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Vapor phase isopropylation of quinoline over modified HY zeolites *

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The vapor phase isopropylation of quinoline was carried out over HY and modified HY zeolites in a fixed-bed reactor at atmospheric pressure. The yield of 2-isopropylquinoline was higher over modified zeolites, especially over doubly-promoted LaKHY zeolite. The maximum yield of 2-isopropylquinoline obtained was 48.8 wt% with 82.9% selectivity. The reaction favors on moderate Lewis acidic sites.

Keywords: zeolite, quinoline, isopropylation, 2-isopropylquinoline

1. Introduction

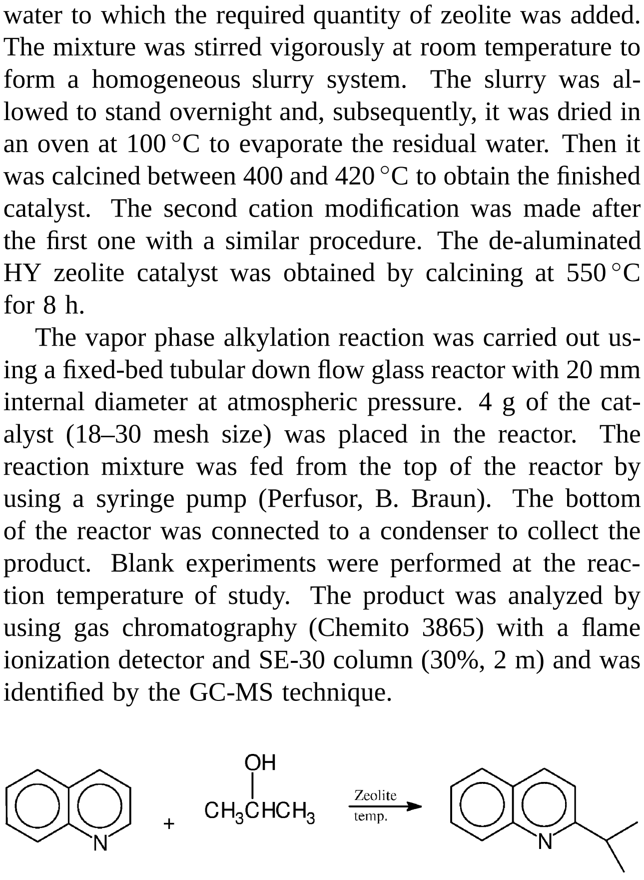
One of the foremost challenging problems being currently faced by the chemical industry is the need for alternative production technologies that are cleaner, safer and more environment friendly. The processes should be efficient in both energy and raw material consumption and result in minimum wastage. Zeolites are introduced in the fine chemical industry due to their numerous advantages over classical Friedel–Crafts catalysts such as easy handling, easy recovery, reusability, less or no corrosion, no disposal problem, high thermal stability and shape selectivity [1–8].

Many pharmaceutical industries use quinoline derivatives. Quinoline carboxylic acids are used in more than 50% in drug intermediates and their use is increasing day by day. There is very little information available on the synthesis of alkylquinolines. The alkylquinolines are present in small quantity in tars from low- and high-temperature carbonization of coal and in coal-liquefaction products [9,10]. Many derivatives of quinolines can be synthesized using the Skraup, Dobner, Knorr and Pfitzinger reaction methods [11]. In a Russian patent alkylquinolines are reported in the alkylation of quinoline from C_1–C_3 alkenes in a vapor phase system by using an Ni–Al catalyst [12]. There is not much published work on alkylation of quinoline, particularly over zeolite catalysts, except our recent report [13]. Furthermore, there is no single report for the synthesis of isopropylquinoline over zeolites. The derivatives of quinolines at second position are more reactive than the other derivatives [14,15]. In this work, we are reporting here for the first time the isopropylation of quinoline (scheme 1) in vapor phase on zeolite systems.

