

Synthesis of resorcinol from *meta*-phenylenediamine in the presence of zeolites

Bryan Brack^{a,*}, David W. Gammon^b, Eric van Steen^a

^a Catalysis Research Unit, Department of Chemical Engineering, University of Cape Town, Private Bag, Rondebosch 7701, South Africa

^b Department of Chemistry, University of Cape Town, Private Bag, Rondebosch 7701, South Africa

Received 17 June 1999; received in revised form 13 September 1999; accepted 4 October 1999

Abstract

Resorcinol can be produced in high yields starting from *meta*-phenylenediamine (MPDA) in the presence of homogeneous mineral acids. The synthesis in the presence of aluminosilicates (e.g., zeolites) offers a solution to the extremely corrosive properties of the mineral acids at reaction temperature (200–275°C). Environmental hazards associated with mineral acids will thus be eliminated. From studies using mineral acids, it was deduced that the rate of reaction is directly proportional to the hydronium ion concentration. The ionisation constants and thus hygroscopic property of the mineral acid determines the degree of resorcinol and MPDA polymerisation. As an alternative, the synthesis can be performed in the presence of aluminosilicates, albeit at higher temperatures. Zeolites H-USY, H-Beta, and amorphous silica-alumina gave good resorcinol yields. During the reaction, the crystal structure of zeolites H-Beta and H-USY is destroyed. H-ZSM-5 is stable under reaction conditions, but the resorcinol yield is rather poor. This can be ascribed to the low adsorption capacity for MPDA in comparison to zeolites H-USY and H-Beta. For all zeolites the dominant part of the reaction may occur on the external surface acid sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Resorcinol; *Meta*-phenylenediamine; Hydrolysis; Zeolites; Adsorption

1. Introduction

Resorcinol is an important building block in the pharmaceutical and dye industry [1]. The main synthesis route is the alkaline fusion of *m*-benzenedisulphonic acid or the hydroperoxidation of diisopropylbenzene [1,2]. In an attempt

to find an alternative, more environmentally benign process for the production of resorcinol, the acid hydrolysis of *meta*-phenylenediamine (MPDA) was investigated.

The first attempts in producing resorcinol using the acid hydrolysis of MPDA were done at the end of the 19th century using mineral acids such as hydrochloric acid, sulphuric acid and stannous chloride. In these experiments, the selectivity for resorcinol was low, and a substantial amount of a tarry resin was produced. Greco [3–6] investigated this reaction in the presence of sulphuric acid, phosphoric acid and

* Corresponding author. Tel.: +27-21-650-3796; fax: +27-21-689-7579.

E-mail address: bbrack@chemeng.uct.ac.za (B. Brack).

ammonium bisulphate. A 75% yield of resorcinol was obtained in the presence of sulphuric acid (molar ratio of sulphuric acid to MPDA of 1.6–1.8 and at temperatures between 200°C and 230°C). Higher yields (~95%) were obtained in the presence of phosphoric acid between 170°C and 250°C. The ratio of phosphoric acid to MPDA is no longer critical, as long as enough acid is available to ensure complete conversion of MPDA. The unique feature of phosphoric acid was ascribed to the fact that only the primary hydrogen in phosphoric acid is strong enough. Ammonium dihydrogenphosphate is formed as a by-product in this reaction. The reaction can also be carried out in the presence of ammonium bisulphate, which can be regenerated by heating it to 310–450°C [6,7].

The above-mentioned mineral acid reaction mixtures are highly corrosive, and lead to the formation of substantial quantities of the ammonium salt as side-products. The reaction using this mixture should not be carried out in stainless steel or monel metal reactors due to the formation of metal-amine complexes. These complexes enhance the formation of resins. Fur-

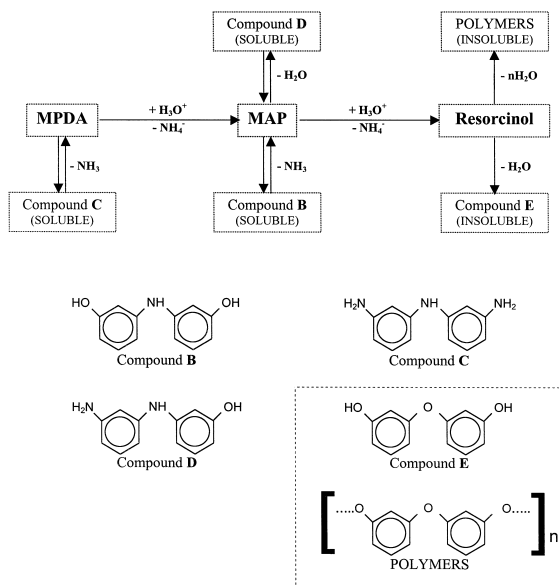
thermore, the separation of resorcinol from the reaction mixture is tedious and energy intensive [3–6]. There is thus an incentive to replace the homogeneous mineral acids with a regenerable, heterogeneous equivalent, such as zeolites or silica-alumina.

The hydrolysis of MPDA is a set of consecutive reactions (see Scheme 1) [3,8]. In the first step MPDA hydrolyses to form *meta*-aminophenol (MAP). MAP is subsequently hydrolysed, yielding resorcinol. In the process, an array of dimerisation and polymerisation side reactions may occur with the phenyl-groups being bonded by –NH– or –O– links. The ether formation is essentially irreversible. The ethers are also far less soluble in water than the polyphenylene-amines. Consequently, mainly diphenyleneamines and insoluble polyethers occur as side-products in the reaction mixture.

