

Zeolite-Catalyzed Chlorination of Toluene by Sulfuryl Chloride: Activity, Selectivity, and Deactivation of ZSM-5

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The chlorination of toluene by sulfuryl chloride was studied using ZSM-5 as the catalyst. A simple rate expression was developed that provides a reasonable quantitative description of the dependence of the initial rate of reaction upon temperature and reactant ratio. The selectivity did not vary significantly as temperature and reactant ratio changed. The effects of framework silica–alumina ratio and exchange cation were also examined. Changing the exchange cation had essentially no effect upon selectivity, but the catalytic activity was higher when K^+ was used as the exchange cation compared to Na^+ or H^+ . Varying the silica–alumina ratio of the zeolite had a very minor effect upon the activity, but the *para*-chlorotoluene/*ortho*-chlorotoluene product ratio increased from 1–1.5 to greater than 2.5 at the highest silica–alumina ratio. In all cases, the catalyst deactivated rapidly, but an oxidative treatment at elevated temperature fully restored the catalytic activity.

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Key Words: toluene chlorination; ZSM-5; deactivation; *para*-selectivity.

INTRODUCTION

In the chlorination of an alkyl aromatic, such as toluene, chlorine may either be added to the alkyl group or substituted onto the aromatic ring. The chlorination of the alkyl group is a free-radical process, and it can be effectively eliminated by conducting the reaction in the dark and by purging the reaction mixture with dried air (1). The oxygen in the air functions as a free radical trap (1–3). The chlorination of the aromatic ring, an electrophilic substitution process, occurs at the *ortho* and *para* positions. Both *ortho*-chlorotoluene and *para*-chlorotoluene are used in the manufacture of a variety of final products including pharmaceuticals, dyes, etc. *para*-Chlorotoluene is more valuable than the *ortho*-chlorotoluene, and consequently much effort has been expended in the development of *para*-selective processes (4) and catalyst/co-catalyst systems (5–15).

Typical commercial processes make use of homogeneous catalysts, such as $FeCl_3$ or $AlCl_3$, and the products are produced in *para*-chlorotoluene/*ortho*-chlorotoluene (*p/o*) isomer ratios of the order of 0.5 (16). This can lead to *ortho* product production that exceeds market demand; under such circumstances, the excess *ortho* product may actually be burned to recover its heat value (17). Further, a large amount of water may be added to the reaction mixture to neutralize the Lewis acid catalyst and separate it from the chlorinated products. The catalyst cannot be economically recovered after this step, and consequently an aqueous waste is generated (18). The development of chlorination catalysts that can be easily separated from the reaction products and that offer enhanced *para*-selectivity would clearly represent a significant economic and environmental improvement.

Heterogeneous catalysts represent one approach to this challenge because their separation from the products should be facile. Zeolite catalysts have received considerable attention because they additionally may affect the selectivity favorably (1, 3–5, 16–43). Zeolite L, in particular, is reasonably active and very selective; using Cl_2 as the chlorinating agent gives *p/o* ~ 1–1.5 (18, 22, 38) and by adding a co-catalyst selectivities as high as *p/o* = 6.6 have been claimed (32). The use of sulfuryl chloride as the chlorinating agent can give *p/o* ~ 6.0 without the use of a co-catalyst (41). It appears that deactivation is a significant factor limiting commercial utilization of zeolite L as a chlorination catalyst (29, 32, 41).

The *para*-selectivity of ZSM-5 in toluene alkylation is a classic example of shape-selectivity (44–47), making it surprising that relatively few studies of chlorination, halogenation, and related reactions using ZSM-5 have been reported (20, 26, 32–36, 38, 48). At higher temperatures, ca. 448 K, chlorine reacts with benzene over ZSM-5 yielding primarily the addition product, hexachlorocyclohexane, and only ca. 13% substitution products (20). However, at 298 K, ZSM-5 catalyzes bromine substitution; the rate is reported to increase as the Si/Al ratio of the ZSM-5 increases while the selectivity is constant at about *p/o* = 1.7 (26). In contrast, a selectivity of *p/o* = 0.69 is reported for chlorination at

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353 K over K-ZSM-5 with monochloroacetic acid as co-catalyst (33).

In the present investigation, the liquid-phase chlorination of toluene by SO_2Cl_2 has been studied, using ZSM-5 as the catalyst. While molecular chlorine is preferred for commercial processes, sulfonyl chloride is convenient as a laboratory chlorinating agent (49). The activity, selectivity, and deactivation of the catalyst have been studied as a function of temperature and reactant ratio. The effects of varying the framework Si/Al ratio and the identity of the exchange cation have also been examined. Fresh and spent catalysts have been characterized to determine the underlying causes for catalyst deactivation, and a method has been developed whereby the catalytic activity and selectivity can be fully restored.

METHODS

The procedures for studying rate and selectivity and for characterization of the catalysts used in this investigation are essentially the same as those employed in previous studies of zeolite-catalyzed chlorination of toluene by SO_2Cl_2 , except that ZSM-5 has been used as the catalyst. The experimental methods are summarized briefly here, as they have been reported more completely elsewhere (1, 41, 42, 50). Since the catalysts differ from those used in previous studies, their preparation is described in greater detail.

