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Pulse Reaction Studies on Variations of Initial Activity/Selectivity of O_2 and H_2 Pretreated Ga-Modified ZSM-5 Type Zeolite Catalysts in Propane Aromatization

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Influence of O_2 and H_2 pretreatments (at 600°C for 10 h) on the initial activity and product selectivity and their variation with time on stream (0–180 min) of H–gallosilicate (H–GaMFI), H–galloaluminosilicate (H–GaAlMFI), and Ga/H–ZSM-5 catalysts (with bulk Si/(Al + Ga) = 34.5 ± 2.5) in the propane aromatization (at 600°C) has been investigated, using a microreactor operated in both the pulse and continuous reaction modes. The catalysts have been characterized for their acidity (measured in terms of pyridine chemisorbed at 400°C), framework and nonframework Ga and Al, and surface Si/Ga ratio. The initial propane conversion/aromatization activity and aromatics selectivity of the H–GaMFI are decreased but that of the H–GaAlMFI and Ga/H–ZSM-5 are increased significantly due to the H_2 pretreatment for all the Ga-modified zeolite catalysts. The variation of the activity and product selectivity of all the three catalysts with the time on stream is found to be strongly dependent upon the pretreatment. Among the catalysts, H–GaAlMFI shows superior performance in the propane aromatization. © 1996 Academic Press, Inc.

INTRODUCTON

Gallium-modified ZSM-5 type zeolite catalysts, Ga-impregnated H–ZSM-5 (Ga/H–ZSM-5), physically mixed Ga_2O_3 and H–ZSM-5, and ZSM-5 type H–gallosilicates (H–GaMFI) and H–galloaluminosilicates (H–GaAlMFI) zeolites show high activity in the aromatization of lower alkanes (1–3), which is a process of great commercial importance. A beneficial effect of high temperature hydrogen pretreatment to physically mixed Ga_2O_3 and H–ZSM-5 and Ga/H–ZSM-5 zeolites on their alkane aromatization activity/selectivity has been observed earlier in a number of studies (1, 4–6). However, the influence of H_2 pretreatment on the alkane aromatization activity/selectivity for the H–GaMFI and H–GaAlMFI zeolites has not been investigated so far. It is also interesting to know the effect of H_2 pretreatment on zeolites that have gallium in their framework.

For gallium exchanged/impregnated H–ZSM-5 and physically mixed Ga_2O_3 and H–ZSM-5 zeolites, the H_2 treatment is believed to cause a surface migration of gallium species in the zeolite channels, resulting in a highly dispersed gallium phase located close to the acid sites (7–12). A significant increase in the dehydrogenation and hydrogenolysis activity, but a small decrease in the protonic acidity of physically mixed Ga_2O_3 and H–ZSM-5 catalyst due to H_2-treatment have been observed (13). Hydrogen is produced in an appreciable quantity in alkane aromatization over these Ga-modified zeolites (1). Hence, the state of gallium and its dispersion are also expected to be changed during the alkane aromatization process, particularly in the initial short period. It is, therefore, interesting to know the initial activity (at zero reaction time) and its variation with time on stream in alkane aromatization over H–ZSM-5 with externally added gallium and also over the H–GaMFI and H–GaAlMFI zeolites pretreated with both H_2 and O_2. Information on the initial state (or initial activity/selectivity) of the catalyst can be obtained using a pulse microreactor combined with GC (14).

This investigation was undertaken with the above objective. The H–GaMFI, H–GaAlMFI, and Ga/H–ZSM-5 zeolites pretreated with H_2 and O_2 have been compared to determine the influence of gas pretreatment under oxidizing and reducing atmospheres (i.e., under O_2 or H_2) on initial activity/selectivity and its variation with time on stream in the propane aromatization process, using a microreactor operated in both pulse reaction and continuous reaction modes.

EXPERIMENTAL

The Ga-impregnated H–ZSM-5 (Ga/H–ZSM-5, with 1.0 wt% Ga and Si/Al ratio of 48) was prepared by impregnating NH_4–ZSM-5, with gallium nitrate solution by the

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incipient impregnation technique. The NH_4–ZSM-5 (NH_4^+ exchange = 96% and crystal size = 5–7 μm) was obtained by exchanging ZSM-5 (prepared by the hydrothermal synthesis according to the patent of Argauer and Landolt (15)) repeatedly (four times) with 1 *M* ammonium nitrate solution at 80°C. The H–gallosilicate (H–GaMFI, with Si/Ga ratio of 33) and H–galloaluminosilicate (H–GaAlMFI, with Si/Al = 68 and Si/Ga = 82) were obtained from the NH_4 form. The NH_4–GaMFI and NH_4–GaAlMFI zeolites (NH_4^+ exchange = 95% and crystal size = 5–8 μm) were prepared by exchanging GaMFI and GaAlMFI zeolites (obtained by hydrothermal synthesis from a gel (pH 9–10), consisting of Na–trisilicate (Fluka), gallium nitrate (Aldrich) with or without aluminum nitrate (BDH), TPA–Br (Aldrich), sulfuric acid, and deionized water, in a stainless steel autoclave at 180°C for 24 h, followed by washing and drying the resulting zeolite crystals at 120°C for 4 h and calcining at 550°C in static air for 15 h to remove the occluded organic template) with 1 *M* ammonium nitrate solution at 80°C for 1 h; the ion exchange was repeated four times. All the zeolites (after the impregnation or the ion exchange) were pressed binder-free, crushed to particles of 0.2–0.3 mm size, and calcined in static air at 600°C for 4 h to get the zeolite catalysts in their H-form. The H_2 or O_2 pretreatment of the zeolites was performed *in situ* in a flow of pure H_2 or O_2 at 600°C for 10 h.

The MFI framework structure of the zeolites has been confirmed by XRD analysis and FTIR spectra. The bulk composition of the zeolites was determined by the chemical analysis of Si by the complete dissolution method (16), Ga by gravimetry using 5,7 dibromo-8-hydroxyquinoline as a complexing agent (17, 18), Al by gravimetry using 8-hydroxyquinoline as a complexing agent (19), and Na by flame photometry. The incorporation of Ga into the framework of the GaMFI and GaAlMFI zeolites was confirmed by observing the ^{71}Ga MAS NMR peak at +156 ppm, which corresponds to tetrahedral gallium in the zeolite framework. The framework Si/Al, Si/Ga, and Si/(Al + Ga) ratios of the zeolites were obtained from ^{29}Si MAS NMR peaks for Si(0Ga or Al) at about −112 ppm and Si(1Ga and/or Al) at about −104 ppm (20). The ^{71}Ga and ^{29}Si MAS NMR spectra were obtained using a Bruker MSL 300 MHz NMR instrument. The surface Si/Ga ratio of the catalysts was determined by XPS of Si (2*p*) and Ga (2*p*), using a VG-Scientific ESCA-3 MKII electron spectrometer. The number of strong acid sites on the zeolites was determined by the chemisorption of pyridine at 400°C using the GC pulse method (21).

