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NOTE

Influence of Low and High Temperature Coking of H-GaMFI Propane Aromatization Catalyst on Its Surface and Catalytic Properties

H-Gallosilicate (MFI) (i.e., H-GaMFI) zeolite shows high activity/selectivity in the aromatization of lower alkanes (1–8), which is a processes of great practical importance. The high aromatization activity of this catalyst is attributed to its high dehydrogenation activity due to the presence of highly dispersed nonframework Ga-oxide species (which are formed during hydrothermal synthesis and/or pretreatments to the zeolite) along with the zeolitic acid sites (or framework Ga), resulting in a bifunctional catalyst. However, this zeolite undergoes fast catalyst deactivation in the propane aromatization (3, 4, 8). The catalyst deactivation is attributed mainly to the coke formation on the zeolite (8). Earlier, a few studies (3, 4, 8–10) have been reported on the deactivation of H-GaMFI zeolite in the propane aromatization at 500–550°C for a short time-on-stream (10 h). It is interesting to know the effect of catalyst deactivation due to coking in the propane aromatization for much longer periods both at low (at 400°C) and high (at 550°C) temperatures on the product selectivity and also on the surface (viz., sorption capacity, acidity/acid strength distribution) and catalytic properties of the zeolite. The present investigation was undertaken for this purpose.

Preparation and characterization of H-GaMFI zeolite (bulk Si/Ga = 33, framework Si/Ga = 51, Na/Ga = 0.07, crystal size 6–7 μm, particle size = 0.2–0.3 mm) have been described earlier (8). For obtaining the low temperature coked (LTC) and high temperature coked (HTC) zeolite in the propane aromatization, the reaction at 400°C for 240 h and at 550°C for 125 h, respectively, was carried out continuously in a tubular quartz reactor (i.d. = 13 mm) using 33 mol% propane and 67 mol% N_2 gas mixture as a feed at a gas hourly space velocity of 3100 cm^3 (STP) $\cdot g^{-1} \cdot h^{-1}$ by the procedure described earlier (8). The carbon deposited on the deactivated catalysts was determined by microanalysis. The catalytic activity/selectivity data in the absence of catalyst deactivation (i.e., initial activity/selectivity) were obtained at different space velocities by carrying out the propane aromatization under steady state for a short period (5 min) and then replacing the reactant by pure N_2 during the period of product analysis by GC.

The fresh and deactivated (LTC and HTC) zeolite samples were characterized for their acidity/acid strength distribution by measuring step-wise thermal desorption (STD) and chemisorption of pyridine (at 100–400°C) using the GC adsorption/desorption methods (8, 11, 12). The N_2 sorption capacity of the fresh and deactivated zeolite samples, pretreated in pure N_2 at different temperatures (200–600°C) for 1 h was measured in terms of the amount of N_2 sorbed from a N_2–He mixture (30 mol% N_2) at liquid nitrogen temperature, using a Monosorb Surface Area Analyzer (Quanta-Chrome Corp., USA). The catalytic activity of the fresh and deactivated zeolite samples in the acid catalyzed model reactions, viz. isooctane cracking (at 400°C) for characterizing external acidity, and *o*-xylene isomerization (at 400°C) and toluene disproportionation (at 500°C) for measuring the overall acidity, and also, in the aromatization of propylene and methanol (at 400°C) were determined using a pulse micro-reactor described earlier (8).

Because of the deactivation at 400°C for 240 h, the propane conversion is reduced from 0.5% to 0.3% and the concentration of aromatics in products is decreased from 0.23 wt% to 0.1 wt%. Whereas, due to the deactivation at 550°C for 125 h, the decrease in the propane conversion and the concentration of aromatics is from 45.0% to 6.6% and 28.6% to 0.7%, respectively. As expected the deactivation at the lower temperature is found to be slow. The influence of the catalyst deactivation due to coking at 550°C on the product selectivity, distribution of aromatics, and p-X/m-X ratio is found to be quite similar to that observed earlier (8–10).

In order to establish the influence of the catalyst deactivation due to coking on the product selectivity, the zeolite deactivated at the different extents is compared with the fresh zeolite for their product selectivity at the same conversion in Table 1. The results clearly show a strong influence of the catalyst deactivation on the product selectivity and also on the dehydrogenation/cracking (D/C) and aromatization/cracking (A/C) activity ratios. Because of the deactivation, the selectivity for aromatizaiton and C_4 hydrocarbons and also the activity ratios are decreased; whereas the selectivity for propylene and $C_1 + C_2$ hydrocarbons is increased. However, a comparison of the distribution of aromatics at the same propane conversion showed no significant effect of the catalyst deactivation due to coking on the aromatics distribution.