2. Experimental

2.1. Reagents

The acid catalysed hydrolysis of MPDA (obtained from AECI) was studied in the presence of mineral acids, such as H₂SO₄ (98%), H₃PO₄ (85%) and (NH₄)H₂PO₄ p.a. (all obtained from Saarchem) as a benchmark for the reaction in the presence of zeolites and amorphous silica-alumina. Zeolites H-ZSM-5 (Südchemie, Si/Al = 13, $S_{\text{BET}} = 303 \text{ m}^2/\text{g}$, $d_{\text{crystal}} = 1\text{--}3 \text{ }\mu\text{m}$), H-ZSM-5 (Südchemie, Si/Al = 22, $S_{\text{BET}} = 312 \text{ m}^2/\text{g}$, $d_{\text{crystal}} = 0.5 \text{ }\mu\text{m}$), H-USY (Akzo Nobel, Si/Al = 5.6, $S_{\text{BET}} = 607 \text{ m}^2/\text{g}$, $d_{\text{crystal}} = 0.5 \text{ }\mu\text{m}$) and zeolite H-Beta (Südchemie, Si/Al = 14.4, $S_{\text{BET}} = 557 \text{ m}^2/\text{g}$, $d_{\text{crystal}} < 0.3 \text{ }\mu\text{m}$) were employed. For comparison, an amorphous silica-alumina (Kalichemie, Si/Al = 6.9, $S_{\text{BET}} = 367 \text{ m}^2/\text{g}$) was used. Prior to their characterisation and use in the reaction, the solids were calcined in air at 180°C for 2 h followed by another 12 h at 450°C. After calcination, the solids were stored in a desiccator over a waterbed for 24 h to allow for rehydration.



Scheme 1. Overall simplified reaction mechanism for hydrolysis of MPDA to form Resorcinol.

2.2. Characterisation of the alumino-silicates

The crystallinity of the zeolites was examined using X-ray diffraction using a Philips X-ray diffractometer generating Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$) in the 2θ region between 4° and 45° with a step size of 0.1° and operating at 40 kV and 25 mA.

The number of acid sites was determined using temperature programmed desorption (TPD) of NH_3 using the method described previously [9]. The strength of adsorption was determined using the method outlined by Cventanovic and Amenomiya [10] of varying the heating rate. Briefly, 0.25 g of the sample is loaded in the quartz TPD-cell. A 1% NH_3/He mixture is passed over the catalyst at 150°C for 1 h. The physisorbed ammonia is flushed off the sample by flowing pure He (60 ml(NTP)/min) over the sample at 150°C for 12 h. The temperature is subsequently ramped with various ramping rates up to 450°C and kept there for 40 min. The amount of ammonia desorbed as a function of the temperature is monitored using a TCD. Ammonia is trapped in sulphuric acid with known concentration. The total amount of ammonia adsorbed was determined by back-titration of the sulphuric acid with caustic soda.

The adsorption of water was determined by TGA/DTA of the re-hydrated zeolite using a Stanton Redcroft STA-780. A total of 25 mg of the solid was placed into the apparatus, flushed with nitrogen (30 ml (NTP)/min) for 4–5 h before being heated up to 450°C . The temperature ramps were varied to determine the strength of adsorption.

The adsorption of MPDA, MAP, and resorcinol on the zeolites was investigated. Ca. 0.4 g of the re-hydrated zeolite was contacted with a 15 ml aqueous solution of MPDA, MAP, resorcinol, or ammonia. The concentration of these compounds in the solution was varied. Before sealing the sample flask, the headspace was flushed with nitrogen to minimise the oxygen content in the flask [11]. The slurry was equilibrated for 6 days in darkness at a constant

temperature between 30°C and 90°C in an oil bath controlled at $\pm 2^\circ\text{C}$. The concentration of the adsorbent in the liquid was determined using HPLC or titration. The amount adsorbed was determined over the mass balance.

2.3. Reaction studies

The reactions were carried out batch-wise, in a 600 ml Parr autoclave under autogeneous pressure. The reactor was filled with 350 ml de-ionised water. If the reaction was carried out in the presence of a mineral acid, the acid was added in a molar ratio of the primary proton of the acid to MPDA of 6.8 or 3.4. If the reaction was carried out in the presence of a heterogeneous catalyst, 10 g of solid was added. A total of 1 g of MPDA was added. The sealed reactor was flushed with nitrogen to reduce the oxygen content in the reactor. The reactor was then heated up to reaction temperature ($225\text{--}300^\circ\text{C}$). Samples (ca. 15 ml with sample loop flushing) of the reaction mixture were withdrawn after various reaction times using a sampling fret (2 μm). The pH of the sample was then determined.

The reaction compounds were separated using HPLC (Spherisorb 80-3 ODS-2, $L = 250$ mm, i.d. = 4.6 mm) employing a mobile phase gradient. The initial mobile phase being used in the first 4 min of the analysis consisted of 0.05 vol.% H_3PO_4 and 0.1 vol.% triethylamine in de-ionised water. This mobile phase was then gradually changed over a period of 2 min to a mobile phase consisting of 80% de-ionised water (0.1 vol.% H_3PO_4 , 0.1 vol.% triethylamine) and 20% acetonitrile with 0.1 vol.% triethylamine. The compounds were analysed with an UV detector operating at 280 nm.

