Selective alkylation of phenol with cyclohexanol over large-pore zeolites

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The alkylation of phenol with cyclohexanol has been investigated in the liquid phase without solvent over the H forms of various zeolites in the temperature range 140–220 °C. Large-pore zeolites have been shown to be efficient catalysts in such a reaction, and led to the selective formation of *para*-cyclohexylphenol at higher temperatures. The product selectivity was found to be less dependent on the type of the zeolite structure in the case of large-pore zeolites. A maximum of about 85% for the phenol conversion has been obtained over H-Y and H-mordenite zeolites at 200 °C whereas the conversion is about 72% with H-β. The production of *o*-alkylated phenol is favored at lower temperatures and *p*-alkylated product at higher temperatures. The best operating temperature is 200 °C.

KEY WORDS: cyclohexylation; phenol alkylation; zeolites; cyclohexyl phenols.

1. Introduction

Solid acid and base catalysis is one of the economically and ecologically important fields in catalysis, out of which a great number of investigations are related to zeolites and similar structure of solids, due to its non-corrosiveness, environmentally benign nature and reusability. It can also be tuned to give higher activity, selectivity and longer catalyst life. The mesoporous molecular sieves or large-pore zeolites may catalyze reactions of large-size molecules. Attention has recently been paid to large-pore zeolites such as H-mordenite, H-Y and H-β. 4-Cyclohexylphenol or *para*-cyclohexylphenol (*p*-CP) is used as an intermediate in the preparation of dyestuffs (colorants for plastics) and biocides. There are extensive published and patented literature reports on its preparation [1–10]. Several of these methods make use of the highly-polluting and toxic Brønsted acids such as H_2SO_4 [3,6] and H_3PO_4 [4–6] as catalysts. These reported processes lack positional selectivity to the *para*-isomer. By using a solid acid catalyst like zeolite, some of the corrosion and pollution problems can be solved, at the same time improving the *para* selectivity. The introduction of shape selectivity in the case of zeolites would possibly permit the influence of the product composition in favor of the more desired *p*-CP. In the case of alkylation of phenol, it is known that C-alkylation requires stronger acid sites than those for O-alkylation [11–14], although some C-alkylation derivatives might be formed by intramolecular rearrangement of the ethers. The aim of the present investigation was to find out optimal conditions for C-alkylation of phenol in the *para* position by cyclohexanol as alkylating agent using medium- and large-pore zeolites.

2. Experimental

2.1. Materials

The zeolite β and mordenite in their ammonium form were obtained from PQ Corporation and H-Y was obtained from Union Carbide. The zeolites H-ZSM-5 and H-FER were synthesized according to the procedure reported elsewhere [15,16]. The NH_4-form of the zeolites was calcined in air by heating at 550 °C for 6 h. Analytical grade phenol and cyclohexanol (E-merk) were used without further purification.

2.2. Characterization

The phase purity of the samples was ascertained by X-ray diffraction (Rigaku, D-Max/III-VC model) using Cu K_α radiation. Surface area and pore volumes were determined from nitrogen adsorption isotherms measured at liquid nitrogen temperature in an Omnisorp 100 CX sorption apparatus. Prior to adsorption, the samples were degassed under vacuum at 300 °C for 4 h. The Si/Al atomic ratios of the zeolites were determined by combination of atomic absorption spectroscopy (AAS), energy dispersive X-ray analysis (EDX) and X-ray fluorescence (XRF). Crystal sizes were obtained from scanning electron micrographs (SEM) collected on a Cambridge Stereoscan 400 instrument. The physico-chemical characterizations of the catalysts under study

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Table 1
Physicochemical characteristics of zeolites

Catalyst	Si/Al ratio (from XRF)	Surface area (m^2/g)	Ammonia desorption (mmol/g)
H-β	30	707.9	1.83
H-M	28	561.5	1.76
H-Y	2.65	836.8	4.54
H-ZSM-5	100	373.5	1.10
H-FER	17	335.4	1.26

are shown in table 1. Temperature-programmed desorption of ammonia (TPDA) was carried out to evaluate the acidic properties of the zeolites using NH_3 as adsorbate. TPDA was performed on an Autochem 2910 analyzer. In a typical run, about 0.3–0.4 g of sample was placed in a TPD cell and heated *in situ* in an He flow (30 ml/min) at 400 °C for 2 h and then exposed to NH_3 adsorption at 80 °C for 30 min by passing an He stream with ammonia. The excess of ammonia (physisorbed ammonia) was purged under He for 30 min at 105 °C and the TPD profile recorded from 50 to 750 °C while heating at a rate of 10 °C/min under a He carrier of 50 ml per min. The total acidity values are tabulated in table 1.

