Catalysis Letters 19 (1993) 281–291

Reactions of benzyl alcohol and dibenzyl ether over zeolites

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Received 20 March 1993; accepted 19 April 1993

The reaction of benzyl alcohol and dibenzyl ether on several zeolites was studied in the temperature range 300–500°C. The major products were benzaldehyde and toluene due to disproportionation, anthracene due to intermolecular alkylation followed by cyclodehydration, benzyltoluenes due to alkylation followed by hydrogenolysis, and stilbene. The alkylation course was strongly influenced by shape selectivity with the large pore zeolites mainly yielding anthracene and the medium pore zeolites benzyltoluene. The formation of stilbene was a new observation which has a bearing on the mechanism of the methanol-to-hydrocarbon reactions.

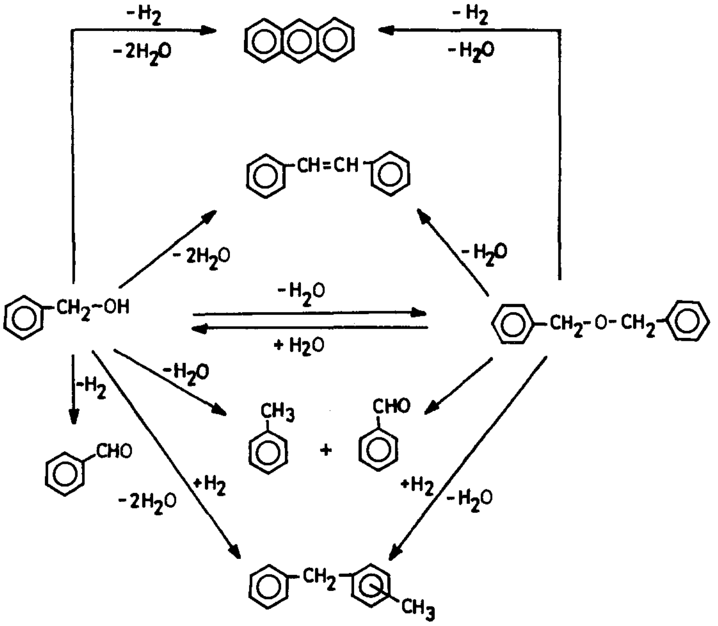
Keywords: Benzyl alcohol, reactions on zeolites; anthracene, from benzyl alcohol; stilbene, from benzyl alcohol; benzyl alcohol, formation of anthracene from; stilbene, formation of anthracene from; zeolites, reaction of benzyl alcohol over.

1. Introduction

Benzyl alcohol undergoes a variety of reactions under acid catalysis, both homogeneous [1,2] and heterogeneous [3–8]. The reaction of benzyl alcohol over alumina has been reported to result in dibenzyl ether (dehydration), benzaldehyde and toluene (disproportionation) and anthracene [5]. The disproportionation reaction has been shown to involve an intermolecular hydride transfer [6] and the selectivity for this reaction increases with the acidity of the catalyst. Formation of anthracene from benzyl alcohol over alumina and over zeolites was first reported by Ganesan and Pillai [5] and was visualized as involving an ortho alkylation to form *o*-benzylbenzyl alcohol followed by cyclodehydration and dehydrogenation. Anthracene formation was the major reaction of benzyl alcohol on acidic forms of alumina and on HY-zeolite at temperatures above 400°C. In view of the wide range of competing reactions undergone by benzyl alcohol over acidic catalysts, it was felt that the use of benzyl alcohol as a probe molecule to examine the behaviour of different zeolites will be rewarding. Here we report a study of the reactions of benzyl alcohol and dibenzyl ether over a number of zeolites in the temperature range of 300–500°C.

