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NOTES

Propane Conversion on Ga-HZSM-5: Effect of Aging on the Dehydrogenating and Acid Functions Using Pyridine as an IR Probe

Gallium-loaded zeolite (Ga-HZSM-5) catalysts have been extensively studied in the recent past, not only in respect of their interesting catalytic activity in the aromatization of C_3–C_5 alkanes (Cyclar Process (*1*)) but also in respect of theoretical considerations. There is clear evidence that in the reaction of alkanes these catalysts behave as bifunctional catalysts, the acid function being provided by the protons and the dehydrogenating function deriving from Ga_2O_3 or Ga^{n+} ions in ionic-exchange positions (*2–4*). Ga-HZSM-5 catalysts deactivate with time on stream (*5*). The deactivation can result from poisoning of the acid centres and/or the dehydrogenating sites by coke deposition or from sintering or phase transformation of the dehydrogenating gallium species. The aim of the present study was to investigate the possible modifications of Ga centres and H^+ sites which may result from the propane reaction. The active centers were studied by infrared spectroscopy of adsorbed pyridine, pyridine adsorption being used to probe both H^+ and Al, Ga Lewis-acid centers (*6*).

Zeolite ZSM-5 was synthesized according the method given in Ref. (*7*). The as-synthesized sample was heated in nitrogen flow while the temperature was increased from 293 to 773 K to decompose the quarternary amine. The material was then calcined in oxygen at 773 K for 2 h to remove carbon residues. Chemical analysis of Al and Si determined by atomic absorption spectroscopy leads to Si/Al = 18. To generate the H-form, the zeolite was ion exchanged with an aqueous solution of NH_4NO_3. The exchange was repeated three times, and the solid was activated at 773 K in oxygen. XRD analysis of the H-form indicated that the solid was highly crystalline. H-ZSM-5 containing Ga was prepared by the incipient wetness impregnation technique using $Ga(NO_3)_3$ aqueous solution (Aldrich). The Ga-HZSM-5 was calcined at 823 K in oxygen for 24 h.

The catalytic experiments were carried out at 823 K in a flow microreactor at atmospheric pressure of C_3H_8, and high WHSV. Reactant and products were analyzed on line with two F.I.D. gas chromatograph equipped with Bentone and Unibeds columns (Alltech, France).

In order to estimate the Brønsted and the Lewis acidity infrared spectra of adsorbed pyridine were used. Samples were pressed into thin wafers (10–20 mg), mounted in a special holder and introduced into the infrared cell. The wafer was outgassed at 803 K, allowed to adsorb pyridine at 373 K, and outgassed at 423 K before recording the IR spectra of adsorbed pyridine on a Fourier transform Bruker spectrometer.

Measurements (823 K and 101 kPa of C_3H_8) were made at low conversion (8–10%) such that secondary reactions were minimized. The conversion was determined immediately after the catalyst was contacted with propane (2–3 min) in order to avoid significant deactivation. In these experimental conditions initial catalytic activities were measured. Figure 1 reports the conversion of C_3H_8 for a series of samples which have experienced various representative modes of activation. Point A shows the conversion over Ga_2O_3-HZSM-5 calcined in oxygen for 16 h at 823 K. Following this treatment the sample was H_2-reduced for 1 h at 823 K and the conversion of C_3H_8 again measured (Point B). It is clear that H_2-reduc-

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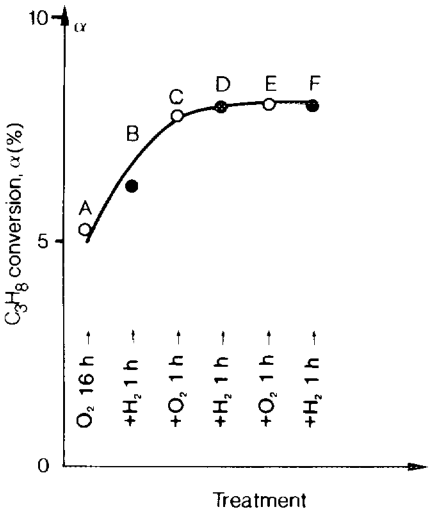


FIG. 1. Rate of propane transformation at 823 K on Ga HZSM-5 as a function of its activation treatment: (A) 16 h under O_2; (B) treatment (A) + 1 h under H_2; (C) treatment (B) + 1 h under O_2; (D) treatment (C) + 1 h under H_2; (E) treatment (D) + 1 h under O_2; and (F) treatment (E) + 1 h under H_2. After each treatment, the same was flushed with N_2 for 15 min.

