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RESEARCH NOTE

Alkylation of Benzene with Formaldehyde over ZSM-5

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Benzyl alcohol is currently produced by hydrolysis of benzyl chloride and the by-products are sodium chloride and carbon dioxide. A "green chemistry" route would be the direct synthesis from benzene and formaldehyde. Therefore, ZSM-5, a medium pore zeolite, was used to evaluate the potential of using shape selective catalysis to control the product distribution obtained by alkylation of benzene with formaldehyde. The restriction of the channels resulted in a synthesis of benzyl alcohol and benzylmethyl ether. Neither of these products is obtained with a Friedel–Crafts' catalyst, such as $AlCl_3$, nor with HY zeolite. Temperature has an effect on benzene conversion, but essentially none on product distribution. Water increases the selectivity to benzyl alcohol but decreases the conversion. Modification of the zeolite with boric acid increases the selectivity to benzylmethyl ether and benzyl alcohol, while modification with phosphorus acid does not, which may be due to the formation of phosphorus acid in the reaction mixture.

Key Words: **alkylation; zeolite; benzylmethyl ether; benzyl alcohol; benzene.**

The alkylation of benzene with formaldehyde catalyzed by conventional Friedel–Crafts' catalysts such as $AlCl_3$ has been well known in organic chemistry. The main product from the reaction is diphenylmethane. Benzyl alcohol (BA), which is an intermediate species of the alkylation, is usually not found among the products, because it is so reactive that once formed it undergoes further reactions immediately with another molecule of benzene or benzyl alcohol to form larger molecules.

Although the reaction of aromatic hydrocarbons with aldehydes has a history as long as that of Friedel–Crafts' catalyst, little attention has been paid to this kind of reaction. One reason may be the complexity of the reaction and many side reactions, which make it useless in commercial application (1). Climent *et al.* (2) studied the reaction of benzene with formaldehyde over HY zeolite catalysts, and the main product was diphenylmethane with yields of 50–60%. They did not indicate that benzyl alcohol was found in their products.

With the advent of medium-pore zeolites, shape-selective catalysis has been an interesting subject of many researchers in catalysis. Some new synthetic routes for organic compounds are being studied using this type of zeolite catalysts (3–6).

This paper reports initial results on the alkylation of benzene with formaldehyde over medium-pore zeolite HZSM-5 catalysts. The HZSM-5 was obtained from PQ Corporation and it had a Al_2O_3–SiO_2 ratio of 80, a residual Na content of 0.05%, and a surface area of 430 m^2/g. Catalysts containing B or P were prepared by impregnating HZSM-5 with their corresponding acidic solutions, followed by drying and calcining at 540°C for 4 h. Paraformaldehyde was used as the source of formaldehyde. At the experimental conditions, paraformaldehyde decomposed to formaldehyde.

The experiment was conducted in a batch stainless steel autoclave reactor. During the reaction the reactor was closed with no material exchange and a stirrer inside the reactor was kept at a constant rotation of 1050 rpm. The reactor was purged each run with high purity nitrogen prior to heating to expel the air in the reaction system. A reactor charge of 30 ml benzene, 20 g paraformaldehyde, 20 ml water, and 4 g catalyst was used for most runs. The reaction temperature was 200°C (if not otherwise indicated), and the reaction pressure was autogenous and was about 5.2 MPa at 200°C. Reaction time was 4 hours (if not otherwise indicated).

With HZSM-5 catalyst, benzene conversion remained at low values as the reaction time increased (Fig. 1). The selectivity for benzyl methyl ether (BME) increased and the selectivity for BA decreased as the reaction time increased. The selectivities for dibenzyl ether (DBE), diphenylmethane (DBM), and benzenedimethanol (also called 1,4 dihydroxy methyl benzene) (BDA) were very low at these reaction times. The product distributions obtained by using HZSM-5 were quite different than reported for conventional Friedel–Crafts' catalysts and HY catalysts (2). This indicates that the HZSM-5 catalyst has played a different role than Friedel–Crafts' catalyst and the HY catalyst in the

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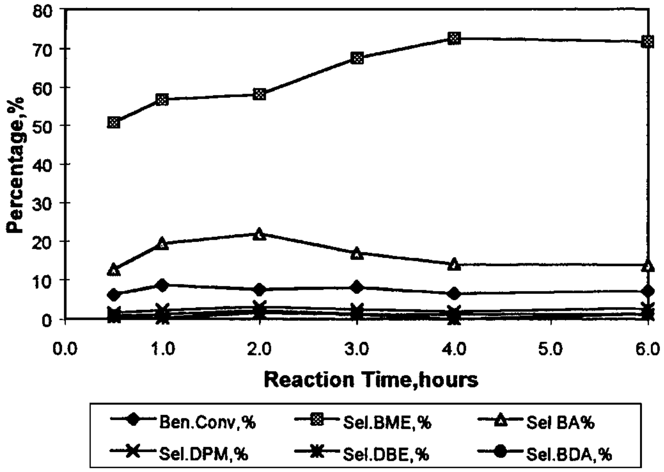

FIG. 1. Effect of reaction time on product selectivity.