The initial (zero reaction time) activity/selectivity of the pretreated zeolites and the variation of the activity/selectivity with time-on-stream in a continuous propane aromatization (at 600°C) have been determined by a pulse reaction of pure propane (>99.99%) at 600°C, using a quartz microreactor (i.d. = 4.5 mm, o.d. = 6 mm and length = 30 cm, packed with 0.1 g catalyst between quartz wool plugs) connected to a gas chromatograph, with an arrangement to operate the reactor in a pulse reaction mode or in a continuous reaction or catalyst pretreatment mode (by bypassing the reactor from the GC unit), as shown in Fig. 1. The microreactor and procedure for *in situ* catalyst pretreatment have been described in detail earlier (22, 23). High purity nitrogen (>99.99), passed over molecular sieves and Oxysorb to remove traces of moisture and oxygen, respectively, is used as a carrier gas (flow rate = 20 $cm^3 \cdot min^{-1}$) in the pulse reaction. The procedure for the propane pulse reaction studies is as follows. The microreactor is bypassed from the GC unit and the catalyst is pretreated in the flow of H_2 or O_2 (flow rate = 30 $cm^3 \cdot min^{-1}$) at 600°C for 10 h. After the pretreatment, the catalyst is flushed with the pure (moisture- and O_2-free) N_2 (50 $cm^3 \cdot min^{-1}$) for 10 min, the reactor is connected to the GC unit, and a pulse of pure propane (0.2 cm^3) is passed over the pretreated catalyst to obtain its initial actvity/selectivity. After the determination of the initial activity/selectvity, the reactor is bypassed from the GC to operate in a continuous reaction mode by passing a mixture of propane and nitrogen (50 mol% propane) continuously over the catalyst at 600°C and gas hourly space velocity (GHSV) of 3100 $cm^3 \cdot g^{-1} \cdot h^{-1}$ (measured at STP). After the continuous propane aromatization reaction for a time-on-stream of 5 min, the reactant gas mixture is replaced by pure N_2 (50 $cm^3 \cdot min^{-1}$) for 10 min to flush the catalyst to remove adsorbed reaction species. Then immediately the reactor was reconnected to the GC and the propane pulse reaction was carried out. This procedure was repeated to obtain the propane pulse reaction data at the different times-on-stream (5, 65, and 185 min) for the continuous propane aromatization to determine the change in the catalytic activity/selectivity due to the change in the catalyst state resulting from the continuous propane aromatization in the initial short reaction period. The three-way valve positions during the above operations are given in Fig. 1. The products of the propane pulse reaction were analyzed by the on-line gas chromatograph (with FID and computing integrator), using Poropak-Q (3 mm × 3 m) and Benton-34 (5%) and dinonylphthalate (5%) on chromosorb-W (3 mm × 5 m) columns for separating C_1–C_4 and aromatics, respectively.

RESULTS AND DISCUSSION

Characterization of Zeolites

The bulk composition of the Ga/H–ZSM-5, H–GaMFI, and H–GaAlMFI zeolites and the influence of pretreatment (in H_2 or O_2) on their framework (FW) composition, nonFW Ga/FW (Ga + Al) (i.e., nonFWGa/H^+) ratio, surface Si/Ga ratio, and strong acidity (measured in terms of

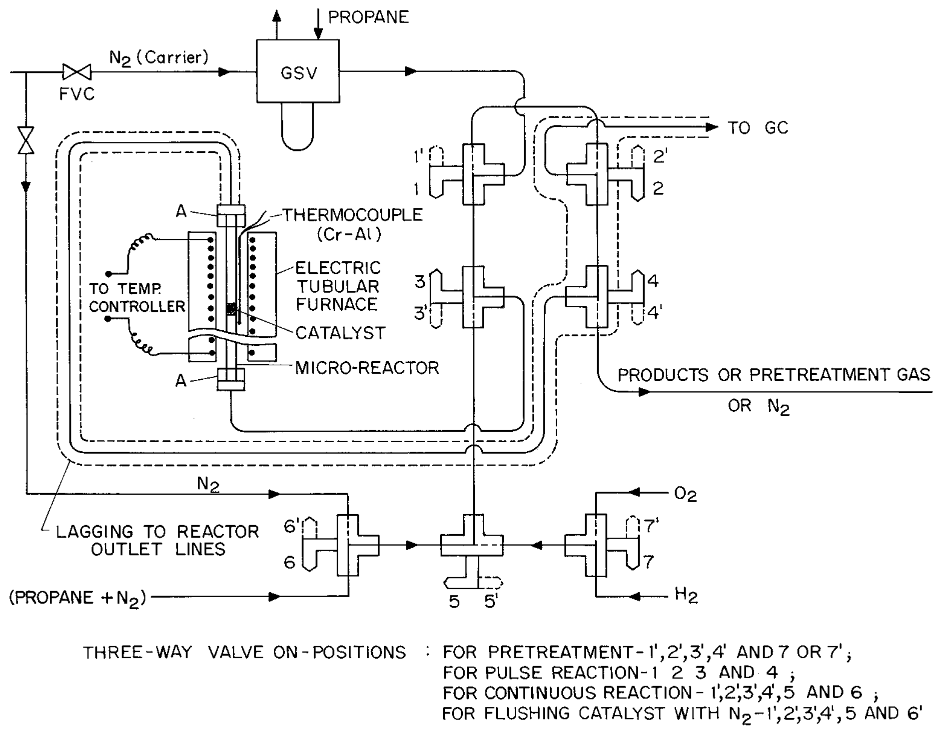

FIG. 1. Microreactor assembly operating in pulse reaction, continuous reaction, and *in situ* catalyst pretreatment modes (GSV = gas sampling valve, A = Ultratorr $\frac{1}{4}''$ to $\frac{1}{8}''$ swagelok connector, all valves with $\frac{1}{8}''$ swagelok end connections and lines with $\frac{1}{8}''$ ss tubings).

pyridine chemisorbed at 400°C) are presented in Table 1. The bulk Si/(Al + Ga) ratio of all the zeolite catalysts is more or less the same (34 ± 2.5).

