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Selective synthesis of 2-methylquinoline over zeolites [*]

P. Ram Reddy, K.V. Subba Rao and M. Subrahmanyam [**]

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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The selective vapour-phase synthesis of 2-methylquinoline by alkylation of quinoline with methanol was carried out over HY, HZSM-5(30), CrHY, CeHY, LaHY, LaKHY and CeHZSM-5(30) zeolites in a fixed-bed reactor at atmospheric pressure. The yields of 2-methylquinoline over modified zeolites, especially those of doubly promoted LaKHY, were found to be higher than those of unmodified zeolites. The maximum yield of 2-methylquinoline obtained was 60.6 wt% at 91.5 wt% selectivity over LaKHY zeolite. The active sites responsible for this methylation were found to be more on Lewis acidic sites available over zeolite systems.

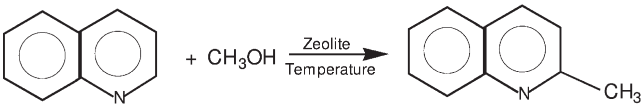
Keywords: zeolite, alkylation, quinoline, 2-methylquinoline

1. Introduction

Alkylations are the most important reactions in organic chemistry while heterogeneously catalysed alkylations by Friedel–Crafts reaction are very well known. Catalysts like $AlCl_3$, $TiCl_4$, BF_3 and $FeCl_3$ used in the conventional Friedel–Crafts alkylation reactions are replaced because of their corrosive nature, economic factors and other environmental protection problems. Zeolites are widely used in the synthesis of specialty and fine chemicals. The introduction of zeolites has proved to be a major breakthrough in acid-catalysed reactions because of their reusability, shape selectivity, high thermal stability, and they can be easily tailored to fit the desired reaction. They also solve a lot of other problems related to waste management in industrial processes [1–9].

Quinolines and alkylquinolines are widely used in metallurgy, polymers, corrosive inhibitors, and toxicology, as analytical reagents, and in the synthesis of agrochemicals. There is very little information available on the synthesis of 2-methylquinoline. The known process for this alkylation involves homogeneous and heterogeneous catalytic systems. Photochemical alkylation of quinoline by irradiation of the solution in benzene with acetic acid gives 20% 2-methylquinoline, 10% 4-methylquinoline and 5% 2,4-dimethylquinoline yield [10]. In the patented report [11], alkylation of quinoline gives 60–80% yield with carboxylic acid in the presence of ammonium persulfate and silver nitrate. Catalytic methylation of quinoline with methanol over a Ni–NiO_2 catalyst at 295 °C gives 2-methylquinoline [12]. Similarly, catalytic methylation by CO–H_2 at 450–470 °C has been reported to give very low yields [13].

As a part of our continued effort to selectively synthesise fine chemicals and their intermediates, in the present work we report for the first time high yields of 2-methylquinoline over zeolites with high selectivity using quinoline and methanol (scheme 1). In the present investigation we have observed high yields of alkylated product compared to the reported literature systems for 2-methylquinoline for the first time over the tested zeolite catalysts. There was no formation of 4-methylquinoline or 2,4-dimethylquinoline over the zeolite catalysts tested.



Scheme 1.

2. Experimental

HY (Si : Al = 2.6) was supplied by PQ corporation, USA, and HZSM-5(30) was supplied by Conteka, Sweden. The modified zeolites were prepared by an impregnation method with La, Ce and Cr metal nitrate salts. The impregnations were carried out at room temperature. Binary cation impregnation of zeolite (LaKHY) was prepared by a stepwise impregnation method. La salt impregnation was followed by K salt. After impregnation the catalysts were calcined at 400 °C for 4–5 h before using them as finished catalysts and the XRD patterns were the same before and after the reaction.

The fixed bed vapour-phase reactions were carried out over zeolite catalysts using a down-flow tubular glass reactor. The quantity of catalyst used for each reaction was 4 g (18–30 mesh size). The conversions were given with respect to quinoline. The reaction mixture of quinoline and methanol was fed from the syringe pump (B. Braun, Germany). Blank experiments were performed at the temperature of alkylation studies. The products were collected at ice-cold water temperature and analyzed by GC (Chemito)

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[**] To whom correspondence should be addressed.

using an SE-30 column. The product analysis was confirmed by GC-MS. The acidities of all the zeolite catalysts such as HY, HZSM-5(30) and cation-promoted zeolites such as CrHY, LaHY, CeHY, LaKHY, CeHZSM-5(30) were measured by the STPD of ammonia method, as reported earlier [14,15].