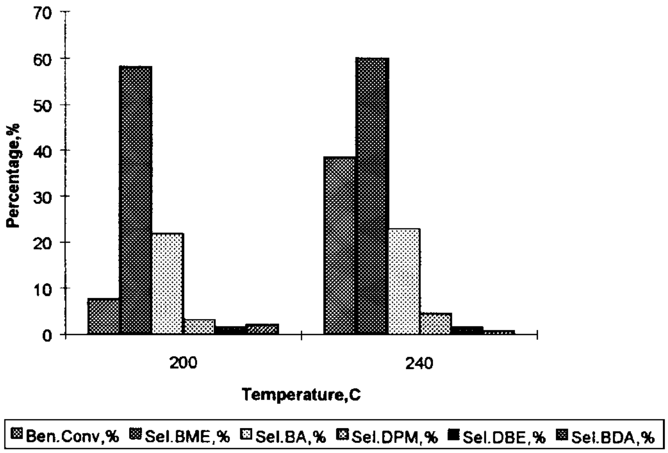

FIG. 2. Comparison of selectivities at two temperatures.

alkylation of benzene with formaldehyde. This is postulated to be due to shape selective catalysis that is characteristic with the use of HZSM-5.

Formation of benzenedimethanol at the reaction conditions is still an interesting observation. No literature has mentioned that benzenedimethanol had been formed from the reaction of benzene and formaldehyde. Its formation in this experiment and the low selectivities for large molecules may be due primarily to the shape-selective catalysis of the HZSM-5 zeolite, since the channels inside HZSM-5 are of 5.1–5.2 Å (7). The HZSM-5 pores are smaller than the diameters of the big molecules such as DBE and DPM, so that these large molecules are restricted in formation over ZSM-5. While over HY catalysts, DPM can be a main product since the channel opening of the HY zeolite is about 7.4 Å (7), which is much larger than that of HZSM-5.

Another interesting observation is that the selectivity for BME is much greater than the selectivity for benzyl alcohol. The reaction mechanism for the formation of benzyl methyl ether has not been reported in the literature and is currently unknown. Research to reveal the reaction mechanism is being performed by the authors.

Reaction temperature significantly affected the conversion of benzene, but had little influence on the product distribution (Fig. 2). The selectivities for BME, BA, DBE, and DPM changed slightly when temperature was increased from 200 to 240°C. Benzene conversion increased by about four-fold when the temperature was increased.

In the alkylation of benzene with formaldehyde by Friedel–Crafts' catalysts such as $AlCl_3$, water is strictly forbidden for it dramatically decreases the catalyst activity. In our experiment, we found the selectivities for small molecules were favored by adding water to the reactor charge. However, the addition of water decreased the conversion of benzene. This is because water occupied the more active sites, resulting in less active sites available for the reaction. When water was added, benzenedimethanol was observed in the reactor mixture. This compound was not observed when no water was added to the reactor. When water was added to the reactor, the reaction solution became much more polar than with no water addition. This polar reaction solution favors benzenedimethanol formation, since benzenedimethanol is a polar compound.

The addition of water reduced the formation of dibenzyl ether and diphenylmethane about four times and increased benzyl alcohol about 4.6 times, while the conversion of benzene was reduced from 11.9 to 7.6%. The effect of water on the product distributions is shown in Fig. 3.

The HZSM-5 modified with P and B by impregnating the zeolite powder with their corresponding oxygen containing acidic solutions. Two catalysts containing B (designed as BHZ) or P (designed as PHZ) were thus prepared. Their catalytic functions along with HZSM-5 are shown in Fig. 4. When P or B is introduced onto the HZSM-5, the conversion of benzene is decreased, especially over the BHZ catalyst, indicating the decrease in the activity of the catalysts. Modification of HZSM-5 with P compounds decreases

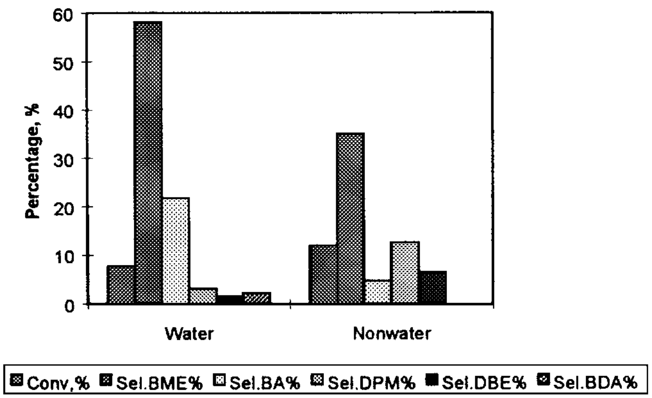

FIG. 3. The effect of water on the product distributions.