2.3. Catalytic runs

The reaction was carried out in a 100 ml stirred autoclave reactor (PARR autoclave, 4842) with stirring and temperature control. In a typical experiment, 50 mmol of phenol and 50 mmol of cyclohexanol were mixed together in the autoclave; the zeolite (10 wt%), freshly calcined and kept at 140 °C under dry air atmosphere, was then added. The autoclave was heated to the required reaction temperature (200 °C) and maintained for 6 h. Reaction conditions other than typical or the standard are shown in the tables or/and figures.

The samples were withdrawn periodically from the autoclave and analyzed on an HP 6890 series GC (HP-1, crosslinked methyl siloxane, 30 m × 0.32 mm × 0.25 μm) with FID. GC-MS (Shimadzu GC-MS QP 2000A) with SE-52 capillary column (25 m) and GC-FTIR (Perkin Elmer Spectrum 2000) were used for identification of the products. The selectivity to a product is expressed as the amount of the particular product divided by the total amount of products and multiplied by 100.

3. Results and discussion

3.1 Effect of catalyst type

Typical reaction results in the alkylation of phenol with cyclohexanol over H-Y, H-β, H-mordenite (H-M), H-ZSM-5 and H-FER zeolites, and non-zeolitic catalysts like silica–alumina (25% alumina) and γ-alumina (1 : 1 molar ratio of reactants, $T = 200\,^{\circ}C$), are summarized in table 2. This reaction gave a substantial amount of monoalkylated products, *o*-cyclohexylphenol (*o*-CP) and *p*-cyclohexylphenol (*p*-CP), along with considerable amounts of cyclohexylphenyl ether (CPE, O-alkylated product), polyalkylated phenols (PCPs) and a few unidentified higher boilers (grouped as others in tables and figures) over large-pore zeolites like H-Y, H-β and H-M. The formation of bulkier polyalkylated phenols was suppressed over the medium-pore zeolites, H-ZSM-5 and H-FER. Also, these catalysts afforded more cyclohexylphenylether (CPE), which may be due to surface reactions of the substrates over these catalysts. The conversion of cyclohexanol is nearly same over these zeolites. The phenol conversion was higher than 80% over H-Y and H-M, while H-β, H-ZSM-5 and H-FER zeolites exhibits a phenol conversion of 70, 54 and 47% respectively. Though H-ZSM-5 possesses a high concentration of strong acid sites, low activity is observed. This is attributed to the fact that the strong acid sites are located within the narrow pores, and thus these are difficult to access for the reactant/product. Similar results are observed over non-zeolite catalysts where the reaction is on the surface, yielding more cyclohexene and CPE (O-alkylated product). The selectivity to *p*-CP is high in the case of large-pore zeolites, and the activity of the catalyst may be written in descending order

Table 2
Reaction results of alkylation of phenol with cyclohexanol over different zeolites at 200 °C[a]

Catalyst	Conversion of cyclohexanol	Conversion of phenol	Product selectivities (wt%)						
			Cyclohexene	CPE	*o*-CP	*p*-CP	PCPs	Others	*o*-/*p*-
H-Y	97.9	85.0	10.6	4	15.9	38.7	21.9	8.9	0.41
H-M	96.6	84.9	7.5	2	16.7	44.8	21.6	7.4	0.37
H-β	98.9	71.4	2.0	0.3	13.9	43.7	31	9.1	0.31
H-ZSM-5	98.6	54.1	84.6	1.9	5.6	7.7	0.2	0	0.73
H-FER	91.0	47.6	93.3	3.9	1.3	1.4	0	0	0.93
Silica–alumina	81.9	54.2	61.1	28.9	7.7	1.3	1	0	5.92
γ-Al_2O_3	98.1	51.5	93.3	1.6	4.2	0.8	0	0	5.25

[a] Reaction conditions: catalyst, 10 wt%, phenol, 50 mmol; cyclohexanol, 50 mmol.