3. Results and discussion

The reaction of quinoline with methanol was carried out over zeolite catalysts such as HY, HZSM-5(30) and cation-promoted zeolites such as CrHY, LaHY, CeHY, LaKHY and CeHZSM-5(30). The results are shown in table 1. All the tested zeolite samples showed catalytic activity for the present alkylation; the HZSM-5(30) system showed less activity for quinoline alkylation compared to the HY system because of its low acidity and small pore size. The measured acidity of all the zeolites is shown in figure 1. The following order of acidity is obtained: LaHY $\geqslant$ LaKHY $>$ CeHY $>$ CeHZSM-5(30) $>$ HY $>$ CrHY $>$ HZSM-5(30). And for catalytic activity, the order at reaction temperature 350 °C is LaKHY $\geqslant$ LaHY $>$ CeHY $>$ HY $>$ CrHY $>$ CeHZSM-5(30) and HZSM-5(30). It has been reported in the literature that zeolites modified by rare earth metal cations such as La and Ce exhibit much higher degree of acidity than transition metal and alkali metal cations [15–18]. This is very much in agreement with our data on acidity of zeolites. Thus the zeolites modified by La and Ce were found to be more catalytically active than unmodified zeolites as in the present alkylation. It has also been reported by several authors that the rare earth forms of Y zeolite are very active for most reactions [19–21]. In the case of transition metal ion impregnated systems, i.e., CrHY zeolite, the catalytic activity suddenly decreased. This sudden decrease may be attributed to its low acidity. Therefore, the alkylation of quinoline is favoured on an acidic system. The results obtained on acidity and catalytic activity at 350 °C are shown in figure 2. It shows that the catalytic activity is falling in line with the order of acidity of the system. In the literature it is mentioned that there exists a direct relationship between acidity and alkylation activity [22]. By doping an alkali metal ion such as K on a preimpregnated zeolite (LaHY), the thermal stability of the doubly promoted zeolite is enhanced and it also helps in reducing the coke formation [8,23]. The modification of LaHY by 1 wt% of alkali metal ion (K) did not show much difference in acidity, therefore the activity is almost the same. The increase in the K content of LaKHY zeolite does not favour the quinoline alkylation since it is an acid-catalysed reaction. In this work the maximum quantity of alkylated product, i.e., 2-methylquinoline, was 60.6 wt% on LaKHY zeolite at 91.5 wt% selectivity. The (Wheland) mechanism of selective formation of 2-methylquinoline is depicted in scheme 2.

It is known that acid-catalysed alkylation by using alcohol as an alkylating agent takes place via a carbonium ion

Table 1
Effect of variation of catalyst on quinoline alkylation.[a]

Catalyst	T_R (°C)	TOS (h)	Quinoline conversion (wt%)	2-MQ yield (wt%)	Selectivity (wt%)
HY	300	1	33.3	33.0	99.0
		4	51.0	37.0	72.5
HY	350	3	42.2	37.1	87.9
		4	32.9	29.3	89.0
CeHY	300	2	30.7	21.7	70.6
		4	35.0	30.2	86.2
CeHY	350	2	58.2	47.0	74.0
		4	50.4	40.5	80.3
CrHY	350	2	58.5	48.8	83.4
		4	29.0	24.3	83.9
LaHY	350	2	58.2	47.0	80.7
		4	58.0	52.3	90.1
LaKHY	300	1	53.0	52.0	98.1
		4	40.3	39.3	97.5
LaKHY	350	1	66.2	60.6	91.5
		4	60.0	52.0	86.6
HZSM-5(30)	350	2	26.0	20.2	77.0
		4	28.5	20.3	71.2
CeHZSM-5(30)	350	1	22.0	20.7	80.0
		4	25.0	21.4	85.6

[a] Quinoline : methanol (molar ratio) = 1 : 3, weight hourly space velocity (WHSV) = 0.5 h^{-1}, T_R = reaction temperature, TOS = time on stream (h), 2-MQ = 2-methylquinoline.

