Alkylation of phenol with cyclohexanol and cyclohexene using HY and modified HY zeolites

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Received 15 December 2001; accepted 3 January 2002

The alkylation of phenol with cyclohexanol and cyclohexene in the presence of HY and dealuminated/ultrastable Y zeolite catalysts was studied over a range of temperature 140–220 °C at atmospheric pressure for reaction times of 2–12 h. The molar ratio of the reactants (cyclohexanol : phenol) was varied from 1 : 1 to 1 : 5. A mixture of isomeric cyclohexylphenol was obtained consisting mainly of 4-cyclohexylphenol. The 2-/4- product ratio decreased with increasing temperature, molar ratio of reactants and increased contact time. The reaction temperature also plays an important role. At lower temperatures, *ortho* product predominates, but at higher temperatures *para* isomer predominates. HY samples dealuminated at medium temperatures (500–700 °C) also increases the *para*-selectivity.

KEY WORDS: alkylation; cyclohexylphenol; zeolite HY; phenol; cyclohexanol; cyclohexene.

1. Introduction

Paracyclohexylphenol (4-cyclohexylphenol) is widely used as an intermediate in the manufacture of dyestuffs, particularly in the manufacture of colorants for plastics, and is also used as biocides and intermediate for dyes. The catalysts used are sulfuric acid [1,2], phosphoric acid [2], polyphosphoric acid [3–5], aluminum salt of diphenyldithiophosphoric acid [6], transitional aluminas [7], and iron and zinc salts [8]. Recently alkylation of *para*-cresol with cyclohexanol/cyclohexene in the presence of H-zeolite Y was reported [9]. Silica-supported BF_3 is also reported for alkylation of phenol using cyclohexene as alkylating agent [10]. But none of these methods report any solid catalytic material, which is eco-friendly and selective to 4-cyclohexylphenol (4-CP).

Many of these drawbacks can be overcome by using recoverable and regenerable solids like zeolites. The use of zeolites and other solid acid catalysts in the manufacture of fine chemicals has been gaining importance in recent years. Zeolites are one of the most promising microporous crystalline materials providing highly selective products. With the aim of achieving both high activity and *para*-cyclohexyl phenol selectivity, the present work is conducted. The use of cyclohexanol/cyclohexene as the alkylating agents, large pore zeolites such as HY, and dealuminated HY as catalysts and under liquid phase conditions, was studied.

2. Experimental

2.1. Catalyst preparation and reagents

The zeolite Na-Y was procured from Union Carbide. It was converted to the ammonium form by continuous exchange (2–3 times) with 2 M ammonium nitrate solution at 80 °C for 16 h. The NH_4-Na-Y zeolite was the parent material for the preparation of the hydrothermally dealuminated samples. Controlled hydrothermal treatment or steaming is the common dealumination method used to prepare industrially important catalysts [11]. Steaming of NH_4-Na-Y at 550 °C for 4 h, followed by exchange with NH_4NO_3 solution and calcination at 550 °C for 12 h, yielded the sample U-550. The U-700 sample was prepared by steaming the U-550 sample at 700 °C for 4 h followed by ammonium nitrate exchange and calcination. The U-700 sample was further steamed at 850 °C for 4 h to yield sample U-850. All these samples were then acid leached by 0.01 N HNO_3 for 4 h.

2.2. Characterization

The crystallinity of zeolites was characterized by X-ray diffraction (Rigaku, D-Max/III-VC model) using Cu K_α radiation. The particle size and morphology of the zeolite catalysts were estimated by scanning electron microscopy (SEM, Cambridge Stereoscan 400). The Si/Al ratio of various zeolites and the degree of dealumination were estimated by a combination of wet, atomic absorption method (Hitachi 800) and ^{29}Si and ^{27}Al MAS-NMR (Bruker Model MSL-300 FT-NMR spectrometer). The sorption characteristics of zeolites were determined by adsorption of nitrogen at the temperature of liquid nitrogen using an Omnisorb CX instrument.

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2.3. Acidity measurement

The acid properties of the catalysts were determined by the temperature-programmed desorption method, with ammonia as a probe molecule (TPDA), using an AutoChem 2910 (Micromeritics, USA) instrument. Each sample was pretreated in a flow of helium at 500 °C for 3 h (50 ml/min). Adsorption of ammonia was performed by passing an He stream with ammonia vapor over the catalyst for 30 min at 80 °C. The sample was flushed with the carrier gas at 105 °C for another 1 h to remove physisorbed ammonia. The TPD profile of ammonia was obtained from 50 to 700 °C at a heating rate of 10 °C/min. The ammonia concentration in the effluent stream was monitored with the thermal conductivity detector and the areas under the peaks were integrated using GRAMS/32 software to determine the amount of ammonia desorbed during TPD.