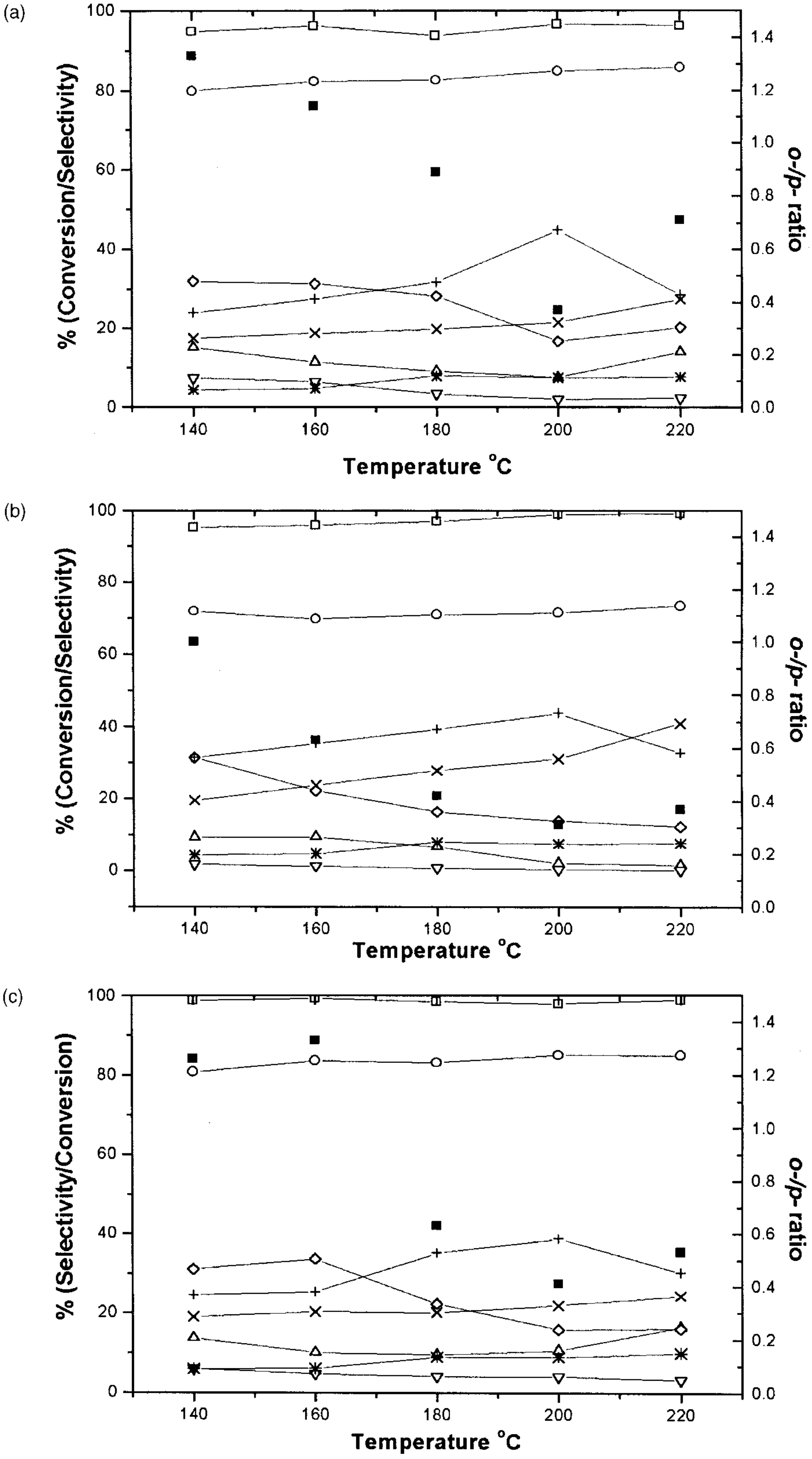

Figure 1. (a) Effect of reaction temperature over H-M for the cyclohexylation of phenol with cyclohexanol. Reaction conditions: phenol/cyclohexanol (molar ratio) = 1; catalyst (H-M) = 10 wt%, time = 6 h. (□) Conversion of cyclohexanol, (○) conversion of phenol, (△) cyclohexene, (▽) CPE, (◇) *o*-CP, (+) *p*-CP, (×) PCPs, (∗) others, (■) *o*-CP/*p*-CP. (b) Effect of reaction temperature over H-β for the cyclohexylation of phenol with cyclohexanol. Reaction conditions: phenol/cyclohexanol (molar ratio) = 1; catalyst (H-β) = 10 wt%, time = 6 h. (□) Conversion of cyclohexanol, (○) conversion of phenol, (△) cyclohexene, (▽) CPE, (◇) *o*-CP, (+) *p*-CP, (×) PCPs, (∗) others, (■) *o*-CP/*p*-CP. (c) Effect of reaction temperature over H-Y for the cyclohexylation of phenol with cyclohexanol. Reaction conditions: phenol/cyclohexanol (molar ratio) = 1 catalyst, (H-Y) = 10 wt%, time = 6 h. (□) Conversion of cyclohexanol, (○) conversion of phenol, (△) cyclohexene, (▽) CPE, (◇) *o*-CP, (+) *p*-CP, (×) PCPs, (∗) others, (■) *o*-CP/*p*-CP.