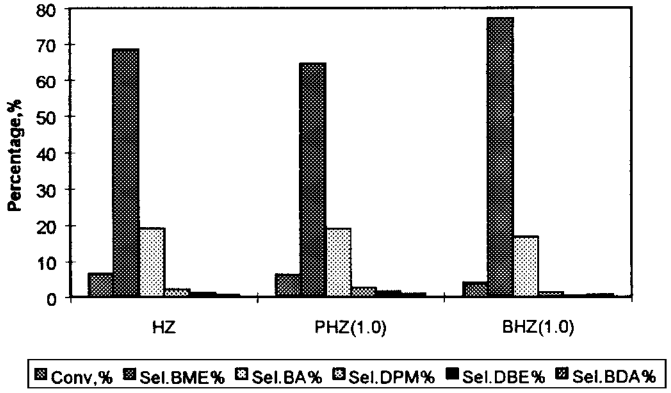

FIG. 4. Effect of different catalysts on selectivities and activities.

strong Brønsted acid sites and increases weak acid sites (8), while modification of HZSM-5 with P compounds decreases both Brønsted acid sites and Lewis acid sites and the channels of the zeolite are narrowed (9–11). This may indicate that alkylation is favored on strong acidic sites. BHZ has narrowed channels and showed better selectivity for BME than HZSM-5 and PHZ, while PHZ showed a lower selectivity for BME than HZSM-5.

Figure 5 shows the changes in benzene conversion and selectivities with different loading amounts of P in the HZSM-5. As the loading amount of P increased, the conversion of benzene changed slightly, indicating that the change in activity of the catalyst was small. The selectivity for BME decreased and for BA a slight decrease was observed compared with the change for BME, while selectivities for large molecules were increased. This indicates that the shape selective catalysis of the catalyst has been decreased. This may be due to the formation of phosphorus acid when P-containing HZSM-5 encountered water in the reactor, because the water was acidic after the reaction.

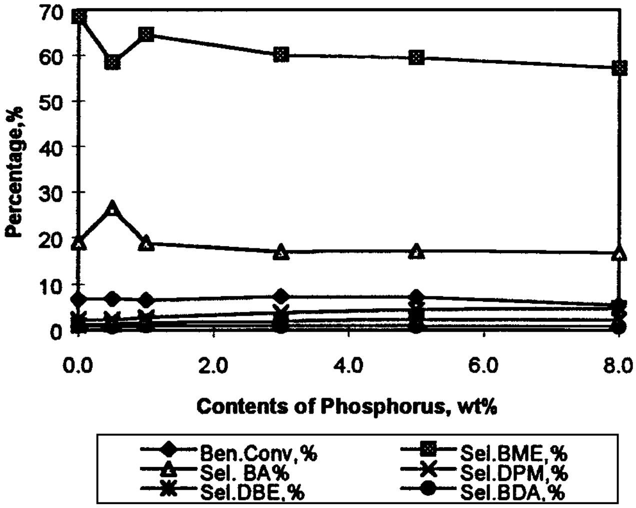

FIG. 5. Effect of phosphorus contents.

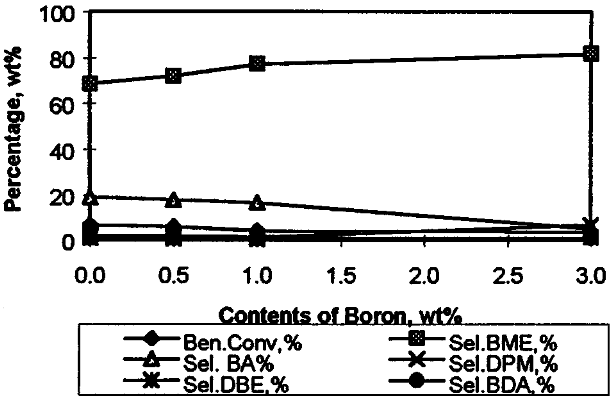

FIG. 6. Effect of boron.

Figure 6 shows the results from catalysts modified with different contents of boron. The conversion of benzene decreased as B content increased. The selectivity for BME was increased, but for BA it decreased. For large molecules selectivities decreased as the content of B in HZSM-5 was increased. The decrease in formation of large molecules indicates an enhancement in shape selective catalysis by the BHZ catalysts.

Alkylation of benzene with formaldehyde can be carried out over ZSM-5 zeolite catalysts. The product distribution over this type of zeolite catalysts is quite different from that over Friedel–Crafts' catalyst and over HY zeolite catalyst. Benzyl methyl ether and benzyl alcohol are the main products over the ZSM-5. This is the result of shape selective catalysis of ZSM-5, whose medium-pore channels do not allow the formation of large molecules such as diphenylmethane, which is the main product over Friedel–Crafts and HY zeolite.

This alkylation has commercial potential for synthesis of benzyl alcohol and benzyl methyl ether. This new synthesis route eliminates the use of chlorinated compounds in the production of benzyl alcohol and benzyl methyl ether. These compounds are used as solvent, fragrances and perfumes, and in the photo industry.

It is obvious that more research needs to be done to reveal the reaction mechanism and optimize the synthesis of the desired products.

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