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Kinetics of alkylation of phenol with methanol over Ce-exchanged NaX zeolite

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The alkylation of phenol with methanol was investigated in vapor phase over a series of cerium-exchanged NaX zeolite with Ce loadings ranging from 0 to 10.43 wt%. The catalyst MX-4 with 8.86 wt% cerium was found to be the best one with total cresols selectivity of 72% at a temperature of 573 K and MeOH to phenol mole ratio of 4:1. The catalyst was also found to be quite stable in the operating range investigated. It was established that the stronger acid sties are required for C-alkylation compared to O-alkylation. From the study of the effects of various parameters, the optimum operating condition for highest cresols selectivity were determined as: MeOH to phenol mole ratio, 4:1; temperature, 623 K; space-time, 10.2 kg h/kgmole under atmospheric pressure. From the kinetic analysis of the experimental data, the apparent activation energy for the reaction was determined as 57.2 kJ/mole.

KEY WORDS: alkylation; phenol; methanol; Ce-exchanged NaX zeolite; cresol; anisole.

1. Introduction

Alkylation of aromatic substrates catalyzed by solid acids such as zeolites constitutes a class of reactions having both academic and industrial importance. Alkylation of phenol is one of such important alkylation reactions producing both C-alkylated products and O-alkylated product [1]. The cresols are used as chemical intermediate for the manufacture of pharmaceuticals, agrochemicals, resins, various additives, polymerization inhibitors, antioxidants and various other chemicals [2–4]. Anisole and other methyl aryl ethers are used as octane boosters for gasoline [5,6].

The alkylation process normally requires Friedel-Craft catalysts such as HCl containing $AlCl_3$, BF_3 and $TiCl_4$. Several problems are associated with these catalysts such as toxicity, corrosiveness, low reaction selectivity, and disposal of effluents. In recent years, catalyst chemists have turned their attention to the use of environment-friendly catalysts such as zeolites in place of mineral acid to fit in well in the concept of environmentally benign system for eco-friendly processes. Vapor phase methylation of phenol has been investigated over various oxides [7–12], zeolites [13–16], phosphates [17], sulfates [18], mixed metal oxides and Al containing hydrotalcites [19–21]. Moreover, the alkylation of phenol is reported to be very sensitive to the acidic and basic properties of the catalysts [1,7,22,23]. Alkylation of phenol with methanol over zeolites produces both C-alkylated (cresols and xylenols) and O-alkylated (anisole) products and cresols being the major product [15]. It is a well-established fact that strong acidity favours the C-alkylation while basic catalysts are found to promote O-alkylation [7,14,24]. Accordingly, anisole formation requires sites with lower acid strengths compared to those necessary for cresol formation [25]. Moreover, many authors using the acidic catalyst reported that high selectivity to anisole in O-alkylation of phenol with alcohol was found in low conversions and the main reactions were ring alkylation to produce cresol and xylenol [18,26,27]. Especially, C-alkylated product is the main product at higher conversions indicating that selectivity is a function of conversion for the acid catalyst.

A review of the literatures also reveals very limited use of more versatile zeolite X for phenol methylation reaction. Moreover, replacement of Na ions of synthetic zeolites (e.g., X and Y) with polyvalent cations from rare earth metals (La, Ce, etc.) has been reported to give materials of superior catalytic activity [28–30]. It was, therefore, thought desirable to study this commercially important reaction using zeolite NaX as catalyst modified by exchanging sodium ions with cerium ions. However, the main objective is to study the effect of cerium loading on acidity and catalytic activity of the exchanged zeolite for the said alkylation reaction. A further objective is to study the effects of various process parameters on the conversion of phenol and the selectivities of different products and to find out optimum conditions for maximum cresols selectivity.