considering the phenol conversion and the ratio of *o*-/*p*-CP as H-M > H-Y > Hβ.

All the above experiments indicated that large-pore zeolite is a promising catalyst for the selective cyclohexylation of phenol to *p*-CP. In our present study, we compare the results of this reaction over large-pore (H-β, H-M and H-Y) zeolites.

3.2. *Effect of temperature*

The effect of temperature in the alkylation of phenol over H-Y, H-β and H-M by cyclohexanol (molar ratio of reactants = 1 : 1) as alkylating agent was studied by performing reactions between 140 and 220 °C. The results are shown in figure 1(a)–(c). It is evident from the figure that the reaction gives *para*-selective product with good selectivities and comparable *o*-/*p*- ratio at 200 °C. But at higher temperature (220 °C), a large amount of PCPs was found, due to further alkylation or transalkylation of the products formed. A small increase in the conversion of phenol with temperature was noticed over these zeolites. At lower temperatures, the formation of cyclohexene is more, which decreases with temperature. The concentration of CPE is less, even at lower temperature, suggesting that C-alkylation predominates over O-alkylation; however, at the higher temperature there was a slight decrease in O-alkylated products, suggesting the isomerization of CPE to C-alkylated phenols. The *o*-/*p*- ratio of CP also decreases with temperature up to 200 °C and a slight increase in the ratio is noticed at higher temperature, 220 °C, due to the formation of PCPs.

3.3. *Effect of molar ratio*

Table 3 summarizes the results of phenol cyclohexylation carried out with various phenol : cyclohexanol ratios from 1 : 1 to 5 : 1. In all cases, *p*-CP was obtained as the major product along with small amounts of *o*-CP and poly-alkylated products. The amount of *o*-CP and other products decreases with increase in the phenol/cyclohexanol molar ratio. It is obvious from table 3 that the formation of ether (CPE), PCPs and other unknown polyalkylated products was minimized with increase in the phenol/cyclohexanol molar ratio. Further, it is also clear that an increase in the phenol/cyclohexanol molar ratio decreases the phenol conversion; however, the conversion of cyclohexanol is always >97%. Maximum *para*-selectivities of above 71 and 75% were achieved over H-M and H-Y zeolites respectively at a phenol/cylcohexanol molar ratio of 5.

3.4 *Effect of reaction time*

Figures 2(a)–(c) show the effect of reaction time for the alkylation of phenol with cyclohexanol at 200 °C. As can be seen from these figures, the phenol conversion increases with time for the catalysts H-M and H-Y, but the phenol conversion is almost the same over H-β zeolite. This may be due to the fact that the reaction is faster over H-β zeolite with time. However, the conversion of cyclohexanol is almost the same during the reaction time (2–12 h) over all these catalysts. The activity of H-M zeolite towards alkylation is less, as seen from the figure, and the formation of cyclohexene is high initially and with time this reacts further to yield alkylphenols.

The *o*-/*p*- ratio decreases with time up to 6 h, which can be attributed to isomerization of the product (*o*-CP) to *p*-CP and other secondary reactions. A further increase of time leads to a slight decrease in selectivity of *p*-CP due to other secondary reactions like isomerization and successive alkylation to PCPs. Also the high concentration of PCPs was found in the product with increasing time due to successive alkylation reactions.