In the case of Ga/H–ZSM-5, the as-synthesized form of ZSM-5 (TPA-ZSM-5) showed the presence of a small amount of octahedral Al (indicated by a ^{27}Al MAS NMR peak at about 0 ppm) and its FW Si/Al ratio (53.0) was not changed significantly by its calcination and/or pretreatment in H_2 or O_2. However, for the GaMFI and GaAlMFI zeolites in their TPA-form, no significant difference is observed in bulk and framework Si/Ga or Si/(Al + Ga) ratios. But in their H-forms, the FW Si/Ga ratio is significantly higher than the bulk Si/Ga ratio and also the FW Si/Ga is influenced by the gas (H_2 or O_2) treatment. Consequently, the non FW/FW Ga ratio is strongly influenced by the pretreatment; the ratio is much higher for the H_2-pretreated catalysts. These observations suggest that the GaMFI and GaAlMFI zeolites are degalliated to an appreciable extent during the conversion of their TPA-form to their H-form; the degalliation of the zeolites due to the

TABLE 1

Data on Characterization of Ga-Modified ZSM-5 Type Zeolites Pretreated in H_2 or O_2

Zeolite	Bulk composition[a]			Pretreatment (H_2 or O_2)	Framework composition[b]			NonFW Ga	Surface	Acidity[d]
	Si/Al	Si/Ga	Si/(Al + Ga)		Si/Al	Si/Ga	Si/(Al + Ga)	FW (Al + Ga) ratio	Si/Ga ratio[c]	(mmol · g^{-1})
Ga/H–ZSM-5	48	97	33	O_2	53	>10,000	53	0.49	56	0.26
				H_2	53	>10,000	53	0.49	67	0.28
H–GaMFI	>10,000	33	33	O_2	>10,000	42	42	0.27	125	0.36
				H_2	>10,000	47	47	0.42	91	0.29
H–GaAlMFI	68	82	37	O_2	68	118	43	0.16	200	0.20
				H_2	68	236	53	0.43	125	0.34

[a] Obtained by chemical analysis.

[b] Obtained from ^{29}Si MAS NMR.

[c] Obtained by XPS.

[d] Measured in terms of pyridine chemisorbed at 400°C.

H_2-pretreatment is larger than that due to the O_2-pretreatment.

It may be noted that, in estimating the FW Si/Ga ratio of H–GaAlMFI, it is assumed that the FW Si/Al ratio is not changed in the conversion of TPA–GaAlMFI to H–GaAlMFI, which is consistent with the ratio observed for Ga/H–ZSM-5. It may also be noted that since the T-sites in the MFI structure are not crystallographically identical, the estimation of framework Si/Ga, Si/Al, or Si/(Al + Ga) ratios from ^{29}Si MAS NMR is not very accurate (24). Nevertheless, the changes in the FW Si/Ga or Si/(Al + Ga) are large enough to give some idea as to the degalliation and the presence of extraframework gallium species.

The observed changes in the surface Si/Ga ratio (obtained from the XPS) for the catalysts due to the pretreatment indicate that for the H_2-pretreated H–GaMFI and H–GaAlMFI zeolites, the surface concentration of Ga is higher than that for the corresponding O_2 pretreated zeolite. But exactly the opposite trend is observed in the case of Ga/H–ZSM-5. These results suggest that there is migration of Ga-oxide species (formed by degalliation) from zeolite channels to the external surfaces of crystallites for the H–GaMFI and H–GaAlMFI zeolites, due to the H_2 pretreatment. The migration of Ga for the Ga/H–ZSM-5 due to H_2 pretreatment is in the reverse direction because of the formation of more volatile Ga-oxide species from the Ga_2O_3 already present on the external surface of the H–ZSM-5 zeolite. This is consistent with that observed earlier (9–11).

The strong acidity of the zeolite catalysts (Table 1) is also influenced by the pretreatment. However, the influence is quite small for the Ga/H–ZSM-5 and H–GaAlMFI catalysts. The observed changes in the acidity due to the pretreatment are the result of degalliation to different extents and/or formation of different extraframework Ga-oxide species having different acidity. The oxidation state of extraframework Ga and its role in the alkane-to-aromatics conversion reaction sequence are not yet clearly understood (25).

Influence of Pretreatment on Initial Activity/Selectivity

Results on the initial (zero time) activity/selectivity of the O_2 and H_2 pretreated Ga-modified zeolite catalysts in propane aromatization (at 600°C), measured under transient conditions by pulse reaction of propane, are presented in Table 2. The initial aromatization activity/product selectivity in propane aromatization is strongly influenced by the pretreatment. When compared with the results obtained due to the O_2 pretreatment, the H_2 pretreatment has the following influence on the initial activity and product selectivity:

—Both the total propane conversion activity and the aromatization activity (or aromatics yield) for the H–GaMFI are decreased appreciably, without affecting its aromatics selectivity. However, the aromatization activity and aromatics selectivity are increased markedly for the H–GaAlMFI and Ga/H–ZSM-5 catalysts. The changes in the catalytic activity are consistent with the changes in the acidity of the catalysts due to the O_2 or H_2 pretreatment.

—The propylene selectivity is increased very markedly for the H–GaMFI and are also increased for the H–GaAlMFI, but to a small extent; whereas the Ga/H–ZSM-5 shows almost no selectivity for propylene.

—The ethylene and methane selectivity are decreased for all the catalysts.

—The ethane selectivity is increased for the H–GaMFI and Ga/H–ZSM-5 catalysts but decreased for the H–GaAlMFI.

—The aromatics/(methane + ethane) mass ratio is increased for all the catalysts; however, the increase is much greater for H–GaAlMFI.

—The methane/(ethane + ethylene) mole ratio for all the catalysts is decreased; the decrease is appreciable, however, for the H–GaMFI and H–GaAlMFI catalysts.

The distribution of aromatics is almost not affected for H–GaMFI, is affected to a very small extent for Ga/H–ZSM-5, and is influenced significantly for H–GaAlMFI (Table 2). In the later case, the concentration of toluene is decreased and that of xylenes is increased.

The increase in the aromatics/(methane + ethane) ratio clearly indicates the beneficial effect of the H_2 pretreatment for all the catalysts because the formation of gases (CH_4 and ethane) having only fuel value is greatly reduced. The aroamtics/(methane + ethane) ratio for the different catalysts (pretreated with H_2) is in the following order: H–GaAlMFI > H–GaMFI > Ga/H–ZSM-5.

The observed superior performance of H–GaAlMFI over Ga/H–ZSM-5 in propane aromatization is attributed mostly to a formation of highly dispersed Ga-species throughout the zeolite channels in close proximity to the protonic acid sites, due to partial degallination (or removal) of framework gallium during the H_2 pretreatment. The increase in the aromatization activity/selectivity of Ga/H–ZSM-5 due to the H_2 pretreatment is also expected to be mostly due to migration of reduced gallium oxide species from the external crystal surface toward the protonic acid sites in the zeolite channels (7–12).