2. Results and discussion

The reactions of benzyl alcohol and dibenzyl ether were studied under gas phase flow condition. A tubular pyrex glass reactor packed with the catalyst in granular form was used. The vapours of the reactant along with a diluent were introduced from the top (downward flow) and the liquid products were condensed and collected for further analysis. Two techniques were employed for the introduction of the reactant. In one, the reactant was mixed with a solvent and introduced as liquid at the top of the reactor using a syringe-type infusion pump. Benzene was used as the solvent in most of the studies. The question of benzene being not an inert solvent, but a reactive one, was considered. Benzene could undergo alkylation by alcohols over zeolites leading to, in the present case, diphenylmethane. Diphenylmethane was indeed a product of the reaction, but a very minor product. This was the case on all the catalysts, under all the conditions studied. In the second procedure, benzyl alcohol vapour was passed into the reactor using nitrogen, by bubbling nitrogen through benzyl alcohol kept in a "saturator" maintained at a constant temperature. The flow rate and bath temperature were so adjusted as to maintain the same contact time as when benzene was used as the diluent. The product compositions of the two types of experiments were very similar. Diphenylmethane was formed even in the reaction using nitrogen as diluent, albeit in smaller quantities. This may be because in addition to benzylation of benzene, demethylation of benzyltoluene can also lead to diphenylmethane. Benzene was also formed



Scheme 1.

as a product which was detected when nitrogen was used as diluent, but was of course missed when benzene was the diluent. Thus, from these studies it appeared that benzene could be safely used as a diluent and did not react to any significant extent under the reaction conditions.

Benzyl alcohol and dibenzyl ether react over oxide catalysts to give a variety of products as illustrated in scheme 1, due to dehydration, dehydrogenation and hydrogenolysis. Toluene, benzaldehyde, anthracene, stilbene and *o*-benzyltoluene (over medium pore zeolite only) are the major products. Other minor products like *m*-benzyltoluene, *o*-benzyltoluene, diphenylmethane, diphenylethane, dibenzyl ether (from benzyl alcohol) and benzyl alcohol (from dibenzyl ether) were also formed.

The product distribution on HY, CeY, HZSM-5 and HZSM-22 are presented in table 1 (benzyl alcohol reactions) and table 2 (dibenzyl ether reactions). The reactions were also done on HEMT, H-Beta, HZSM-12, HEU-1 and NaY-zeolite (the full data are not included here). The product distribution on the large pore zeolites was very similar to those on the Y-zeolite and that on the medium zeolite similar to that on ZSM-5.

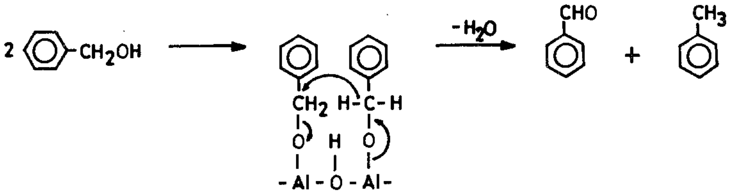
The major reactions of benzyl alcohol may be classified under three headings: (a) dehydration, (b) disproportionation and (c) benzylation.

(a) DEHYDRATION

Intermolecular dehydration to form dibenzyl ether was observed only at the lower temperatures (300 and 350°C). Since the reactions were done at high conversions and since the ether undergoes further reactions, it is not surprising that the ether is not detected at higher temperatures.

(b) DISPROPORTIONATION

Benzyl alcohol undergoes ready disproportionation to benzaldehyde, toluene and water under the reaction conditions. The reaction has been shown to involve, over alumina, a hydride transfer from a surface benzyl oxide species to the positively polarized α-carbon of a neighbouring benzyloxy species (scheme 2). This mechanism may be valid for the zeolite catalyzed reactions also. Since no dehydrogenation is involved, the molar ratio of benzaldehyde/toluene is unity except at



Scheme 2.

