Catalysis Letters 21 (1993) 275–281

Ga_2O_3 / HZSM5 propane aromatization catalysts. Influence of the hydrogen pretreatment on the acid and redox functions

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Received 29 March 1993; accepted 23 June 1993

The activity and selectivity of a mechanical Ga_2O_3/HZSM5 mixture in four model reactions (propane aromatization at 803 K, *n*-heptane cracking and meta-xylene isomerization at 623 K, methylcyclohexane transformation at 773 K) were compared after pretreatment at 873 K under nitrogen and under hydrogen flow. It was thus demonstrated that the hydrogen treatment provoked a significant increase in the dehydrogenating activity of the gallium species but only a small decrease in the protonic acidity. Moreover this hydrogen treatment created a significant hydrogenolysis activity.

Keywords: Propane; aromatics; acid catalysts

1. Introduction

The applied and basic aspects of short-chain alkane aromatization have recently been reviewed [1,2]. With Ga-HZSM5 catalysts aromatization occurs mainly through a bifunctional scheme, Ga species catalyzing the dehydrogenation of the alkane reactants and of the naphthene intermediates and the acid sites catalyzing the oligomerization of alkenes and the cyclization of oligomers. Hydrogen pretreatment at high temperature of these catalysts has a positive effect on their activity and their selectivity for aromatization [3–8]. This effect would be due to a pronounced change in the gallium species (reduction, migration in the zeolite crystallites, decrease in size of the gallium particles...). According to Price and Kanazirev [6], the reduction of gallium is followed by a reaction between the acid OH groups of the zeolite and reduced gallium oxide,

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O\,, \tag{1}$$

$$Ga_2O + 2H^+Z^- \rightarrow 2Ga^+Z^- + H_2O\,. \tag{2}$$

Step (2) would be the limiting step of the process, the reduction of gallium oxide ceasing when all the acid sites are neutralized. However, since the protonic sites are involved in the oligomerization and cyclization steps of the bifunctional pathway, the aromatization activity should decrease with the pronounced neutralization of the protonic sites although the contrary has been observed. Therefore either the neutralization of the protonic sites or the bifunctional scheme is to be questioned [2,6].

Consequently, it is very important to specify what is the effect of hydrogen pretreatment of Ga-HZSM5 catalysts on their protonic acidity. Through infrared spectroscopy it was shown that a simple treatment of a Ga-HZSM5 sample during one hour at 773 K under hydrogen causes a decrease by a factor of 5 in the number of protonic sites [9]. Model reactions, such as *n*-heptane cracking and meta-xylene isomerization, can also be used for characterizing the protonic acidity of solid catalysts [10,11], this method having the advantage of giving information specifically on the active sites.

The first aim of this work is to confirm through the above model reactions the neutralization of the acid sites of Ga-HZSM5 catalysts caused by hydrogen pretreatment and to assess its significance. The catalyst (a Ga_2O_3/HZSM5 mixture) and the temperature of pretreatment (873 K) were similar to those used by Price and Kanazirev [6]. The time of pretreatment (10 h) was chosen following ref. [6] so as to obtain the maximum percentage of Ga_2O_3 reduction hence the complete neutralization of the acid sites. In addition two other model reactions, propane and methylcyclohexane transformations, were used to specify the effect of the hydrogen pretreatment on the dehydrogenating activity of the gallium species.

2. Experimental

The Ga_2O_3/HZSM5 mixture (10 wt% Ga) was prepared by ball-milling β-Ga_2O_3 (Aldrich) with a HZSM5 zeolite (Si/Al = 40) for 3 h. The zeolite was synthesized according to the method of Guth and Caullet [12]. Prior to use the Ga_2O_3/HZSM5 mixture was pretreated for 10 h at 873 K under dry nitrogen or hydrogen flow ($3.6\ \ell\ h^{-1}$).

The model reactions were carried out in a flow reactor under the following conditions:

– Propane transformation: $T = 803$ K; propane pressure = 1 bar; WWH (weight of reactant injected per weight of catalyst and per hour) between 1.7 and $34.3\ h^{-1}$.

– *n*-heptane cracking: $T = 623$ K; heptane pressure = 0.1 bar; nitrogen pressure = 0.9 bar; WWH = $6.85\ h^{-1}$.

– *m*-xylene isomerization: $T = 623$ K; xylene pressure = 0.2 bar; nitrogen pressure = 0.8 bar; WWH between 7.85 and $39.3\ h^{-1}$.

Table 1
Activity (10^{-3} mol h^{-1} g^{-1}) of the Ga_2O_3/HZSM5 mixture after pretreatment under nitrogen or hydrogen flow at 873 K in the transformation of various hydrocarbons

Reactant pretreatment	Propane	*n*-heptane	*m*-xylene	Methylcyclohexane
N_2	16	3.0	36	28
H_2	36	2.6	24	105

– Methylcyclohexane transformation: $T = 773$ K; methylcyclohexane pressure $= 0.2$ bar; nitrogen pressure $= 0.8$ bar; WWH between 10 and 66.4 h^{-1}.