The decrease in the propane conversion and aromatization activity of the H–GaMFI due to the H_2 pretreatment is attributed mostly to removal of some of the framework gallium under the reducing conditions, thus decreasing the number of protonic acid sites responsible for oligomerization and cyclization, and also for propane conversion in the propane aromatization process.

TABLE 2

Initial Activity/Product Selectivity of the O_2- and H_2-Pretreated Ga-Modified ZSM-5 Type Zeolites in Propane Aromatization (at 600°C)

Acidity/selectivity/product ratio/ product distribution	H–GaMFI		H–GaAlMFI		Ga/H–ZSM-5	
	O_2-treated	H_2-treated	O_2-treated	H_2-treated	O_2-treated	H_2-treated
(*A*) *Initial catalytic activity*						
Propane conversion						
Total (%)	99.9	89.7	99.9	98.4	100.0	100.0
To aromatics (%)	68.6	61.5	70.5	82.0	69.0	81.9
(*B*) *Product selectivity ratio*						
Aromatics selectivity (%)	68.7	68.5	71.0	82.9	69.0	81.9
Propylene selectivity (%)	1.8	9.6	1.6	1.9	0.2	0.0
Ethylene selectivity (%)	12.1	10.9	9.1	6.5	4.7	3.1
Ethane selectivity (%)	3.2	4.7	3.3	1.5	3.4	3.9
Methane selectivity (%)	14.1	6.4	15.2	7.4	13.3	11.1
$CH_4/(C_2H_4 + C_2H_6)$ mole ratio	1.63	0.73	2.16	1.64	2.96	2.88
Aromatics/$(CH_4 + C/2H_6)$ mass ratio	4.0	6.2	3.9	9.5	4.1	5.5
(*C*) *Distribution of aromatics* (*wt%*)						
Benzene	68.6	68.0	73.0	74.1	76.7	78.5
Toluene	31.4	31.2	27.0	23.7	23.3	21.5
C_8-aromatics	00.0	00.0	00.0	2.2	00.0	00.0

The product selectivity in propane aromatization is found to be dependent upon the propane conversion (1, 27, 28). However, in the present case, the propane conversion over all the catalysts (pretreated in H_2 or O_2) is 95 ± 5% (Table 2). Hence, the catalysts can be compared for their product selectivity.

Influence of Pretreatment on the Variation of Activity/Selectivity

Influence of time on stream (for a short initial period, 0–180 min) and catalyst pretreatment on the propane conversion (both total conversion and to aromatics), product selectivity, and distribution of aromatics in the propane aromatization (at 600°C) over the H–GaMFI, H–GaAlMFI, and Ga/H–ZSM-5 catalysts is shown in Figs. 2, 3, and 4, respectively. Figure 5 shows the effect of time on stream and catalyst pretreatment on the aromatics/(methane + ethane) mass ratio obtained in the propane aromatization over the catalysts. The variation of the propane conversion and aromatization activity relative to the corresponding initial activity in the catalytic process over the catalysts are presented in Figs. 6 and 7, respectively.

The results (Figs. 2–7) reveal that the catalyst pretreatment has a strong and also complex effect, which also depends on the catalyst, on the variation of catalytic activity/selectivity with the time on stream in the propane aromatization process.

Variation of Catalytic Activity with Time-On-Stream

The propane conversion and aromatization activity of the H_2 and O_2 pretreated catalysts (Figs. 2a, 3a, and 4a) or that relative to the initial ones (i.e., A_t/A_0, where A_t and A_0 are catalytic activity determined at time-on-stream of t and zero, respectively) (Figs. 6 and 7) are found to be changed with increasing time on stream, as follows.

Propane conversion activity: For the H_2-pretreated H–GaMFI, the propane conversion activity increases initially, passes though a maximum, and then decreases, whereas for the O_2-pretreated H–GaMFI, it decreased continuously. For the O_2-pretreated Ga/H–ZSM-5, it decreases markedly. The effect of time on stream and pretreatment on the propane conversion activity of H–GaAlMFI is quite small. The effect of time on stream on the propane conversion activity of H_2-pretreated Ga/H–ZSM-5 is also very small.

Aromatization activity: For H_2- or O_2-pretreated GaMFI, aromatization activity initially increases to a small extent and then decreases, the decrease being very sharp for the H_2-pretreated catalyst. For O_2-pretreated H–GaAlMFI and Ga/H–ZSM-5, it increases sharply and then passes through a maximum. For H_2-pretreated H–GaAlMFI and Ga/H–ZSM-5, it decreases. However, the trends for the decrease are different. Its variation with time on stream is very strongly affected by the pretreatment for the H–GaAlMFI and Ga/H–ZSM-5 catalysts but the pretreatment effect on its variation is relatively much smaller for the H–GaMFI catalyst. The effect of pretreatment in these two cases is opposite (Fig. 7).

The observed decrease in the aromatization activity with increasing time on stream for all the H_2-pretreated catalysts is mostly due to the catalyst deactivation caused by coke