Catalyst Preparation

The ZSM-5 used to prepare the catalysts came from three sources. Two samples were synthesized in the lab using the procedure described by Chen *et al.* (51). The difference between the two is the silica–alumina ratio. These zeolites will be designated as ZSM-5(33) and ZSM-5(97). The values in parentheses are the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios determined experimentally using inductively coupled plasma atomic emission spectroscopy (ICP–AES). Another sample, ZSM-5(356), was obtained from UOP in the Na^+ -exchanged form; its silica–alumina ratio, 356, was also determined experimentally by ICP–AES. The sample ZSM-5(50) was obtained from Zeolyst International in the NH_4^+ -exchanged form with a manufacturer-specified silica–alumina ratio of 50.

The first step in the preparation of each catalyst involved the calcination of the as-synthesized or as-received material. A quantity of zeolite was placed in a muffle furnace in a porcelain dish and heated at a rate of 1 K min^{-1} from room temperature to 378 K and held at this temperature for 2 h. Next, the oven temperature was increased at a rate of 1 K min^{-1} to 773 K. It was then held at this temperature for 18 h. This procedure is expected to burn out any template (tetrapropyl ammonium ions) remaining in the pores following synthesis, or, in the case of ammonium-exchanged ZSM-5, it is expected to decompose the ammonium cations, leaving protons as the exchange cations.

The next step in the preparation of a given catalyst was ion exchange. A 1 M solution of NaCl (99 + %, Aldrich, A.C.S. reagent grade), KCl (99 + %, Aldrich, A.C.S. reagent grade), or NH_4Cl (99.5 + %, Aldrich ACS reagent grade) was prepared, and 1 L of this solution was placed in a 1000 mL flask fitted with a mechanical stirrer and heating mantle. An amount of zeolite, not exceeding 10 g, was added to the 340 to 350 K solution and continuously stirred for 24 h. The zeolite was recovered by vacuum filtration. The preceding exchange procedure was repeated to ensure that most of the exchangeable cation had been replaced by the desired cation. The zeolite was again recovered by vacuum filtration and the exchange procedure was repeated a second time, except that doubly distilled water was used. This “washing” step was used to remove any bulk chloride salts remaining from the two ion exchanges. Once again, the zeolite was recovered by vacuum filtration, after which the wet filter cake was dried overnight in a vacuum oven at room temperature. Finally, the resulting zeolite was calcined again using the procedure already described. In this case, no template was expected to be present, but for ammonium-exchanged samples, the second calcination would again be expected to convert them to a proton-exchanged form.

Catalyst Characterization

The chemical composition of the samples, except ZSM-5(50), was measured by ICP–AES before their use and at selected times after their use. Briefly, the zeolite was mixed with a flux consisting of LiBO_2 and $\text{Li}_2\text{B}_4\text{O}_7$ and fused into a glass bead at 1273 K. The bead was then dissolved in nitric acid and the resulting solution was analyzed in the instrument. Standards 7 and 19 from Plasma Chem Corp. were used for calibration.

X-ray diffraction (XRD) was used to verify the crystal structure and to characterize relative changes in the crystallinity of the samples. Powder diffraction data were collected over a 2θ range from ca. 3.2° to 84.5° using a Stoe diffractometer and $\text{Cu K}\alpha$ radiation. Highly crystalline MgO was mixed with the samples and used as an internal standard. Comparison of the powder XRD patterns to those for ZSM-5 reported by Szostak (52) revealed no features other than those attributable to ZSM-5 or to the MgO used as an internal standard. Relative crystallinity was calculated using the method described by Szostak (52).

The apparent BET surface area was measured using a volumetric adsorption apparatus. Stepwise thermal desorption of ammonia and sulfur dioxide were also used to characterize the adsorption sites on the samples. Typically the samples, housed in a simple tubular reactor, were first heated to 373 K at a rate of 2 K min^{-1} , held at that temperature for 2 h, heated further to 873 K at the same rate, held there for 1 h, and cooled to room temperature, all under

flowing, purified He. The reactor was then purged with the gas to be adsorbed for 5 min, after which it was isolated from the rest of the system while it contained the adsorbing gas at a pressure of 50 psig. The gas was allowed to adsorb for 30 min before helium flow was reestablished. Sufficient time was taken to establish a stable baseline on the thermal conductivity detector attached to the reactor outlet. The temperature was then increased rapidly to 323 K and held at that temperature until the detector signal returned to baseline. The detector response during this period was integrated; the area was assumed to be proportional to the amount of desorbed gas. The temperature was then increased by 50 K and held until a stable baseline was achieved, again integrating the detector response. This was repeated, initially using steps of 50 K and later steps of 100 K, to a final temperature of 873 K.