Table 3
Effect of molar ratio of the reactants for alkylation of phenol with cyclohexanol over large-pore zeolites

Catalyst	Mole ratio	Conversion of cyclohexanol	Conversion of phenol	Product distribution selectivities (%)						
				Cyclohexene	CPE	*o*-CP	*p*-CP	PCPs	Others	*o*/*p*
H-M	1 : 1	96.6	84.9	7.5	2	16.7	44.8	21.6	7.4	0.37
	2 : 1	97.4	48.2	5.2	1.9	16.5	52.7	16.8	6.9	0.31
	3 : 1	98.9	26.9	3.9	1.4	14.6	66.9	8.2	5	0.22
	5 : 1	99.5	18.6	2	2	13.5	75.3	4.1	3.1	0.18
H-β	1 : 1	98.9	71.4	2	0.3	13.9	43.7	31	9.1	0.31
	2 : 1	99.1	47.9	4.6	4.7	12.8	48	20.9	8	0.27
	3 : 1	99	27.1	6.5	3.4	14	56.6	12.7	6.8	0.24
	5 : 1	99.8	18.7	5.1	3.8	13.1	66.2	7.1	4.7	0.19
H-Y	1 : 1	97.9	85	10.6	4	15.9	38.7	21.9	8.9	0.41
	2 : 1	98.5	45.3	6.4	3.3	14.9	52.2	15.8	7.4	0.28
	3 : 1	99.3	27.4	4.3	2.3	13.7	63.4	11.8	4.5	0.21
	5 : 1	99.5	19	2.6	1.4	12.9	71.1	8.7	3.3	0.18

Note: Reaction conditions: temperature, 200 °C; time, 6 h; catalyst, 10 wt%.