The reaction products were analyzed on line by gas chromatography with a Varian 3400 equipped with a 30 m fused silica capillary column DB Wax in the case of *m*-xylene isomerization and with a 50 m fused silica capillary column PLOT Al_2O_3/KOH for the other reactions.

3. Results

Four model reactions were used to characterize the Ga_2O_3/HZSM5 mixture after hydrogen or nitrogen pretreatment: propane aromatization at 803 K, *n*-heptane cracking and *m*-xylene isomerization at 623 K, methylcyclohexane transformation at 773 K. Table 1 shows that the initial rates of propane and methylcyclohexane transformation are greater after hydrogen pretreatment while those of *n*-heptane cracking and meta-xylene isomerization are lower. Whatever the reaction and the pretreatment the activity of the Ga_2O_3 component is much smaller than that of the Ga_2O_3/HZSM5 mixture.

For all the reactions except for meta-xylene isomerization the product distribution depends on the pretreatment. In propane aromatization propene (resulting

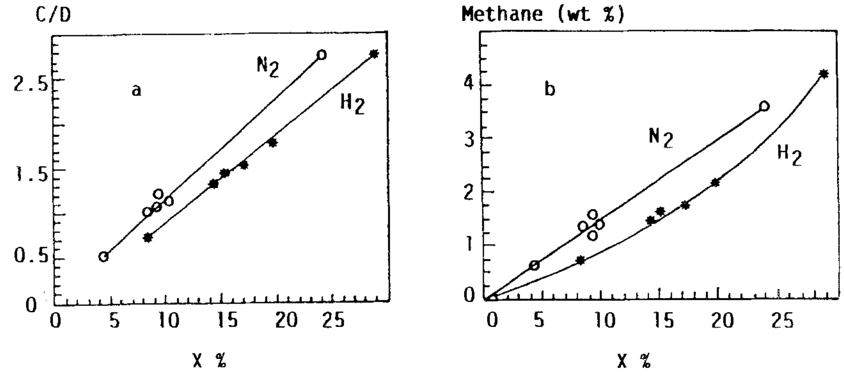


Fig. 1. Propane transformation at 803 K on the Ga_2O_3/HZSM5 mixture pretreated under nitrogen or hydrogen flow. (a) Cracking/dehydrogenation rate ratio C/D versus conversion, (b) methane yield versus conversion.

Table 2
n-heptane cracking at 623 K over a Ga_2O_3/HZSM5 mixture pretreated under nitrogen or hydrogen flow at 873 K. Product distribution (mol%) for a conversion of 3.5%

Pretreatment	C_1	C_2	C_3	C_4	C_5	C_6	iC_7	C_3C_4	o/s	$\sum iC_4/\sum nC_4$
N_2	0	3.3	52.7	34.7	5.6	0.6	3.1	1.5	1.05	1.0
H_2	1.1	4.7	47.7	37.7	4.8	0.6	3.4	1.3	1.2	1.7

from propane dehydrogenation D) and methane + ethylene in equimolar amounts (resulting from cracking C) are the only primary products for both pretreatments. A lower value of C/D is obtained after hydrogen pretreatment (fig. 1a). However, after this pretreatment a secondary mode of methane formation appears (fig. 1b). The selectivity towards aromatics is slightly greater, towards unwanted products (methane C_1 and ethane C_2) it is lower, which gives a greater aromatics/(C_1+C_2) ratio after hydrogen pretreatment.

Whatever the pretreatment the main products of n-heptane cracking are C_3 and C_4 alkenes and alkanes. However, certain differences can be observed: formation of methane and faster formation of ethane, greater alkene/alkane ratio (o/s), lower C_3/C_4 and greater iC_4/nC_4 after hydrogen pretreatment (table 2).

Para- and ortho-xylenes are practically the only products of meta-xylene transformation. The para/ortho ratio does not depend on the pretreatment; in both cases it decreases when the conversion increases.

Methylcyclohexane is directly transformed into C_1–C_6 cracking products and into C_6–C_8 aromatics. Only traces of dimethylcyclopentanes and of C_7 aliphatic hydrocarbons are found. The product distribution depends on the pretreatment:

– The aromatization/cracking rate ratio is equal to 2.0 after hydrogen pretreatment as against 0.8 after nitrogen pretreatment (fig. 2).

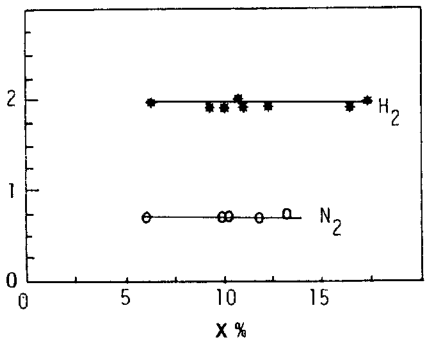


Fig. 2. Methylcyclohexane transformation at 773 K on the Ga_2O_3/HZSM5 mixture pretreated under nitrogen or hydrogen flow. Aromatization/cracking rate ratio A/C versus conversion.