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TABLE 1

Influence of Catalyst Deactivation due to Coking on Product Selectivity in Propane Aromatization over H-GaMFI at 550°C (Feed: 33 mol% propane + 67 mol% N_2)

	$X = 30\%$		$X = 15\%$		$X = 6.6\%$	
	Fresh	Deactivated (33%)	Fresh	Deactivated (66%)	Fresh	Deactivated (85%)
Product selectivity (%)						
Aromatics	52.0	49.1	34.0	31.7	16.3	11.5
Propylene	19.7	25.0	34.6	41.6	58.0	66.3
$C_1 + C_2$	17.4	22.9	16.4	23.4	15.2	18.7
C_4	10.9	3.0	15.0	3.3	10.5	3.5
Activity ratios						
D/C	4.8	3.4	5.1	3.3	5.6	4.4
A/C	3.0	2.1	2.1	1.4	1.1	0.6

Data on the coke deposition and N_2 sorption (at liquid N_2 temperature) for the HTC and LTC zeolite with or without pretreatment in N_2 (free from the traces of oxygen) at different temperatures (200–600°C) are presented in Table 2. The carbon deposition on the LTC zeolite is much smaller than that on the HTC zeolite. In case of the LTC zeolite, the carbon deposition can be removed to a large extent and also the amount of N_2 sorbed is increased significantly simply by the N_2 treatment at higher temperatures. However, for the HTC zeolite, the influence of N_2 pretreatment is very small. Also, the amount of N_2 sorbed in the HTC zeolite is much smaller than that in the fresh and LTC zeolites. This indicates heavy blockage of channels of the HTC zeolite by coke.

The acid strength distribution on the fresh, LTC, and HTC zeolites, is presented in Fig. 1a. The columns in the figure show acid strength distribution of the sites involved in the chemisorption at 100°C. Each of the columns of the acid strength distribution represents the number of acid sites measured in terms of pyridine desorbed in the corresponding temperature steps. A variation of the pyridine chemisorption with temperature for the three zeolites is shown in Fig. 1b. Both the STD of pyridine and the chemisorption of pyridine at different temperatures (Fig. 1) reveal that the acid strength distribution on the zeolite is quite broad and it is strongly influenced by the coke deposition and also by the temperature of coking or the extent of coke deposition. Because of the coke deposition, both the total and strong acid sites (measured in terms of the pyridine chemisorbed at 100°C and 400°C, respectively) are decreased.

The fresh and deactivated (LTC and HTC) zeolites have also been characterized for their acid function by carrying out the following acid catalyzed model reactions over them in a pulse microreactor: isooctane cracking (at 400°C) for studying external (or intercrystalline) acid sites, and toluene disproportionation and *o*-xylene isomerization (at 400°C)

TABLE 2

Data on Characterization of Fresh and Coked H-GaMFI Zeolites

H-GaMFI zeolite	N_2 pretreatment[a] temp. (°C)	Carbon deposited (wt%)	N_2 sorbed (at liq. N_2 temp.) ($\mathrm{mmol \cdot g^{-1}}$)
Fresh	400	0.0	2.97
LTC	without pretreatment	0.65	—
	200	0.65	2.31
	400	0.50	2.51
	600	0.28	2.80
HTC	without pretreatment	7.4	—
	200	7.4	0.4
	600	7.0	0.5

[a] Pretreatment given in a flow of pure N_2 (free from the traces of O_2) for 1 h.