3. Results

3.1. Characterisation of the solids

Table 1 gives an overview of the characterisation of the solids using desorption measure-

Table 1
Characterisation of the solids used in this study by desorption measurements

	Al content (mmol/g)	NH ₃ -TPD		H ₂ O-desorption	
		Chemisorption (mmol NH ₃ /g)	ΔH_{ads} (kJ/mol)	After N ₂ flushing (mmol H ₂ O/g)	ΔH_{ads} (kJ/mol)
Silica-alumina	2.18	1.54	62	2.24	46
H-ZSM-5 (Si/Al = 13)	1.21	0.85	89	3.35	27
H-USY	2.63	1.72	44	6.32	45
H-Beta	1.10	0.78	75	4.27	44

ments. The amount of ammonia chemisorbed corresponds to the aluminium content of the silica-aluminates. The strength of adsorption was determined by applying NH₃-TPD at various heating rates as described by Cventanovic and Amenomiya [10]. The acid strength decreases from H-ZSM-5 to H-Beta to H-USY. H-Beta has an intermediate acid strength, which has been reported before [12].

The affinity of the solids for water was determined using TGA/DTA of the re-hydrated samples, again applying the method of Cventanovic and Amenomiya [10]. The water uptake decreased in the order H-USY > H-Beta > H-ZSM-5, showing the expected decrease in the hydrophilic properties of the zeolites with increasing Si/Al ratio.

Fig. 1 gives the respective mole fraction dependency of the aqueous solutes MPDA, MAP, and resorcinol on the uptake by the zeolites. The adsorbed amount is plotted against the mole fraction of the solute in solution. The amount of MPDA adsorbed (see Fig. 1A) is for H-Beta larger than H-USY which in turn is larger than H-ZSM-5. From the initial slope of the curve, taking into consideration the differences in the total uptake, it can be deduced that the strength of adsorption follows the order H-Beta > H-USY > H-ZSM-5. The order of strength between H-Beta and H-USY could have been expected based on the NH₃-TPD. The adsorption of MPDA on ZSM-5 is much smaller. This might be attributed to adsorption solely on the external surface of ZSM-5. The measured solution pH was ca. 6.0 for H-Beta, 7.0 for H-USY and 8.5 for H-ZSM-5. This also affects the

adsorption isotherms since the equilibrium $\text{H}_2\text{O} + \text{C}_6\text{H}_4(\text{NH}_2)_2 = [\text{C}_6\text{H}_4(\text{NH}_2)(\text{NH}_3)]^+\text{OH}^-$ is favoured at low pH.

Fig. 1B shows the amount of MAP adsorbed as a function of the mole fraction of MAP in the

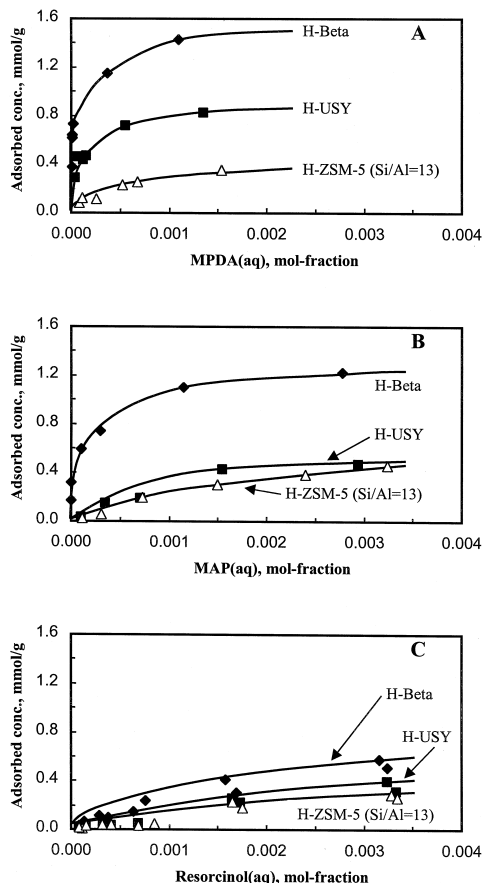


Fig. 1. Adsorption–equilibrium data for aqueous (A) MPDA, (B) MAP, and (C) Resorcinol on H-Beta (◆), H-USY (■) and H-ZSM-5 (Si/Al = 13) (Δ) at 70°C.

aqueous phase. The order of the strength of adsorption and the concentration of the monolayer are similar to those obtained for MPDA although the adsorption is generally weaker. This can be attributed to the difference in basicity of the two compounds. (pK_a of $MPDA^+ = 8.89$; pK_a of $MAP^+ = 9.63$ [13]). It must be remembered, however, that adsorption of the non-ionic MAP can also occur by adsorption of the hydroxy-group onto the hydrophobic oxygen anions [14,15].

Depending on the pH, the adsorption of resorcinol onto zeolites (see Fig. 1C) is less strong than the adsorption of the amino compounds. This can be ascribed to the low basicity of this compound in relation to the amino compounds. Although a similar trend can be observed, the differences between the zeolites become minimal.