Table 1
Reactions of benzyl alcohol over zeolites[a]

Catalyst	Temp (°C)	Conv. (%)	Yield (mol%)[b]								
			toluene	benzal-dehyde	OBT + MBT	PBT	DBE	DPE	anthracene[c]	stilbene	unaccounted[d]
HY-zeolite	300	72	18	17	0	0	12	0	6	0	19
	350	92	22	21	1.5	2.5	3	0	31	0	11
	400	96	9	9	1.5	2	0	0	52	9	13.5
	450	98	7	14	2	1.5	0	0	47	12	14.5
	500	98	8	17	1.5	1.5	0	0	45	11	14
HZSM-5	300	56	11	11	3	4	12	1	tr	0	14
	350	78	16	15	6	13	7	5	tr	0	16
	400	92	20	22	7	28	0	2	tr	2	11
	450	94	17	26	4	31	0	2	tr	3	11
	500	96	14	29	3	27	0	0	tr	5	18
HZSM-22	300	78	20	20	1	3	21	tr	tr	0	13
	350	89	24	26	1	7	12	tr	tr	4	15
	400	100	27	27	3	21	0	tr	tr	7	15
	450	100	17	23	5	31	0	tr	tr	10	14
	500	100	13	20	4	29	0	tr	tr	18	16
CeY-zeolite	300	83	19	20	1.1	2.8	11	tr	12	0	17.1
	350	97	22	21	2	3.6	0	tr	34	4	10.4
	400	98.5	6	7	4.5	2	0	tr	61	7	11
	450	100	6.5	10	6	4.5	0	tr	52	5.5	15.5
	500	100	4.5	17	5	6	0	tr	43	3	21.5

[a] Reagent = 5 ml of benzyl alcohol in 20 ml of benzene, catalyst = 3 g, flow rate = 20 ml/h.

[b] Mole percentage based on benzyl alcohol.

[c] tr = traces.

[d] Small amount of diphenylmethane, higher boiling components which did not appear on the gas chromatograph, gases, coke and mechanical losses. PBT = *p*-benzyltoluene, OBT = *o*-benzyltoluene, MBT = *m*-benzyltoluene, DBE- dibenzyl ether, DPE = diphenylethane.

Table 2
Reactions of benzyl ether over zeolites [a]

Catalyst	Temp (°C)	Conv. (%)	Yield (mol%) [b]								
			toluene	benzaldehyde	benzyl alcohol	OBT + MBT	PBT	DPE [c]	anthracene	stilbene	unaccounted [d]
HY-zeolite	300	73	20	19	6	2	3.5	1.5	7	1	13
	350	96	26	25	2	7	9	0	8	2	17
	400	98	26	24	1	5	6	0	17	5	14
	450	100	12	15	0	4	3	0	45	10	11
	500	100	10	12	0	3.5	3	0	41	17	13.5
HZSM-5	300	77	15	16	6	4	9	2	8	1	16
	350	93	23	23	1	6	12	3	11	3	11
	400	100	14	9	1	9	28	1	16	6	16
	450	100	10	7	1	8	19	0	28	9	18
	500	100	11	9	0	6	21	0	26	8	19
CeY-zeolite	300	88	21	22	4	3.5	2	3.5	9	0	11
	350	96	25	24	2	8	3	1	16	0	13
	400	100	11	12	0	7	3.5	2	48	0	16.5
	450	100	8	10	0	5	4.5	0	54	7	11.5
	500	100	9	12	0	4	3.5	1.5	41	4	25
HZSM-22	300	87	25	25	12	0	4	tr	4	2	13
	350	96	31	30	5	1	6	tr	8	3	12
	400	100	14	14	5	6	19	tr	12	13	17
	450	100	9	8	4	7	28	tr	15	14	15
	500	100	8	8	0	6	30	tr	17	17	14

[a] Reagent = 5 ml of dibenzyl ether in 20 ml of benzene, catalyst = 3 g, flow rate = 20 ml/h.

[b] Mole percentage based on dibenzyl ether.

[c] tr = traces.