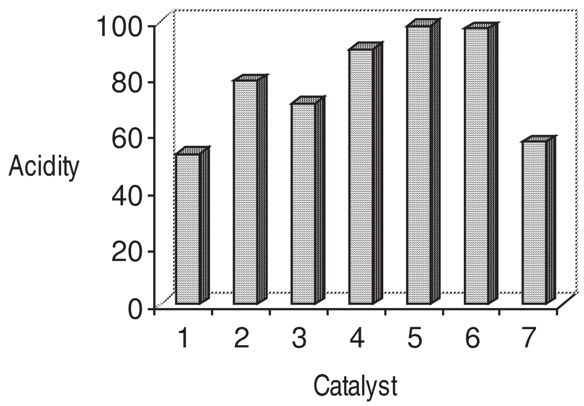


Figure 1. Acidity of the zeolite catalysts (mmol/g): (1) HZSM-5(30), (2) CeHZSM-5(30), (3) HY, (4) CeHY, (5) LaHY, (6) LaKHY, (7) CrHY.

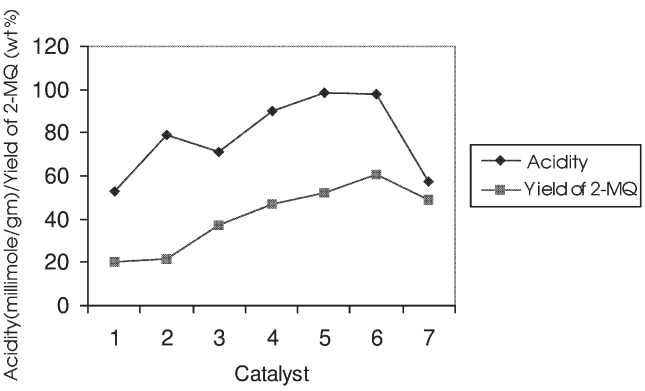
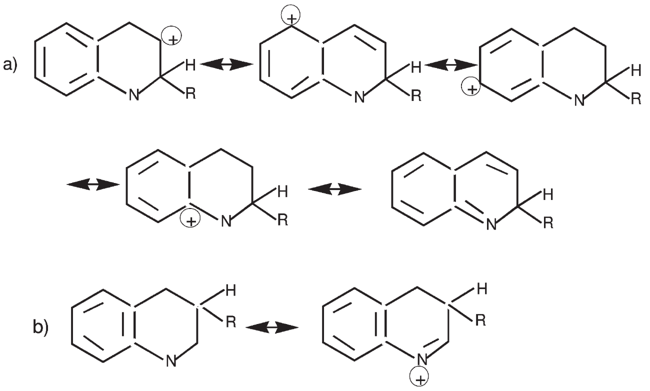


Figure 2. Correlation between the acidity and catalytic activity of the zeolite catalysts for 2-MQ yield: (1) HZSM-5(30), (2) CeHZSM-5(30), (3) HY, (4) CeHY, (5) LaHY, (6) LaKHY, (7) CrHY.



Scheme 2. Electrophilic attack at (a) position 2 and (b) position 3 in methylquinoline formation in Wheland intermediate mesomeric forms.

generated by protonation of the oxygen and is followed by dehydration [24]. The carbonium ion thus formed is responsible for the electrophilic substitution. From the above resonance structures, it can be seen that the electrophilic attack at position 2 leads to five resonating structures, whereas attack at position 3 forms only two [25]. Therefore, the product 2-methylquinoline formation probabilities are relatively more in comparison with 3-methylquinoline product. More insight into the alkylation was obtained by carrying out the reaction at various temperatures, molar ratios of quinoline and methanol, and weight hourly space velocities (WHSV) to achieve the highest yield of 2-methylquinoline on the LaKHY system. Furthermore, the life of the catalyst was checked by following the product distribution during time on stream.