Rate and Selectivity Measurements

Prior to use in reaction studies, toluene (99%, Aldrich) was stored over dried molecular sieve 4A to eliminate any excess moisture. Sulfuryl chloride (97%, Aldrich) was distilled twice, no more than 4 h before its use. Air was used as a reactor purge gas; it was passed through a bed of activated molecular sieve 4A, activated carbon, and Drierite in order to eliminate moisture. High-purity helium, used as carrier gas in the gas chromatograph (gc), was further purified using a Supelco high-capacity carrier gas purifier. In a typical experiment using this purge and operating in the dark, the final mole fractions of *ortho*- and *para*-chlorotoluene were of the order of 5%; the mole fractions of benzyl chloride and combined dichlorotoluenes were on the order of 0.04 to 0.05%.

The reactor system consisted of a three-necked, round-bottomed flask. The dried air entered through one neck and was introduced into the liquid through a fritted tube. A mechanical stirrer entered through a second neck, and the gas exited through a condenser attached to a third neck. In this way, the loss of liquid was minimal. In a typical run, the catalyst was first loaded into the empty reactor and dried *in situ* at 573 K for 18 h. After cooling to reaction temperature, the toluene was charged and the air purge started. Freshly distilled sulfuryl chloride was then added to start the reaction. The reactor was operated in the dark in a semi-batch mode, typically for 2 h. Small liquid samples (200 μ L) were withdrawn at selected times using a syringe. The withdrawn liquid was immediately added to a small volume of quench solution (2.0 mL of *n*-hexane and 2.0 mL of aqueous 5 M NaOH, 0.63 M Na₂S₂O₃), which stopped the reaction and extracted the organics into the hexane. The organic component was analyzed using a gc with an Alltech SE-54 Econo-Cap capillary column and a flame-ionization detector interfaced to a computer via the program PeakSimple (SRI). The use of separately prepared standard solutions allowed calculation of the number of moles of toluene, benzyl

chloride, *ortho*-chlorotoluene, and *para*-chlorotoluene in the reactor at the time when the sample was withdrawn.

At the end of a kinetic run, the catalyst was typically recovered via centrifugation. In some cases, the recovered catalyst was immediately used in another kinetic run. To do so, it was returned to the reactor in a small volume (ca. 5 mL) of toluene. Dried air flowed through the reactor overnight, causing the toluene to evaporate (no coolant was flowing in the condenser during this period). By the next morning, the catalyst was dry, and a new run was started by adding toluene and proceeding from that point as before. When the catalyst was not going to be used in any additional kinetic runs, its final mass was determined and it was stored in a desiccator pending additional characterization.

Kinetic Data Analysis

The raw data included the temperature (all runs were isothermal); the initial amounts of zeolite, toluene and sulfuryl chloride charged to the reactor; and the measured number of moles of toluene, benzyl chloride, *ortho*-chlorotoluene, and *para*-chlorotoluene at the sampling times for that run. The following equations were used to analyze the data:

$$n_i = n_i^0 - a[1 - \exp(-bt)] \quad [1]$$

$$r_i = \frac{1}{\omega} \frac{dn_i}{dt} = -\frac{ab}{\omega} \exp(-bt) \quad [2]$$

$$r_i^0 = -\frac{ab}{\omega} \quad [3]$$

$$(p/o)_{\text{integral}} = \frac{n_{p-C_7H_7Cl}}{n_{o-C_7H_7Cl}} \quad [4]$$

$$(p/o)_{\text{instantaneous}} = \frac{r_{p-C_7H_7Cl}}{r_{o-C_7H_7Cl}} \quad [5]$$

Equation [1] was fit to the data for the moles of toluene versus time. In that equation n_i is the moles of species i at time t , n_i^0 is the number of moles charged to the reactor, and a and b are adjustable constants. This empirical equation was found to fit the data very well in this study as well as in several past studies using different zeolites (41, 42). Equation [1] was similarly fit to the data for the moles of each of the chlorotoluenes as a function of time. The rates of toluene consumption, *ortho*-chlorotoluene formation, and *para*-chlorotoluene formation were found by taking the derivative of Eq. [1] with respect to time and normalizing. This is shown in Eq. [2] where r_i is the instantaneous rate of production of species i and ω represents the normalization factor. In this study, all rates are expressed as turnover frequencies, taking one site to be associated with each aluminum cation in the zeolite. That is, in this study ω has been set equal to the moles of aluminum present in the catalyst charged to the reactor. By setting $t = 0$ in Eq. [2], the instantaneous initial rate of production, r_i^0 ,

could be determined as given in Eq. [3]. The selectivity was characterized using either the integral p/o ratio, Eq. [4], or the instantaneous p/o ratio, Eq. [5].

RESULTS AND DISCUSSION

Activity, Selectivity, and Deactivation of Na-ZSM-5(356)

Figure 1 presents the results from a typical experiment. The moles of toluene, *ortho*-chlorotoluene, and *para*-chlorotoluene present in the reactor at each sampling time are plotted against the elapsed time since the start of the experiment. The particular data shown are from a run at 323 K using Na-ZSM-5(356), but they are representative of all runs performed in this study. It is apparent from the figure that the catalyst deactivates rapidly. At the end of the two-hour experiment the number of moles is not changing very much with time, yet there is a large amount of unreacted toluene remaining. The reaction is not nearing thermodynamic equilibrium, even at the end of the experiment, suggesting a severe deactivation occurs.