2. Experimental

The commercial zeolites HY and HZSM-5 supplied by PQ Corporation of USA and Conteka of Sweden are modified by an impregnation method with 1–3 wt% cations such as La, Ce, Cr and K. The required quantity of metal salt (respective nitrate salt) was taken and dissolved in distilled water to which the required quantity of zeolite was added. The mixture was stirred vigorously at room temperature to form a homogeneous slurry system. The slurry was allowed to stand overnight and, subsequently, it was dried in an oven at 100 °C to evaporate the residual water. Then it was calcined between 400 and 420 °C to obtain the finished catalyst. The second cation modification was made after the first one with a similar procedure. The de-aluminated HY zeolite catalyst was obtained by calcining at 550 °C for 8 h.

The vapor phase alkylation reaction was carried out using a fixed-bed tubular down flow glass reactor with 20 mm internal diameter at atmospheric pressure. 4 g of the catalyst (18–30 mesh size) was placed in the reactor. The reaction mixture was fed from the top of the reactor by using a syringe pump (Perfusor, B. Braun). The bottom of the reactor was connected to a condenser to collect the product. Blank experiments were performed at the reaction temperature of study. The product was analyzed by using gas chromatography (Chemito 3865) with a flame ionization detector and SE-30 column (30%, 2 m) and was identified by the GC-MS technique.



Scheme 1.

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3. Results and discussion

3.1. Catalyst characterization

The acidity of all the zeolite catalysts was measured by the method of stepwise temperature-programmed desorption (STPD) of ammonia, as reported in the literature [16], and the values of the zeolites are shown in table 1. The zeolites modified by rare earth cations show slightly higher acidity than the unmodified zeolites [13,17–20] and the acidity of transition metal modified zeolites is found to be less than those of unmodified zeolites, as in the following order: LaHY $\geqslant$ LaKHY > CeHY > HY > CrHY > HZSM-5(30). In K-modified zeolite systems, the acidity does not change further compared to that after the earlier addition of La salt to the zeolite. It may be due to the fact that the available acidic sites are already neutralized with the La addition. The X-ray diffraction of all the modified zeolites was measured and the crystallinity was found to be the same. The surface area of the zeolite samples was measured by the BET method. The modified zeolite surface area decreases compared to unmodified zeolites and the values are given in table 2.

3.2. Catalyst activity

The reaction of quinoline with isopropanol was carried out over zeolite catalysts HY, CeHY, LaHY, CrHY, LaKHY, DHY (de-aluminated HY) and HZSM-5(30) and the results are shown in table 3. Time-on-stream product distributions correspond to the second and fourth hour samples. The following order of activity was observed for this isopropylation at 350 °C temperature: LaKHY > LaHY > CeHY > DHY > HY > CrHY > HZSM-5(30). This trend is similar to our previous work on quinoline methylation [13]. HZSM-5(30) zeolite shows very low activity for this isopropylation reaction which may be due to its small ring size. The activity depends on the zeolite acidity and, as shown in figure 1, Ce- and La-modified HY zeolites exhibit slightly higher activity than that of unmodified zeolites and the trend matches very well with other literature reports [13,20–23]. The amount of lanthanum used here is only 3 wt%; if we increase the lanthanum content, the acidity of zeolite increases and there are possibilities to form the di- and poly-alkylated products in quinoline alkylation at high acidic content of solid catalysts [24]. In our system here, 2-isopropylquinoline is obtained with 48.8 wt% yield on LaKHY zeolite, as is shown in scheme 2. By addition of 1 wt% of potassium to the zeolite the acidity does not change. Moreover, it decreases the coking [17]. Here the percentage of alkali is restricted to only 1 wt% and, if we enhance the alkali content, then the zeolite surface is not favorable for this isopropylation reaction and it acts like a base-catalyzed reaction. In fact, the isopropylation

Table 1
Acidity of zeolite catalysts which are used in quinoline isopropylation.

Catalyst	Acidity (mmol/g)			Total acidity
	150–250 °C	250–350 °C	350–450 °C	
HY	42.03	19.47	9.47	70.99
LaHY	48.54	27.40	22.50	98.44
CeHY	46.79	23.59	19.90	90.29
LaKHY	47.45	28.30	21.80	97.55
CrHY	34.74	15.23	7.51	57.48
HZSM-5(30)	29.9	12.9	10.35	53.15

Table 2
Surface areas of the zeolite catalysts which are used for quinoline isopropylation.

