Alkylation of benzene by benzyl chloride over H-ZSM-5 zeolite with its framework Al completely or partially substituted by Fe or Ga

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Liquid-phase benzylation of benzene by benzyl chloride to diphenylmethane over H-ZSM-5, H-gallosilicate(MFI), H-galloaluminosilicate(MFI), H-ferrosilicate(MFI) and H-ferroaluminosilicate(MFI) zeolites at 80 °C has been investigated. A complete or partial substitution of Al in H-ZSM-5 zeolite by Fe or Ga results in a drastic increase in the catalytic activity of the zeolite in the benzylation process. The redox function of the zeolite is relatively more important than its acid function in the benzylation process.

Keywords: benzylation of benzene, H-ZSM-5, H-gallosilicate(MFI), H-galloaluminosilicate(MFI), H-ferrosilicate(MFI), H-ferroaluminosilicate(MFI)

1. Introduction

Liquid-phase alkylation of aromatic compounds, using homogeneous acid catalysts, is a commonly practiced Friedel–Crafts type reaction in organic synthesis [1]. However, the commonly used homogeneous acid catalysts (viz. $AlCl_3$, BF_3 and H_2SO_4) pose several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. Development of reusable solid acid catalysts having high activity for the Friedel–Crafts reaction is, therefore, of great practical importance. Worldwide efforts have been made to achieve this goal using different solid catalysts, such as heteropoly acid salts [2–4], sulfated ZrO_2 or Fe_2O_3 [5], Fe-containing MCM-41 [6,7], ion-exchanged clays [8] and clayzic [9] for benzylation of benzene and HY, H-beta and H-ZSM-5 zeolites [10] for benzylation of toluene. However, the zeolite catalysts showed a poor activity in the benzylation reactions [10]. The alkylation of an aromatic compound containing an electron-donating group (e.g., alkyl, alkoxy, OH, etc.) can be accomplished with ease but of that without such aromatic-ring-activating group (e.g., benzene) is difficult [1]. It is interesting to note that, inspite of its very strong acidity, H-ZSM-5 zeolite shows almost no activity for the benzylation of benzene [10]. We report here our preliminary results, indicating a drastic increase in the catalytic activity of H-ZSM-5 zeolite when its framework Al is completely or partially substituted by Ga or Fe and also indicating the importance of redox function of the zeolite over its acid function for the benzylation reaction.

2. Experimental

The H-ZSM-5 (H-AlMFI) and ZSM-5 type H-gallosilicates (H or H.Na-GaMFI), H-galloaluminosilicates (H-GaAlMFI), H-ferrosilicate (H-FeMFI) and H-ferroaluminosilicate (H-FeAlMFI) zeolites (table 1) were prepared and characterized by procedures similar to that described earlier [11–13]. The strong acid sites on the zeolites were measured in terms of the pyridine chemisorbed at 400 °C. The liquid-phase benzylation reactions over the zeolite catalysts were carried out in a magnetically stirred glass reactor (capacity: 25 cm^3) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free N_2 ($30\ cm^3\,min^{-1}$) through the liquid reaction mixture at the following reaction conditions: reaction mixture $=$ 13 ml of moisture-free benzene and 1.0 ml of benzyl chloride, amount of catalyst $=$ 0.1 g and temperature $=$ 80 °C. Before using the catalyst, it was pretreated at 450 °C in a flow of moisture-free helium for 1 h to remove the adsorbed moisture. The reaction was started by injecting benzyl chloride in the reaction mixture, containing benzene and the catalyst, under reflux condition (at 80 °C). The course of the reaction was followed by measuring quantitatively the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by N_2 in a 0.1 M NaOH solution containing phenolphthalein indicator) as a function of time and also by analyzing the reaction mixture for unconverted benzyl chloride and benzylation products at the end of the experiment by gas chromatography. There was a good agreement between the benzyl chloride conversion obtained from the acid–base titration and the GC analysis. The conversion data were corrected for a small time lag

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Table 1
Results of the benzylation of benzene over H-AlMFI, H-FeMFI, H-FeAlMFI, H-GaMFI, H.Na-GaMFI and H-GaAlMFI zeolite catalysts.