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2. Experimental

2.1. Materials

The NaX zeolite used in the present study was obtained from S. D. Fine Chemicals Pvt. Ltd., India. It was in the form of 1.5 mm extrudate. Phenol and methanol used in this study were both obtained from Qualigens Fine Chemicals, Mumbai, India. Both of these chemicals were of 'Analytical Reagent' grade.

2.2. Catalyst preparation

The NaX zeolite was first dried to remove moisture and kept ready for cation exchange. The catalyst particles were first refluxed with 2% NH_4NO_3 solution for 6 h, for three times, each time with a fresh 2% NH_4NO_3 solution with subsequent calcining of the particles at 623 K in between. The catalyst particles thus obtained after a total of 18 h heating and containing about 5–6% of Na (determined by flame photometer) were boiled with a required percentage of cerium ammonium nitrate solution for about 16 h, thereby modifying the HX zeolite [31]. This was then dried and calcined at 623 K and ready for use in the reactor. The X-ray diffraction pattern of the Ce-exchanged NaX zeolite exactly matched with that of the virgin NaX zeolite (Figure 1), indicating no structural change during ion exchange. Catalysts treated with 2, 5, 7, 10 and 12% cerium ammonium nitrate solutions were designated as MX-1, MX-2, MX-3, MX-4 and MX-5,respectively.

2.3. Determination of cerium in the exchanged catalysts

Accurately 2 g of freshly calcined catalyst containing cerium was taken in a conical flask and digested with concentrated HCl for about an hour. The digested material was then diluted with distilled water and filtered through a filter paper. The filtrate containing the cerium in solution was transferred to a 500 mL beaker, and its volume was raised to about 250 mL by adding distilled water. To this solution, 50 mL of saturated oxalic acid solution was added, which gave rise to a white precipitate of cerium oxalate. The precipitate was filtered through a Whatman no. 40 ashless filter paper and was thoroughly washed with distilled water. The white precipitate along with the filter paper was then ignited over a previously weighed silica crucible at 1173 ± 10 K to a constant weight. On heating, cerium oxalate was converted to Ce_2O_3. The percentage of cerium was then calculated from the weight of Ce_2O_3 [32].

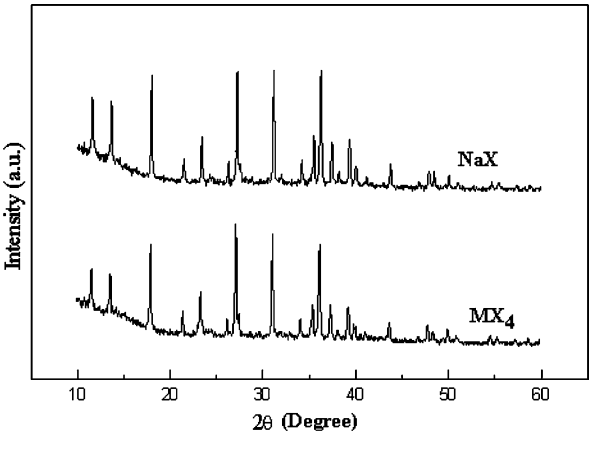


Figure 1. X-ray diffraction patterns of virgin and Ce-exchanged NaX zeolite.

2.4. Determination of BET surface area

The surface areas of various Ce-exchanged NaX as well as that of parent NaX zeolites were measured by BET method (Flowsorb-II, Micromeritics, 230–000000–00, Nor Cross, GA, USA).

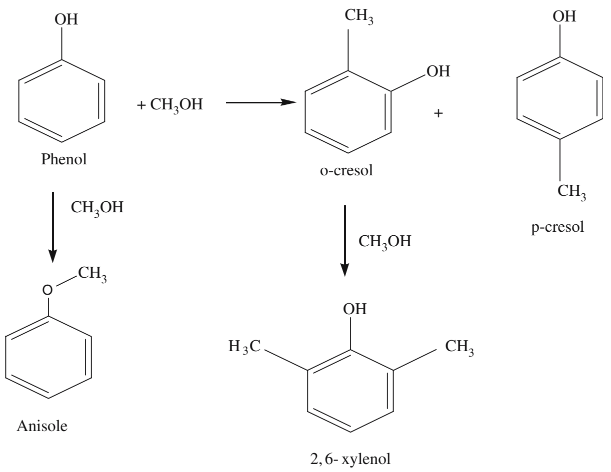
2.5. Temperature programmed desorption (TPD) of ammonia