This deactivation is also apparent when the rate of reaction is calculated using Eqs. [1] and [2]. The fit of equation [1] to the experimental data is shown in Fig. 1; the fitting parameters for toluene for this particular run were $a = 0.0123$ mol and $b = 0.0392$ min⁻¹. These parameters can be used to calculate the rate of reaction over the course of the reaction using equation [2]. The result is shown in Fig. 2, along with several other runs. A replicate run using a fresh catalyst also is shown to indicate the typical variability from run to run. While there is some variability in the initial rates, both fresh samples deactivate rapidly over the course of the run. The figure also shows that when the catalyst was recovered at the end of the experiment and immediately reused in additional successive experiments, virtually none

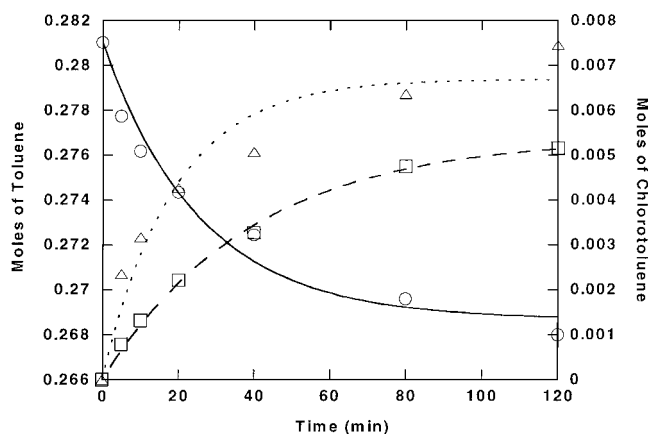


FIG. 1. Moles of toluene (circles), *ortho*-chlorotoluene (squares), and *para*-chlorotoluene (triangles) in the reactor during the course of chlorination by sulfuryl chloride (initially 0.281 moles) using 1 g Na-ZSM-5(356) catalyst at 323 K. The symbols represent the experimental data; the lines show the fit of Eq. [1] to the data.

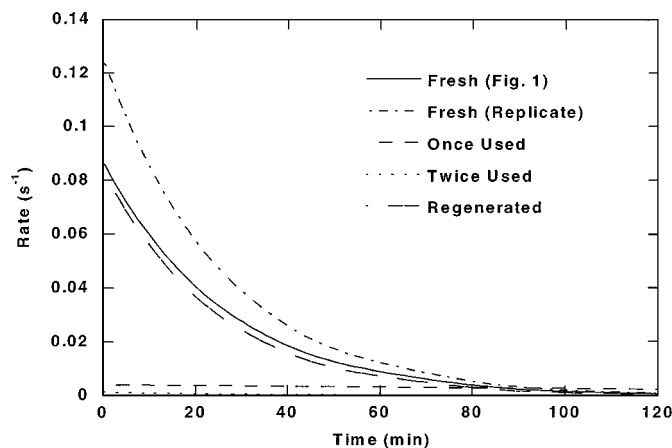


FIG. 2. Rate of reaction during chlorination by sulfuryl chloride using Na-ZSM-5(356) at 323 K in a series of three back-to-back runs without regeneration and for a regenerated catalyst. (A replicate run is shown for the fresh catalyst.)

of the lost activity was regained. The initial rates in the back-to-back experiments were one and one-half and two orders of magnitude smaller than the initial rate with fresh catalyst. Rapid deactivation was also observed when using Na-X, Na-Y, and NaK-L zeolites as catalysts (41, 42). For those catalysts, fouling of the pores accompanied by dealumination and eventual structural degradation was identified as the cause for the deactivation. There are significant differences between ZSM-5 and these other zeolites.

A major difference between ZSM-5 and the other zeolites is that it proved possible to completely restore the activity of ZSM-5. After use in three consecutive experimental runs, the zeolite was recovered and placed in a ceramic boat inside a tube furnace. The sample was then heated in dried air in stages to 773 K over 8 h and held there for 6 h. The so-treated catalyst was then used again in a chlorination experiment, and the rate is shown in Fig. 2. It can be seen that the activity profile is virtually identical to that of the fresh sample. Table 1 presents the results of chemical

TABLE 1

Results of Catalyst Characterization

Catalyst	State	Silica/alumina ratio	Na/Al or K/Al	Apparent BET area (m ² g ⁻¹)
Na-ZSM-5(33)	Fresh	33	0.79	253
Na-ZSM-5(97)	Fresh	97	1.00	351
	Used twice			203
	Regenerated			336
Na-ZSM-5(356)	Fresh	356	1.00	423
	Used twice			256
	Regenerated			389
K-ZSM-5(33)	Fresh	34	0.76	
H-ZSM-5(33)	Fresh	28		
K-ZSM-5(50)	Fresh			419

analysis and apparent BET area measurements on several catalysts. It can be seen in the table that the apparent surface area of the ZSM-5 sample decreased very significantly as it deactivated. The regeneration treatment restored the apparent BET surface area of the ZSM-5 catalysts to their fresh values. A similar loss in apparent surface area was also observed with zeolites X, Y, and L, but with those materials, the regeneration treatment did not restore the apparent surface area to its initial value. To within experimental error, the relative crystallinity of the ZSM-5 samples did not change upon repeated use. This, too, is different from the other materials, particularly zeolites X and Y, where the crystallinity decreased substantially upon repeated use.