4. Effect of temperature on quinoline alkylation

The effect of temperature on quinoline alkylation was studied over LaKHY, and the results have been summarized in table 2. The conversion of quinoline below 300 °C temperature is less favourable. This may be attributed to the high boiling nature of quinoline, i.e., 236 °C, and also due to the non-availability of enough Lewis acidic centers required for the reaction at this temperature. Brønsted and Lewis acidic sites are generated during the calcination of the catalyst. Brønsted acid sites are generated by the dissociation of water molecules and Lewis acid sites are generated by dehydroxylation of the lattice at higher temperatures. The nature of acid sites depends on the thermal pretreatment; Brønsted acid sites are converted into Lewis acid sites at high temperatures [18]. In this context, it is to be stated that the reaction was carried out at temperatures of 300, 350 and 400 °C. At temperature above 350 °C the selectivity of the reaction decreased from 91.5 to 54.4 wt%. For the present alkylation the other by-products, i.e., di- and trimethylquinolines, are present. The conversion of quinoline also gradually decreased to 46.2 wt% from the highest obtained value of 60.8 wt% at temperatures above 350 °C, which may be due to deposition of coke on the catalyst [26,27]. The coke deposit on acidic sites of zeolites leads to a decrease in the number of available active sites by coverage or blocking of the pores of zeolites resulting in a decrease of catalytic activity for the reaction. Also, it is seen that the acidity measured beyond 400 °C represents strong acid sites, and it suggests that they may not be useful during the methylation of quinoline. It may be inferred that only moderate Lewis acidic sites are the active sites responsible for this methylation. The maximum yield of 2-methylquinoline was observed at 350 °C, where more Lewis acidic sites exist. In our previous work on toluene alkylation, Lewis acidic sites were found to be suitable as in the present case of quinoline alkylation. In contrast, the acylations of furan and pyrrole are found to be more active on Brønsted acidic centers [15,23].

Table 2
Extent of alkylation of quinoline at various temperatures over LaKHY zeolite.[a]

T_R (°C)	TOS (h)	Quinoline conversion (wt%)	2-MQ yield (wt%)	2-MQ selectivity (wt%)
300	1	53.0	52.0	98.1
	4	40.3	39.3	97.5
350	1	66.2	60.6	91.5
	4	60.0	52.0	86.6
400	1	60.8	24.6	41.0
	4	46.2	25.2	54.4

[a] Quinoline : methanol (molar ratio) $= 1:3$, WHSV $= 0.5\ \mathrm{h}^{-1}$.

5. Variation of methanol : quinoline feed molar ratio and weight hourly space velocity

As seen from the results shown in tables 3 and 4, the molar ratio of quinoline and methanol was varied from 1 : 1 to 1 : 4. The maximum yield of 2-methylquinoline was observed at 1 : 3 molar ratio. Similarly, by changing the weight hourly space velocity (WHSV) from 0.25 to 1 h^{-1} the conversion of quinoline decreased due to low contact time of feed over the catalyst. The optimum WHSV value obtained was 0.5 h^{-1} to get the best yield of alkylated product.

A catalytic activity study was conducted for more than 8 h in order to record the life of the LaKHY zeolite at

Table 3
Feed molar ratio (quinoline : methanol) on alkylation product over LaKHY zeolite.[a]

Molar ratio	TOS (h)	Quinoline conversion (wt%)	2-MQ yield (wt%)	2-MQ selectivity (wt%)
1 : 1	1	17.9	13.1	73.0
	4	0.0	0.0	0.0
1 : 2	1	55.0	54.0	98.0
	4	31.9	26.2	82.1
1 : 3	1	66.2	60.6	91.5
	4	60.0	52.0	86.6
1 : 4	1	22.0	15.7	71.3
	4	18.0	15.1	84.0

[a] $T_R = 350\ °\mathrm{C}$, WHSV $= 0.5\ \mathrm{h}^{-1}$.

Table 4
Effect of weight hourly space velocity (WHSV) of reactants on alkylation.[a]

WHSV (h^{-1})	TOS (h)	Quinoline conversion (wt%)	2-MQ yield (wt%)	2-MQ selectivity (wt%)
0.25	1	35.7	35.0	98.0
	4	30.5	26.1	85.5
0.50	1	66.2	60.6	91.5
	4	60.0	52.0	86.6
0.75	1	26.0	20.2	77.0
	4	27.1	21.0	77.4
1.00	1	30.7	21.7	70.6

[a] Catalyst = LaKHY, $T_R = 350\,°C$, quinoline : methanol (molar ratio) = 1 : 3.

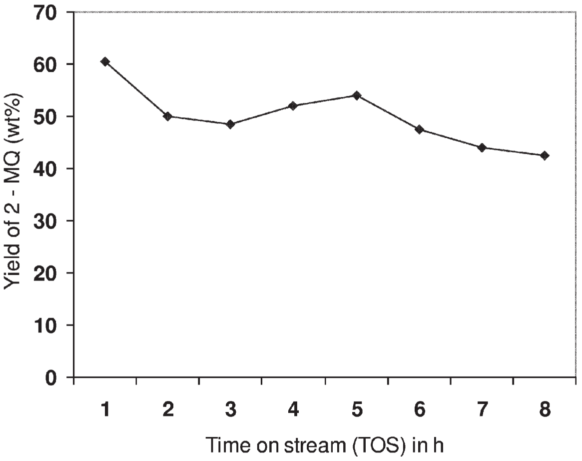


Figure 3. Yield of 2-methylquinoline with time on stream during quinoline alkylation over LaKHY.