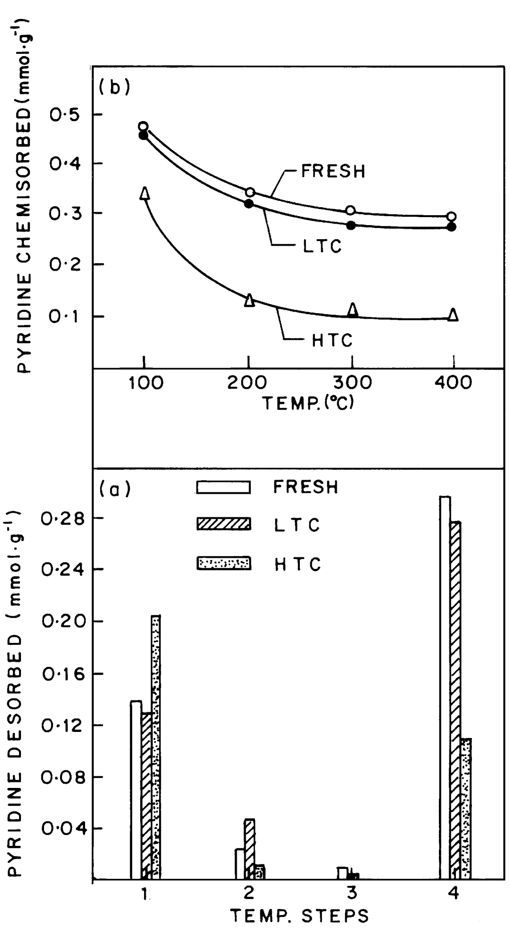

FIG. 1. (a) Step-wise thermal desorption of pyridine (chemisorbed at 100°C) from the fresh and coked H-GaMFI zeolites (temperature steps: (1) $100°\mathrm{C} < T_\mathrm{d} \leq 200°\mathrm{C}$; (2) $200°\mathrm{C} < T_\mathrm{d} \leq 300°\mathrm{C}$; (3) $300°\mathrm{C} < T_\mathrm{d} \leq 400°\mathrm{C}$; and (4) $400° < T_\mathrm{d} \leq T_\mathrm{d}^*$, T_d^* = temperature at which all the chemisorbed pyridine is desorbed). (b) Temperature dependence of pyridine chemisorption on the fresh and coked H-GaMFI zeolites.

TABLE 3

Results of Pulse Reactions (at 400°C) over Fresh and Coked H-GaMFI Zeolites

		Isooctane cracking		o-Xylene isomerization		Toluene disproportionation	
Zeolite	T_N[a] (°C)	Conversion (%)	Reaction rate ($mmol \cdot g^{-1} \cdot h^{-1}$)	Conversion (%)	Reaction rate ($mmol \cdot g^{-1} \cdot h^{-1}$)	Conversion (%)	Reaction rate ($mmol \cdot g^{-1} \cdot h^{-1}$)
Fresh	400	2.2	7.1	12.4	55.1	1.8	9.0
LTC	400	1.4	4.5	10.7	47.5	1.5	7.5
LTC	600	2.2	7.1	11.8	52.2	1.8	9.0
HTC	400	0.8	2.6	6.8	30.1	1.3	6.5
HTC	600	0.8	2.6	6.7	29.7	1.3	6.5

		Propylene aromatization			Methanol aromatization		
Zeolite	T_N[a] (°C)	Conversion (%)	Reaction rate ($mmol \cdot g^{-1} \cdot h^{-1}$)	Aromatics in hydrocarbons (wt%)	Conversion (%)	Reaction rate ($mmol \cdot g^{-1} \cdot h^{-1}$)	Aromatics in hydrocarbons (wt%)
Fresh	400	90.7	1077	41.8	100	1314	27.8
LTC	400	87.4	1038	36.6	100	1314	24.6
LTC	600	89.4	1062	41.0	100	1314	27.4
HTC	400	69.7	828	26.3	100	1314	20.2
HTC	600	69.5	825	26.1	100	1314	20.1

[a] N_2 pretreatment temperature.

Note. Pulse reaction conditions: amount of catalyst 0.1 g; pulse size: 0.4 μl and 0.2 cm^3 for liquid and gaseous reactant, respectively; carrier N_2 gas flow: 20 $cm^3 \cdot min^{-1}$.

for studying the overall acidity of the zeolites. The results of the model reactions are presented in Table 3. In all the reactions, the catalytic activity of the zeolite is decreased due to the coke deposition. The decrease is, however, smaller for the LTC zeolite. In case of the LTC zeolite, the catalytic activity in all the model reactions is increased, approaching almost to that of the fresh zeolite, by increasing the N_2 pretreatment temperature from 400 to 600°C. On the contrary, there is only a little or no increase in the activity of the HTC zeolite by increasing its N_2 pretreatment temperature.