These results suggest that the deactivation of ZSM-5 involves fouling of the pores, but that it does not involve dealumination and structural degradation. These latter processes could not be reversed by an oxidation treatment like the one used here resulting in restored activity and apparent surface area. It is suspected that polychlorinated toluenes are formed within the pores during a chlorination experiment. Indeed, in other experiments involving the chlorination using molecular chlorine as the chlorinating agent the used catalyst was subjected to a solvent extraction procedure using hexane at 50°C. Polychlorinated aromatics were detected in the extract in amounts as high as 31 $\mu\text{mol g}^{-1}$ of catalyst. These higher molecular weight species may then accumulate and block access to the pores, resulting in deactivation of the catalysts. The regeneration process is expected to combust such residues and thereby to make the pore structure accessible again. The superior resistance of ZSM-5 to structural degradation is not unexpected (53, 54); it has been reported that ZSM-5 can be exposed to added HCl at 773 K without affecting the activity or selectivity of the catalyst for nucleophilic substitution of chlorobenzene (54).

The fits of Eq. [1] to the data for *ortho*-chlorotoluene and *para*-chlorotoluene in Fig. 1 can be used to calculate the instantaneous selectivity during the reaction (p/o ratio) using Eqs. [2] and [5]. The instantaneous selectivity calculated in this way has been shown to be a better indicator of catalyst performance over time than is the measured p/o ratio at each sampling point (41). The measured p/o represents an integral over the entire experiment, and when the catalyst is deactivating rapidly, it can be dominated by the initial selectivity. Consequently, the integral selectivity is not characteristic of the selectivity at the time of sampling. Figure 3 therefore shows the instantaneous selectivity during the same set of experiments shown in Fig. 2. The initial selectivity is quite good, $\sim p/o = 2.6$ (and even higher for the regenerated catalyst). These initial selectivities are higher than those reported for bromination (24–27) and for chlorination using molecular chlorine with a

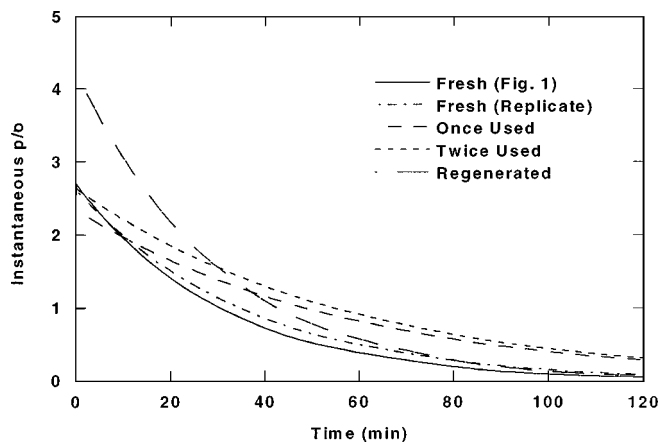


FIG. 3. Instantaneous selectivity during chlorination by suluryl chloride using Na-ZSM-5(356) at 323 K in a series of three back-to-back runs without regeneration and for a regenerated catalyst. (A replicate run also is shown for the fresh catalyst.)

monochloroacetic acid co-catalyst (33). This may be due, at least in part, to the use of suluryl chloride as the chlorinating agent, in that chlorination with suluryl chloride often leads to higher *para*-selectivity (41) than chlorination with Cl_2 .

When NaK-L and other zeolites were re-used without regeneration, the selectivity was observed to be much lower than with the fresh catalyst. In the present case, the selectivity is essentially the same. This might be a consequence of the differences in mode of deactivation; the dealumination process may have a more pronounced effect within the pores, forcing a larger percentage of the reaction to occur on the external surface. The fouling process, in turn, may affect the external and internal surfaces equally, but the greater amount of internal surface area may lead to a greater percentage of the reaction occurring on the internal surface (where selectivity is higher) as the catalyst deactivates. The higher initial selectivity after regeneration is not understood at present, but it can be seen that it is rapidly dissipated.