tion of the catalyst resulted in a significant increase of its catalytic activity for the propane reaction. Subsequent O_2-oxidation of the reduced sample produced an additional increase of the conversion (Point C), but further H_2–O_2 activation cycles (Points D, E, F, . . .) gave almost no additional increase. The catalytic behaviour of the Ga-HZSM-5 catalyst varied markedly with the H_2–O_2 activaton mode. The dehydrogenating properties of Ga-HZSM-5 have been attributed to the simultaneous presence of H^+ acid centres and Ga species (*2–4*). It has been suggested that the promoting effect of the activation in O_2 and H_2 results from an increase in the dispersion of Ga species due to their spreading and migration into the zeolite channels toward ion exchange positions (*8*). Although the mechanism of Ga species migration was not fully understood it was suggested that reduced Ga^{n+} species reacted with H^+ of the zeolite, thus lowering the number of protons available for the reaction (*9*), H^+ being replaced by Ga^{n+}.

The catalytic behaviour with time on stream of Ga-HZSM-5, optimized by successive O_2–H_2 treatments at 823 K, has been studied (Fig. 2). The reaction temperature was 823 K and C_3H_8 pressure 101 kPa as before, but the WHSV was lowered in order to increase the conversion of propane. Figure 2 shows that one third of the activity was lost after two hours on stream. The deactivated sample was regenerated *in situ* by oxidation at high temperature of the coke formed on the zeolite. The conditions of coke-burning were 673 K in N_2 followed by 10% vol. of O_2 in N_2 at 1 liter h^{-1} flow rate while the temperature was increased by 1 K per minute up to 823 K (see below for TPO results). The sample was then maintained at 823 K for 1 h. The regenerated, "coke-poisoned Ga-HZSM-5" was again exposed to C_3H_8 at 823 K using the same experimental conditions as those used previously. The C_3H_8 conversion with time on stream was measured, and the experimental curve superimposed exactly on the curve of Fig. 2. The Ga-HZSM-5 was submitted to 8 cycles of C_3H_8 reaction followed by regeneration by oxidation at high temperature. After the 8th cycle the curve of conversion versus

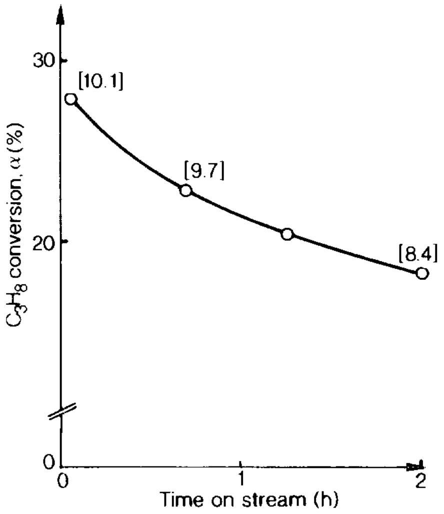


FIG. 2. Change in the conversion of C_3H_8 as a function of time on stream. The numbers in brackets are relative to the methane selectivity (see text).

time on stream still superimposed on that in Fig. 2 which clearly indicates that in the experimental conditions described the Ga-HZSM-5 which has experienced loss of $\frac{1}{3}$ of its actvity could be totally regenerated. The oxidation of the deposited coke was studied by temperature-programmed oxidation (TPO) using a TGA/DTG instrument coupled with a mass spectrometer. The TPO curve showed a maximum at 803 K. The weight of carbon deposited on the Ga-HZSM-5 after two hours on stream in C_3H_8 at 823 K was estimated to be 2.5 ± 0.2 wt%.

To investigate the influence of "coke deposition" on the acid function of H^+ and/or the dehydrogenating function of the Ga species of the Ga-HZSM-5 catalyst infrared studies of adsorbed pyridine were performed on a series of samples which had been submitted to C_3H_8 reaction for different times on stream. It is well known that the adsorption of pyridine on H-ZSM-5 produces several IR bands in the region 1700–1400 cm^{-1}, one at 1550 cm^{-1} being characteristic of the pyridinium ion and another at 1450 cm^{-1} signifying pyridine coordinatively bonded to Lewis acid sites. The main results are gathered in Table 1. The number of protons present in H-ZSM-5 and 1.6 wt% Ga-HZSM-5, as revealed by the absorbance value of the IR band at 1550 cm^{-1}, are almost identical. This result leads to the important conclusion that upon impregnation with Ga salt followed by calcination in O_2, the proton acidity of H-ZSM-5 remained, to a first approximation, unchanged. The very small increase of the IR band intensity at 1450 cm^{-1} was attributed to pyridine adsorbed on Ga species, these being considered as Lewis-acid centres (*6, 10*).

