Activity Stabilization of Ga-MFI Zeolite Catalyst Modified by Chemical Vapor Deposition

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The chemical vapor deposition of silica on Ga-MFI zeolite was carried out using tetraethyl orthosilicate. The enhancement in para selectivity during toluene alkylation with the extent of silica deposition was closely monitored. The effect of reaction temperature on the behavior of silica deposited Ga-MFI zeolite was established. A deactivation trend in toluene conversion was observed when the zeolite was employed for alkylation for longer periods. The reasons for catalytic deactivation and stability enhancement by in situ coking are discussed.

Isomorphous substitution of a framework element in a zeolite is very interesting from the point of modification of acid properties.[1)] There has been considerable effort to use isomorphous substituted MFI zeolites for various hydrocarbon conversion reactions. We have previously reported the use of Ga-MFI zeolite for the synthesis of *p*-diethylbenzene by ethylbenzene ethylation.[2)]

The unique feature of Ga-MFI zeolite is its shape selectivity. This feature of the zeolite can be further enhanced by incorporating compounds like P_2O_5, MgO or B_2O_3, by adsorbing a bulky organic base on the external surface sites, or by increasing the crystallite size or silica deposition.[3—5)] Among the various techniques employed for enhancing the shape selectivity, chemical vapor deposition (CVD) of silica has several distinct advantages over the other techniques.[6)] According to Hibino et al.,[7)] silica deposits on the external surface as a thin layer which deactivates acid sites on the external surface. The deposited silica layer consists of siloxane bonds, whereas the zeolite is composed of siloxane and Si–O–Al bonds. This results in the variation in bond lengths or angles between silica layer and zeolite framework. The siloxane bond of the silica layer protrudes into the pore, due to this, the pore opening is narrowed.

The present paper deals with the shape selectivity enhancement of Ga-MFI zeolite by CVD during toluene alkylation with methanol. It was observed that the time on stream behavior of the CVD modified zeolite showed a deactivating trend. An effort was made to stabilize the catalytic activity during alkylation. This paper encompasses the details of chemical vapor deposition, controlled coking and the related acidity modulation and stabilization of catalytic activity.

Experimental

The isomorphous substituted high silica Ga-MFI zeolite used in this study was synthesized following the reported procedure.[8)] It was characterized for structural, morphological, and acidity features by physicochemical techniques such as XRD, SEM, ESCA, FT-IR, and TPD of ammonia. The SiO_2/Ga_2O_3 ratio was determined by a combination of wet chemical analysis and atomic absorption spectrophotometry.

The as-synthesized zeolite was converted to active proton form by calcining at 793 K for 8 h and ion exchanging with 10% NH_4NO_3, followed by another calcination at 793 K for 8 h. The alkylation reaction as well as chemical vapor deposition was carried out in a tubular, fixed bed, glass reactor at atmospheric pressure. In each run, 1 g zeolite in proton form was loaded in the reactor.

Before silylation the zeolite in proton form was pretreated at 813 K with 90 ml min^{-1} nitrogen gas flow for two hours. The chemical vapor deposition on the zeolite was carried out using tetraethyl orthosilicate as silicon source. A 10% $Si(OC_2H_5)_4$ solution in 75 : 25 toluene and methanol was vaporized and passed through the catalyst bed maintained at 513 K. The silicate solution was fed at a rate of 4 ml h^{-1} to the vaporizer; a flow rate of 90 ml min^{-1} hydrogen was maintained so that there was uniform contact of the vapour with the catalyst. After the catalyst had been in contact with the vapor for the desired period, the hydrogen flow was changed to nitrogen. The nitrogen gas was replaced by air; then the reactor temperature was raised to 813 K and kept at this temperature for 10 h to decompose tetraethyl orthosilicate to silica.[9)]

To carry out the alkylation reaction, a mixture of reactants, toluene and methanol was fed by a Sage syringe pump, vaporized and passed through the catalyst bed maintained at the reaction temperature. Before this step, the catalyst was activated at 773 K for 2 h with 90 ml min^{-1} nitrogen. The products of the reaction were condensed at the reactor outlet and analyzed with a Varian Vista 6000 gas chromatograph equipped with FID and LB-500 capillary column.