The most significant result to this point is the regenerability of ZSM-5. All other zeolites studied have deactivated irreversibly. The relatively high selectivity is a second benefit. NaK-L gives higher selectivity under certain conditions, but it deactivates and cannot be regenerated. The silica-alumina ratio in the ZSM-5 framework and/or the identity of the exchange cation was next varied in order to study their effect upon activity, selectivity and deactivation. In all cases, it was observed that the catalysts deactivated in the same manner as already discussed. Therefore, in the following sections only the initial activity and initial selectivity will be considered. These properties were calculated in the same way as above, but only the values at $t = 0$ will be considered.

Effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio and Exchange Cation upon Na-ZSM-5 Performance

Sodium-exchanged forms of ZSM-5 with three different silica–alumina ratios (33, 97, and 356) were prepared and characterized. The data in Table 1 suggest that the ZSM-5(33) sample might contain extra-framework aluminum. Specifically, for Na–ZSM-5(33) the Na/Al ratio is less than unity and for K–ZSM-5(33) the K/Al ratio is less than unity and essentially the same as the Na/Al ratio of Na–ZSM-5(33). When all aluminum is present in the zeolite framework, the cation/aluminum ratio should equal unity. This expectation is met for the other two samples, Na–ZSM-5(97) and Na–ZSM-5(356), but not for ZSM-5(33). Additionally, the apparent BET surface area of Na–ZSM-5(33) was lower than expected and lower than that of the other two samples. It seems likely that these materials contain small particles of Al_2O_3 that are not part of the framework. Nonetheless, the results for ZSM-5(33) are presented here with the other two samples. Additionally, K^+ - and H^+ -exchanged forms of ZSM-5(33) were prepared and catalytically evaluated prior to the characterization of their chemical composition, and the results for these samples are included here, as well.

The initial rate of reaction for the fresh samples is shown in Fig. 4. Based upon the mechanism for homogeneously catalyzed chlorination, it is assumed that the exchange cations in these catalysts function as Lewis acid sites and that they are the active sites for reaction. Consequently, it is expected that the turnover frequencies used here, which are based upon the aluminum content (equal to the sodium content), should be equal if the composition and temperature are equal. The data show that this is true for Na–ZSM-5(356) and Na–ZSM-5(97), but the rate for Na–ZSM-5(33) is lower. If, as suspected, the last sample contains extraframework aluminum, then there may be two reasons for its lower turnover frequency. First, the number of ex-

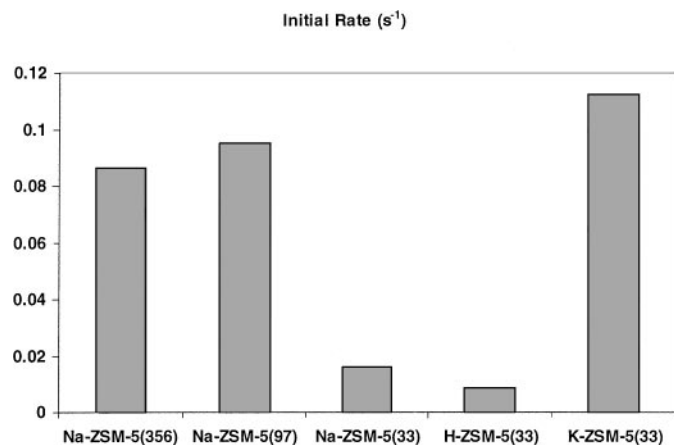


FIG. 4. Initial rate of chlorination of toluene by sulfuryl chloride at 323 K using fresh samples of ZSM-5 with varying silica–alumina ratios and with different exchange cations.

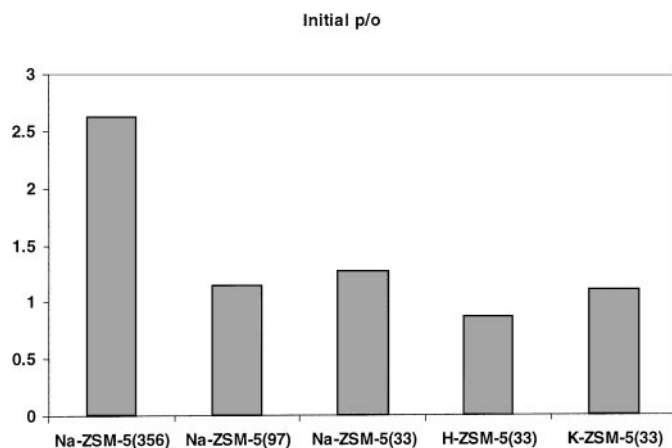


FIG. 5. Instantaneous initial selectivity during chlorination of toluene by sulfuryl chloride at 323 K using fresh samples of ZSM-5 with varying silica–alumina ratios and with different exchange cations.

change cations will be lower than the number of aluminum atoms in the framework, and hence the turnover frequency in the figure will be underestimated. Second, the presence of the extraframework material may block access to some fraction of the pores, leading to further underestimation of the turnover frequency. The apparent BET area supports this possibility.