[d] Small amount of diphenylmethane, higher boiling components which did not appear on the gas chromatograph, gases, coke and mechanical losses. PBT = *p*-benzyltoluene, OBT = *o*-benzyltoluene, MBT = *m*-benzyltoluene, DBE-diphenylethane.

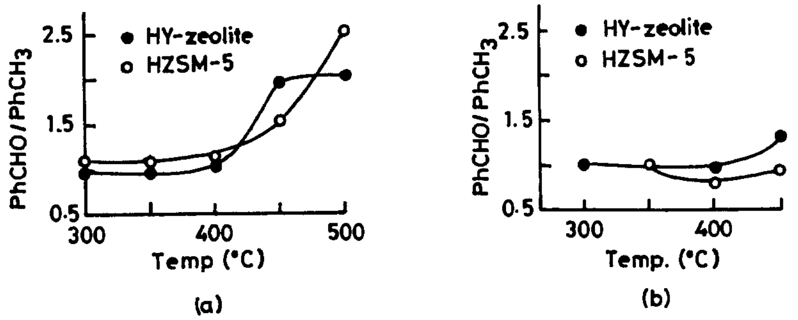


Fig. 1. Reaction of (a) benzylalcohol and (b) dibenzyl ether.

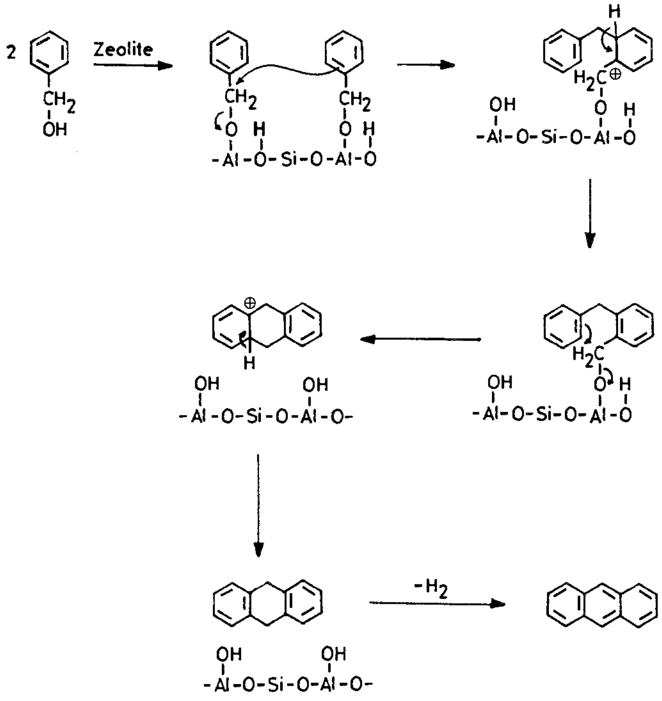
temperatures above 450°C. Above 450°C this ratio goes above unity due to a competing unimolecular dehydrogenation of benzyl alcohol to benzaldehyde and hydrogen. This has been found to be true over all the zeolites. However, there is a significant difference in the behaviour of benzyl alcohol and dibenzyl ether at high temperatures, with respect to the benzaldehyde / toluene ratio.

At higher temperatures (>400°C), this ratio is higher than unity when benzyl alcohol is used as the probe molecule as expected, fig. 1. But when dibenzyl ether is used, even at these temperatures the ratio remains close to unity. This is probably due to the fact that when dibenzyl ether is the reactant two benzyloxy groups are available close to each other for disproportionation to occur (scheme 2). When benzyl alcohol is used, this need not be the case and the alternate reaction, dehydrogenation, competes favourably with disproportionation.

