JOURNAL OF CATALYSIS **157**, 283–288 (1995)

Further Evidence on the Change of Acid Properties of H–ZSM-5 by Ga and Pt

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Received October 31, 1994; revised July 27, 1995; accepted July 28, 1995

The effects of oxidizing and reducing treatments over Ga/H–ZSM-5 aromatization catalysts are studied. The respective roles of the dehydrogenation function and of the acid function are discussed and it appears that the acid function is depressed through the reducing treatment. To explain the role of gallium in propane activation, the concept of the dual-site mechanism is preferred to the concept of the "porthole" mechanism. © 1995 Academic Press, Inc.

INTRODUCTION

It was recently reported that H–ZSM-5 supported gallium is highly active and selective for the aromatization of light alkanes (1–5). Significant aromatic yields were also obtained from the reaction of C_2–C_3 alkanes over Pt–HZSM-5 (6–8). The following mechanism is generally accepted: dehydrogenation of the alkanes into alkenes on the gallium or on the platinum component, oligomerization of the alkenes, and cyclization on the acid component of the zeolite (9). It was further argued that gallium species (as well Pt centers) catalyze the recombination of H adatoms, thus promoting the desorption of H_2 (5, 10). Furthermore, dehydrogenation of the alkane is considerably enhanced by the addition of gallium to H–ZSM-5, while cracking is inhibited. (1, 2). In addition, the concept of a dual-site mechanism was introduced, in order to account for the strong enhancement of the rate of propane dehydrogenation when Ga species and H^+ centers were simultaneously present on the zeolite surface (11).

An important effort has been made to describe the interaction of the dehydrogenating species with the zeolite and particularly with the OH acid sites. The answer to this important question remains controversial, in particular when the catalysts have been submitted to H_2-treatment at high temperature. According to Price and Kanazirev (12) and to Mériaudeau and Naccache (13), H_2-reduction of Ga_2O_3/H–ZSM-5 resulted in the formation and migration of Ga^{+1} species with the subsequent replacement of H^+ by Ga^{+1}. Consequently the total number of acid OH groups decreased, as demonstrated by the decreased intensity of the infrared band at 3610 cm^{-1}. In a further study Mériaudeau *et al.* (14) confirmed these conclusions by showing that the rate of *m*-xylene isomerization over Ga_2O_3/H–ZSM-5 was considerably decreased when the reaction was made over an H_2-reduced Ga_2O_3/H–ZSM-5 sample. By contrast, Barre *et al.* (15) indicated that the H_2-reduction of Ga_2O_3/H–ZSM-5 has only a minor effect on the zeolite acidity since the rate of *m*-xylene isomerization over the H_2-reduced sample was lowered by only a factor of 1.5 as compared with the rate over the oxidized sample. Similarly Meitzner *et al.* (5), by studying the isomerization of 2-methyl-2-pentene, a well established acid-catalyst reaction, concluded that the initial proton acid-site density of H–ZSM-5 is almost unchanged following impregnation with Ga_2O_3 as well as following reduction of the impregnated sample. Because of the crucial importance of the acid function on the catalytic performances of Ga_2O_3/H–ZSM-5 and Pt/H–ZSM-5, and because of these published contradictory results, we have reinvestigated the catalytic properties of Ga_2O_3/H–ZSM-5 samples, oxidized and reduced forms. The dealkylation reaction of ethylbenzene is often used to probe the acidity of solids. Furthermore, in order to obtain additional evidence on the possible effect of the hydrogen removal from the catalyst surface on the overall reaction of propane following the "porthole" concept (10), the cracking and the dehydrogenation of propane over Pt/H–ZSM-5 were studied.

EXPERIMENTAL

ZSM-5 was synthesized according to the patent literature. It was converted to the acid form by ion exchange to give the ammonium form, followed by calcination. Chemical analysis gave a Si/Al ratio of 16. Aqueous ion exchange of H–ZSM-5 with $[Pt(NH_3)_4]^{2+}$ resulted in