3.2. Reaction studies

Fig. 2 shows the resorcinol yield as function of time at reaction temperatures 225°C and

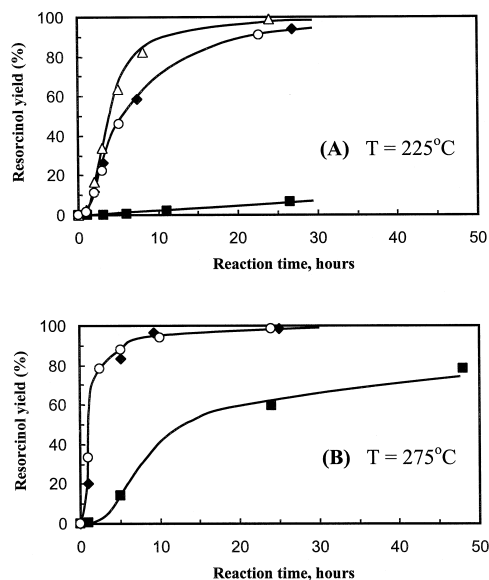


Fig. 2. Resorcinol yield versus time at a reaction temperature of (A) 225°C, (B) 275°C using H_2SO_4 (Δ), H_3PO_4 (\diamond), $NH_4H_2PO_4$ (\blacksquare) with an acid to MPDA mole ratio of 6.77; and H_2SO_4 (\circ) with an acid to MPDA mole ratio of 3.39.

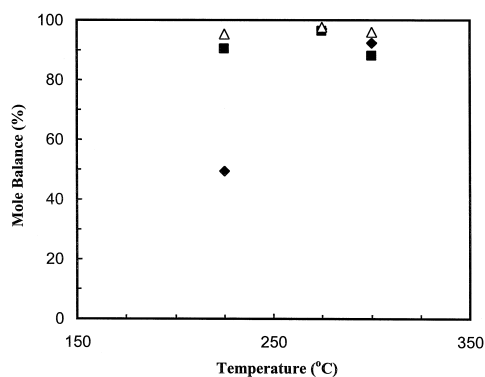


Fig. 3. Mole balance after 25 h reaction time over H-Beta (\diamond), H-USY (\blacksquare) and H-ZSM-5 (Si/Al = 13) (Δ).

275°C, respectively. The 1-h heating period required to bring the reaction mixture from ambient temperature to reaction temperature forms part of the reaction time shown in the figures below. The rate of resorcinol formation increases with an increase in both temperature and acid strength. Higher acid to MPDA mole ratios (H_2SO_4 in Fig. 2A) increases the reaction rate. The reaction rate using phosphoric acid is identical to sulfuric acid when the sulfuric acid to MPDA mole ratio is half that of phosphoric acid to MPDA mole ratio. In the case of ammonium dihydrogen phosphate, the resorcinol yield and reaction rate is drastically increased when the reaction temperature increased from 225°C to 275°C. No resorcinol is produced without the addition of an acid. When using an 6.77 acid to MPDA mole ratio, the pH for H_2SO_4 , H_3PO_4 and $NH_4H_2PO_4$ are 1.4, 1.7, and 5.2, respectively. The pH stays essentially constant during the reaction. Mole balances reveal that hardly any side products are formed.

The mole balances obtained for the zeolites after 25 h reaction time are shown in Fig. 3. All compounds detected in the reaction mixture (MPDA, MAP, resorcinol, Compound C and Compound D) were back-calculated to the number of moles of MPDA required to obtain the concentrations of the compounds in solution at the end of the reaction. For example, 2 moles of MPDA are required to produce 1 mole of Compound C. The mole balance was then obtained

by dividing the back-calculated MPDA quantity at the end by the initial amount of MPDA used. Only the reaction involving H-Beta at 225°C shows a poor mole balance of 48%. Since the zeolites are brown after the reaction, it may be concluded that the lost moles are due to chemisorbed compounds on the zeolite surface.

The resorcinol yields versus reaction time obtained for the alumino-silicates as shown in Fig. 4 are not based on the initial amount of MPDA since the solution mole balance changes during the course of the reaction. Instead, the obtained resorcinol yield was calculated by dividing the resorcinol amount by the total back-

calculated MPDA amount of the bulk solution at the end of the reaction. By doing so, the adsorbed amount onto the solids when establishing a solid-solution equilibrium at reaction temperature can be corrected. The deviation in the mole balances is greatest for the first two sampling points after which the mole balances return to those given in Fig. 3.