2.4. Catalytic runs

The alkylation reactions were carried out under batch conditions in a PARR autoclave (Model No. 4842, USA) in the temperature range 140–220 °C at autogeneous pressure. Both cyclohexanol and cyclohexene were used as alkylating agents to study the mechanism and the effect of nature on alkylating agents. A typical reaction mixture contains phenol (1.88 g, 20 mmol) and cyclohexanol (2.0 g, 20 mmol) or cyclohexene (1.68 g, 20 mmol) in the reactor. To this mixture 10 wt% of freshly activated catalyst (200 °C, 2 h) was added. The reaction temperature was then raised slowly to the desired value. All the chemicals were obtained from E-Merck (AR grade) and used without further purification.

2.5. Analysis

The samples of the reaction mixture were isolated from the catalyst after 6 h by quenching the reactor in ice-cold water and the collected samples were analyzed by HP 6890 series GC (HP-1, crosslinked methyl siloxane, $30\,\text{m} \times 0.32\,\text{mm} \times 0.25\,\mu\text{m}$). The GC-MS measurements were performed on a GCMS-QP2000A mass spectrometer equipped with a Shimadzu 14A gas chromatograph. The products were further identified by GC-FTIR (Perkin-Elmer FTIR spectrometer, Spectrum 2000, equipped with Perkin-Elmer GC-IR system 2000 and Perkin-Elmer Autosystem Chromatograph). 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. Catalyst characterization

The physicochemical properties of the catalyst used in this study are presented in table 1. The XRD patterns reveal that the crystallinity is maintained in all dealuminated samples, but drops down a little in the sample treated at 850 °C. The unit cell constant, which is the indication of dealumination, was calculated to be 24.68, 24.38, 24.34 and 24.21 Å for these hydrothermally dealuminated samples HY, U-550, U-700 and U-850 respectively. The NH_3-TPD spectra of HY, Na-Y, U-550, U-700 and U-18 catalysts are shown in figure 1, while the temperature of desorption maxima (T_{d_i}) and the amount of desorbed ammonia (total acidity) are summarized in table 2. The spectrum of Na-Y exhibits a maximum at 249 °C; thereafter ammonia desorption decreases slowly. The HY catalyst showed two main desorption peaks at 297 and 398 °C (medium and strong acid sites), whereas the dealuminated HY catalyst U-700 shows these peaks at 212 and 309 °C, which were shifted to lower temperatures. Interestingly, the sample U-550 showed decreased acidity as compared with U-700, which is steamed at a higher temperature, showing peaks at 192 and 364 °C. On the other hand, the TPD profile of the steamed samples U-850 exhibits two main desorption peaks at 134 °C (less intense) and 346 °C.

3.2. Catalytic activity

Table 3 shows the activities and selectivity of the products with various catalysts studied in the alkylation of phenol with cyclohexanol. The reaction products are cyclohexylphenyl ether (CPE), a mixture of *ortho*- and *para*-cyclohexylphenol (2-CP and 4-CP) and

Table 1
Physical characteristics of HY and dealuminated HY zeolites

Sample	Temperature (°C)	Unit cell formula (from NMR)	Unit cell constant (Å)	Unit cell volume (Å)	Framework Si/Al	Deal. (%)	SA (BET) (m^2/g)
Na-Y	–	$Na_{42}[(AlO_2)_{56}(SiO_2)_{136}]$	24.71	15 093	2.4	–	825.2
Na-HY	500	$Na_{20}[(AlO_2)_{54}(SiO_2)_{138}]$	24.68	15 036	2.56	3.6	836.9
U-550	550	$Na_2[(AlO_2)_{20}(SiO_2)_{172}]$	24.38	14 493	8.75	64.3	554.3
U-700	700	$Na_{1.49}[(AlO_2)_{10}(SiO_2)_{182}]$	24.34	14 428	18.69	82.1	555.8
U-850	850	$Na_{1.22}[(AlO_2)_7(SiO_2)_{185}]$	24.21	14 202	52.06	87.5	385.3

All the samples were steamed for 4 h.