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0021-9517/95 $12.00

Pt/H–ZSM-5 samples. The concentration and the amount of the platinum solution were adjusted in order to obtain a series of samples containing 0.05, 0.1, 0.3, and 0.6 wt% Pt. The Pt/H–ZSM-5 samples containing 0.1 and 0.6 wt% Pt were, after reduction under hydrogen (see below), back exchanged with NaCl aqueous solution and are designated Pt/Na–ZSM-5. The samples were heated under flowing oxygen to 623 K and then reduced under H_2 at 623 K, T being then increased to 773 K; Pt dispersion measured by H_2 adsorption approached 100% dispersion for all samples. The solids used for H_2 chemisorption studies were then flushed with N_2 and transferred into the microreactor; then, after being flushed with N_2, they were re-reduced under a flow of H_2, the temperature being increased from 293 to 773 K. Ga_2O_3/H–ZSM-5 was obtained by impregnating H–ZSM-5 with a solution of $Ga(NO_3)_3$. The samples were then dried at 373 K. Samples containing respectively 2.5 and 5 wt% gallium were prepared. Before any measurement, samples were submitted to the following activation:

—Oxidized form: the dried Ga_2O_3/H–ZSM-5 was calcined under a flow of O_2 at 873 K, the temperature being increased from 293 K to 873 K (ramping 2°C/min); the catalyst was maintained at this temperature for 8 h and then cooled to the reaction temperature (773 K for propane, 623 K for ethylbenzene, or room temperature for sorption measurement).

—Reduced form: the sample was first oxidized as described, flushed with N_2, and then reduced under flowing H_2 overnight at 873 K. The reduced sample was then cooled to reaction temperature.

Before the catalytic reaction was started the samples were always flushed with N_2 for 10 min.

Catalytic evaluation was performed in a continuous flow microreactor at atmospheric pressure. The reactants and products were analyzed on line by gas chromatography. The conversion was maintained at less than 5% by varying the space velocity WHSV. At low conversion the initial products resulting from the reaction at 773 K of propane over Pt/H–ZSM-5 were propene and methane + ethene. Trace amounts of aromatics were detected. The reaction of ethylbenzene was carried out in the temperature range 623–723 K over Ga_2O_3/H–ZSM-5 samples either in its oxidized form or in its reduced form. The carrier gas was nitrogen. The acid-catalyzed dealkylation of ethylbenzene produced benzene and ethylene. The sorption capacity of the different solids was measured using *n*-hexane and a Sartorius microbalance. Oxidized and reduced samples, activated as described above, were transferred in the microbalance cell; they were flushed with N_2, heated again under a flow of either O_2 or H_2 for 4 h at 773 K, and then outgassed at 773 K ($P = 0.1$ Pa) for 2 h before the *n*-hexane absorption experiments were started. The absorption isotherms were obtained by increasing *n*-hexane vapor pressure up to 10 kPa.

RESULTS AND DISCUSSION

The catalytic behavior of H–ZSM-5 and of oxidized Ga/H–ZSM-5 and reduced Ga/H–ZSM-5 in the propane reaction at 773 K is compared in Table 1. Table 1 confirms the well established observation that adding gallium to H–ZSM-5 enhances considerably the rate of dehydrogenation of propane into propene, while the rate of cracking of propane into methane and ethylene is only slightly changed. The assumption that Ga species participate to the dehydrogenation step of propane is thus reinforced. It has been previously shown (11) that oxidized Ga/H–ZSM-5 samples contain almost exclusively Ga_2O_3 clusters and probably few Ga^{3+} in cationic position. Hence the acidity H^+ of the starting material H–ZSM-5 was only slightly decreased by adding Ga_2O_3. Methane was exclusively formed from the cracking of C_3H_8 catalyzed by H^+. Since the number of protons was almost unchanged on H–ZSM-5 and oxidized Ga/H–ZSM-5, the rate of CH_4 formation should remain almost identical on both samples, in agreement with the results shown in Table 1.

Table 1 shows that for the oxidized samples, independently of the Ga loading, the rate of methane formation is slightly decreased and the rate of propane transformation is increased; these results are in agreement with the literature. By contrast the reduced samples experienced catalytic changes which were dependent on the gallium loading:

—for the 2.5 wt% Ga sample, the rate of methane formation is decreased while the rate of propane transformation is not much modified;

—for the highest Ga loading (5 wt%) there is a decrease of both methane formation and propane formation in agreement with a previous report (16).