Results and Discussion

The zeolite Ga-MFI prepared is of high Si/Ga ratio of 90. The XRD pattern indicated the absence of phases other than MFI. The morphology of the crystallites were of twinned elongated prism. The length was 10—12 u and breadth 4—6 u. The total acidity as estimated by temperature programmed desorption in terms of milli mole equivalents of ammonia per gram of Ga-MFI was 0.35.

Toluene alkylation with methanol was carried out over chemical vapor deposited Ga-MFI zeolites. The deposition period was varied to incorporate different extents of silica on the zeolite. The results of the runs are depicted in Fig. 1. With progressive deposition of silica over Ga-MFI, *p*-xylene selectivity as defined by the fraction of *p*-xylene in total xylenes increased from 56 to 90%. The enhancement in para selectivity was accompanied by decrease in toluene conversion. This can be attributed to the fact that the chemical vapor deposition of tetraethyl orthosilicate followed by calcination deposits silica, which narrows the pore opening size. The reduced pore opening size affects the diffusion of reactants and products inside and outside the zeolite channels. The change in the pore opening size can easily be followed by a standard test involving probe molecules of known dimensions.[10)]

In order to study the effect of reaction temperature on the performance of chemical vapor modified Ga-MFI zeolite, the runs were carried out in the temperature range 350 to 450 °C (Fig. 2). With a raise in temperature from 350 °C, there is an increase in toluene conversion up to 425 °C; above this temperature toluene conversion started decreasing, as more and more alkylating agent goes to secondary reactions such as oligomerization and aromatization. Even though xylene selectivity showed a similar profile, *p*-xylene selectivity decreased due to the reduced constraint index CI at higher temperature, resulting in lowering of the difference in diffusivity between *m*- and *p*-xylene.[11,12)]

The alkylation activity of the chemical vapor deposited Ga-MFI zeolite was studied continuously for 24 h. It was observed that with time on stream the alkylation activity as reflected by toluene conversion of silica deposited Ga-MFI zeolite decreased at a rate faster than for Ga-MFI zeolite (Fig. 3). This phenomenon was observed at all the temperatures in the range 350—450 °C and can be attributed to pore opening size reduction due to silica deposition. As the pore opening size is reduced, the reactant molecules are retained inside the zeolite for a longer time and the coke is easily formed and deposited on the stronger sites. This coke grows further and covers the active sites; with this, catalytic activity drastically reduces. An XPS study of coke on Al-MFI zeolite provides strong evidence that the coke fills the ZSM-5 channel system initially before any significant amount of coke is formed on the external surface.[13)] It has been reported by Derouane et al.[14)] that, in case of ZSM-5 zeolite, deactivation occurs initially through limitation of the access to the active sites, then follows blockage of the access to the sites of channel intersection in which coke molecules are situated. The dependency of para-selectivity in toluene alkylation on acidity as a function of time on stream is reported in Table 1. With increase in on stream period, the para selectivity is enhanced and the acidity is decreased due to coking of the acidic sites.