Ammonia TPD of the modified catalysts was performed in a CHEM-BET 3000 instrument (Quanta Chrome, USA). In a typical experiment, 0.1 g of the powdered catalyst sample was taken inside a quartz "U" tube and degassed at 723 K for 1 h with helium gas flow followed by cooling to low temperature (~303 K). The gas flow was then changed to 1 mol% ammonia in nitrogen for 1 h. After this, the helium gas flow was resumed once again for 30 min at the same temperature to remove loosely adsorbed ammonia molecules from the catalyst surface. The catalyst sample was then heated to 373 K under helium flow and kept at that temperature until the steady state was attained. The sample was then heated from 373 to 1173 K at a heating rate of 10 K/min. The desorbed ammonia was detected by a TCD analyzer.

2.6. Experimental procedure and product analysis

The catalytic experiments were carried out in a fixed-bed, continuous down-flow cylindrical stainless steel (SS 316) tubular reactor (0.025 m ID and 0.33 m in length). The reactor was fitted with a preheater in the upstream and a condenser at its outlet. The reactor was heated electrically from outside and insulated to prevent heat loss. In a typical run, about 0.03 kg of catalyst was loaded into the reactor and supported by inert beads on either side of the bed. The bed temperature was measured by a thermocouple placed in a thermowell extending from the top of the reactor to the centre of the bed. The aromatic-alcohol mixture was introduced with the help of a metering pump and vaporised in the preheater before contacting the catalyst.

The reactant vapors along with nitrogen entered the reactor from the top. The product vapors, along with unreacted reactants, were condensed in the condenser and the liquid samples collected were analyzed in a Gas



Scheme 1.

Chromatograph unit fitted with a 4.2 m × 3.2 *mm* SS column containing Benton 34 and 7% dinonyl phthalate stationary phase on Celite-545 solid support using a flame ionisation detector (FID). The material balance was checked and it was > 96%.

The terms 'phenol conversion' and products 'selectivity' are defined as Phenol conversion (%) = [(pheol in feed − phenol in product)/ phenol in feed] × 100 Selectivity (%) = [desired product/ total aromatics (excluding phenol)in product] × 100.

3. Results and discussion

In the alkylation of phenol with methanol, *o*-cresol was detected as the major product followed by *p*-cresol, 2,6-xylenol and anisole. Based on these products, the following reaction scheme was proposed for the reaction system under investigation:

3.1. Acitivity of modified catalysts

The experiments were carried out to compare the activities of different Ce-exchanged catalysts for the phenol methylation reaction. The possible reactions are presented in Scheme 1. As can be seen from Table 1, the conversion of phenol increases with increase in cerium content of the exchanged zeolite.

Table 1
Cerium contents, acidity and activity of various modified catalysts

Catalyst	Cerium content (wt%)	Relative acidity	Phenol conversion (%)
NaX	Nil	1.0	1.7
MX-1	1.74	1.22	14.0
MX-2	4.56	1.58	23.6
MX-3	6.70	1.83	32.0
MX-4	8.86	2.20	42.0
MX-5	10.43	2.45	45.0

Conditions: Pressure, 1 atm; temperature, 623 K; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4; space-time, 10.2 kg h/kgmole.