Evidence for the increase of Ga species dispersion upon H_2-reduction has been reported (17). The presence of highly dispersed Ga species was supposedly responsible for the increase in the rate of propane dehydrogenation because Ga species acted as a porthole for the recombination of H adatoms formed in the dehydrogenation step catalyzed by H^+ (10). By contrast our work shows conclusively that the rate of propane dehydrogenation decreased upon H_2-reduction of Ga/H–ZSM-5. A marked decrease in the rate of cracking is also observed. The concept of the dual-site mechanism (11) apparently could be applied. The likely explanation for the decrease in the rates of cracking and dehydrogenation is that, upon H_2-reduction, Ga species, in their reduced form, migrate within the zeolite channel and exchange with H^+, thus lowering the number of H^+ available for the reaction. This caused a decreased rate of cracking, since the rate of the reaction is

TABLE 1

Transformation of Propane on Ga/H-ZSM-5 Catalysts

Catalyst and treatment	H-ZSM-5		2.5 wt% Ga/H-ZSM-5		5 wt% Ga/H-ZSM-5	
	O_2	H_2	O_2	H_2	O_2	H_2
Rate[a] of propane transformation	65	65	300	320	308	66
Rate[a] of methane formation	61	61	45	17	41	5.2

[a] mmol $h^{-1}g^{-1}$.

directly proportional to the number of H^+, and a simultaneous decrease in the rate of dehydrogenation, because the average active sites, H^+-Ga^+ ensembles, must be decreased by the removal of H^+. It has been shown earlier that the dehydrogenation center is probably a dual site composed of a gallium ion and a proton (16), indicating that a delicate balance between Ga ions and protons is needed. Clearly the picture given above for the difference in the catalytic performances of Ga/H-ZSM-5 in its oxidized and reduced forms agrees with previous infrared data indicating that the amount of acid OH in Ga/H-ZSM-5 decreases upon H_2-reduction at higher temperature.

In order to reinforce the conclusion that the total acidity of Ga/H-ZSM-5 is substantially lowered following reduction by H_2 and subsequent migration and exchange of Ga^{+1} with H^+, the dealkylation reaction of ethylbenzene in the temperature range 523–673 K was studied. The ethylbenzene dealkylation into benzene and ethylene catalyzed by H^+ is well documented in the literature. In a previous work (14) we studied the isomerization of *m*-xylene in order to test the acidity of pentasil-based catalysts. However, it is known that the isomerization of *m*-xylene over medium-pore zeolites is often diffusion controlled, which renders the zeolite acidity hazardous to quantify from rate measurement. The Arrhenius plots for the rate of ethylbenzene dealkylation over H-ZSM-5 and Ga/H-ZSM-5 oxidized and reduced forms are represented graphically in Fig. 1 and the rate of benzene formation is given in Table 2.

For oxidized samples, the addition of gallium to the H-ZSM-5 sample slightly decreased the ethylbenzene dealkylation rate. The activation energy over H-ZSM-5 and oxidized Ga/H-ZSM-5 was almost the same. One could consider that upon impregnation of H-ZSM-5 with $Ga(NO_3)_3$ solution and activation in oxygen, a few protons of the zeolite were replaced by Ga^{3+}, thus slightly lowering the total acidity. The H_2-reduction of Ga/H-ZSM-5 has a pronounced effect on the rate of ethylbenzene dealkylation, Fig. 1, while the activation energy for the reaction changed little. It is clear that the amount of H^+ present on reduced Ga/H-ZSM-5 is considerably less than that present on H-ZSM-5 and Ga/H-ZSM-5 (oxidized form). Another possible cause for the decrease of the dealkylation rate could be found by assuming that the porosity of the reduced sample is less (decrease of the porosity due to pose blocking resulting from the migration of Ga within the zeolite channels). In order to clarify this point, we have measured the *n*-hexane sorption capacity for the different