(c) BENZYLATION PRODUCTS

The other major products of the reaction, namely, anthracene, benzyltoluenes and stilbene can be considered to be benzylation products. Both benzyl alcohol and dibenzyl ether are known to give, on adsorption over zeolites, the same surface species namely benzyl oxide. *o*-benzylbenzyl oxide species formed by the interaction between two such surface alkoxide species can undergo dehydrative cyclization followed by aromatization to form anthracene (scheme 3). Ganesan and Pillai [5] reported that the attempts to isolate the intermediate *o*-benzylbenzyl alcohol were not successful due to its ready conversion to anthracene under the reaction conditions. However, the gas chromatographic analysis showed its presence in traces in the product mixture. They showed that when the intermediate alcohol, prepared independently was subjected to the same experimental conditions, anthracene was obtained quantitatively.

In the case of large pore zeolites anthracene formation was one of the major reactions when benzyl alcohol and dibenzyl ether were the reactants. Assuming that the first step in anthracene formation is ortho benzylation, this high yield of anthra-



Scheme 3.

cene is indicative of a high degree of selectivity for ortho alkylation on the large pore zeolites and is most likely due to the proximity of the ortho position to the alkylating agent.

Over medium pore zeolites, anthracene is absent or very little when benzyl alcohol was the reactant. However, a small amount of anthracene was formed when dibenzyl ether was the reactant.

Formation of anthracene from benzyl alcohol seems to be a reaction strongly controlled by shape selectivity considerations (see table 3). There is a distinct differentiation between the large pore zeolites (Y, EMT, and Beta) and the medium pore zeolites (ZSM-5, EU-1 and ZSM-22) with ZSM-12 coming in between. The low yield on NaY could be due to reduced acidity or due to reduced space availability inside the pores. In the case of alumina catalysts, increased sodium doping was found to decrease the anthracene yield and was attributed to reduction in acidity [5]. Changing the feed molecule to dibenzyl ether did not affect the anthracene selectivity on the large pore zeolites. However, on the medium pore zeolites, this made a big difference. Several possibilities may be considered.

(i) Anthracene formation from benzyl alcohol involves interaction between two molecules adsorbed on the surface close to each other in an appropriate orientation. This is not achieved in the confined space available in medium pore zeolites. In

Table 3
Selectivity for anthracene and benzyltoluene at 100% conversion (450°C) over different zeolites [a]

Reactant		CeY	HY	NaY	HEMT	H-Beta	HZSM-12	HEU-1	HZSM-5	HZSM-22
benzyl	ANTH	52.0	47.0	16.0	50.0	44.0	38.0	9.0	tr	tr
alcohol	BTS	10.5	3.5	11.5	6.0	7.0	11.0	20.0	35.0	36.0
dibenzyl	ANTH	54.0	45.0	37.0	40.0	45.0	41.0	18.0	28.0	15.0
ether	BTS	9.5	7.0	14.0	15.0	7.0	7.0	10.0	27.0	35.0

[a] ANTH: anthracene, BTS: benzyltoluenes and tr: traces.

the case of the dibenzyl ether reaction, the two benzyl species are delivered to the active sites of the catalyst in one packet and are probably oriented in the required manner.

(ii) The mechanism of anthracene formation from benzyl alcohol (scheme 3) may be different from that for dibenzyl ether. As discussed below, other pathways can also be considered for anthracene formation (scheme 5).

(iii) In the case of dibenzyl ether the reaction may be taking place on the external surface of the medium pore zeolites and not inside the pores.

Some experiments were done to verify the third possibility by poisoning the external surface of HZSM-5 catalyst using 1,10-phenanthroline. This bulky base has been shown to be effective to block the external acid sites of ZSM-5 catalyst and thereby induce para-selectivity in toluene alkylation with ethylene [9]. When a reagent mixture consisting of 5 ml dibenzyl ether, 20 ml benzene and 0.5 g 1,10-phenanthroline was passed over HZSM-5 (3 g), the product distribution as well as the total conversion changed. When the concentration of 1,10-phenanthroline was increased twofold, total conversion came down further but the product distribution was unaffected. There was heavy carbon deposit on the catalyst when 1,10-phenanthroline was used. The catalyst powder was caked into a black mass. This seems to be the cause of the reduction in conversion. While these studies cannot be considered to be definitive, the fact that anthracene was formed from dibenzyl ether even when the catalyst was poisoned by 1,10-phenanthroline suggests that at least part of the anthracene formation has taken place inside the pores of the catalyst.