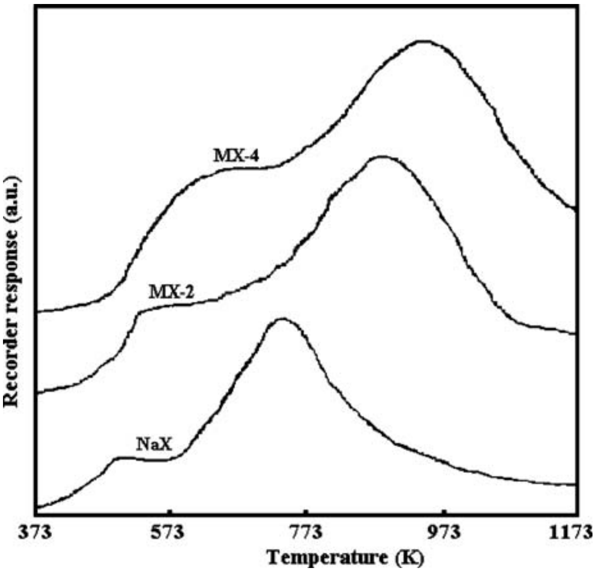


Figure 2. Temperature programmed desorption profiles of ammonia for various catalysts.

Temperature-programmed desorption (TPD) of ammonia was also studied with NaX as well as Ce-exchanged NaX zeolites and Figure 2 shows the representative TPD profiles of three catalysts. The desorption of ammonia corresponding to different peaks of the profiles is indicative of energy levels at which ammonia is bound to acid sites. The profiles indicate that the catalysts contain mainly two types of acid sites of varying strengths. The strengths of the acid sites increase with Ce-exchange as the desorption peaks shift gradually towards the higher temperatures with increasing cerium content of the catalysts. Moreover, the number of acid sites also increases as the peak area increases with Ce-exchange. Areas under both the peaks for all catalysts were measured and the acidity relative to virgin NaX was determined from the ratio of the peak areas as reported in Table 1. It is evident from Table 1 that the acidity of the catalysts increases with increase in cerium loadings. The increase in catalytic activity is, therefore, due to the increase in both quantity and strength of the acid sites by cerium exchange.

The turnover frequency (TOF) for phenol conversion was evaluated on the basis of cerium (phenol conversion on NaX alone was subtracted) and plotted as a function of cerium content as shown in Figure 3. As can be seen from this plot, the TOF decreases as the cerium content of the exchanged zeolite increases. This indicates that all of the cerium present in the catalyst does not take part in enhancing the activity of the catalyst. The BET surface areas of the exchanged zeolites were also measured and found to vary between 450 and 360 m^2/g (figure 3) while the parent NaX zeolite was having a surface area of

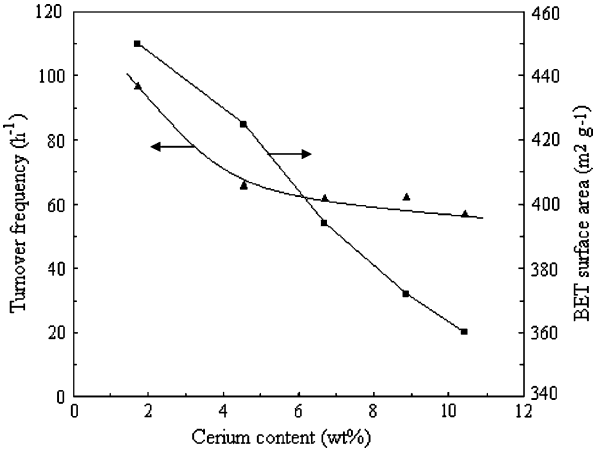


Figure 3. Variation of turnover frequency and surface area with cerium loading Condition: Temperature, 623 K; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4; space-time, 10.2 kg h / kgmole; catalyst weight, 0.03 kg.

478 m^2/g. The decrease in surface area may be due to blocking of some pores by adsorbed cerium compounds, which do not take part in catalyzing the reaction and are, therefore, responsible for decrease in TOF.