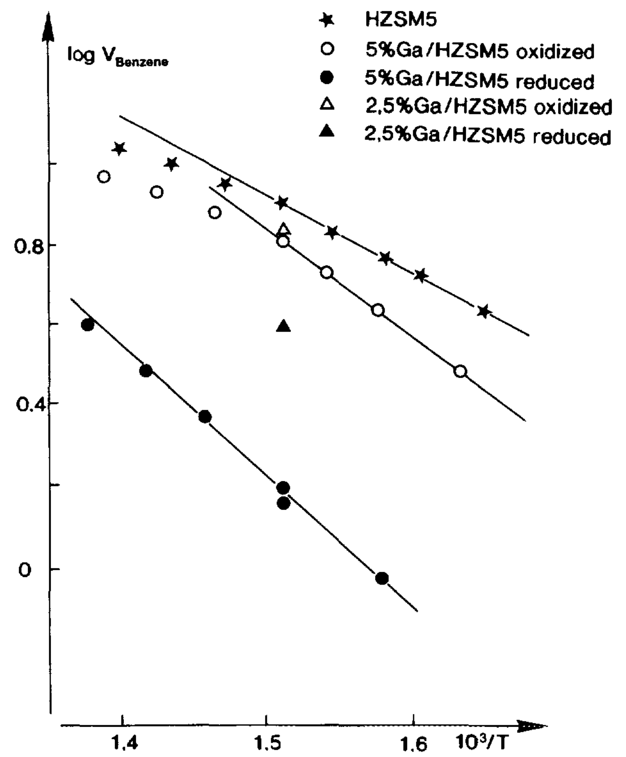

FIG. 1. Arrhenius plot: Rate of benzene formation as a function of the reaction temperature for H-ZSM-5 (★) and Ga/H-ZSM-5 catalysts after oxidative (○, △) and reducing (●, ▲) treatments. Rate in mmol h^{-1} g^{-1} catalyst. Experimental conditions: catalyst weight 10 or 20 mg, flow rate 2 or 4 liter/hr. Feed: ethylbenzene/H_2/N_2 (0.5/5/95.5 kPa).

TABLE 2

Transformation of Ethylbenzene over Ga/H–ZSM-5 Catalysts

Catalyst and treatment	H–ZSM-5		2.5 wt% Ga/H–ZSM-5		5 wt% Ga/H–ZSM-5	
	O_2	H_2	O_2	H_2	O_2	H_2
Rate of benzene formation in mmol h^{-1} g^{-1}	8	8	6.4	3.1	6.2	1.6

Note. T = 662 K, feed E_B + N_2, P_{E_B} = 2.8 kPa.

samples. Results are reported in Table 3; the value obtained for the H–ZSM-5 solid is in good agreement with the value reported by Choudhary and Singh (18). Table 3 indicates that the sorption capacity of the H–ZSM-5 was only slightly modified by addition of Ga; the highest decrease (about 30%) was observed for the sample containing 5 wt% Ga and H_2-reduced. It is clear that the change in the rate of ethylbenzene dealkylation cannot be explained by pore blocking.

It has also been checked that the X-ray structure of the zeolite remains unchanged after having added Ga (5 wt%) and performed the reduction treatment.

The experimental results obtained here by the dealkylation of ethylbenzene are also consistent with the observed decrease of the infrared band intensity of acid OH in H–ZSM-5 when Ga was added and the sample was reduced (14). It was argued (5) that the number of bridged OH, in H–ZSM-5, may decrease while the Brønsted acidity previously associated with OH is constant, considering that gallium hydride species O—GaH are in fact replacing a fraction of these bridging OH.

However, these hypotheses do not apply to our infrared results (14) and to the catalytic measurements given in this work. The simple conclusion which explains the decrease of the acidity and of the catalytic activity in the acid-type reaction is that upon H_2-reduction, reduced gallium species migrate in the zeolite channels and experience an exchange reaction with the protons, as follows:

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O \quad [1]$$

$$Ga_2O + 2H\text{-}OZ \rightarrow 2GaOZ + H_2O. \quad [2]$$

The H–ZSM-5 used in this study contains 2.7 wt% Al, each framework Al atom generating one proton. Assuming that the proton exchange with the monovalent gallium cation occurred following Eq. [2], the fully Ga exchanged sample would contain 6.9 wt% Ga. Hence the maximum proton exchange which may occur on the 5 wt% Ga impregnated sample, following Eqs. [1] and [2], will be 72%. It would result that, if the chemistry described by Eqs. [1] and [2] occurred, only 28% of the initial acidity of the Ga/H–ZSM-5 sample would remain after H_2-reduction. This results of the dealkylation of ethylbenzene indicate that the H_2-reduced Ga/H–ZSM-5 sample retains about 21% of the activity shown by the oxidized sample, in relatively good agreement with the calculated lost of acidity due to H_2-reduction. The sample which contained 2.5 wt% Ga showed some deviation but nevertheless presented a catalytic activity for ethylbenzene dealkylation which decreased substantially upon H_2-reduction. The role of the Ga species, during propane conversion, was analyzed in terms of a porthole which, by catalyzing the removal of hydrogen from the catalyst surface, increased the conversion of propane into propene, the cracking reaction into methane being consequently lowered (5, 19). The authors concluded that Pt would probably act in a similar manner;

TABLE 3

Sorption Capacity of the Different Samples as a Function of the Treatment

Sample and treatment	H–ZSM-5		2.5 wt% Ga/H–ZSM-5		5 wt% Ga/H–ZSM-5	
	O_2	H_2	O_2	H_2	O_2	H_2
Sorption capacity mmol h^{-1}	1.3	1.3	1.2	1.05	1.15	0.9

Note. $P_{n\text{-hexane}}$ = 10 kPa, T = 300 K.