p-benzylation

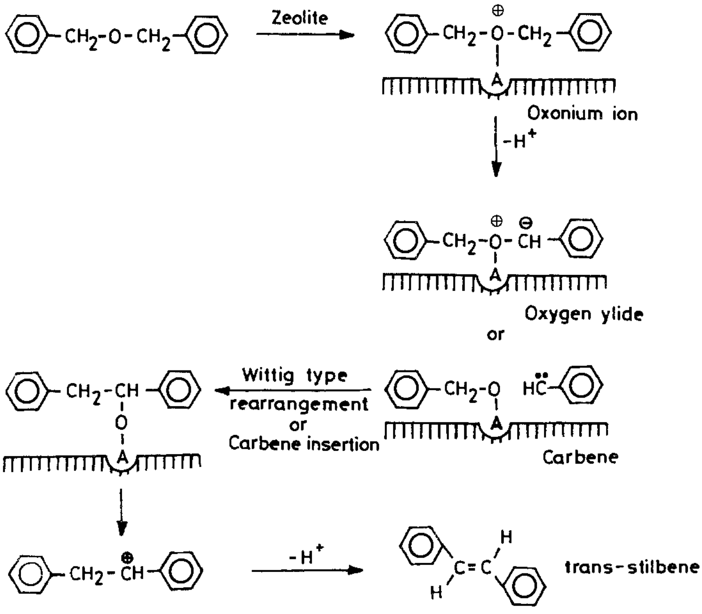
Benzyltoluenes, mainly the para isomer, were obtained in all the reactions. Assuming that the preferred site of benzylation is ortho as discussed above, the ortho benzylated product has two pathways in which it can undergo further reaction namely (i) cyclization to anthracene and (ii) hydrogenolysis to *o*-benzyltoluene which may undergo further isomerization to meta- and (mainly) para-benzyltoluene (due to shape selectivity reasons). On the medium pore zeolites the major alkylation product is *p*-benzyltoluene and not anthracene. The reverse is true in the large pore zeolites. It is likely that once the *o*-benzylbenzyloxy species is formed, it can attain the orientation required for the transition state for cyclodehydrations to anthracene in the pores of the large pore zeolite. This seems to be not the case in the medium pore zeolite due to space restrictions and hence it undergoes reaction by the alternate pathway, namely hydrogenolysis followed by isomerizations.

α-benzylation: stilbene formation

Stilbene was a significant product in all the reactions. Diphenylethane was also formed in some of the experiments. Diphenylethane could be the product of thermally generated benzyl radicals. The possibility of stilbene being formed by the dehydrogenation of diphenylethane was considered. However, in experiments when diphenylethane (in benzene) was passed over HY-zeolite under the reaction condition, no stilbene was formed. Hence alternate pathways for the formation of stilbene were considered.

The formation of stilbene can be considered as an α-benzylation as discussed below. Stilbene from benzyl alcohol is formally similar to ethylene from methanol, which is the basis of the methanol-to-gasoline (MTG) reaction over zeolites.

The mechanism of the MTG reaction has been extensively investigated [10]. Dimethyl ether has been shown to be the first intermediate. This may undergo α-elimination to form a carbene which can be stabilized by complexation with a dimethyl ether molecule and then undergo an insertion reaction to lead to methyl ethyl ether, and thence, ethylene, which by further acid catalyzed conversions gets



Scheme 4.

transformed to higher hydrocarbons. An alternate mechanism that has been suggested involves an oxygen ylide, which undergoes Wittig or Stevens type rearrangement followed by decomposition to furnish ethylene. Extension of this mechanism to dibenzyl ether and benzyl alcohol as shown in scheme 4, will lead to the formation of trans-stilbene. An interesting outcome of this line of thinking is that ortho-benzylation and anthracene and *o*-benzyltoluene formation can take place by a related Sommelet–Hauser type rearrangement as shown in scheme 5.