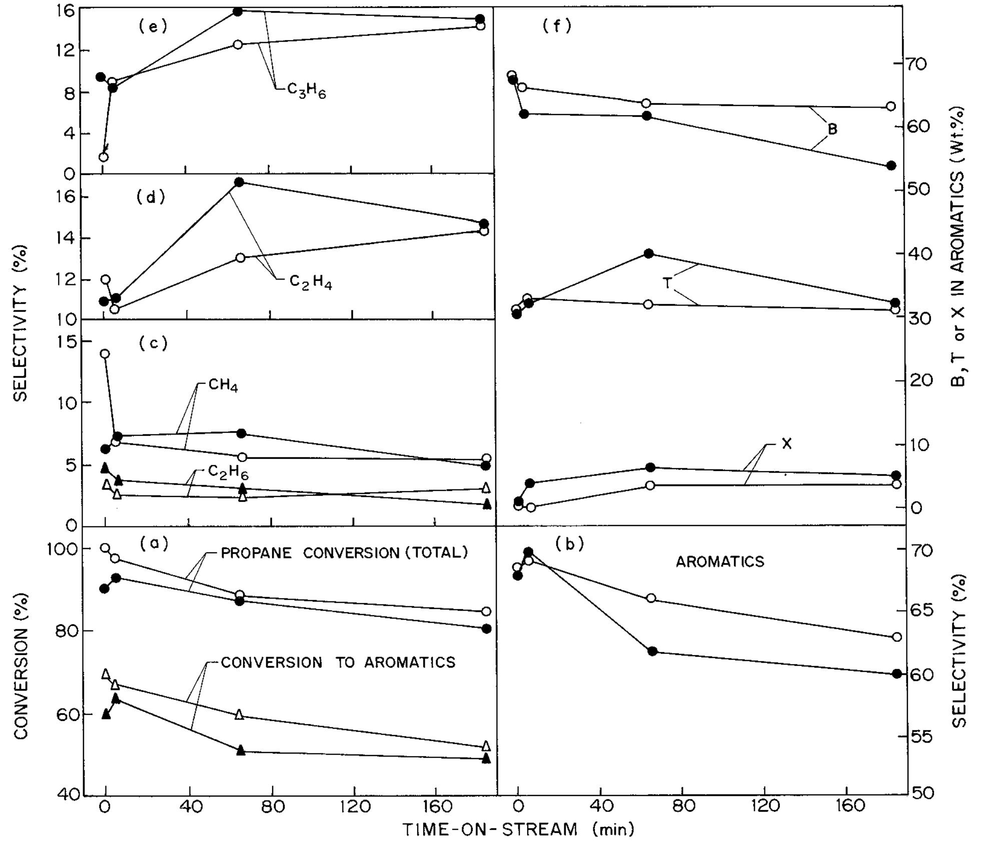

FIG. 2. Influence of time-on-stream on the conversion, selectivity, and distribution of aromatics in propane aromatization over the O_2- and H_2-pretreated H–GaMFI. (Open symbols for O_2-pretreated catalyst and solid symbols for H_2-pretreated catalyst.)

deposition during propane aromatization. After the removal of coke by oxidative treatment of the catalysts (at 550°C with 5% in N_2 for 1 h), the catalyst activity is recovered almost completely. The initial small increase in the activity of H_2-pretreated H–GaMFI (Figs. 2a, 6, and 7) may be due to a change in the state of the catalyst in the initial reaction period. However, the exact reason for this change is not known. The observed initial sharp increase followed by the continuous increase in aromatization activity for an appreciably long period (more than 1 h) for the O_2-pretreated H–GaAlMFI and Ga/H–ZSM-5 catalysts (Figs. 3a, 4a, and 7) is expected to be mostly due to the change in the catalyst state resulting in increased intrinsic catalytic activity due to their *in situ* (during the catalytic process) pretreatment by the hydrogen produced in the aromatization process. The effect produced by the H_2 formed during the process is expected to be similar to that observed due to the H_2 pretreatment of these catalysts discussed earlier. Thus, the results reveal that the O_2-pretreated H–GaAlMFI and Ga/H–ZSM-5 catalysts are activated during the initial period of the propane aromatization process. After a reaction period (or time on stream) of about 1 h, the catalytic activity is decreased, mostly due to the catalyst deactivation by coking. It may be noted that the variation (with time on stream) in the total propane conversion activity of all the H_2- and O_2-pretreated catalysts is relatively much smaller than in the aromatization activity (Figs. 6 and 7).

Variation of Product Selectivity with Time-On-Stream

The results (Figs. 2b–2e, 3b–3e and 4b–4e) reveal that the product selectivity in the propane aromatization is very strongly influenced by both the catalyst pretreatment and the catalyst activation/deactivation (or the time on stream), and its variation also depends upon the catalyst used and the catalyst pretreatment. The important observations on this are summarized below.

With increased time on stream:

(i) the aromatic selectivity passes through a maximum (with an initial sharp increase) for the O_2-pretreated H–GaAlMFI and Ga/H–ZSM-5 and also for both the H_2- and O_2-pretreated H–GaMFI, but decreases continuously for the H_2-pretreated H–GaAlMFI and Ga/H–ZSM-5;

(ii) the propylene selectivity is passed through first a minimum and then a maximum for the H_2-pretreated H–

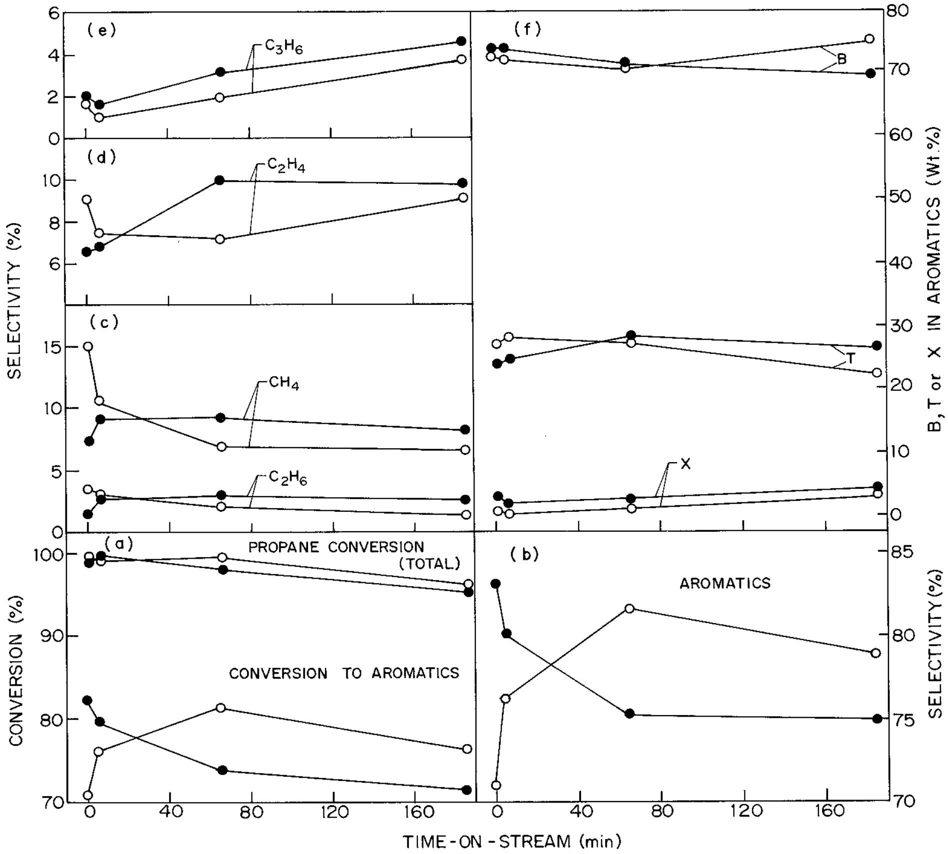

FIG. 3. Influence of time-on-stream on the conversion, selectivity, and distribution of aromatics in propane aromatization over the O_2- and H_2-pretreated H–GaAlMFI. (Open symbols for O_2-pretreated zeolite and solid symbols for H_2-pretreated catalyst.)