TABLE 4

Transformation of Propane on Pt–H-ZSM-5 Catalysts

Catalyst wt% Pt	H-ZSM-5 0	H-ZSM-5 0.05	H-ZSM-5 0.1	Na-ZSM-5 0.1	H-ZSM-5 0.3	H-ZSM-5 0.6	Na-ZSM-5 0.6
Rate[a] of propene formation	16	27	575	380	1107	1867	1120
Rate[a] of methane formation	61	36	25	0.9	22	59	10

Note. T = 773 K, $P_{C_3H_8}$ = 101 kPa.
[a] mmol h^{-1} g^{-1}.

the "porthole" effect accounts for the enhanced yield of the dehydrogenation reaction. The reaction of propane over Pt/H-ZSM-5 zeolite was investigated. In order to better appreciate the reaction occurring on the metal, the acidity of Pt/H-ZSM-5 was neutralized in several experiments by exchanging Pt/H-ZSM-5 with Na^+ ions. The conversion was kept low, less than 5%, in order to limit secondary reactions. The initial reaction step occurring in the aromatization of propane over Pt/H-ZSM-5 catalysts is the dehydrogenation of C_3H_8 into propene, this reaction always being accompanied by the undesirable cracking of propane into dead end methane and ethene. Table 4 shows the relative rates of production of propene and methane by reaction of propane at 773 K over a series of Pt/H-ZSM-5 samples.

It is apparent from Table 4 that the addition of a small amount of platinum to H-ZSM-5 leads to a substantial increase in C_3H_6 production. It is important to point out here that the rate of C_3H_6 formation increased almost linearly with the Pt content. This is consistent with the observed fact that the dehydrogenating properties of the platinum surface are far better than those showed by H-ZSM-5. Hence from the results obtained over Pt/H-ZSM-5 catalysts it is rather difficult, if not impossible, to distinguish in the dehydrogenation reaction the part played by the acid sites from the occurring on the Pt surface. The approach to the above question was made partially possible by exchanging H^+ with Na^+. If one considers that sodium exchange has no effect on the Pt surfazce properties, the experimental values for the production of propene on 0.1 and 0.6 wt% Pt supported on hydrogen and sodium forms of the catalysts indicates a dehydrogenation activity due to H^+ 195 mmol h^{-1} g^{-1} catalyst and 747 mmol h^{-1} g^{-1} catalyst for, respectively, 0.1 wt% Pt/H-ZSM-5 and 0.6 wt% H-ZSM-5. These values are much larger than the value observed on H-ZSM-5 without added Pt, which is 16 mmol h^{-1} g^{-1} catalyst. The promotion must obviously be attributed to the presence of Pt, and the effect outlined by Meitzner *et al.* (5) for Ga/H-ZSM-5, where Ga acts as a porthole to increase the rate of recombination and desorption of H adatoms, could also be applied to the platinum system. The authors (5) claimed also that the efficient porthole removal of hydrogen produced by the dehydrogenation of propane should reduce the cracking step, thus increasing the selectivity to olefins and aromatics. In agreement with these suggestions, Table 4 shows that the presence of a small quantity of Pt decreased the production of CH_4. The excess CH_4 observed with 0.6 wt% Pt/H-ZSM-5 is probably due to the nonnegligible hydrogenolysis reaction occurring on the Pt surface, due to the relatively high Pt loading.

CONCLUSIONS

Pt/H-ZSM-5 catalysts are excellent dehydrogenating materials, the efficiency for dehydrogenation being mainly brought about by the platinum surface. However, dehydrogenation of propane catalyzed by H^+ still occurs, the removal of H adatoms being favored by recombination over Pt sites according to the porthole concept.

Apparently this concept is less applicable to Ga/H-ZSM-5, the (H^+–Ga) dual site playing the most important role. Reduction of Ga/H-ZSM-5 resulted in the formation of Ga^+ species which migrated and exchanged with H^+ sites. The proton acidity as measured by the reaction of ethylbenzene is thus lowered. The corresponding decrease in the propane transformation rate observed for the 5 wt% Ga/H-ZSM-5 sample (reduced form) strongly suggests that the propane transformation requires both Ga sites and protons; thus, as shown earlier, a good balance between Ga sites and protons should exist in order to have an effective catalyst for propane transformation.

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