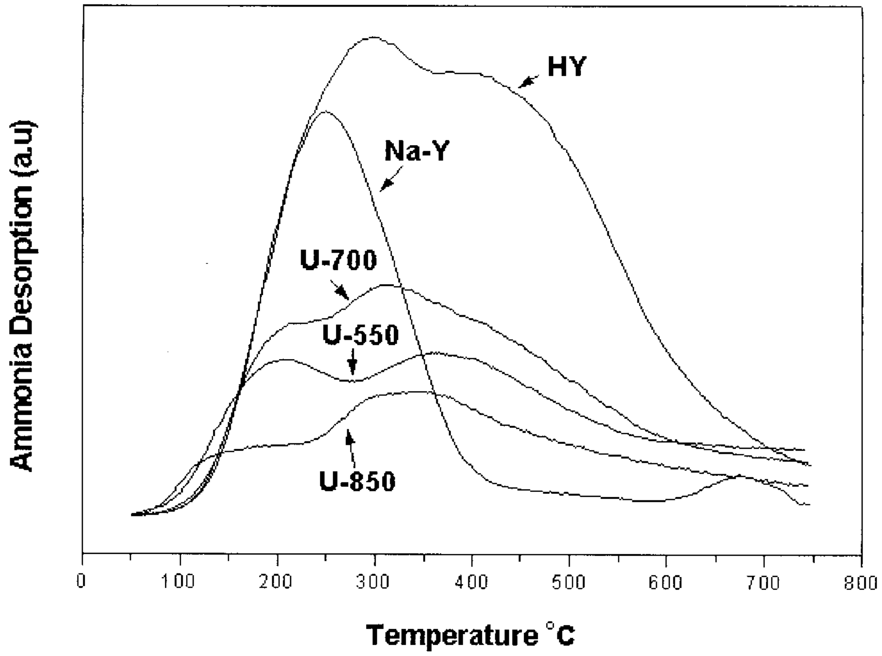


Figure 1. Normalized NH_3-TPD spectra of HY and dealuminated HY zeolites.

poly-alkylated cyclohexylphenols (PACPs). Small amounts of others (unknown high boilers) are also observed over all zeolite catalysts. The phenol conversion was more than 80% over all catalysts except Na-Y and U-850 (41 and 32.7% phenol conversion respectively). All these catalysts exhibit high conversion rates of cyclohexanol (<95%). Cyclohexene was formed as the major product in the case of the Na-Y catalyst. Other zeolites (HY) and HY zeolite dealuminated at moderate temperature (U-550, U-700) showed selective formation of 4-CP and the 2-/4- ratio is 0.34–0.41, whereas the catalyst HY steamed at a higher temperature (U-850) showed more formation towards 2-CP with less conversion of phenol, and the 2-/4- ratio was 2.24. This may be partially due to the decrease in the crystallinity of the sample and high dealumination percentage (88%), due to which mesoporosity increases. Most of these non-selective surface reactions predominate. So, the observed *ortho*-selectivity can be correlated to this phenomenon. HY and samples dealuminated at medium temperatures (500–700 °C) catalyze the reaction more efficiently than other samples. However, the selectivity for 4-CP was found to be nearly the same for these samples (U-550 and U-700). When the reaction was performed over γ-Al_2O_3 under identical conditions, the major product was cyclohexene (93.3%) and the 2-/4- ratio was 5.25.

Table 2

NH_3-TPD: temperature of desorption maxima and amount desorbed

Catalyst	T_{d_1} (°C)	T_{d_2} (°C)	Total acidity (mmol/g)
Na-Y	249.7	–	1.80
HY	297.4	398.4	4.54
U-550	192.5	364.5	1.17
U-700	209.3	314.5	1.97
U-850	–	346.1	0.68

$150 < T_{d_1} < 300$ °C; $T_{d_2} > 300$.

Table 3

Effect of various catalysts for alkylation of phenol by cyclohexanol

Catalyst	Conversion of cyclohexanol	Conversion of phenol	Product selectivities (wt%)						
			Cyclohexene	CPE	2-CP	4-CP	PCPs	Others	2-/4-
Na-Y	97.5	41.0	59.6	12.0	11.4	16.1	0.9	0.0	0.71
HY	97.9	85.0	10.6	3.0	15.9	38.7	21.9	9.9	0.41
U-550	99.9	83.2	12.7	4.1	15.6	42.7	17.9	7.0	0.37
U-700	99.9	81.2	14.0	3.7	15.2	44.3	15.6	7.2	0.34
U-850	97.7	32.7	28.5	8.7	42.2	18.8	1.8	0.0	2.24
γ-Al_2O_3	98.1	51.5	93.3	1.7	4.2	0.8	0.0	0.0	5.25

Reaction conditions: pressure 1 atm, temperature 200 °C, phenol/cyclohexanol (molar ratio) = 1, catalyst 10 wt%, time = 6 h.

The Si/Al molar ratio in the framework of zeolite influences important properties of zeolites (especially the number of active centers and cations). It is widely accepted that the strength of a given acid site depends on the number of aluminum atoms present in the next nearest neighbors (NNN), the stronger centers being those with smaller numbers of aluminum atoms in the NNN. Therefore, it is obvious that variation in the framework Si/Al ratio must produce samples with different catalytic activities [12]. Steaming of zeolites concurrently leaches aluminum, which in turn reduces the number of Al–O bonds. This results in the shrinkage of the unit cell size and consequently decreases micropore volume. Four zeolites, HY, U-550, U-700 and U-850, can be considered (table 1) and the activity of the zeolites decreased as follows: U-700 > U-550 > HY > U-18 > U-850 (table 3) for the selective formation of 4-CP.