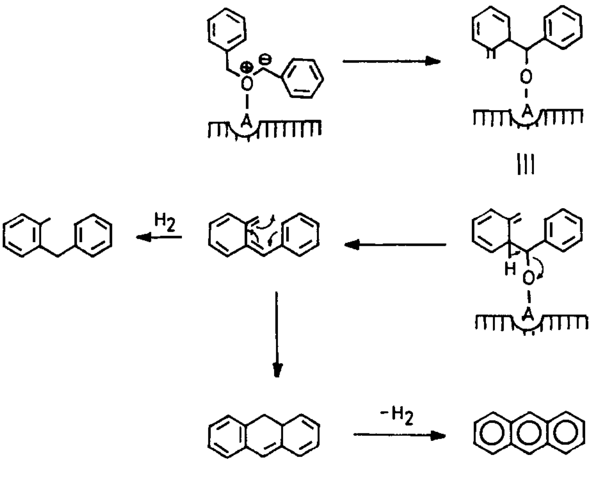
3. Experimental

3.1. CATALYSTS

ZSM-5 and Y-zeolites were obtained as gifts from IPCL-CATAD Division, Thane, India and Union Carbide, USA respectively. ZSM-12, ZSM-22, EU-1, zeolite beta and EMT zeolites were synthesised by standard procedures. The catalysts were activated in a stream of dry and purified air at 500°C for 4 h before use.

3.2. EXPERIMENTAL PROCEDURE

The reactions were carried out in a flow reactor consisting of a pyrex tube of 2.5 cm diameter and 40 cm length kept in a cylindrical furnace mounted in a slanting manner. About 3 g of the catalyst was kept in the middle isothermal region of the reactor. The space above the catalyst was packed with pyrex glass beads which acted as a preheater zone. Provision was made to read the inside temperature of the catalyst zone using a thermocouple. The catalyst was activated at 500°C and the temperature was brought to the reaction temperature in a stream of pure and dry



Scheme 5.

nitrogen. The liquid mixture was introduced at the top of the reactor by means of an infusion pump. A syringe pump (Electronic Engineering Corporation, Madras-600 041, India) was used in the present study. The liquid products were collected in a water cooled receiver and analysed by GC. Gaseous products formed during the reaction were collected in a burette by the downward displacement of water. After each reaction, the catalyst was reactivated by passing pure and dry air at 500°C through the catalyst tube for 3–4 h.

3.3. PRODUCT ANALYSIS

Products were analysed using HPLC (Zorbax ODS 4.6 mm X 15 cm column, 80 : 20 methanol : water solvent system, spectrophotometric detector, LC 5A, Shimadzu, Japan) and GLC with a flame ionization detector. The column used was Ultra 2 (cross linked 5% Ph Me Silicone) 50 m×0.2 mm×0.33 μm film thickness and the GC used was a Hewlett Packard, 5890 Series II, gas chromatograph. Identifications and estimations were made by comparison of retention times and peak areas calibrated with the help of authentic samples. Structures were further confirmed by spectral data (UV–visible, IR and ^{1}HNMR) of pure compounds isolated from the reaction product mixture by column chromatography.

Acknowledgement

The authors gratefully acknowledge generous gifts of zeolites by Union Carbide Corporation, Tarrytown, New York and Indian Petrochemicals Corporation Ltd. CATAD Division, Thane, India. The authors also thank Professor Weitkamp, University of Stuttgart, Germany, for providing the facilities for the synthesis of the other zeolites. RS thanks IIT Madras and GTZ Germany for his deputation to Germany from September 1991 to February 1992.

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