The resorcinol yield as well as the reaction rate increases upon changing the temperature from 225°C to 275°C through to 300°C. This change is most pronounced for the case of H-Beta where the resorcinol yield after 25 h increases from 8 mol% at 225°C to above 80 mol% at 275°C while approaching 90 mol% at 300°C. For H-Beta at 225°C, the low yield in resorcinol (Fig. 4A) coupled with the low mole balance in Fig. 3 suggests that the MPDA is strongly adsorbing. At the same time, the initial reaction rate at a particular temperature in the case of H-Beta is greater than all the other alumino-silicates used. Remarkably, the resorcinol yield of H-USY after 25 h reaction time (~9 mol%) is greater than that of H-Beta at 225°C; however, less substantially increases to 25 mol% resorcinol yield at 275°C and 300°C. The H-ZSM-5 with Si/Al = 13 is a rather poor catalyst for the acid catalysed hydrolysis of MPDA, offering resorcinol yields between 1 and 3 mol% irrespective of the temperature. The other H-ZSM-5 zeolite with Si/Al = 22 and very similar properties to H-ZSM-5 (Si/Al = 13) has been tested at 300°C (Fig. 4C) and shows a remarkable higher resorcinol yield after 25 h (~65 mol%). The only difference between the two H-ZSM-5 zeolites was observed by 4-methylquinoline TPD [9], where the number of external surface acid sites of H-ZSM-5 (Si/Al = 22) was found to be approximately 15 times that of H-ZSM-5 (Si/Al = 13). This could have been expected based on the difference in the average crystallite size of these zeolite samples (H-ZSM-5 (Si/Al = 13) $d_{\text{crystal}} = 1-3 \mu\text{m}$; H-ZSM-5 (Si/Al = 22) $d_{\text{crystal}} = 0.5 \mu\text{m}$). It can thus be concluded that the reaction in the presence of H-ZSM-5 takes place on the external

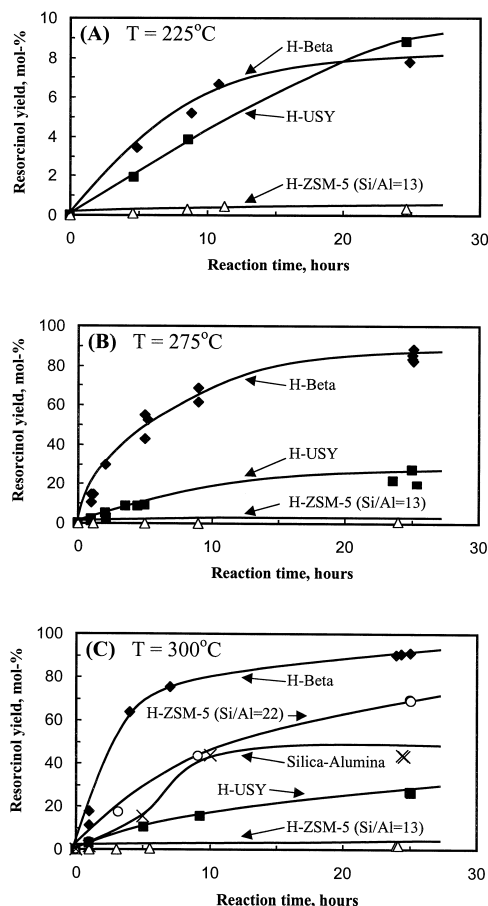


Fig. 4. Resorcinol yield versus time at reaction temperatures of (A) 225°C, (B) 275°C, and (C) 300°C using 10 g H-Beta (\blacklozenge), H-USY (\blacksquare), H-ZSM-5 (Si/Al = 13) (\triangle), H-ZSM-5 (Si/Al = 22) (\circ) and amorphous Silica-Alumina (\times), 1 g MPDA and 350 ml de-ionised water under autogeneous pressure ($V_{\text{reactor}} = 600 \text{ ml}$).

surface of the zeolite. The overall rate of the H-ZSM-5 (Si/Al = 22) reaction at 300°C is greater than that of H-USY and silica-alumina but less than that of H-Beta. Amorphous silica-alumina shown in Fig. 4C seems to have a slow initial reaction rate; however, increases substantially after 5 h to level out at 40 mol% resorcinol yield after 10 h. During the reaction the pH changes from pH ~ 7 at the start to pH ~ 9 at the end of the reaction. Reactions with γ -Al₂O₃ led to no MPDA conversion.

4. Discussion

The solid catalysts were characterised by adsorption of the relevant compounds. The adsorption behaviour of MPDA, MAP, and resorcinol could not be modelled using the Langmuir isotherm. The attempt to evaluate the strength of adsorption using the Clausius–Clapeyron relationship [16] was unsuccessful since both the Langmuir and graphically determined isosters did not decrease monotonically with increasing temperature. This can be attributed to the variation in the fugacity coefficient due to bulk and thus surface excess solute–solvent interaction considerations [17], as well as heterogeneous surface interaction parameters. Zeolites and activated carbon also serve as reactant-concentrating ‘‘vessels’’ where a phase change inside the pore structure may occur so that the solvent–solute system outside the pore structure is different to the one found inside the pore structure [17,18]. In most cases, this is found true up to the melting point temperature of the organic compounds (m.p. MPDA = 62.8°C, m.p. MAP = 122°C [19]). The Langmuir equation also makes the assumption of a 1 to 1 molecular exchange, while the molecular diameters of the organic compounds are approximately three times the size of a water molecule.

Although the adsorption behaviour could not be modelled, a qualitative interpretation of the data is still possible. The maximum uptake for all the organic compounds follow the order

MPDA > MAP > resorcinol. The difference cannot be ascribed to geometric differences in the organic molecules, but must be attributed to the difference in affinity of the zeolite in the adsorption of the binary mixture of the organic molecule and water. The strength of adsorption can be estimated from the initial slope in the graphs of the amount adsorbed versus the concentration, taking into consideration the maximum loading. It can thus be deduced that the strength of adsorption decreases in the order MPDA > MAP > resorcinol.