GaMFI, but increased continously (with initial sharp increase) for the O_2-pretreated H–GaMFI; passed through a minimum for both the H_2- and O_2-pretreated H–GaAlMFI, but through a maximum for the H_2-pretreated Ga/H–ZSM-5;

(iii) the ethylene selectivity passes through a minimum for the O_2-pretreated H–GaMFI and H–GaAlMFI and also for the H_2- and O_2-pretreated Ga/H–ZSM-5, but passes through a maximum for the H_2-pretreated H–GAMFI and H–GaAlMFI catalysts;

(iv) the methane selectivity decreases continuously (with initial sharp decrease) for the O_2-pretreated H–GaMFI and H–GaAlMFI, but passed through a maximum for the H_2-pretreated H–GaMFI and H–GaAlMFI, a minimum for O_2-pretreated Ga/H–ZSM-5, and both maximum and minimum for the H_2-pretreated Ga/H–ZSM-5.

The ethane selectivity, however, is affected to a relatively smaller extent due to the pretreatment or catalyst activation/deactivation during the propane aromatization.

The results in Fig. 5 show a strong influence of the catalyst pretreatment and the catalyst activation deactivation during propane aromatization on the aromatics/(methane + ethane) mass ratio. It is very essential to get high value for this ratio in order to decrease the formation of undesirable methane and ethane, which have only fuel value, so that the economics can be improved. The increase in time on stream causes the ratio to pass through a maximum for the H_2- and O_2-pretreated H–Ga/H–ZSM-5 and causes the O_2-pretreated H–GaMFI (with a sharp initial increase) to increase continuously for the O_2-pretreated H–GaAlMFI and the H_2-pretreated H–GaMFI and to pass through a maximum (with a sharp initial increase) for the O_2-pretreated H–GaMFI. The influence of pretreatment on the variation of the ratio for the Ga/H–ZSM-5 is quite small, but for the other two catalysts is very large and almost opposite.

Figures 2f, 3f, and 4f reveal that the distribution of aromatics (BTX) produced in the process is influenced by both the catalyst pretreatment and the catalyst activation/deactivation during the process. The influence is however, very pronounced for the Ga/H–ZSM-5 but relatively much smaller for the H–GaAlMFI.

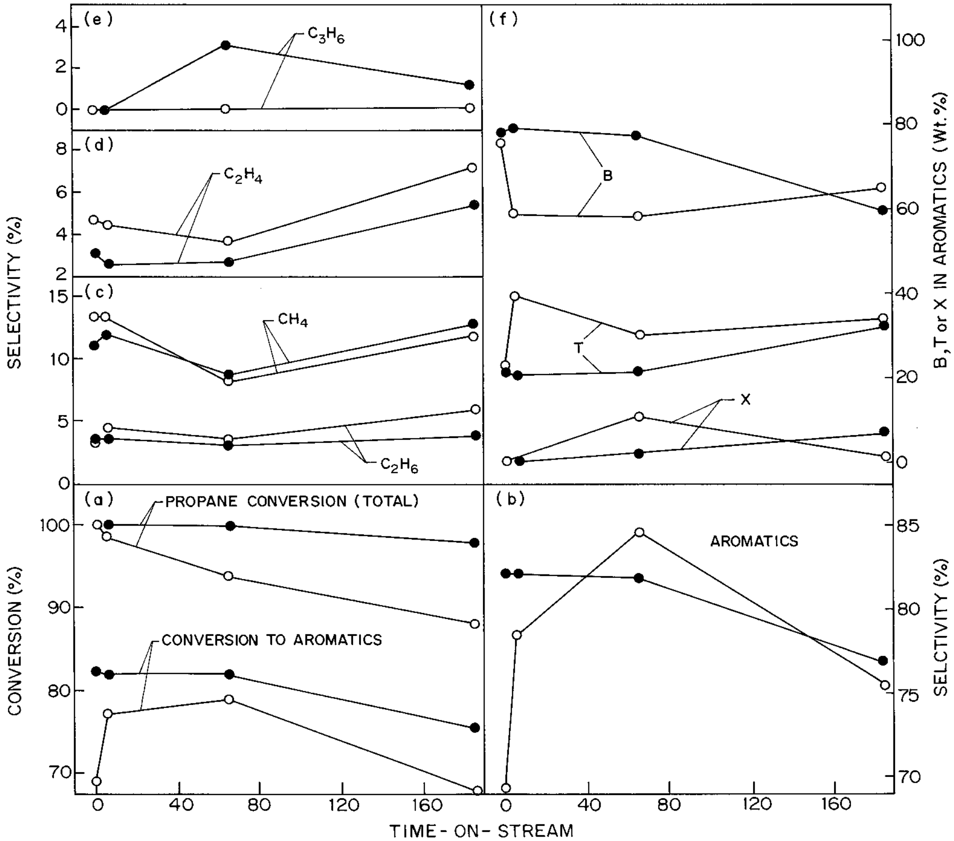

FIG. 4. Influence of time-on-stream on the conversion, selectivity, and distribution of aromatics in propane aromatization over the O_2- and H_2-pretreated Ga/H–ZSM-5. (Open symbols for O_2-pretreated catalyst and solid symbols for H_2-pretreated catalyst.)

Comparison of Catalysts for their Initial Activity/Selectivity and Deactivation

Initial Activity/Selectivity

Based on the results (Table 2 and Figs. 2–7), the catalysts pretreated with H_2 or O_2 are compared for their initial activity/selectivity as follows.

(*A*) *H_2-pretreated catalysts:*

Propane conversion activity	H–GaAlMFI ≃ Ga/H–ZSM-5 > H–GaMFI
Propane aromatization actvity	H–GaAlMFI ≃ Ga/H–ZSM-5 ≫ H–GaMFI
Aromatics selectivity	H–GaAlMFI > Ga/H–ZSM-5 ≫ H–GaMFI
Aromatics/(CH_4 + C_2H_6) mass ratio	H–GaAlMFI > H–GaMFI > Ga/H–ZSM-5

(*B*) *O_2-pretreated catalysts:*

Propane conversion activity	H–GaAlMFI ≃ Ga/H–ZSM-5 ≃ H–GaMFI
Propane aromatization actvity	H–GaAlMFI > Ga/H–ZSM-5 ≥ H–GaMFI
Aromatics selectivity	H–GaAlMFI > Ga/H–ZSM-5 ≃ H–GaMFI
Aromatics/(CH_4 + C_2H_6) mass ratio	H–GaAlMFI ≃ Ga/H–ZSM-5 ≃ H–GaMFI

It may be noted that the O_2-pretreated catalysts have different nonFW Ga/FW(Ga + Al) ratios but the H_2-pretreated ones have more or less similar nonFW Ga/FW(Ga + Al) ratios. The comparison of the catalysts, particularly the H_2-pretreated ones, as their nonFW Ga/FW(Ga + Al) is more or less the same, leads to the conclusion that the catalysts containing extraframework Ga-species in association with the FW Al (i.e., stronger zeolite acid sites) are more active as well as more selective in the propane-to-aromatics conversion.