Zeolite catalyst	Zeolite composition			Zeolite calcination temp. (°C)	Strong acid sites on zeolite (mmol g^{-1})	Time required for benzyl chloride conversion (min)		Induction period for benzylation reaction (min)
	Si/Al ratio	Si/(Ga or Fe) ratio	H^+-exchange (%)			50%	90%	
H-AlMFI (H-ZSM-5)	22.0	∞	>99.0	550	0.31	No reaction for 2 h		
H-FeMFI	∞	16.5	>99.0	550	0.29	6.7	25	0.9
H-FeAlMFI	26.2	28.1	>99.0	550	0.26	30.3	104	5.5
H.Na-GaMFI (I_{a1})	∞	33.0	95.0	550	0.29	31.2	82.5	6.1
H.Na-GaMFI ($I_{a'}$)	∞	33.0	95.0	750	0.09	55.7	143	10.1
H.Na-GaMFI (I_{a2})	∞	33.0	55.0	550	0.16	41.3	109	7.5
H.Na-GaMFI (I_{a3})	∞	33.0	5.0	550	0.04	112	–	13.1
H-GaMFI (II)	∞	50.5	>99.0	550	0.25	44.0	107	8.8
H-GaAlMFI (I)	46.8	15.7	>99.0	550	0.44	22.8	56.2	4.1
H-GaAlMFI (II)	34.5	23.0	>99.0	550	0.46	33.0	97.2	5.8
H-GaAlMFI (III)	17.1	51.2	>99.0	550	0.48	99.7	285	8.7

(1.1 min) between the evolution of HCl in the reaction and the analysis of the evolved HCl by the titration.

3. Results and discussion

Results showing the dependence of the conversion of benzyl chloride on reaction time in the benzylation of benzene over the different ZSM-5 type zeolite catalysts were presented in figure 1. In all the cases, the product formed was mainly diphenylmethane. In case of the Ga-containing zeolites, the formation of di- and higher alkylated benzenes was negligibly small (<2 wt% of the products) and there was no formation of polybenzyl chloride. However, in case of the Fe-containing zeolites, the formation of di- and higher alkylated benzenes and polybenzyl chloride was quite significant (5–8 wt% of the products obtained at the end of the reaction).

The conversion vs. reaction time curves (figure 1) for all the zeolites show a short induction period (1–13 min) for the reaction, followed by an exponential rise in the conversion with time and then slow increase in the conversion upto the end of the reaction. The observed trend is typical of an autocatalytic reaction and a similar trend has been observed earlier for the benzylation reactions using homogeneous Lewis acid catalysts [14] and heterogeneous solid acid catalysts [5,15].

The zeolite catalysts are compared for their benzene benzylation activity in table 1. The comparison reveals that the H-ZSM-5 zeolite shows almost no activity in the benzylation of benzene, but its benzylation activity is drastically increased because of a partial or complete substitution of its framework Al by Fe or Ga. From the comparison of the results for the different zeolites (table 1), the following important observations can be made:

- Among the Fe- or Ga-substituted zeolites, the ones having lower Si/(Fe or Ga) ratio showed higher benzylation activity, indicating the importance of Fe or Ga concentration in the zeolite for its benzylation activity; the higher the Fe or Ga concentration, the higher the benzylation activity of the zeolite.
- For the zeolites with different Si/(Fe or Ga) ratios, there is no direct relationship between the zeolite acidity and the benzylation activity. However, for the zeolites having the same Si/Ga ratio but different acidity (i.e., H.Na-GaMFI with different H^+ exchange or calcined at different temperatures), the benzylation activity of the zeolite is increased with increasing zeolitic acidity.
- The reaction induction period varies from catalyst to catalyst, depending upon its activity; in general the higher the activity, the lower the reaction induction period.

The above observations clearly show that although the zeolitic acidity is also important, the concentration of Fe or Ga in the zeolite is more important for the benzylation reaction. The observed reaction induction period, which varies from catalyst to catalyst, indicates that the catalysts are activated during the initial reaction period, probably by their chloridation; a presence of chlorine in traces in the used catalysts (after washing) was detected.