Catalyst	Surface area (m^2/g)	Catalyst	Surface area (m^2/g)
HY	409.5	CrHY	223.0
LaHY	272.2	DHY*[a]	198
CeHY	245.3	HZSM-5(30)	427.3
LaKHY	175.5		

[a] DHY* = de-aluminated HY zeolite.

Table 3
Effect of variation of catalyst on quinoline isopropylation.[a]

Catalyst	TOS (h)	Conversion of quinoline (wt%)	Yield 2-IPQ (wt%)	Selectivity 2-IPQ (%)	Others (wt%)
HY	1	44	38	86.3	6
	4	26	19.1	73.4	6.9
LaHY	2	49	42	85.7	7.0
	4	41	34.2	83.4	6.8
CeHY	2	46	40.3	87.6	5.7
	4	38	32.8	86.3	5.2
LaKHY	**2**	**54.5**	**48.8**	**89.5**	**5.7**
	4	48	39.2	81.6	8.8
CrHY	2	38	24.9	65.5	13.1
	4	31.4	19.8	63.0	11.6
HY*	2	48	39.4	82.0	8.6
	4	34	25.7	75.5	8.3
HZSM-5(30)	2	18.2	13.0	71.4	5.2
	4	15.4	11.2	72.7	4.2

[a] Reaction temperature = 350 °C, feed molar ratio = 1 : 3, WHSV = 0.5 h^{-1}.

[b] 2-IPQ = 2-isopropylquinoline.

[c] Others = 4-IPQ, di- and poly-alkylated products, etc.

[d] HY* = de-aluminated HY zeolite.

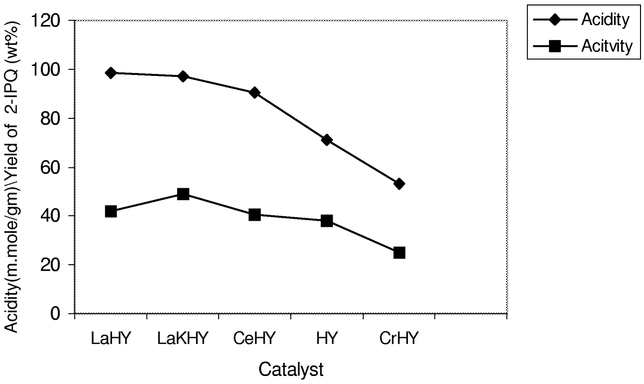
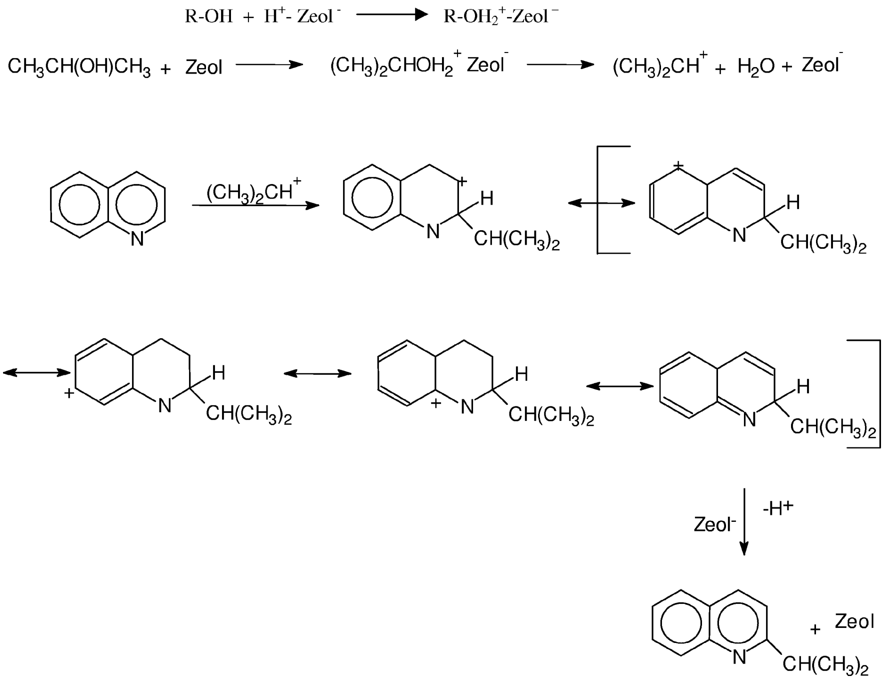


Figure 1. Acidity and catalytic activity correlation in quinoline isopropylation over zeolite catalysts.