By contrast, the sample which had been submitted to O_2–H_2 treatment and had shown the highest activity in the C_3H_8 reaction (Fig. 1) experienced a decrease of the IR band intensity at 1550 cm^{-1}. This decrease corresponded to the exchange of H^+ by Ga^{n+} species during the catalyst activation in H_2. Simultaneously we observed that the intensity of the IR band at 1450 cm^{-1} increased markedly due to the increase of Lewis-acid centres resulting from a better dispersion of Ga^{n+} species, Ga^{n+} being atomically dispersed when localized in zeolite-exchange positions. To establish the effect of "carbonaceous residues" on the H^+ acidity and Lewis acidity (Al^{3+}, Ga^{n+}) the characteristic changes in the IR spectra of adsorbed pyridine caused by reaction with C_3H_8 for 2 h was studied. Table 1 indicates that the IR band absorbance at 1550 cm^{-1} decreased by 50% (from 1.2 to 0.6); this effect was reversible upon calcination in oxygen at 823 K. When the deactivated sample was regenerated in oxygen at 823 K, the 1550 cm^{-1} band, upon pyridine adsorption, regained its original intensity.

TABLE 1

Absorbance/mg of Catalyst for the Pyridine IR Vibrations at 1550 and 1450 cm^{-1} for Pure HZSM-5 and Ga-HZSM-5 as a Function of the Nature of the Thermal Treatment

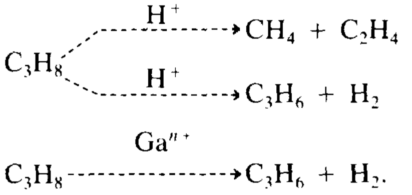
Sample	10^2 × absorbance/mg of catalyst for pyridine vibration	
	1550 cm^{-1}	1450 cm^{-1}
HZSM-5	2.0	0.4
1.6 wt% GaHZSM-5 calcined at 823 K under O_2 (corresponding to Point A in Fig. 1)	1.9	0.6
1.6 wt% GaHZSM-5 after O_2 and H_2 treatments (Point E in Fig. 1)	1.2	1.7
1.6 wt% GaHZSM-5 after 2 h on stream (Point B in Fig. 2)	0.6	1.2
1.6 wt% GaHZSM-5 aged and regenerated using the described procedure	1.85	1.7

An important decrease (30%) is also observed for the IR band absorbance at 1450 cm^{-1}. As pointed out above, both Al^{3+} and Ga^{3+} ions contribute to this IR band so it is difficult to estimate the number of Ga^{3+} ions which have been poisoned during the propane reaction; however, even if one assumes that the poisoning of Ga^{3+} ions is responsible for the total decrease of the vibration absorbance at 1450 cm^{-1}, this maxium decrease would be smaller than that observed for the vibration at 1550 cm^{-1}, indicating that the Lewis acidity is less decreased than the Brønsted acidity.

The infrared study has shown a significant decrease in the number of protons and Ga^{n+} species. Furthermore it appeared that the Brønsted acidity decreased much more than the dehydrogenating function. We have concluded that the coverage of H^+ and Ga^{n+} by carbonaceous residue causes the deactivation of the bifunctional Ga-HZSM-5 catalyst.

It is also important to examine the deactivation process of Ga-HZSM-5 in view of the selectivity change occurring during C_3H_8 reaction. Figure 2 reports the selectivity to CH_4 (numbers in brackets) as a function of time on stream, S_{C_1} selectivity being defined by $S_{C_1} = P_{C_1}/3P_{C_3}$, where $P_{C_1} = CH_4$ pressure and P_{C_3} = pressure of C_3H_8 converted. The numbers given in Fig. 2 indicate a small decrease of the methane selectivity.

The reaction of propane over Ga-HZSM-5 catalyst proceeds by the following equations (*11*):



$$C_3H_8 \xrightarrow{H^+} CH_4 + C_2H_4$$

$$C_3H_8 \xrightarrow{H^+} C_3H_6 + H_2$$

$$C_3H_8 \xrightarrow{Ga^{n+}} C_3H_6 + H_2.$$

Hence the main source of CH_4 is the cracking of C_3H_8 on acid centres while that of C_3H_6 is the dehydrogenation of propane on Ga^{n+} centres. One may conclude that a decrease in the selectivity to CH_4 would reflect a decrease in the ratio : acid function/ dehydrogenating function. The results reported in Fig. 2 suggest that the acid function was more poisoned than the dehydrogenating function by deposition of coke.

In conclusion, this work indicates that during propane aromatization over Ga-HZSM-5 catalysts, both functions (acid function and dehydrogenating function) are deactivated, as evidenced by IR studies of adsorbed pyridine. The decrease of the propane conversion with time on stream confirms this finding and the change in C_1 selectivity with time on stream indicates that the acid function is more deactivated than the dehydrogenating function, a conclusion which is in agreement with IR results indicating that the Brønsted acidity is decreased by 50% compared to 30% for the Lewis acidity which reflects the dehydrogenating function.

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