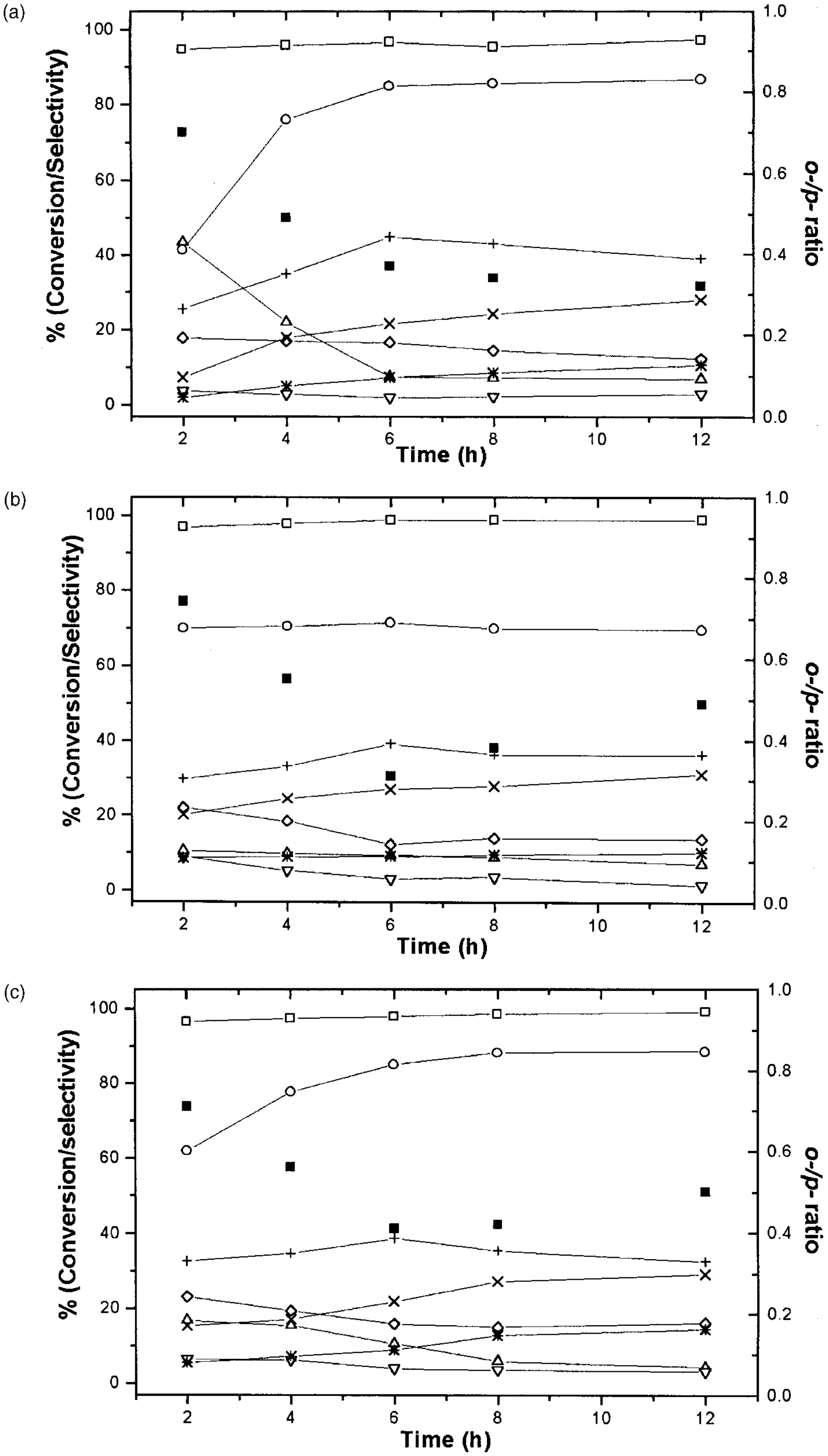

Figure 2. (a) Effect of reaction time over H-M for the cyclohexylation of phenol with cyclohexanol. Reaction conditions: temperature = 200 °C, phenol/cyclohexanol (molar ratio) = 1, catalyst (H-M) = 10 wt%. (□) Conversion of cyclohexanol, (○) conversion of phenol, (△) cyclohexene, (▽) CPE, (◇) *o*-CP, (+) *p*-CP, (×) PCPs, (∗) others, (■) *o*-CP/*p*-CP. (b) Effect of reaction time over H-*β* for the cyclohexylation of phenol with cyclohexanol. Reaction conditions: phenol/cyclohexanol (molar ratio) = 1, catalyst (H-*β*) = 10 wt%, time = 6 h. (□) Conversion of cyclohexanol, (○) conversion of phenol, (△) cyclohexene, (▽) CPE, (◇) *o*-CP, (+) *p*-CP, (×) PCPs, (∗) others, (■) *o*-CP/*p*-CP, (c) Effect of reaction time over H-Y for the cyclohexylation of phenol with cyclohexanol. Reaction conditions: temperature = 200 °C, phenol/cyclohexanol (molar ratio) = 1, catalyst (H-Y) = 10 wt%. (□) Conversion of cyclohexanol, (○) conversion of phenol, (△) cyclohexene, (▽) CPE, (◇) *o*-CP, (+) *p*-CP, (×) PCPs, (∗) others, (■) *o*-CP/*p*-CP.

Table 4
Effect of catalyst concentration

H-M (%)	Conversion of cyclohexanol	Conversion of phenol	Product distribution selectivities (%)						
			Cyclohexene	CPE	*o*-CP	*p*-CP	PCPs	Others	*o*-/*p*-
5	94.3	77.1	14.5	8.6	21.6	38.7	12.8	3.8	0.56
10	96.6	84.9	7.5	2.0	16.7	44.8	21.6	7.4	0.37
15	98.1	89.8	6.6	1.7	20.1	40.9	19.1	11.6	0.49
20	100	90.9	4.8	0.8	20.4	34.6	24.5	14.9	0.59

3.5. *Influence of catalyst concentration*

Table 4 shows the influence of H-M zeolite concentration under the optimal conditions ($T = 200\,^\circ\mathrm{C}$; phenol/cyclohexanol molar ratio = 1; time = 6 h). As shown in this table, the increase in catalyst amount increases the phenol conversion (from 77.1% at 5 wt% to 90.9% at 20 wt%) and the formation of cyclohexene and CPE decreases. There is an increase in polyalkyation and other side reactions *versus* the monoalkylation step.

3.6 *Mechanism*

From the above studies and with good probability the following mechanism can be postulated. The first step is the protonation of cyclohexanol generating a carbocation, which reacts with the nucleophilic sites of the phenol. Alternatively, the carbocation dehydrates to reactive cyclohexene, which can also be an alkylating agent under the reaction condition. Cyclohexene reacts with phenol through either an O-alkylation or a C-alkylation pathway to give rise to the desired alkylphenols. It is also highly probable that the O-alkylated product (CPE) under the acidic environment and at high-temperature conditions may undergo a Fries-type migration to the alkylphenols.

4. Conclusions

The alkylation of phenol with cyclohexanol as the alkylating agent can be carried out efficiently over large-pore zeolites to selectively yield *para*-cyclohexyl phenol. Lower temperatures yielded more *ortho*-alkylated product and it decreases with temperature. The increase of phenol concentration in the reaction mixture leads to more selective formation of *para*-cyclohexyl phenol. The optimum reaction conditions under our study for this reaction were temperature 200 °C; time 6 h; molar ratio of phenol/cyclohexanol 3 : 1.

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