In comparing different exchange cations, the same sample of ZSM-5(33) was used, and so these factors are expected to be the same for all three cations. The turnover frequency for the K^+ -exchanged sample is greater than that of the H^+ - and Na^+ -exchanged forms. Stepwise thermal desorption of ammonia and of sulfur dioxide did not reveal any differences between the catalysts that could be correlated with activity or selectivity differences. The higher activity of K–ZSM-5(33) was replicated in a second experiment using fresh catalyst. However, it must be noted that the activity of K–ZSM-5(50) is of the same order of magnitude as that of Na–ZSM-5(33). There may be significant differences between the two samples of ZSM-5 with respect to uniformity of composition as well as crystallite size since the ZSM-5(33) was synthesized in the lab while the ZSM-5(50) was purchased from Zeolyst. The trend shown in Fig. 4 involves a single batch of the same zeolite. It might prove interesting to prepare and evaluate H- and Na-exchanged forms of ZSM-5(50) to see whether the same trend is observed with that material.

The initial selectivity for all the samples is shown in Fig. 5. The selectivity was much higher for the ZSM-5 with the highest silica–alumina ratio and was apparently not affected by the exchange cation in the ZSM-5(33) catalysts. The time constant, b , in Eq. [1] can be used as a crude indicator of the rate of deactivation. Figure 6 does not reveal any systematic variation in the time constant, consistent with the observation that each catalyst had deactivated by nearly two orders of magnitude over the course of a two-hour

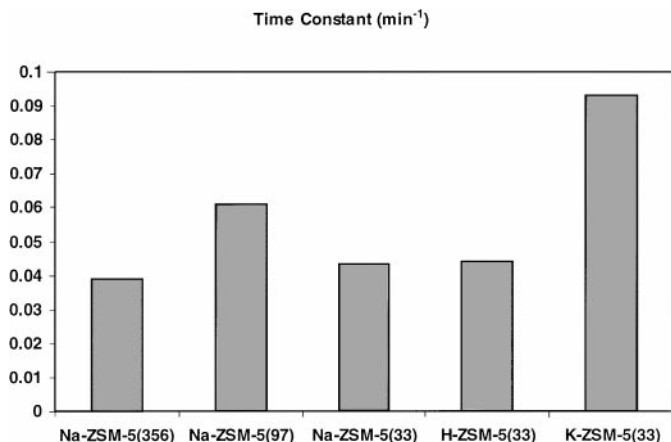


FIG. 6. Time constant, b , from Eq. [1] for the chlorination of toluene by sulfuryl chloride at 323 K using ZSM-5 samples with varying silica-alumina ratios and exchange cations.

kinetic run. In summary, the highest activity was associated with the K^+ -exchanged form of ZSM-5 while the highest selectivity was associated with high silica-alumina ratio. This leads to a trade-off in catalytic performance in that the highest selectivity is realized with a catalyst with few sites per gram.

Effects of Temperature and Reactant Ratio upon K-ZSM-5(50) Performance

The effects of temperature and reactant ratio were studied using K-ZSM-5(50) in a series of experiments wherein the total feed concentration was fixed, but the molar ratio of toluene to sulfuryl chloride was varied. Measurements were made at ratios of 9:1, 1:1, and 1:9 with each ratio studied at 313, 323, and 333 K. The initial rates are shown in Fig. 7. The data are not consistent with a simple sec-

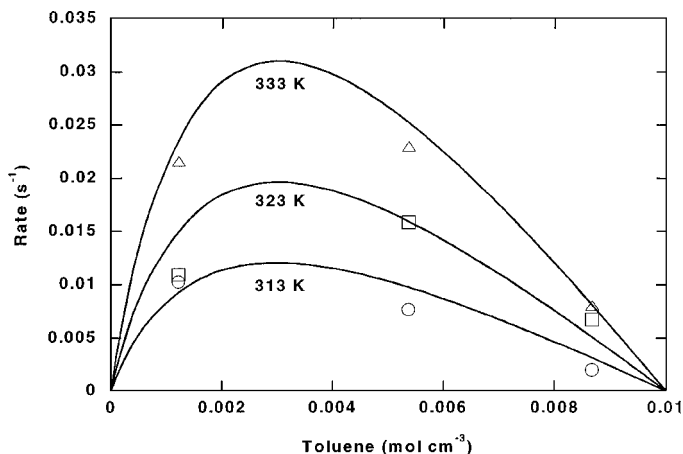
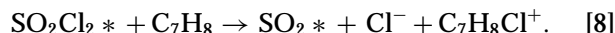
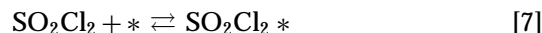
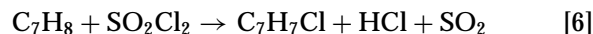


FIG. 7. Initial rate of chlorination of toluene by sulfuryl chloride using K-ZSM-5(50) at different temperatures and with different ratios of toluene to sulfuryl chloride. The symbols represent the experimental data; the lines show the fit of the kinetic model to the data.

ond order rate expression, so other rate expressions were considered. In homogeneous catalytic chlorination using a Lewis acid, molecular chlorine interacts with the catalyst to generate a positively charged chlorine that can effectively attack the aromatic ring. The rate-limiting process is usually taken to involve the interaction between the activated chlorine atom and toluene, leading to the formation of an arenium cation (55–57):