For Catalyst Deactivation Due to Coking

The catalyst order for the deactivation of aromatization activity for the H_2- and O_2-pretreated catalysts (Fig. 7) is as follows:

H_2-pretreated catalysts	H–GaMFI > H–GaAlMFI > Ga/H–ZSM-5
O_2-pretreated catalysts	H–GaMFI ≃ Ga/H–ZSM-5 > H–GaAlMFI.

For the deactivation of propane conversion activity, the catalysts can be ordered as follows.

H_2-pretreated catalysts	H–GaMFI ≫ Ga/H–ZSM-5 ≃ H–GaAlMFI
O_2-pretreated catalysts	H–GaMFI > Ga/H–ZSM-5 > H–GaAlMFI.

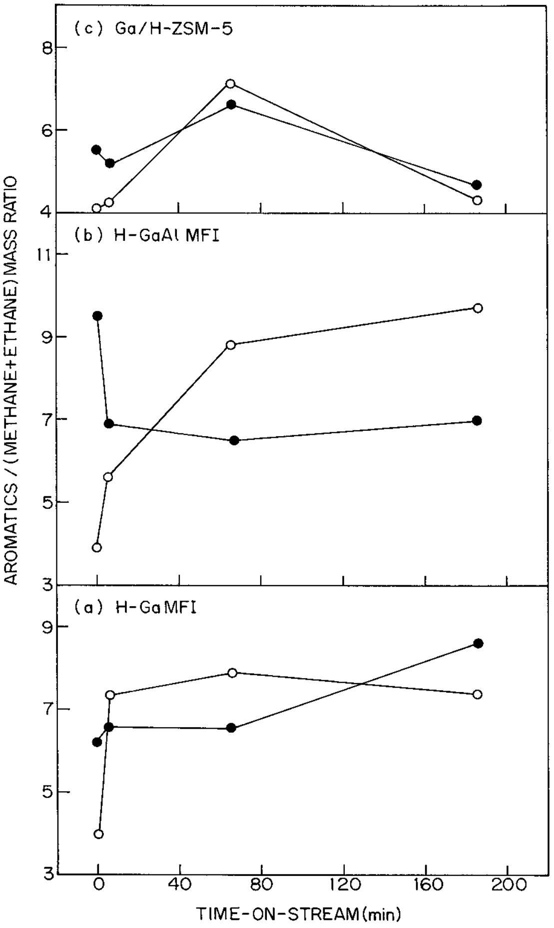

FIG. 5. Influence of time-on-stream on aromatics/(methane + ethane) mass ratio in the aromatization of propane over O_2-pretreated (open symbol) and H_2-pretreated (solid symbol) Ga-modified zeolite catalysts.

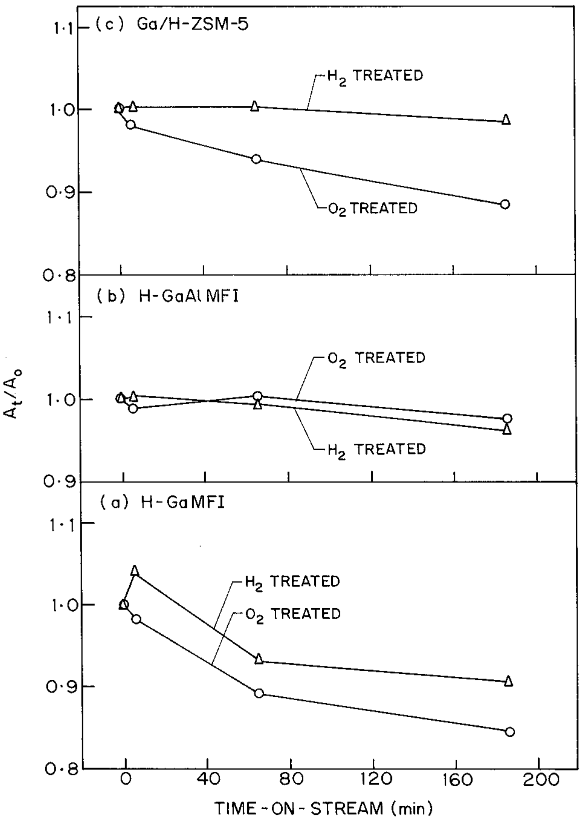

FIG. 6. Variation with time-on-stream the total conversion of propane, relative to that at $t = 0$, over the O_2- and H_2-pretreated Ga-modified zeolite catalysts.

The deactivation of the propane conversion activity of the H–GaAlMFI is not influenced significantly by the pretreatment. The comparison of O_2-pretreated catalysts for their deactivation is, however, not very reliable because the activation and deactivation processes occur simultaneously during the initial reaction period.

The above comparison reveals that H–GaAlMFI, which shows superior performance, has a very high potential for developing a highly active and selective catalyst for lower alkane aromatization. In order to obtain desirable converson and aromatics selectivity in lower alkane aromatization, the catalyst must contain strong acid sites with high density and also highly dispersed active gallium species in close proximity of the zeolitic acid sites, thus maintaining a balance between the acid and dehydrogenating function (1, 26–28). This could very well be achieved in the case of H–GaAlMFI; the density of strong acid sites can be controlled by the framework Si/Al ratio and the highly dispersed active gallium species can be obtained by degallination of the zeolite under controlled conditions.

It may be noted that the pulse microreactor results may not reflect exactly the activity/selectivity of the zeolites under steady-state conditions. Nevertheless, for the purpose of comparing the initial activity/selectivity, such studies are very useful.

CONCLUSIONS

This investigation leads to the following important conclusions.

1. The initial aromatization activity/selectivity and product distribution in propane aromatization over H–GaMFI, H–AlMFI, and Ga/H–ZSM-5 catalysts are strongly influenced by their high temperature pretreatment with O_2 or H_2.

2. The variation of activity (both propane conversion and aromatization) and product selectivity with time on stream are strongly affected by the catalyst pretreatment and the catalyst activation (caused by the interaction of