X-ray diffraction spectra before and after the reaction at 300°C were taken for H-ZSM-5, H-USY and H-Beta and compared with spectra found in literature [20]. As observed in Fig. 5, H-ZSM-5 (both, for Si/Al = 13 and for Si/Al = 22) retains its characteristic X-ray fingerprint after the reaction. The crystallinity of H-Beta decreases while H-USY becomes totally amorphous. The change in BET-surface area and the loss in the crystallinity of H-ZSM-5, H-Beta and H-USY are given in Table 2. BET surface area shows a similar trend to the XRD findings. It can be concluded that the pore structure of H-USY and silica-alumina collapses during the reaction. This may explain the poor resorcinol yield of H-USY when compared to H-Beta.

Fig. 2 shows an increase in reaction rate with increasing concentration (H₂SO₄) and tempera-

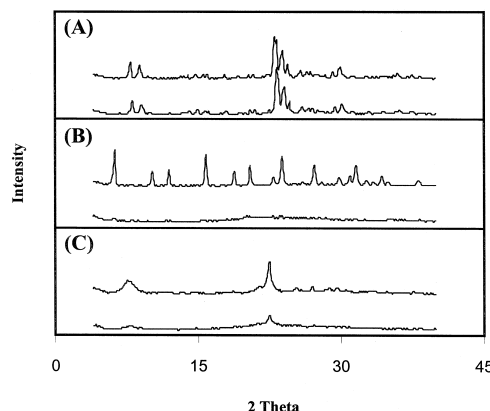


Fig. 5. X-ray diffraction spectra taken of (A) H-ZSM-5 (Si/Al = 13), (B) H-USY, and (C) H-Beta before the reaction (top curve) and after the reaction for 25 h at 300°C (bottom curve).

Table 2

BET surface area before and after reaction for 25 hours at 300°C and loss in crystallinity due to reaction at 300°C for 25 hours

	BET surface area (m ² /g)		Loss in crystallinity ^a (%)
	Before reaction	After reaction	
H-Beta	557	151	60
H-USY	607	61	100
H-ZSM-5 (Si/Al = 13)	303	284	5
H-ZSM-5 (Si/Al = 22)	312	298	5
Silica-Alumina	367	33	–

^aAs determined from the difference in the relative intensity of the XRD-peaks.

ture. Changing the acid from H₂SO₄ (pK_a = –2 at 25°C [21]) to H₃PO₄ (pK_a = 2.12 at 25°C [21]) to H₂NH₄PO₄ (pK_a = 7.4 at 25°C [21]) result in different rate constants. Under the very dilute reaction conditions, the first ionisation of phosphoric acid may be considered complete whereas sulfuric acid tends to fully dissociate into H₃O⁺ and SO₄^{2–} ions (pK_a of HSO₄[–] = 1.92 at 25°C [21]) resulting in two moles hydronium ions being formed for every one mole of sulfuric acid. This is precisely what is observed during experimentation. The reaction rate of sulfuric acid and phosphoric acid are identical if the acid to mole ratio of phosphoric acid is twice that of sulfuric acid. The rate of reaction is thus related to the concentration of hydronium ions present in solution. At the same time the acid ensures the removal of the basic ammonia and drives the thermodynamically unfavourable reaction forward. It must be kept in mind, however, that the self-ionisation of constant (pK_w at 200°C = 11.30 [22]) as well as the acid dissociation constant (pK_a(H₂NH₄PO₄) at 275°C = 8.57 [23]) change considerably at elevated temperatures.

Contrary to previous reports [3,6,8] no tarry resins were obtained when using sulfuric acid since the extremely low concentration allowed for the full dissociation of sulfuric acid into its ions, thus satisfying the acids strong affinity for water. When this condition is not met, the hygroscopic property of sulfuric acid promotes the

etherification of the produced resorcinol. Consequently, it is important that after a certain conversion of MPDA, the liberated NH₃ has sufficiently neutralised the H₂SO₄ to prevent etherification of the formed resorcinol. Due to the moderate dissociation constant K_a of phosphoric acid, the acid provides the reaction with the required hydronium ions for the acid–base reaction, however, it cannot polymerise the formed resorcinol.

Experimental and thermodynamic studies have proven that the removal of ammonia is vital for the reaction to proceed towards the formation of resorcinol. Under the very dilute reaction conditions described in this paper (26.4 mmol MPDA per litre water) the resorcinol yield in the ideal gas phase has been estimated to be 98%. This will be lower in the liquid phase. Nevertheless, the TPD determined chemisorbed ammonia that can be present on 10 g of zeolites is considerably less than the 18.5 mmol required for complete reaction as seen in the case of H-Beta. Some ammonia desorb at reaction temperature, which explains the rise in the pH from pH = 7 at the start of the reaction to pH = 9 towards the end.