3.2. *Effect of cerium loading on product selectivity*

The effect of cerium loading on product selectivity is shown in Figure 4. It is evident from this figure that with increase in cerium content of the modified zeolite, the selectivities of C-alkylated products increase and that of O-alkylated product decreases. The increase in C-alkylation is due to generation of stronger acid sites in the catalysts with more and more cerium exchange. Garcia *et al.* [25] have reported that anisole formation requires sites of lower acid strengths compared to those necessary for cresol formation. Similar observations have been reported by Pierantozzi and Nordquist [7] and Balsama *et al.* [14]. It can also be seen from figure 2 that the selectivity of cresols more or less remains constant from a cerium loading of 8.85 % (MX-4) onwards. As our objective was to get maximum cresols, further experiments were carried out with MX-4 catalysts only.

3.3. *Time on stream behavior of MX-4*

Times on stream runs were conducted over MX-4 for 3 h at 623 K and atmospheric pressure with a MeOH to phenol mole ratio of 4:1 as shown in Figure 5. After a slight decrease, the catalyst activity was found to attain a constant value. Figure 5 also shows the change in products selectivity with time on stream. Products selectivities were also found to attain steady state values after an hour or so. The catalyst is, therefore, quite stable at the reaction conditions.

3.4. *Effect of methanol to phenol mole ratio*

Effect of methanol to phenol mole ratio in the feed mixture was studied by varying the mole ratio from 1:1 to 8:1 as shown in Figure 6. The conversion of phenol was found to increase steadily with increase in methyl alcohol content of the reaction mixture.

The change in methyl alcohol to phenol molar ratio in the feed was found to change the selectivities of different products. An increase in the amount of methyl alcohol in the feed had negative influence on the selectivity of anisole as it decreased from 28% at a ratio of 1:1 to 6% at 8:1. The selectivity of 2,6-xylenol increases with increase in MeOH/phenol ratio due to increased availability of alkylating group for further alkylation of *o*-cresol (Scheme 1). As a result, the selectivity of

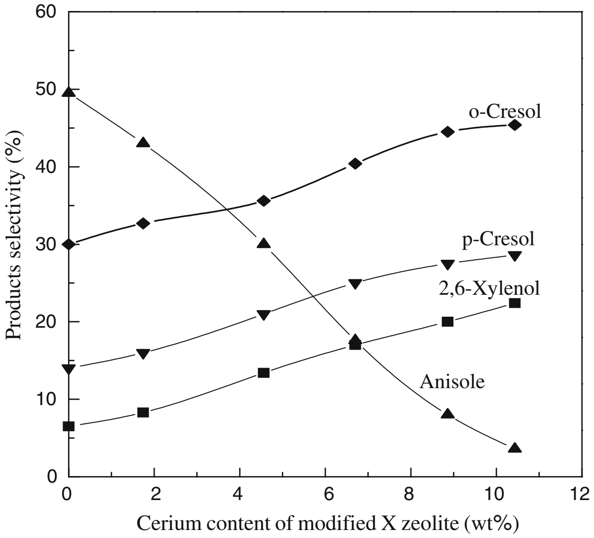


Figure 4. Effect of cerium content of catalysts on products selectivities Condition: Pressure, 1 atm; temperature, 623 K; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4; space-time, 10.2 kg h / kgmole.