3.3. *Effect of reaction time*

Figure 2 shows the activity and product selectivity (wt%) of zeolite HY catalyst as a function of time for the alkylation of phenol with cyclohexanol at 200 °C and an equimolar ratio of phenol to cyclohexanol. Formation of cyclohexene was high initially and decreased with time. Cyclohexanol conversion is almost constant, whereas the conversion of phenol increases with time. There is an increase in the wt% of 4-CP up to 8 h and then a decrease; this is because of the formation of a large amount of PCPs due to secondary reactions such as dealkylation and transalkylation of the products formed.

3.4. *Effect of reaction temperature*

The alkylation of phenol with cyclohexanol was carried out in the temperature range 140–220 °C over HY zeolite (figure 3(a)) and was compared with U-700 zeolite under identical reaction conditions (figure 3(b)). It can be seen from the data in figure 3(a) that the selectivity of 2-CP decreases (varies from 31% at 140 °C to 15.9% at 200 °C) and that of 4-CP increases (varies from 24.5% at 140 °C to 38.7% at 200 °C) with temperature. However, the selectivity towards 4-CP decreases slightly at higher temperature (38.7% at 200 °C and decreases to 30.1% at 220 °C) with a concomitant increase in the selectivity of PCPs. The conversion of phenol and cyclohexanol is almost the same in the temperature range studied. When the reaction was carried out over U-700 zeolite (figure 3(b), the conversion of phenol and selectivity to 4-CP increases with temperature with a decrease in 2-/4- ratio, which is comparatively less than HY zeolite at all reaction temperature.

When cyclohexene was used as an alkylating agent (figure 3(c)), in the temperature range 140–220 °C and under similar conditions, both conversions of phenol and cyclohexanol increased from 75.1% and 80.2% at 140 °C to 88.6% and 94.5% respectively at 200 °C. However, at a higher temperature, 220 °C, the conversion of phenol dropped to 83.5%, which shows an increase in phenol amount in the reaction mixture, accompanied