The formation of resorcinol from MPDA is a consecutive reaction of MPDA → MAP → resorcinol (see Scheme 1, Fig. 6). A fit of the concentration/time data to the kinetic equations for consecutive reactions has been attempted. Although the reaction is consecutive, it seems that the overall process follows a rake type of reaction, hence the relatively high initial formation of resorcinol in Fig. 6. Principally, it would be expected that the initial rate of MAP formation should be greater when using mineral acids than using heterogeneous acids due to adsorption, desorption, and mass transfer constraints present for heterogeneous solid. Comparing the mineral acids with zeolites at the same reaction temperature of 275°C clearly illustrates that more MAP has been produced after 1 h using the zeolites than for the case of phosphoric acid. The measured maximum of MAP formed when using phosphoric acid is around 10 mol%, while

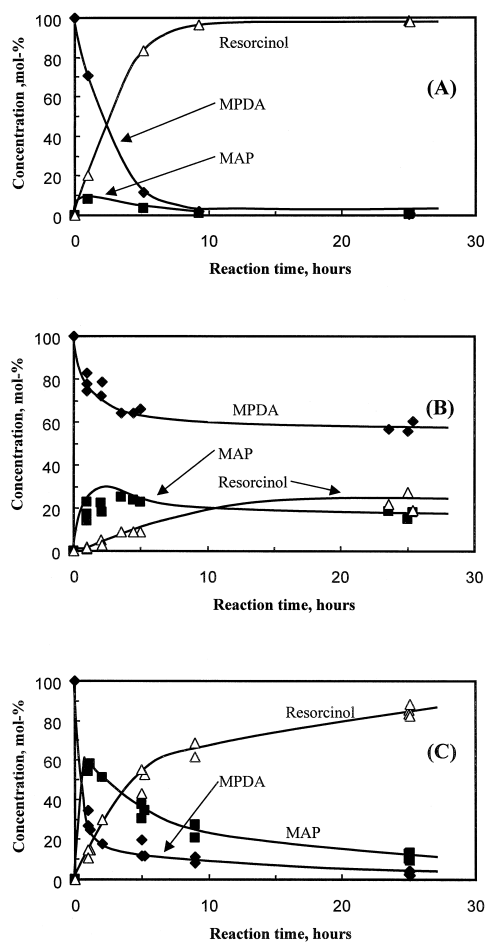


Fig. 6. Concentration versus reaction time of (A) Phosphoric acid, (B) H-USY, and (C) H-Beta to illustrate the difference in MAP and Resorcinol yields when comparing a mineral acid to a heterogeneous acid.

that of H-USY and H-Beta is 30 mol% and 60 mol%, respectively. The minor yield of MAP in the presence of acids can be attributed to the fast secondary conversion of MAP to resorcinol.

When observing from the adsorption-equilibrium data (Fig. 1A) that at 70°C and equivalent reactor MPDA concentration 4 mmol MPDA adsorbs onto 10 g H-USY and 8 mmol MPDA adsorbs onto 10 g H-Beta, and comparing this to Fig. 6, this might explain the observed high initial rate of formation of MAP. The adsorption process will happen during the start-up procedure and after reaching a certain temperature the chemisorbed MPDA can desorb

as MAP combined with some resorcinol. The temperature of significant desorption is largely dependent on the acid strength of the zeolite determined (see Table 1). Thus, the mole balance of H-USY at 225°C is at 90 mol% while that of H-Beta is only 48 mol%.

Upon taking a reactor sample at 200°C (using H-Beta) during the ramping period, the mole balance of the bulk solution was only 22% of the initial mole balance. Products of MAP (35 mol%) as well as resorcinol (6 mol%) were observed. The slow increase in the mole balance during the reaction towards the respective final mole balance can be explained by realising that as the reaction proceeds increasing amounts of resorcinol is produced. The resorcinol in turn does not adsorb as strongly onto the zeolites as MPDA or MAP (compare Fig. 1).

H-USY is very unstable and is unsuitable for the described reaction conditions as seen from BET and XRD results discussed above. Similar trends are observed in Fig. 6B showing a large initial conversion of MPDA, however the curve flattens to a plateau after 5 h while at the same time the consecutive reaction from MAP to resorcinol stops. This implies that H-USY is virtually inactive after 5-h reaction time. Amorphous silica-alumina is similar to H-USY. It however does not deactivate as quickly.

H-Beta with 0.78 mmol acid sites per gram has fewer acid sites than H-USY (1.72 mmol/g). Nevertheless, full conversion of MPDA is achieved. Although H-Beta, after the reaction, shows a 73% loss in BET surface area (90% loss for H-USY) with a loss in crystallinity of 60% (100% for H-USY), the fact that the crystal size of H-Beta (< 0.3 μm) is smaller compared to 0.5 μm for H-USY must not be underestimated. Consequently, the external surface area of H-Beta is at least two times larger than that of H-USY. This means that there are at least as many acid sites on the external surface of H-Beta as on H-USY. In conjunction with the higher stability of H-Beta this might explain the higher activity of this catalyst compared to H-USY.

Although the crystallinity and surface area of H-ZSM-5 before and after the reaction are maintained, the resorcinol yield is very poor. The intermediate pore zeolite with a kinetic diameter of 5.6 Å [14] will pose considerable molecular diffusion limitations when considering the space required by the relatively bulky MPDA molecule in admixture with liquid water molecules competing for acid sites in a low Si/Al zeolite [24]. Pore size limitation of H-ZSM-5 is understood when taking *meta*-xylene with a kinetic diameter of 7 Å [12] as a comparison to MPDA in solution.