The chlorinating agent is sulfuryl chloride, Eq. [6], but by direct analogy, Eqs. [7] and [8] could be written for the heterogeneous catalytic reaction. Equation [7] shows equilibrated adsorption of sulfuryl chloride, and Eq. [8] shows the rate-limiting formation of an arenium cation. A number of different rate expressions can be derived from this reaction sequence, including the following:

$$-r_{C_7H_8} = \frac{k K C_{C_7H_8} C_{SO_2Cl_2}}{1 + K C_{SO_2Cl_2}} \quad [9]$$

Too few conditions were studied to permit a serious mechanistic interpretation of the kinetics. Equation [9] was found to describe the limited kinetic data adequately, but here it will be treated as an empirical rate model. The coefficients k and K were assumed to vary according to Arrhenius-like expressions, and the resulting four-parameter model was fit to the nine experimental data. The result is shown in Fig. 7. The fit is reasonable, but additional data using a wider range of compositions and temperatures would be necessary to firmly establish its validity, and other kinds of experiments would be required in order to probe the details of the reaction mechanism. For the fit shown in Fig. 7, the activation energy associated with the rate coefficient, k , is 41.7 kJ mol⁻¹, and the enthalpy change associated with K is equal to 1.7 kJ mol⁻¹. In comparison, an apparent activation energy of 56.9 kJ mol⁻¹ has been reported for the uncatalyzed chlorination of toluene by Cl₂ in acetic acid (58) and 22.6 kJ mol⁻¹ has been reported for chlorination using Cl₂ and an AlCl₃ catalyst in CCl₄ solution (59).

Table 2 shows that the selectivity was essentially the same for all temperatures and feed ratios. This differs from the behavior of NaK-L where the p/o increased to over 6 at high concentrations of sulfuryl chloride. It was speculated that with NaK-L, the effect of high SO₂Cl₂ concentration upon selectivity was related to its high dielectric constant. This might provide a more polarizable environment around the toluene and thereby affect selectivity in the same way that varying the solvent can affect selectivity. Extending this reasoning, it is possible that the pores of ZSM-5 are too

TABLE 2
Effect of Reactant Ratio and Temperature Upon Deactivation and Selectivity of K-ZSM-5(50)

Toluene concentration mol cm ⁻³	Constant <i>b</i> in Eq. [1] (min ⁻¹)			Initial <i>para</i> -/ <i>ortho</i> -chlorotoluene selectivity		
	313 K	323 K	333 K	313 K	323 K	333 K
0.00868	1.88×10^{-03}	9.82×10^{-03}	5.90×10^{-03}	1.4	1.4	1.4
0.00537	7.44×10^{-03}	8.76×10^{-03}	8.99×10^{-03}	1.4	1.3	1.2
0.00121	3.18×10^{-02}	2.73×10^{-02}	3.72×10^{-02}	1.5	1.5	1.3

narrow to allow additional SO₂Cl₂ molecules to approach toluene closely enough to produce a similar effect.

Finally, Table 2 shows that there are some trends in the deactivation behavior as the composition is varied. Generally, at each temperature the constant, *b*, increases as the toluene concentration decreases (and the sulfuryl chloride concentration increases). This is consistent with the idea that deactivation is caused primarily by formation of polychlorinated aromatics that block the pores. As the concentration of chlorinating agent increases and the concentration of toluene decreases, it becomes more likely that polychlorinated materials will form, and thus it would be expected that the catalysts would deactivate more rapidly.

ZSM-5 is a more promising catalyst for chlorination of toluene than Na-X, Na-Y, or NaK-L mainly because it can be regenerated after deactivation whereas the others cannot. However, the reaction takes place at near-ambient conditions while the regeneration requires treatment at an elevated temperature in air or oxygen. Furthermore, the rate of deactivation is so high that a continuous process could only be implemented if catalyst regeneration and recycle were integrated into it. This kind of integration is very elegantly employed in the catalytic cracking process. For chlorination, the extreme differences in temperature and phase between the reaction and the regeneration stages would appear to make such integration practically impossible. It might be interesting to determine whether the chlorination process could be effected in the vapor phase, in which case it would be easier to integrate catalyst regeneration with the reaction process.

CONCLUSIONS

ZSM-5 catalyzes the chlorination of toluene by sulfuryl chloride, but like several other zeolites, it deactivates rapidly during the reaction. The deactivation appears to be caused by the accumulation of polychlorinated products that block access to the pores. Exposure to air at elevated temperature fully restores both the catalytic activity and the selectivity. The initial rate of reaction is highest when potassium is the exchange cation. A rate expression has been presented that permits modeling of the initial kinetics with reasonable quantitative accuracy. The selectivity is not significantly affected by the reactant composition, the

temperature, or the identity of the exchange cation, but it is significantly higher on a high-silica form of ZSM-5 than on other samples of the same zeolite.

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