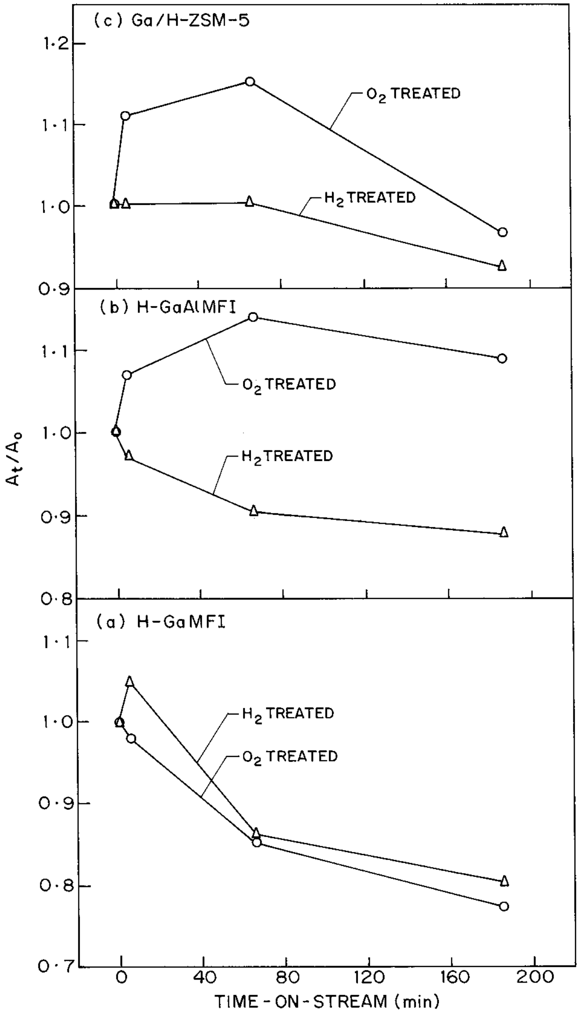

FIG. 7. Variation with time-on-stream the conversion of propane to aromatics, relative to that at $t = 0$, over the O_2- and H_2-pretreated Ga-modified zeolite catalysts.

hydrogen, produced in the aromatization, with the catalysts pretreated with O_2) are deactivation (due to coking), depending upon the catalyst.

3. The initial aromatization activity and selectivity are appreciably increased due to the H_2 pretreatment given to the H–GaAlMFI and Ga/H–ZSM-5 catalysts and also due to the activation (by the H_2 produced in the reaction) of these catalysts (when pretreated with O_2), in the aromatization process during a short initial reaction period. However, the H_2 pretreatment results in a decrease in both the propane conversion and aromatization activity of the H–GaMFI.

4. The aromatics/(methane + ethane) mass ratio for all the catalysts is increased by their H_2 pretreatment and also by the catalyst activation by the H_2 produced during the aromatization process (for a short initial period) over the O_2 pretreated catalysts.

5. Comparison of the catalysts for their initial activity/selectivity and aromatics/(methane + ethane) ratio and variation of these parameters with time-on-stream in the propane aromatization process leads to the following order for the catalysts for their choice: H–GaAlMFI > Ga/H–ZSM-5 > H–GaMFI. Zeolite (MFI) catalysts containing extraframework Ga-species in association with framework Al (i.e., stronger protonic acid site) rather than with framework Ga are more active as well as more selective in the propane aromatization. Galloaluminosilicates (MFI) have high potential for developing commercial propane (or lower alkanes) aromatization catalysts having desirable activity/selectivity and life.

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REFERENCES

1. Guisnet, M., Gnep, N. S., and Alario, F., *Appl. Catal.* **89,** 1 (1992).
2. Ono, Y., *Catal. Rev. Sci. Eng.* **34,** 179 (1992).
3. Giannetto, G., Monque, R., and Galiasso, R., *Catal. Rev. Sci. Eng.* **36**(2), 271 (1994).
4. Kanazirev, V., Price, G. L., and Dooley, K. M., *J. Chem. Soc. Chem. Commun.* 712 (1990).
5. Kanazirev, V., Price, G. L., and Dooley, K. M., *Stud. Surf. Sci. Catal.* **69** 277 (1991).
6. Joly, J. F., Ajot, H., Alario, F., Aittaleb, D., Gnep, N. S., and Guisnet, M., "Proceedings, 9th International Zeolite Conference, Montreal, 1992, Vol. II." (R. Von Ballmoose, J. B. Higgins, and M. M. J. Treacy, Eds.), p. 501. Butterworth/Heineman, Boston, 1993.
7. Dooley, K. M., Chang, C., and Price, G. L., *Appl. Catal.* **84,** 17 (1992).
8. Jia, S., Wu, S., and Meng, Z., *Appl. Catal. A. Gen.* **103,** 259 (1993).
9. Joly, J. F., Ajot, H. Merlen, E., Raatz, F., and Alario, F., *Appl. Catal.* **79,** 249 (1991).
10. Meriaudeau, P., and Naccache, C., *Appl. Catal.* **73,** L13 (1991).
11. Kanazirev, V., Pifter, R., and Forster, H., *J. Mol. Catal.* **69,** L15 (1991).
12. Kanazirev, V., Dimitrova, R., Price, G. L., Khodakov, A. Yu., Kustov, L. M., and Kazansky, V. B., *J. Mol. Catal.* **70,** 111 (1991).
13. Barre, M., Gnep, N. S., Magnoux, P., Guisnet, M., Sansare, S. D., and Choudhary, V. R., *Catal. Lett.* **21,** 275 (1993).
14. Choudary, V. R., and Doraiswamy, L. K., *Ind. Eng. Chem. Prod. Res. Dev.* **10,** 218 (1971).
15. Argauer, R. G., and Landolt, G. R., U.S. Patent 3,702,886 (1972).
16. Van Hooff, J. H. C., and Roelofsen, J. W., *Stud. Surf. Sci. Catal.* **58,** (1991).
17. Gastinger, E., *Z. Anal. Chem.* **126,** 373 (1944).
18. Duval, C., "Inorganic Thermogravimetric Analysis," 2nd ed., p. 416. Elsevier, Amsterdam, 1963.
19. Vogel, A. I., "Text Book of Quantitative Inorganic Analysis," 3rd ed., p. 514. Longmans, Green, London, 1961.
20. Liu, X-S., and Klinowski, J., *J. Phys. Chem.* **96,** 3403 (1992).

21. Choudhary, V. R., and Nayak, V. S., *Appl. Catal.* **4,** 31 (1982).
22. Choudhary, V. R., Sansare, S. D., Rajput, A. M., and Akolekar, D. B., *Appl. Catal.* **69,** 187 (1991).
23. Choudhary, V. R., and Rane, V. H., *J. Catal.* **135,** 310 (1992).
24. Thomas, J. M., and Jiu, X-S., *J. Phys. Chem.* **90,** 4843 (1986).
25. Iglesia, E., Baumgartner, J. E., and Price, G. L., *J. Catal.* **134,** 549 (1992).
26. Meriaudean, P., and Naccache, C., ‘‘Catalysis Deactivation’’ (C. H. Bartholomew and J. B. Bhutt, Eds.), p. 767. Elsevier, Amsterdam, 1991.
27. Giannetto, G., Montes, A., Gnep, N. S., Florentino, A., Cartraud, P., and Guisnet, M., *J. Catal.* **145,** 86 (1993).
28. Choudhary, V. R., Kinage, A. K., Sivadinarayana, C., Devadas, P., Sansare, S. D., and Guisnet, M., *J. Catal.* **158,** 34 (1996).