Scheme 2.

Table 4
Effect of temperature on quinoline isopropylation over LaKHY.[a]

T_R (°C)	TOS (h)	Conversion of quinoline (wt%)	Yield 2-IPQ (wt%)	Selectivity 2-IPQ (%)	Others[b] (wt%)
250	4	15	11.4	76.0	3.6
	2	11	8.5	77.2	2.5
300	2	49	41.4	84.4	7.6
	4	42	34.8	82.8	7.2
350	**2**	**54.5**	**48.8**	**89.5**	**5.7**
	4	48.0	39.2	81.6	8.8
400	2	56	36.2	64.6	19.8
	4	51.9	30.0	57.8	21.9

[a] T_R = reaction temperature, molar ratio = 1 : 3, WHSV = 0.5 h^{-1}.
[b] Others = 4-IPQ, di- and poly-alkylated products, etc.

of quinoline is an acid-catalyzed reaction. In view of all this, the other controlling parameters such as variation of temperature, variation of feed molar ratio, i.e., quinoline to isopropanol, and weight hour space velocities (WHSV) were studied to get the best activity and selectivity over LaKHY zeolite system.

3.3. Effect of temperature on quinoline isopropylation

Isopropylation of quinoline was carried out at temperatures of 250, 300, 350 and 400 °C. The product formation was found to be affected by the reaction temperature and it is shown in table 4. From the data it is found that temperature below 300 °C is not suitable, because of the availability of Brønsted acid sites and these are not active for this reaction. In fact, it is reported that the Friedel–Crafts alkylation of quinoline favors on moderate Lewis acid sites [13]. At 300 °C the conversion is low and the alkylated yield is considerable. Furthermore, at 350 °C the alkylated product yield is found to be a maximum of 48.8 wt% with the selectivity of 82.9%; from this temperature Brønsted acid sites will transform into Lewis acid sites [23] which are suitable for Friedel–Crafts alkylation [13,25]. At higher temperature, i.e., above 350 °C, the available acid sites are strong [16,23,26,27]. Therefore, we can say the reaction favors on moderate Lewis acid sites. At 400 °C the Lewis acid sites are the predominant and strong active sites which are high in number. This may be the reason for the formation of di- and poly-alkylated products at high temperature [24] and these block the zeolite channels thus causing coke formation, resulting in the deactivation of the zeolite catalyst [28,29].

3.4. Variation of feed molar ratio and weight hour space velocity (WHSV) on quinoline isopropylation

The variation of molar ratio and weight hour space velocity plays a key role in the product formation in many catalytic reactions. Here the molar ratios of quinoline to isopropanol, weight hour space velocities were varied and the results are depicted in figures 2 and 3. At 1 : 1 concentrations of quinoline to isopropanol the conversion of quinoline decreases with time-on-stream. The maximum yield of alkylated product was found to be at 1 : 3 molar ratio. Further increase in isopropanol concentration, decreases the yield and selectivity of alkylated product. This may be due to the formation of di- and poly-alkylated products which deactivates the zeolite catalyst. Thus the 1 : 3 molar ratio composition was chosen as optimum. Similarly the WHSV of the reactant varied from 0.5 to 1 and the maximum yield of alkylated product is found to be at 0.5 h^{-1}. This contact time may be selective due to the inherent property of the catalyst for the observed product yields.