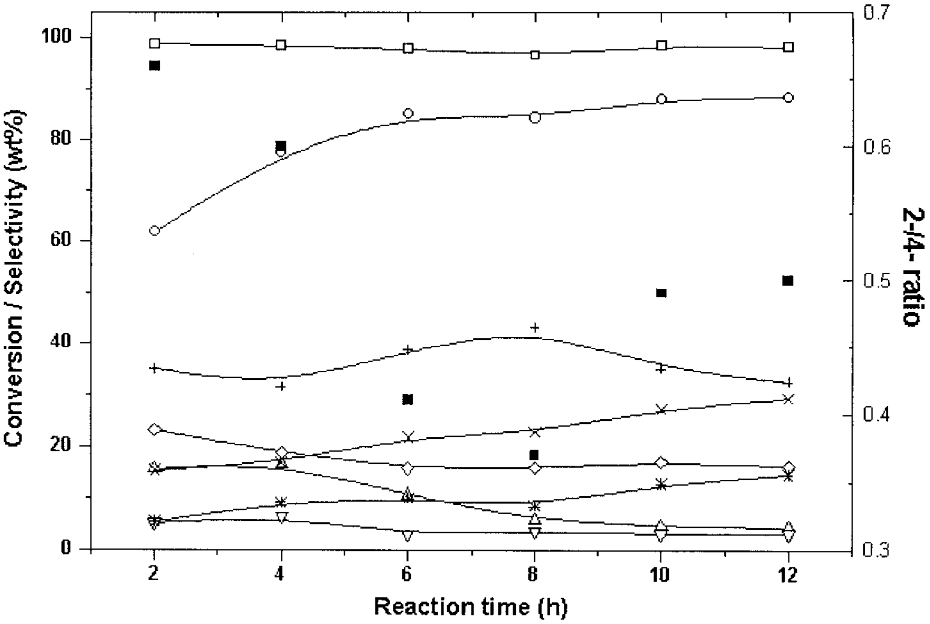
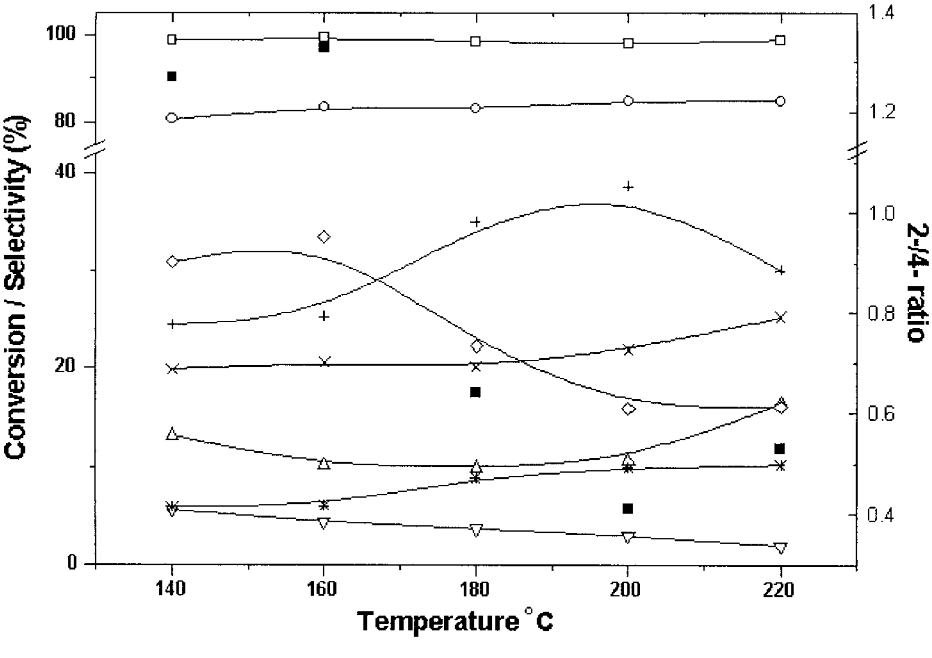
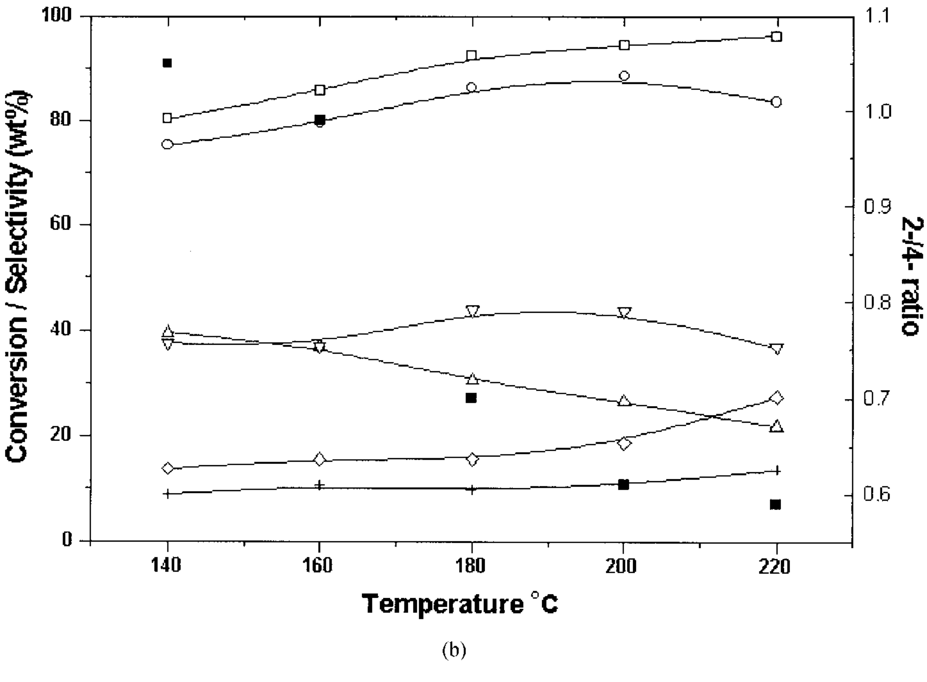


Figure 2. Alkylation of phenol by cyclohexanol over HY zeolite as a function of reaction time. (□) Converted cyclohexanol, (○) converted phenol, (△) cyclohexene, (▽) CPE, (◇) 2-CP, (+) 4-CP, (×) PCPs, (∗) others, (■) 2-CP/4-CP. Reaction conditions: temperature = 200 °C; phenol/cyclohexanol (molar ratio) = 1, catalyst (HY) = 10 wt%.



(a)