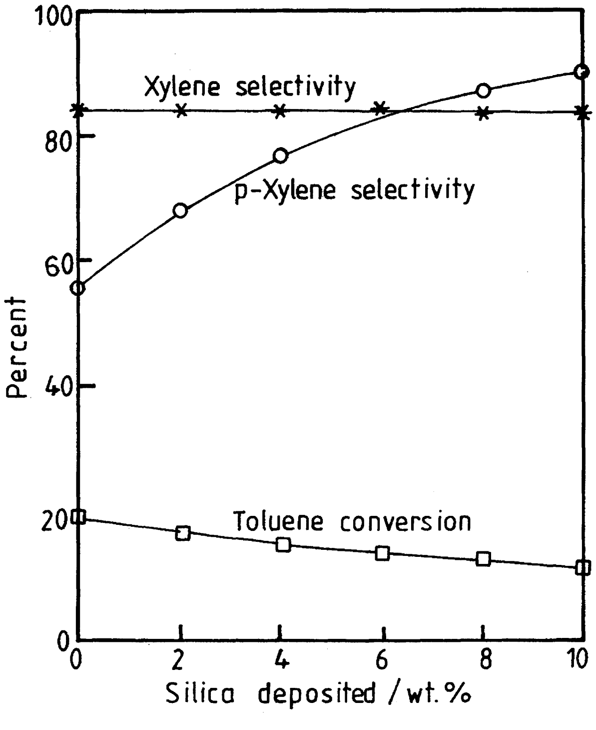

Fig. 1. Para selectivity enhancement and the extent of silica deposition. Temperature = 400 °C, WHSV = 2.5 h^{-1}, Mole ratio Toluene : Methanol = 4.

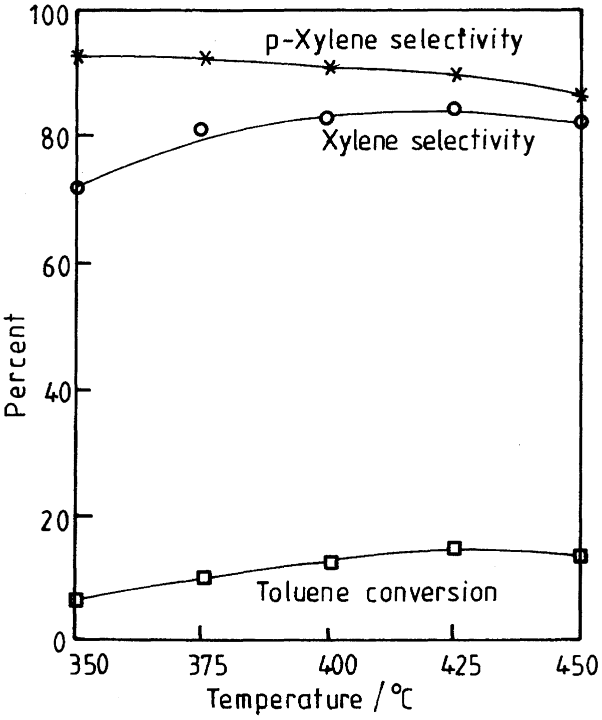

Fig. 2. Effect of reaction temperature on the performance of chemical vapor deposited Ga-MFI zeolite. WHSV = 2.5 h^{-1}, Mole ratio Toluene : Methanol = 4, Silica deposition = 8%.

In the present case the coke formation seems to be coming from methanol, which is used as an alkylating agent. It has been reported by Chen[15)] that, depending on the ratio of toluene to methanol in the feed mixture and the reaction severity, only a fraction of the methanol participated in toluene alkylation reaction, with the remaining being converted to light hydrocarbons. Methanol, being a smaller

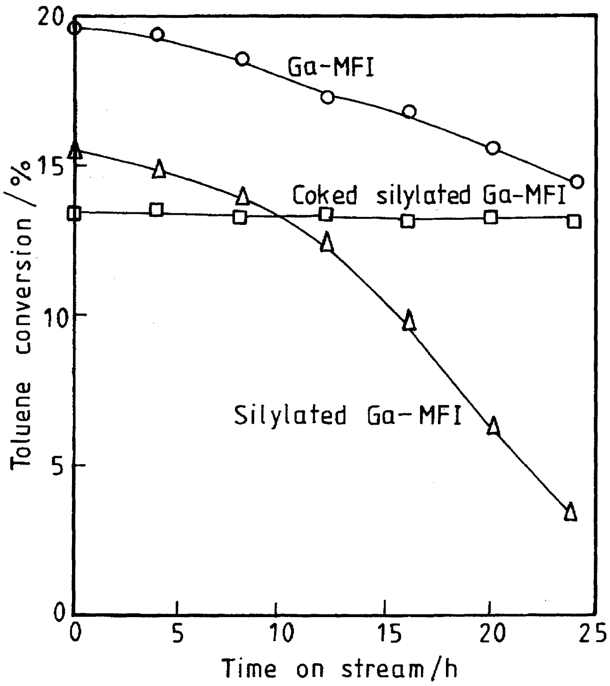

Fig. 3. Time on stream behavior of Ga-MFI zeolite, silylated Ga-MFI zeolite with and without coking. Temperature=425 °C, WHSV = 2.5 h^{-1}, Mole ratio Toluene : Methanol = 4, Silica deposition = 8%.