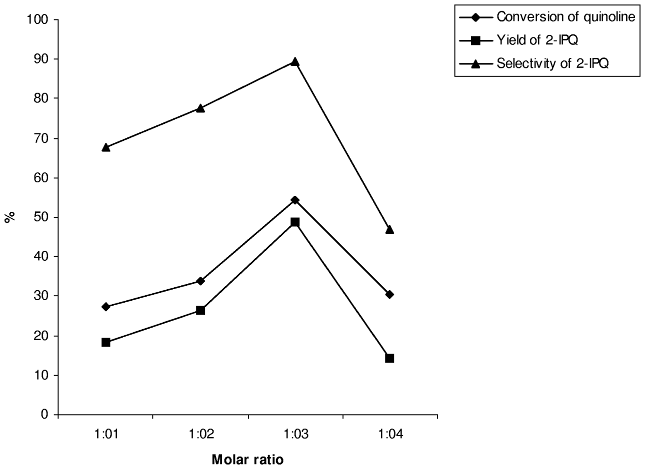


Figure 2. Variation of molar ratio of quinoline to isopropanol on quinoline isopropylation over LaKHY zeolite catalyst at 350 °C and WHSV 0.5 h^{-1}.

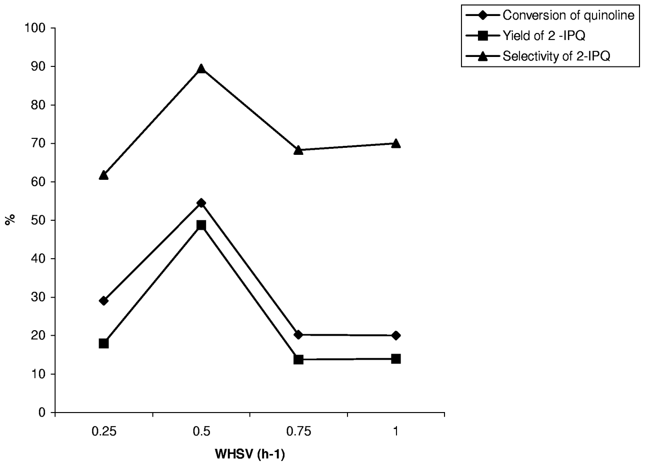


Figure 3. Variation of weight hour space velocity (WHSV) on quinoline isopropylation over LaKHY zeolite catalyst at 350 °C and of 1 : 3 molar ratio of quinoline to isopropanol feed.

By optimizing the parameters like temperature, molar ratio and weight hour space velocity, the alkylated product yield, i.e., 2-isopropylquinoline, still does not exceed 50 wt% and this may be mainly due to the shape selectivity of the zeolites. It is stated in the literature [30,31] that for isopropylation of large molecules such as naphthalene and biphenyl the delaminated HY zeolite is favorable, but in the present case there was no improvement of 2-isopropylquinoline product yield during quinoline isopropylation using de-alumination. It is known that the de-alumination of zeolites increases its acidic strength [32,33], whereas in the present case of quinoline isopropylation does not favor high acidic strength because of formation of isomers [24].

3.5. Reaction mechanism

It is known that the acid-catalyzed Friedel–Crafts alkylation of aromatics with an alcohol occurs via a carbonium ion electrophile generated by protonation of the oxygen and followed by the removal of water, and this electrophile attacks the aromatic ring that acts as a nucleophile [30]. The alkylation of quinoline catalyzed by zeolites takes place on acidic sites. Medium and large pore modified zeolites are the *ortho*- and *para*-directing groups in the alkylation reactions [31,32]. Thermodynamically and kinetically the quinoline isopropylation of both second and fourth positions is likely to occur on zeolite catalysts [33]. But by using modified zeolite samples and by variation of parameters, the isomers can be arrested [34]. Also the zeolites used in this reaction have mild acidic centers. Therefore, in the present case only the secondary position has the major product selectivity and it has been shown in scheme 2. At higher temperatures the selectivity decreases. This may be due to the formation of other isomers, which do not come from the zeolite channels resulting the zeolite deactivation.

4. Conclusions

Modified zeolites are suitable for quinoline alkylation compared to unmodified zeolites. LaKHY is the best catalyst for the isopropylation of quinoline. Selectivity as well as conversion decreases above 350 °C. Moderate Lewis acidic sites are responsible for quinoline isopropylation. The maximum yield of isopropylquinoline obtained was 48.8 wt% over LaKHY at 350 °C temperature with a molar ratio of 1 : 3 of quinoline to isopropanol and at WHSV of 0.5 h^{-1}. The yield of 2-isopropylquinoline decreased with time on stream after 4 h of run duration.

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