Due to the low external acid sites on H-ZSM-5, diffusion constraints are enhanced. This is due to the requirement for the formed ammonia to either desorb into the bulk solution or migrate to an acid site inside the pore structure before another organic molecule can take its place. Nevertheless, when performing another reaction using H-ZSM-5 (Si/Al = 22) with very similar properties to H-ZSM-5 (Si/Al = 13) the obtained resorcinol yield was 48%. The only difference between the two zeolites was determined by 4-methylquinoline TPD, where the external surface acid sites of the H-ZSM-5 (Si/Al = 22) was found to be approximately 15 times that of the original H-ZSM-5 (Si/Al = 13). SEM images confirmed this since the crystal size of H-ZSM-5 (Si/Al = 13) ranges between 1 and 3 μm while that of H-ZSM-5 (Si/Al = 22) is 0.5 μm.

Due to the strong acid sites and strong affinity of amines to poison acid sites [25,26], the reaction temperature might have to be increased above 300°C.

5. Conclusion

The mineral acids illustrate the effect of the hydronium ion concentration on the reaction rate, making the amine substitution a second order reaction. Replacement of the mineral acids by zeolites is possible. The activity is found to be H-Beta > H-USY > Si/Al > H-ZSM-5.

Niwa et. al. has found similar trends when studying the reaction where aniline is produced using phenol and ammonia [15]. However, the collapse of the crystal structure is inevitable under the reaction condition mentioned. H-ZSM-5 proves to be the only zeolite that remains stable under the reaction condition, yet its activity remains low, particularly due to reduced acid site accessibility. As a recommendation, the problem can be solved using small H-ZSM-5 crystals with large external surface area and/or raising the temperature above that of the present investigation.

Acknowledgements

Financial support for this research program from AECI, THRIP and FRD is gratefully acknowledged.

References

- [1] R.W. Layer, in: Kirk–Othmer Encyclopedia of Chemical Technology 2, 4th edn., Wiley, New York, 1992, pp. 473–482.
- [2] J. Varaganat, in: Kirk–Othmer Encyclopedia of Chemical Technology 13, 3rd edn., Wiley, New York, 1981, pp. 39–69.
- [3] N.P. Greco, Verfahren zur Herstellung von Resorcin, German Patent 1 808 389 (1968).
- [4] N.P. Greco, Resorcinol Manufacture, US Patent 3 462 497 (1969).
- [5] N.P. Greco, Resorcinol Preparation, US Patent 3 862 245 (1970).
- [6] N.P. Greco, Hydrolysis of meta-Phenylendiamine, US Patent 3 862 246 (1975).
- [7] R.D. Young, in: Kirk–Othmer Encyclopedia of Chemical Technology 2, 3rd edn., Wiley, New York, 1978, pp. 533–535.
- [8] L.F. Fieser, M. Fieser, in: Organic Chemistry, Heath and Company, Boston, 1944, pp. 428–432.
- [9] R.W. Weber, J.C.Q. Fletcher, K.P. Möller, C.T. O'Connor, Microporous Mater. 7 (1996) 15.
- [10] R.J. Cventanovic, A. Amenomiya, Adv. Catal. 17 (1967) 103.
- [11] R.D. Vidic, M.T. Suidan, U.K. Traegner, G.F. Nakhla, Water Res. 24 (1990) 1187.
- [12] S.G. Hedge, R. Kumar, R.N. Bhat, P. Ratnasamy, Zeolites 9 (1989) 231.
- [13] A. Adrien, E.P. Serjeant, in: The Determination of Ionization Constants: A Laboratory Manual, 3rd edn., Chapman & Hall, London, 1983, pp. 136–164.

- [14] E. Narita, N. Horiguchi, T. Okabe, *Chem. Soc. Jpn.* 787 (1985).
- [15] M. Niwa, N. Katada, S. Iijima, H. Igi, *Stud. Surf. Sci. Catal.* 105 (1997) 1227.
- [16] C. Wittrock, H.-H. Kohler, *J. Phys. Chem.* 97 (1993) 7730.
- [17] V.P. Ravi, R.V. Jasra, T.S.G. Bhat, *J. Chem. Technol. Biotechnol.* 71 (1998) 173.
- [18] P.B. Venuto, *Microporous Mater.* 2 (1994) 297.
- [19] R.H. Perry, D. Green, in: *Perry's Chemical Engineers' Handbook*, 6th edn., McGraw-Hill, Singapore, 1984, pp. 3–41.
- [20] M.M.J. Treacy, J.B. Higgins, R. von Ballmoos, in: *Collection of Simulated XRD Powder Patterns for Zeolites*, 3rd edn., Elsevier, New York, 1996.
- [21] D.F. Shriver, P.W. Atkins, C.H. Langford, in: *Inorganic Chemistry*, 2nd edn., Oxford University Press, Oxford, 1994, pp. 188–194.
- [22] B. Kuhlmann, E.M. Arnett, M. Siskin, *J. Org. Chem.* 59 (1994) 3098.
- [23] E.L. Shock, H.C. Helgeson, *Geochem. Cosmochim. Acta* 52 (1988) 2009.
- [24] N.Y. Chen, *J. Phys. Chem.* 80 (1976) 60.
- [25] R.C. Mordi, J. Dwyler, R. Fields, *J. Catal.* 143 (1993) 627.
- [26] F. Fetting, C. Merz, *Chem. Eng. Technol.* 19 (1996) 526.