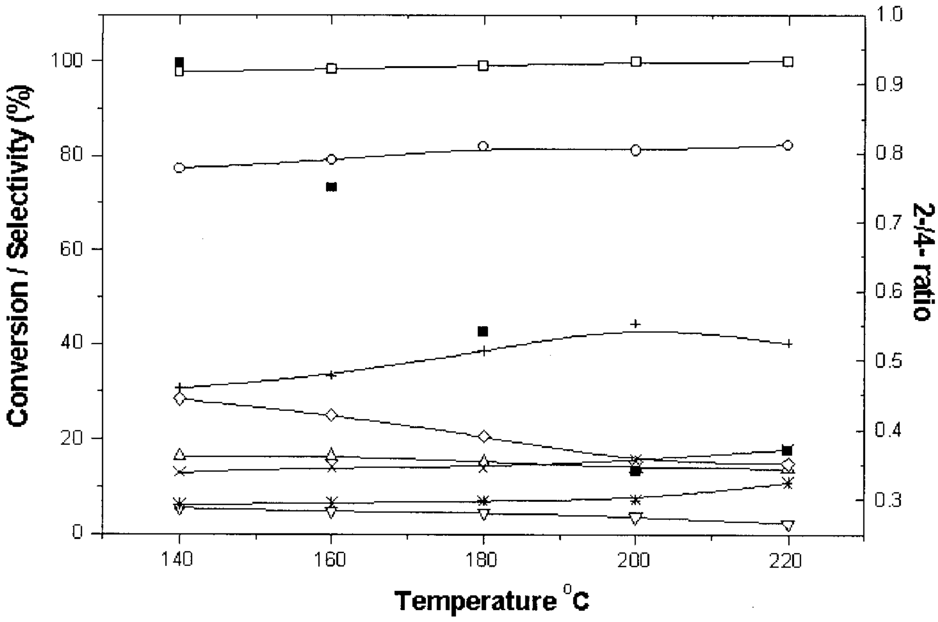


(b)

Figure 3. (a) Effect of reaction temperature on alkylation of phenol with cyclohexanol over HY zeolite. (□) Converted cyclohexanol, (○) converted phenol, (△) cyclohexene, (▽) CPE, (◇) 2-CP, (+) 4-CP, (×) PCPs, (*) others, (■) 2-CP/4-CP. Reaction conditions: phenol/cyclohexanol (molar ratio) = 1, catalyst (HY) = 10 wt%, time = 6 h. (b) Effect of reaction temperature on alkylation of phenol with cyclohexene over HY zeolite. (□) Converted cyclohexene, (○) converted phenol, (△) 2-CP, (▽) 4-CP, (◇) PCPs, (+) others, (■) 2-CP/4-CP. Reaction conditions: phenol/cyclohexanol (molar ratio) = 1, catalyst (HY) = 10 wt%, time = 6 h.

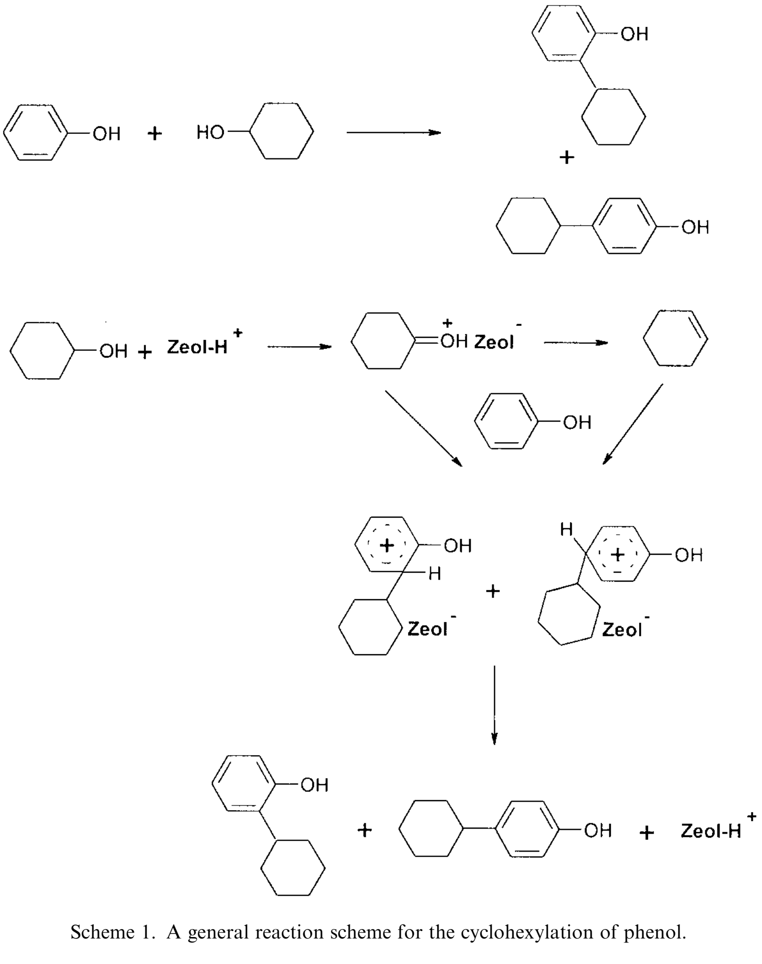
by an increase in the selectivity of PCPs, with a concomitant decrease in 2- and 4-CP, confirming the secondary reactions with an increase of temperature. Also there is no formation of cyclohexylphenylether (CPE). The yield towards CPs (2- + 4-) is considerably higher (66.5 and 55.3% respectively at 200 °C) with respect to cyclohexene and phenol than with respect to cyclohexanol and phenol (53.5 and 46.4% respectively at 200 °C), showing that cyclohexene is an effective alkylating agent.