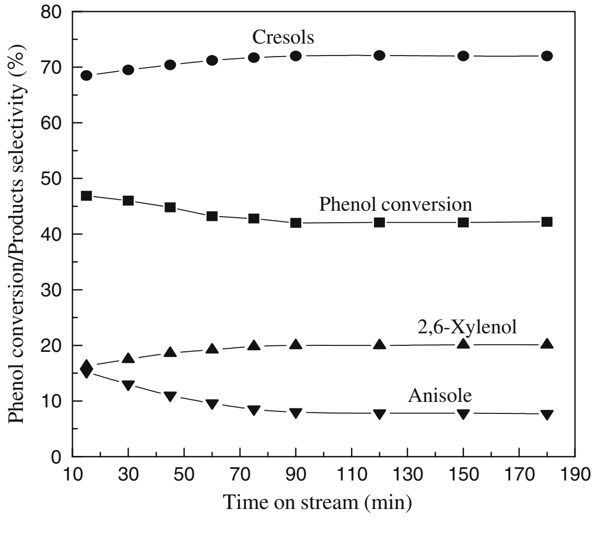


Figure 5. Time on stream behavior of MX-4 Conditions: Pressure, 1 atm; temperature, 623 K; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4; space-time, 10.2 kg h/ kgmole.

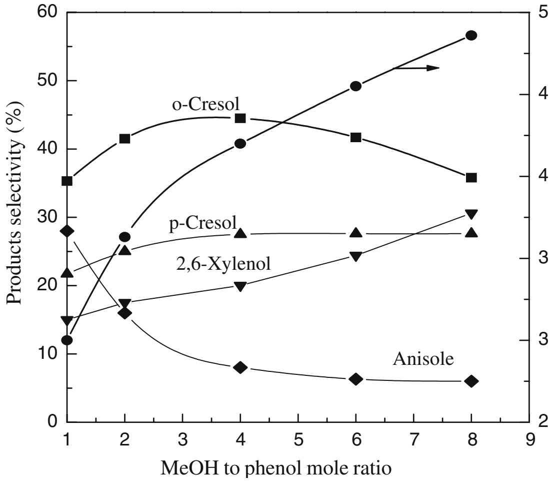


Figure 6. Effect of methanol to phenol mole ratio on phenol conversion and products selectivities Condition: Pressure, 1 atm; temperature, 623 K; catalyst, MX-4; nitrogen to feed mole ratio, 0.4; space-time, 10.2 kg h/ kgmole.

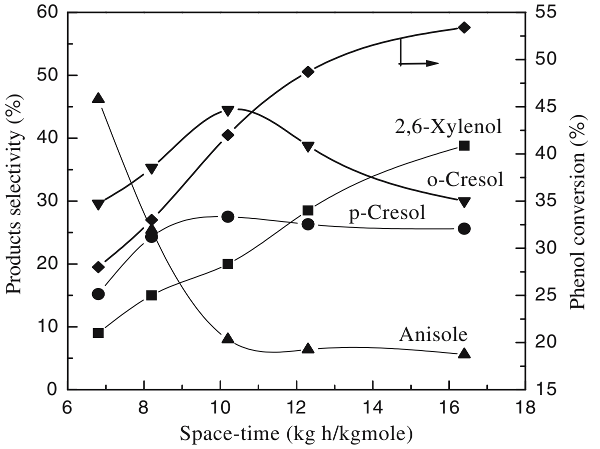


Figure 7. Effect of space-time on phenol conversion and products selectivities Condition: Pressure, 1 atm; temperature, 623 K; catalyst, MX-4; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4.

o-cresol decreases with increase in MeOH/phenol ratio, after passing though a maximum at a mole ratio of 4:1. The selectivity of *p*-cresol, however, increases first and then remains almost unchanged with change in feed composition. A steady increase in total cresols/anisole values from 2.0 to 10.6 and in selectivity of 2,6-xylenol from 15.0 to 30.6% indicates that the formation of C-alkylated products including the double alkylated product is dependent upon the availability of excess methylating agent [33].

