaction scheme operating is 1,2-shift.

Like *para*-toluidine in this case also the conversion over the three isomorphous substituted zeolites has been compared. The results are summarized in the form of Fig. 5. The conversion is lowest for Fe-ZSM-5 and highest for Al-ZSM-5, while Ga-ZSM-5 exhibited a trend

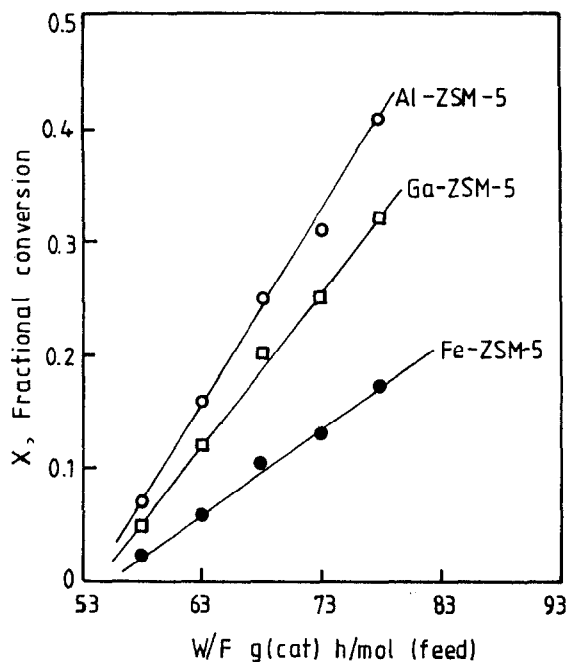


Fig. 5. Plot of fractional conversion versus space time for the three metallosilicates.

in between. The rate of *ortho*-toluidine conversion which is given by the slope of the plot of fractional conversion versus space time (W/F)

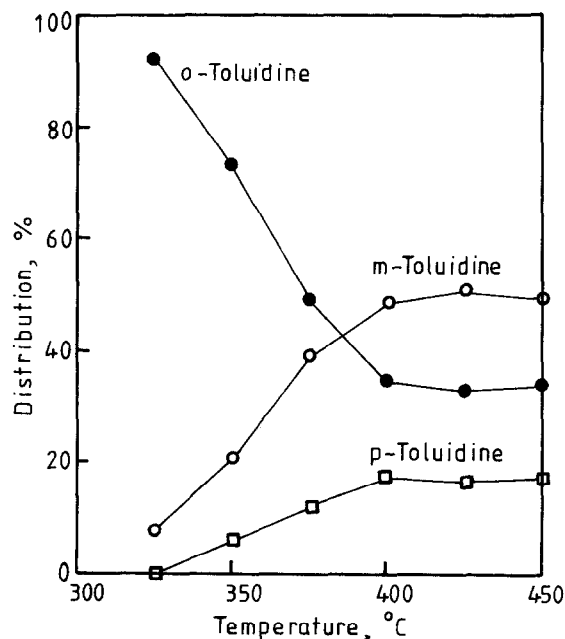


Fig. 4. Influence of reaction temperature on *ortho*-toluidine conversion over Al-ZSM-5.

is highest for Al-ZSM-5 followed by Ga-ZSM-5 and Fe-ZSM-5. The results once again confirmed that there is a relationship between toluidine isomer conversion and metallosilicate acidity.

#### 4. Conclusions

At lower temperature *para*-toluidine is selectively got converted to *meta*-toluidine over Al-ZSM-5. Also *ortho*-toluidine conversion resulted in only *meta* isomer. *Ortho*- and *para*-toluidine can get transformed to each other via *meta*-toluidine. At around 400°C both *ortho*- and *para*-toluidine isomerized to equilibrium composition of toluidines. Lower contact time and lower temperature favour less conversion of toluidine isomers. This conversion also depends on the concentration of isomers in aniline. There is a very good relationship between the metallosilicate acidity and toluidine isomer conversion. The conversion is more on the metallosilicate of higher acidity, while it is less on the metallosilicate of lower acidity.

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