Based on the above studies a general reaction scheme is shown in scheme 1. The first step in the reaction is the dehydration of cyclohexanol to cyclohexene. This further reacts with phenol to yield cyclohexylphenol. The other consecutive reaction is the alkylation of cyclohexanol to



(c)

Figure 3. (c) Effect of reaction temperature on alkylation of phenol with cyclohexanol over U-700 zeolite. (□) Converted cyclohexanol, (○) converted phenol, (△) cyclohexene, (▽) CPE, (◇) 2-CP, (+) 4-CP, (×) PCPs, (∗) others, (■) 2-CP/4-CP. Reaction conditions: pressure 1 atm, phenol/cyclohexanol (molar ratio) = 1, catalyst (HY) = 10 wt%, time = 6 h.



Scheme 1. A general reaction scheme for the cyclohexylation of phenol.

Table 4
Effect of phenol/cyclohexanol molar ratio in the selectivity of 4-CP over HY

Phenol : cyclohexanol	Conversion of cyclohexanol	Conversion of phenol	Product selectivities (wt%)						
			Cyclohexene	CPE	2-CP	4-CP	PCPs	Others	2-/4-
5 : 1	96.4	15.9	1.1	0.2	16.4	80.7	1.5	0.1	0.20
3 : 1	97.6	24.7	2.8	0.7	16.5	71.9	7.5	0.6	0.23
2 : 1	99.0	39.2	10.5	1.1	15.9	54.2	12.4	5.9	0.29
1 : 1	99.9	81.2	14.0	3.7	15.2	44.3	15.6	7.2	0.34

Reaction conditions: pressure 1 atm, temperature 200 °C, catalyst (HY) 10 wt%, time = 6 h.

yield both cyclohexylphenyl ether (CPE) or cyclohexyl phenols (CPs) depending on the reaction conditions. (The cyclohexylphenyl ether concentration decreases with temperature (figure 3(a)).) This is evidenced when cyclohexanol was used as the alkylating agent (the conversions of phenol is high) and when cyclohexene was used as the alkylating agent (the conversion of phenol is comparatively less as the etherification step is not there). With an increase of temperature both the rates of alkylation and dehydration increase as is evidenced by the increase in other alkylated products. But at all the temperatures under study the rate of alkylation with cyclohexanol is higher than the rate of dehydration, which is favored by the Brønsted acidity.

3.5. Effect of phenol/cyclohexanol molar ratio

The results of the influence of phenol/cyclohexanol or cyclohexene molar ratios on the alkylation of phenol and product selectivities over the catalyst U-700 are summarized in table 4. The conversion of phenol decreased, whereas the selectivity to 4-CP increased with increasing molar ratio of phenol to cyclohexanol. The product selectivity to 4-CP reached a maximum of 80% at phenol conversion of 16%. The 2-/4- ratio also decreases with an increase of phenol concentration in the reaction mixture.

3.6. Influence of catalyst concentration

Table 5 shows the influence of U-700 zeolite concentration under the optimal conditions ($T = 200\,^{\circ}$C; phenol/cyclohexanol molar ratio = 1; time = 6 h). As shown in this table, the increase in catalyst amount increases the phenol conversion (from 71.7% at 5 wt% to 96.9% at 20 wt%) and the formation of cyclohexene, whereas a decrease in other product selectivities is noted. There is an increase in polyalkylation and other side reactions *versus* the monoalkylation step with an increase in catalyst concentration due to availability of more acid sites for the secondary reactions to take place.

3.7. Influence of reaction time

Figure 4 depicts the influence of reaction time over the HY zeolite under the optimum reaction conditions ($T = 200\,^{\circ}$C; phenol/cyclohexanol molar ratio = 1; time = 6 h). It is observed that the conversion of phenol increases with reaction time. However, the selectivity to 4-CP decreases after 8 h of reaction time, and that of PCPs and others increases there after showing that longer contact time leads to polyalkylated products due to secondary reactions.

3.8. Recycling

In order to examine the regenerability of the catalyst, the solid phase was separated from the reaction mixture by filtration, washed with ethylacetate, dried at 120 °C and finally calcined at 500 °C for 3–4 h to remove the carbonaceous deposits before further use. The results of the catalyst recycling experiment are shown in table 6. The conversion of phenol decreased sharply from 85 to 75% on the first recycle, after which it almost remains

Table 5
Effect of catalyst concentration on cyclohexylation of phenol over HY zeolite

HY (wt%)	Conversion of cyclohexanol	Conversion of phenol	Product selectivities (wt%)						
			Cyclohexene	CPE	2-CP	4-CP	PCPs	Others	2-/4-
5	99.7	71.7	25.9	8.1	17.9	36.1	8.6	3.4	0.50
10	99.9	81.2	14.0	3.7	15.2	44.3	15.6	7.2	0.34
15	100.0	90.6	12.9	1.3	18.3	35.4	20.8	11.3	0.52
20	100.0	96.9	6.6	0.6	16.2	29.8	28.2	18.6	0.54

Reaction conditions: pressure 1 atm, temperature 200 °C, phenol/cyclohexanol (molar ratio) = 1, time = 6 h.