3.5. *Effect of temperature on phenol conversion and product selectivity*

The phenol methylation reaction was carried out at different temperatures in the range of 573–723 K and at a MeOH to phenol mole ratio of 4:1. As can be seen from Table 2, the conversion of phenol increases with increase in temperature in the range studied as expected. It can also be seen from Table 2 that the selectivities of all products but 2,6-xylenol decrease with temperature. The selectivity of *o*-cresol decreased from 49.0 to 35.5% as the temperature was increased from 573 to 723 K, while the corresponding decrease in selectivity of *p*-cresol was from 32.5 to 16.5%. A similar decreasing trend in the selectivity of anisole from 11.3 to 6.3% was observed. The selectivity of 2,6-xylenol on the other hand increased from 7.2 to 41.6% for the same temperature change. The ratio of the selectivities of total cresols to anisole in this temperature range showed that the formation of C-alkylated products was much more than that of the O-alkylated product. Although the selectivities of cresols recorded a decrease with rise in temperature, the ratio of the selectivity of *o*-cresol to that of *p*-cresol exhibited an increase from 1.51 at 573 K to 2.15 at 723 K indicating that the formation of *o*-cresol remained the favored reaction path even at high temperature compared to the formation of *p*-isomer.

3.6. *Effect of space-time*

The effect of space-time on the conversion of phenol and selectivities of the products is shown in Figure 7 for the space-time range of 6.8–16.4 kg h/kgmole. The conversion of phenol was found to increase with space-time as expected. As the space-time increases, the selectivity of *o*-cresol increases first, attains a maximum value and then decreases while that *p*-cresol attains almost a steady

Table 2
Effect of temperature on phenol conversion and products selectivity

Temperature (K)	Phenol conversion (%)	Selectivity (%) of			
		o-Cresol	*p*-Cresol	2,6-Xylenol	Anisole
573	37.2	49.0	32.5	7.2	11.3
623	42.0	44.5	27.5	20.0	8.0
673	45.6	40.5	21.3	31.2	7.0
723	49.5	35.5	16.5	41.6	6.3

Conditions: Pressure, 1 atm; catalyst, MX-4; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4; space-time, 10.2 kg h/kgmole.

state value after an initial rise (figure 7). Highest selectivity for cresols was found with a space-time of 10.2 kg h/kgmole. Higher values of the ratio of the selectivities of total cresols to anisole (9.0) and the selectivity of *o*-cresol (44.5%) established that an intermediate space-time of 10.2 kg h/kgmole was suitable for the production of *o*-cresol. The formation of xylenol was favored by a large contact time between the catalyst and the feed whereas formation of *o*-cresol required an optimum contact time, which was neither very small nor very large as shown in figure 7.

3.7. Kinetic analysis

The effect of space-time on phenol conversion has been discussed in the previous section. The following differential equation was used to describe the rate of reaction of phenol in a plug flow reactor by assuming pseudo-first order kinetics:

$$-\mathrm{d}C_A/\mathrm{d}(W/F_{Ao}) = kC_A \qquad (1)$$

where W is the weight of the catalyst (kg), F_{Ao} is the flow rate of phenol (A) in the feed (kgmole of phenol/h) and C_A is the concentration of phenol (kgmole/m^3). Integration of equation (1) yields,

$$-\ln(1 - X_A) = k(W/F_{Ao}) \qquad (2)$$

where X_A is the fractional conversion of phenol. A plot of –ln (1-X_A) against W/F_{Ao} over MX-4 catalyst gave a straight line passing through the origin as shown in Figure 8. From the slope of the straight line, the rate constant for the phenol alkylation reaction was determined as 9.04×10^{-3} kgmole/kg h. Similar rate constant values have also been reported in the literature [34]. The rate of reaction of phenol is, therefore, first order with respect to phenol and zero order with respect to methanol. Hence the rate equation can be written as

$$-r_A = kC_A \qquad (3)$$

Employing the equation from power law kinetics, equation (3) can be rewritten as

$$-r_A = A_o \exp(-E/\mathrm{RT})C_A \qquad (4)$$

where A_o is the Arrhenius frequency factor and E_a is the apparent activation energy. For the reaction in the plug flow reactor, equation (4) can be modified as

$$(F_{Ao}/W)X = A\exp(-E_a/\mathrm{RT})C_A \qquad (5)$$

Now writing C_A in terms of initial concentration of phenol (C_{Ao}) and rearranging equation (5) we get,

$$\ln[X_A/(1 - X_A)] = \ln A_1 - E_a/\mathrm{RT} \qquad (6)$$

where A_1 is a constant. A plot of ln [X_A/(1-X_A)] against (1/T) gave a straight line as shown in Figure 9. From the slope of the line, the apparent activation energy was calculated as 57.2 kJ/mole. Similar activation energy values have been reported by Velu and Swamy [21].