The high benzylation activity of the Ga- or Fe-substituted zeolites is attributed to the presence in their channels of non-framework Ga or Fe oxide species (which are formed due to degalliation or deferriation of framework Ga or Fe of the corresponding zeolites during their calcination/pretreatment [11,12]) in combination with the zeolitic protons. The activation of the benzene nucleus on the Fe or Ga oxide species, having redox function, present in a close vicinity of the zeolite protons is responsible for the observed high catalytic activity or drastic increase in the activity. Although the Fe-substituted ZSM-5 type zeolite shows higher benzylation activity than the Ga-substituted one, the latter shows higher selectivity for diphenylmethane with almost no self-polymerization of benzyl chloride and, hence, it is to be preferred for the benzylation reaction. Further detailed investigation on the benzylation of benzene and substituted benzenes is necessary to understand the reaction mechanism and product distribution in the benzylation reaction over these zeolite catalysts and also the reaction induction period, which varies from catalyst to catalyst.

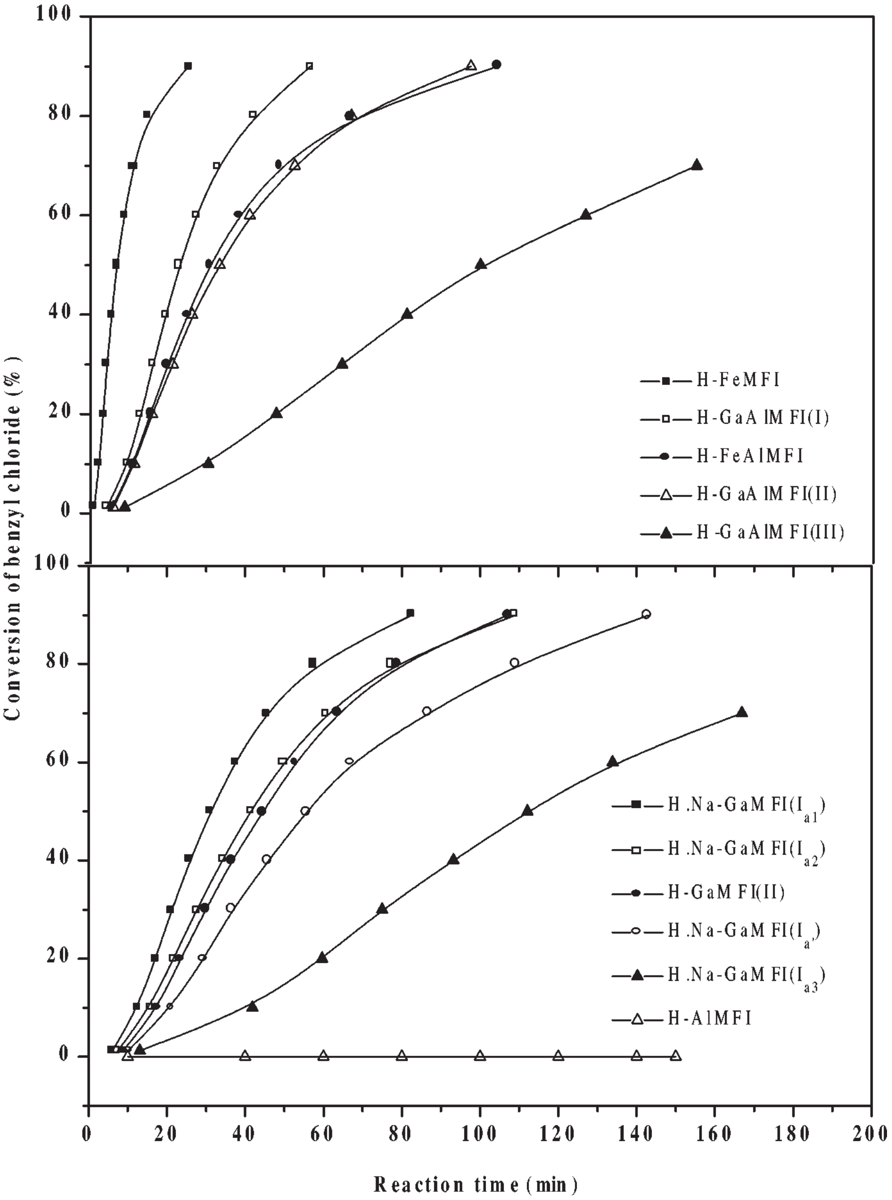

Figure 1. Conversion vs. reaction time plots for the benzylation of benzene (at 80 °C) over H-ZSM-5 and Fe- and Ga-substituted ZSM-5 type zeolites.

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