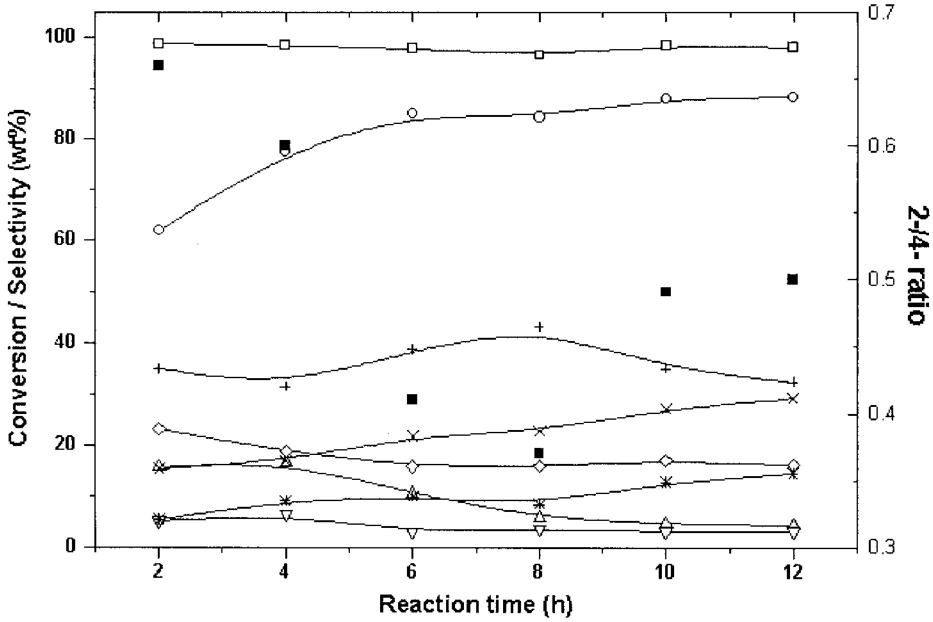


Figure 4. Effect of reaction time on alkylation of phenol with cyclohexanol over HY zeolite. Reaction conditions: pressure 1 atm, phenol/cyclohexanol (molar ratio) = 1, catalyst (HY) 10 wt%.

Table 6
Influence of the recycled catalyst (U-700) in the alkylation of phenol with cyclohexanol

Recycle	Conversion of cyclohexanol	Conversion of phenol	Product selectivities (wt%)						
			Cyclohexene	CPE	2-CP	4-CP	PCPs	Others	2-/4-
Fresh	99.9	81.2	14.0	3.7	15.2	44.3	15.6	7.2	0.34
1	100.0	75.6	16.7	5.9	15.5	40.3	13.4	8.2	0.38
2	99.5	73.9	18.9	7.1	15.3	38.6	12.3	7.8	0.40
3	99.0	71.6	23.1	7.7	14.6	35.0	12.1	7.5	0.42

Reaction conditions: pressure 1 atm, temperature 200 °C, phenol/cyclohexanol (molar ratio) = 1, catalyst (HY) 10 wt%, time = 6 h.

constant. However, the selectivity to 4-CP or the 2-/4- ratio remains nearly unaffected. The catalyst can be recycled effectively after washing with ethylacetate, dried and calcined at 500 °C for 3–4 h.

4. Conclusions

The liquid-phase alkylation of phenol with cyclohexene or cyclohexanol as alkylating agents can be carried out efficiently over HY zeolites. The alkylation of phenol with cyclohexanol or cyclohexene leads to the formation of a mixture of 2- and 4-monoalkylated products, in which 4-cyclohexylphenol is found to be major. The optimum reaction conditions are $T = 200\,^{\circ}\mathrm{C}$; phenol/cyclohexanol or cyclohexene molar ratio = 1 : 3 and time = 6 h. At lower temperatures, over HY, 2-CP predominates and at higher temperatures the *para*-isomer, 4-CP, predominates. Parameters such as reaction time, reaction temperature and molar ratio of the reactants increased the selectivity towards 4-CP. Also, HY zeolite steamed at medium temperatures (550–700 °C) showed an increase in selectivity of 4-CP.

Acknowledgments

R.A. thanks CSIR, New Delhi, for a Senior Research Fellowship. The authors would like to thank Dr. K.V.R. Chary, IICT, Hyderabad, India, for providing the TPD results.

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