Table 1. Para-Selectivity and Acidity of Silica Modified Ga-MFI Zeolite as a Function of Time on Stream Period

Time on stream h	Para isomer selectivity %	Acidity mmol equiv g^{-1}
0	93.3	0.34
9	94.6	0.21
16	96.8	0.16
20	98.1	0.13
24	99.8	0.09

molecule than toluene, can diffuse faster inside the narrowed channels of Ga-MFI and goes for olefins formation. These olefins oligomerize to coke. The internal coke formation by the polymerization of small olefins on MFI zeolite is well-known.[16)]

In order to stabilize the catalytic activity, several techniques were used. Among the various techniques which worked most effectively was the controlled in situ coking of Ga-MFI zeolite. The controlled coking is carried out by disproportionating ethylbenzene, which goes through dealkylation/realkylation mechanism. Some of the eliminated ethyl group produces ethylene and, from this, olefin coke is formed. The coke is deposited on the higher strength acid sites inside Ga-MFI channel and the zeolite acidity is modulated. It may be noted here that the main difference between ethylene produced from ethylbenzene and, olefins and ethylene formed from methanol is the quantity. During ethlybenzene conversion over Ga-MFI zeolite, the major reaction is disproportionation via dealkylation/realkylation mechanism, only a very small quantity of ethylene is produced from the $-C_2H_5$ group detached from the aromatic ring, while the reactions of methanol over Ga-MFI zeolite formed considerable quantities of ethylene and other olefins. Accordingly, the pattern of the acid sites coking is different in the above two cases. The change in acidity of the zeolite after coking is established from temperature programmed desorption (TPD) of ammonia profiles (Fig. 4). The TPD pattern consisted of a low and a high-temperature peak corresponding to strong and weak acid sites (total acidity of silylated zeolite was 0.34 milli mole equivalent of ammonia per gram). The in situ coking alters the distribution of both strong and weak acid sites (total acidity of coked silylated zeolite was 0.22 milli mole equivalent of ammonia per gram). The time-on-stream behavior of a silylated coked Ga-MFI zeolite is presented in Fig. 3. The zeolite, having more strong acid sites, favor cracking/coking reactions, the zeolite possessing more of medium strength acid sites is desired for alkylation, while the zeolite containing more acid sites of lower strength is preferred for isomerization reaction. Controlled coke formation during ethylbenzene conversion covers the sites of higher strength. Due to this, the coked zeolite contains more acid sites of the strength required for alkylation and exhibits enhanced stability.

Conclusions

The chemical vapor deposition of silica on Ga-MFI zeolite enhanced the para selectivity during alkylation of toluene with methanol. The para selectivity decreased with enhancement in reaction temperature in the range 350—450 °C. The best alkylation activity was observed around 425 °C. The chemical vapor deposition narrows the pore opening size and affects the catalyst stability. Thus a deactivating trend in tol-

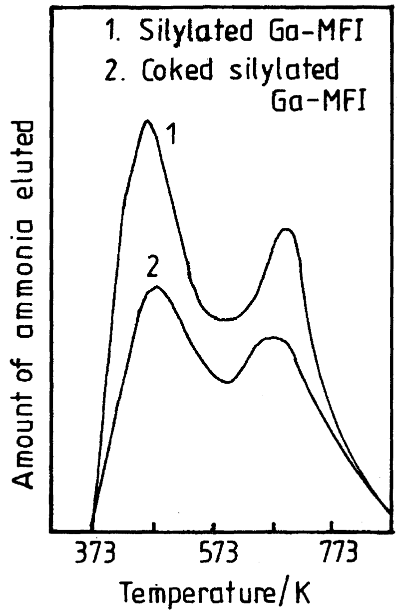

Fig. 4. Temperature programmed desorption patterns of 8% silylated Ga-MFI with and without coking.

uene conversion was observed. In situ coking of the zeolite enhanced its stability during alkylation.

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