350 °C and at 0.5 h^{-1} WHSV, 1 : 3 molar ratio of quinoline to methanol feed composition. It has been found that the initial yields gradually decreased over a period of time and the same is depicted in figure 3. This deactivation may be due to the formation of coke at the acidic sites of zeolites over a period of time.

6. Conclusions

The following conclusions may be drawn from the data generated. Modified zeolites are suitable for quinoline alkylation compared to bare zeolites. Lewis acidic sites are responsible for the present alkylation reaction. LaKHY is the active catalyst for the selective synthesis of 2-methylquinoline with high yields. Selectivity as well as conversions decrease at high temperatures, i.e., above 350 °C. Conversion and yields gradually decrease over a period of 8 h. The maximum yield of 2-methylquinoline obtained was 60.6 wt% at 91.5 wt% selectivity over LaKHY at 350 °C temperature with 1 : 3 molar ratio of quinoline : methanol at 0.5 h^{-1} WHSV.

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References

[1] Y. Ono, Catal. Tech. (1997) 31.
[2] S.J. Kulkarni, S.B. Kulkarni, P. Ratnaswamy, H. Hattori and K. Tanabe, Appl. Catal. 8 (1983) 43.
[3] W.W. Kaeding, C. Chu, L.B. Young and S.A. Butter, J. Catal. 69 (1981) 392.
[4] W.W. Kaeding, C. Chu and L.B. Young, J. Catal. 89 (1984) 267.
[5] R. Fang, H.W. Kouwenhoven and R. Prins, Stud. Surf. Sci. Catal. 84 (1994) 1441.
[6] J.H. Kim, S. Namba and T. Yashima, Bull. Chem. Soc. Jpn. 61 (1988) 1051.
[7] J. Cejka, B. Wichterlova and S. Bednarova, Appl. Catal. 79 (1991) 215.
[8] P. Ram Reddy, S.J. Kulkarni and M. Subrahmanyam, Ind. J. Chem. Tech. 5 (1998) 69.
[9] M.E. Davis, Acc. Chem. Res. 26 (1993) 111.
[10] H. Nozaki, Tetrahedron Lett. (1967) 4259.
[11] F. Minisci, Italian Patent 906418 (1 February 1972).
[12] R.C. Myerly and K. Weinberg, US Patent 3428641 (18 February 1969).
[13] D.K. Chapman, US Patent 3718704 (27 February 1973).
[14] S. Narayanan and K. Deshpande, Appl. Catal. 135 (1996) 125.
[15] P. Ram Reddy, M. Subrahmanyam and S.J. Kulkarni, Catal. Lett. 54 (1998) 95.
[16] W. Klading, Acta Cient. Veenz. 30 (1979) 74.
[17] W. Klading, J. Phys. Chem. 80 (1976) 262.
[18] C. Gauthier, B. Chiche, A. Finiels and P. Geneste, J. Mol. Catal. 50 (1989) 219.
[19] D.A. Hickson and S.M. Csicery, J. Catal. 10 (1965) 27.
[20] P.B. Venuto, L.A. Hamilton, P.S. Landis and J.J. Wise, J. Catal. 5 (1966) 484.
[21] K. Gaare and D. Akporiaye, J. Mol. Catal. 109 (1996) 177.
[22] S. Narayanan, V. Durga Kumari and A. Sudhakar Rao, Appl. Catal. 111 (1994) 133.
[23] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, J. Chem. Soc. Chem. Commun. (1993) 1456.
[24] A. Mitra, S. Subrahmanian, Satyanarayana, V.V. Chilukuri and D.K. Chakrabarthy, Appl. Catal. 153 (1997) 233.
[25] F. Richard, H. Carreyre and G. Pérot, J. Catal. 159 (1996) 427.
[26] B. Gielen and M.G. Pakerkar, Zeolites 9 (1989) 208.
[27] W.F. Hölderich, J. Roseler, G. Heitmann and A.T. Liebens, Catal. Today 37 (1997) 353.