In order to know the influence of the low and high temperature coking of the zeolite on its aromatization activity, pulse propylene and methanol aromatization reactions (at 400°C) were carried out over the fresh, LTC, and HTC zeolites under identical conditions. Results of the aromatization of propylene and methanol are included in Table 3. In both the reactions, the formation of aromatics is decreased due to the coke on the zeolite, the decrease being smaller for the LTC zeolite but quite appreciable for the HTC zeolite. Methanol is converted completely over both the fresh and coked zeolites. However, the propylene conversion is decreased due to the precoking of the zeolite, the decrease being larger for the HTC zeolite. The influence of the N_2 pretreatment on the aromatization activity of the coked zeolites in both the reactions and also on the propylene conversion is very much similar to that observed for the acid catalyzed model reactions (Table 3). A comparison of the results for the LTC and HTC zeolites with those of the fresh zeolite shows a strong influence of the high temperature coking of the zeolite on its surface and catalytic properties.

The decrease in the N_2 sorption due to the coking indicates that at least a part of the coke is located in the zeolite channels. In the case of the HTC zeolite, its channels are heavily blocked due to the coke molecules. Whereas, for the LTC zeolite, the channel blockage by the coke formation is very small and, moreover, a large fraction of this coke can be removed even by the nonoxidative treatment (i.e., N_2 pretreatment), particularly at high temperatures. However, only a very small part of the coke could be removed from the HTC zeolite by its nonoxidative treatment at 600°C.

The decrease in the zeolitic acid sites due to the coking, determined by both the pyridine chemisorption and the acid catalyzed model reactions (viz., o-xylene isomerization and toluene disproportionation), is attributed to the blockage of part of the acid sites by the coke in the zeolite channels, thus making them unavailable for the pyridine chemisorption or reactants. The observed increase in the activity in the model reactions (Table 3) and also in the aromatization reactions (Table 3) of the LTC zeolite with increasing the N_2 pretreatment temperature reveals that the blocked acid sites are freed due to the removal of volatile coke molecules from the zeolite. The results of the pyridine and model reactions for the zeolite acidity are complementary to each other.

The external acidity of the zeolites is characterized by the iso-octane cracking reaction because iso-octane cannot penetrate the ZSM-5 type zeolites even at 400°C (13, 14). The iso-octane cracking occurs on strong acid sites (13, 14). The decrease in iso-octane cracking activity due to coking (Table 3) shows that the strong acid sites on the external surface of the zeolite are decreased due to their blockage by the coke on the external surface. The decrease of the external acidity for the high temperature coking is substantially higher than that for the low temperature coking (Table 3). This is expected because of the deposition of coke to a larger extent on the external surface at high temperature. It is admitted that coke molecules formed at low temperature are mainly located inside the zeolite channels, while at high temperature they could be located near and on the outer surface (15, 16).

Because of the coking (at 550°C), the catalytic activity of the zeolite in the aromatization of propane is reduced drastically. The aromatization activity in both the propylene and methanol aromatization reactions is also decreased. This is expected because of the unavailability of both the zeolitic acid sites and dehydrogenation sites (i.e., extra framework Ga-oxide species) for the reactants due to their blockage by the coke molecules. The product selectivity and the D/C and A/C activity ratios in the propane aromatization (at the same propane conversion) are found to be strongly influenced by the coking (Table 1). This is consistent with our earlier observations (8, 10, 14) that the aromatics selectivity and D/C activity ratio in the propane aromatization over H-GaMFI zeolite are increased with increasing the zeolitic acidity. However, the aromatics distribution is not affected significantly due to the coking.

This investigation leads to the following important conclusions: Because of the coking of H-GaMFI zeolite in the propane aromatization, both the internal (intracrystalline) and external (inter crystalline) zeolitic acid sites are decreased due to their blockage by coke molecules. The N_2 sorption capacity of the zeolite is also reduced due to the presence of coke or coke precursors in the zeolitic channels. The coke deposition at 550°C for (125 h) is much higher than that at 400°C (for 240 h) and, hence, the coking at higher temperatures causes a much larger decrease in the internal and external zeolitic acidity, N_2 sorption capacity, and catalytic activity in the aromatization of propane. The product selectivity and dehydrogenation/cracking and aromatization/cracking activity ratios in the propane aromatization are also strongly influenced, but the distribution of aromatics is not changed due to the high temperature coking.

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