Table 3
Methylcyclohexane transformation at 773 K over a Ga_2O_3/HZSM5 mixture pretreated under nitrogen or hydrogen flow at 873 K. Product distribution (mol%) for a conversion into cracking products of 6.6%

Pretreatment	C_1	C_2	C_3	C_4	C_5	C_6	o/s[a]
N_2	15.1	17.2	41.0	21.6	3.4	1.7	2.1
H_2	45.1	14.6	26.1	13.5	0.3	0.4	0.9

[a] Alkene/alkane ratio.

– The percentage of benzene in the C_6–C_8 aromatic products is equal to 45% after hydrogen pretreatment as against 15% after nitrogen pretreatment.

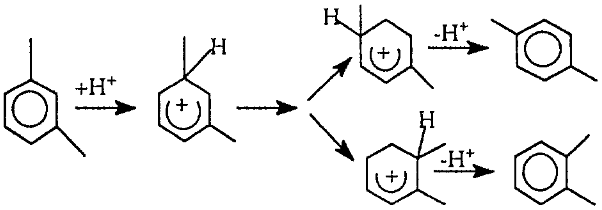
– The percentage of methane in the cracking products is much greater after hydrogen pretreatment, the alkene/alkane ratio being lower (table 3).

4. Discussion

The most significant effect of the hydrogen pretreatment is to increase the dehydrogenating activity of the gallium species. This is shown in particular for reactions carried out at high temperatures. Thus the rate of formation of propene from propane at 803 K is at least 5 times greater after hydrogen pretreatment; the cracking/dehydrogenation rate ratio is significantly decreased being close to zero at low conversion (fig. 1a). The production of aromatics from methylcyclohexane at 773 K is 4–5 times faster after hydrogen pretreatment and the aromatization/cracking rate ratio is 2.5 times greater. As shown by the lower alkene/alkane ratio (o/s table 3) part of hydrogen resulting from methylcyclohexane dehydrogenation is consumed by the hydrogenation of the olefinic cracking products. Even at 623 K the increase in the dehydrogenating activity of the gallium species can be observed. Thus the alkene/alkane ratio in the products of *n*-heptane cracking is greater after hydrogen pretreatment (o/s table 2).

The hydrogen pretreatment creates also a significant hydrogenolysis activity. Obviously as hydrogenolysis consumes hydrogen it can only appear when there is hydrogen production during the transformation of model compounds. This hydrogenolysis activity is responsible for the large amount of methane in the methylcyclohexane cracking products (table 3) and for the significant change in the C_6–C_8 aromatic distribution. It explains also the secondary formation of methane during propane aromatization (fig. 1b). Even at 623 K during *n*-heptane cracking methane can be observed as one of the products.

Lastly hydrogen pretreatment affects also the acid sites. This is shown clearly by the decrease in the rate of meta-xylene isomerization (1.5 times lower). It is well known that this reaction occurs on protonic sites through the following mechanism [10,13]:



Taking into consideration this mechanism it is very unlikely that the reaction rate is affected by redox sites.

Hydrogen pretreatment causes also a decrease in the activity for *n*-heptane cracking at 623 K. Although this reaction is, like *m*-xylene isomerization, an acid-catalyzed reaction, the decrease in activity is less pronounced. This can be explained by two contrary effects on the activity, one negative due to a neutralization of the acid sites, the other positive due to a change in the reaction mechanism because of the presence of redox sites. This positive effect has already been shown with PtHY zeolite catalysts [10]. It was attributed to the formation on the redox sites of heptenes which are easily protonated and transformed into cracking products. Changes in the product distribution similar to those observed in this work (increase in the iC_4/nC_4 ratio...) were also found. With methylcyclohexane cracking because of the higher temperature the positive effect of the redox sites dominates.

An important point to be emphasized is that the decrease in the activity of the acid sites caused by hydrogen pretreatment is much smaller than the decrease of acidity expected from the model proposed by Kanazirev and Price [6] and than the decrease in the number of protonic sites shown by Meriaudeau and Naccache [9]. The remaining active acid sites are sufficient for catalyzing the oligomerization of alkenes and the cyclization of oligomers involved in the bifunctional scheme of propane aromatization. The increase in the aromatization activity caused by the hydrogen treatment can be related to the increase in the rate of dehydrogenation of propane, which is most likely the limiting step of propane aromatization.

5. Conclusion

Hydrogen pretreatment at high temperature of a Ga_2O_3/HZSM5 mixture causes a significant increase in the dehydrogenating activity and unexpectedly creates an important hydrogenolysis activity. Furthermore this treatment has only a limited effect on the activity of the acid sites. The increase in the aromatization activity can be explained through the bifunctional scheme generally proposed for propane aromatization.

Acknowledgement

This work was carried out thanks to the financial support of the Indo-French Centre for the Promotion of Advanced Research/Centre Franco-Indien pour la Promotion de la Recherche Avancée.

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