4. Conclusions

The present study shows that alkylation of phenol with methanol over cerium exchanged zeolite catalyst can give high selectivity of C-alkylated products by increasing the acidity of the NaX zeolite through cerium exchange. The effects of various parameters such as cerium loading, MeOH to phenol mole ratio in the feed, temperature and space-time on phenol conversion and products selectivities were studied. Total cresols to anisole ratio showed that lower acid strength favored

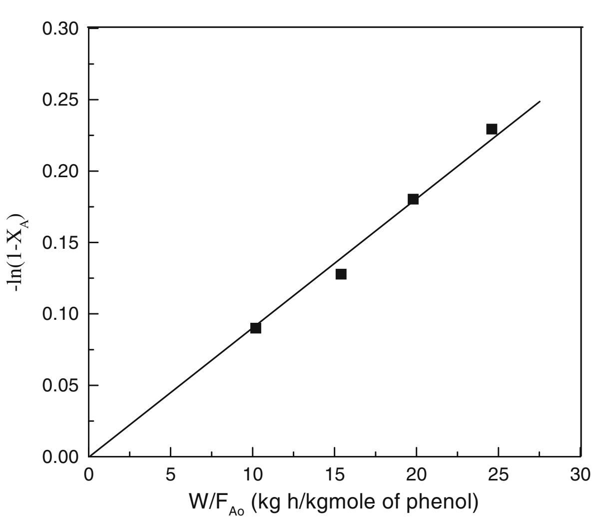


Figure 8. Pseudo-first order kinetic plot for conversion of phenol Condition: Pressure, 1 atm; temperature, 623 K; catalyst, MX-4; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4.

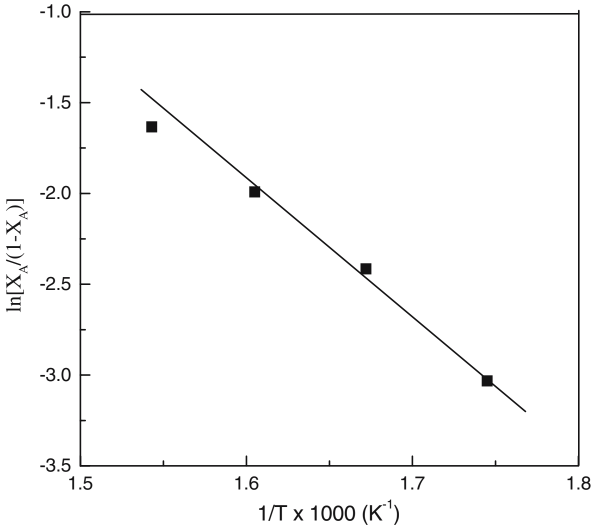


Figure 9. Arrhenius plot for the phenol conversion Conditions: Pressure, 1 atm; catalyst, MX-4; MeOH to phenol mole ratio, 4:1; nitrogen to feed mole ratio, 0.4; space-time, 3.1 kg h/kgmole.

O-alkylation, while C-alkylation required stronger acid sites of the catalyst. The selectivity of the double alkylated product was found to be more at higher temperatures, higher concentrations of alkylating agent in the feed and higher acidity of the catalyst. A space-time of 10.2 kg h/kgmole was found to be optimum for highest cresols selectivity over the best catalyst MX-4. The catalyst MX-4 could be a potential one for the phenol methylation reaction with high selectivity for cresols.

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