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Gallium-containing zeolites – valuable catalysts for the conversion of cycloalkanes into a premium synthetic steamcracker feedstock

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Abstract

Gallium is incorporated into zeolite H-ZSM-5 by reductive solid-state ion exchange, i.e., by heating a physical mixture of gallium oxide and H-ZSM-5 in a hydrogen flow at 600°C. The samples are characterized by AES/ICP, XRD, FTIR and MAS NMR spectroscopy. Methylcyclohexane is converted over these catalysts in a hydrogen atmosphere at 6 MPa and 250 to 400°C, yielding a high-quality synthetic steamcracker feedstock (consisting mainly of ethane, propane and *n*-butane). Mechanistic aspects of the reaction are discussed, and the importance of non-classical Haag-Dessau cracking is emphasized. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Gallium-containing zeolites are well-known catalysts in the Cyclar process for the production of aromatics from small alkanes [1], and an excellent review on the incorporation of gallium into zeolites has been published recently by Fricke et al. [2]. This prompted us to study the performance of such zeolites in the opposite reaction, i.e., the ring opening of cyclic hydrocarbons. This is a process with ever increasing attractiveness, since a considerable oversupply of aromatics has to be expected for the next few years, which has mainly two origins: Firstly, with the advent of the Auto Oil Programme of the European Union, the aromatics content of gasoline has to be reduced from 45 vol.% in 1999 to 42 and 35 vol.% in 2000 and 2005, respectively [3]. Secondly, with the forecasted growth rate of the demand for ethene [4] and propene [5] in the next 10 years of about 4.5% and 4.7%, respectively, the amount of pyrolysis gasoline simultaneously produced in steamcrackers will necessarily increase as well. For the conversion of aromatics into a premium synthetic steamcracker feedstock (consisting mainly of ethane, propane and *n*-butane), two process variants have recently been introduced. In variant 1, the aromatics are directly converted with hydrogen on a shape-selective zeolite catalyst in a bifunctional form [6]. In variant 2, cycloalkanes, which can easily be obtained from aromatics by state-of-the-art hydrogenation processes, are converted on similar zeolite catalysts in a monofunctional acidic form [7]. In both cases, pyrolysis gasoline can be recycled in the same process unit. We report here on

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the influence of gallium located on extra-framework positions on the catalytic properties of zeolite H-ZSM-5 in the hydroconversion of methylcyclohexane as a model hydrocarbon for prehydrogenated pyrolysis gasoline. In contrast to earlier work, where methylcyclohexane has been converted at ambient pressure mainly into aromatics on zinc- or gallium-containing zeolites [8–10], a high hydrogen partial pressure is applied to avoid aromatics formation.

2. Experimental

Zeolite ZSM-5 ($n_{Si}/n_{Al} = 20$) was hydrothermally synthesized as reported earlier [11] and ammonium-ion-exchanged. Gallium was incorporated according to Price and Kanazirev [12] by heating a physical mixture of 205 or 5 mg gallium oxide and 3.0 g zeolite NH_4-ZSM-5 in a quartz tubular reactor for 12 h at 400°C in a flow of nitrogen and for additional 6 h at 600°C in a flow of hydrogen. The resulting catalysts, 4.9Ga/H-ZSM-5 and 0.14Ga/H-ZSM-5, had gallium contents of 4.9 and 0.14 wt% (referenced to the mass of the dry catalyst), respectively, as determined by AES/ICP (Plasma 400, Perkin-Elmer). A diffractometer D5000 (Siemens) operating with CuK_α radiation at 40 kV and 30 mA was used to obtain the XRD data. The MAS NMR experiments were performed on a Bruker spectrometer MSL-400 at resonance frequencies of 104.3 and 400.1 MHz for ^{27}Al and ^{1}H NMR spectroscopy, respectively. The FTIR spectra were recorded in a vacuum apparatus at 200°C with an FTIR spectrometer Vector 22 (Bruker) using self-supporting wafers (≈ 10 mg/cm^2) activated in vacuum ($\approx 1.5 \times 10^{-4}$ Pa) at 400°C. The catalytic experiments were performed in a flow-type apparatus with a fixed-bed reactor. The mass of the dry catalyst (particle size between 0.20 and 0.32 mm), the total pressure, the partial pressure of methylcyclohexane at the reactor inlet and the WHSV amounted to 500 mg, 6.0 MPa, 65 kPa and 0.68 h^{-1}, respectively. Product analysis was achieved by high-resolution capillary gas chromatography (Hewlett-Packard) with a HP PONA column. The carbon content of the used catalysts was obtained with an Elementar Vario EL instrument.

3. Results and discussion

3.1. Characterization of the catalysts

Heating a physical mixture of gallium oxide and zeolite H-ZSM-5 at 600°C in flowing hydrogen results in a solid-state reaction. This has been reported earlier [12–15] and can be confirmed by XRD experiments: the reflections of gallium oxide present in the physical mixture at angles 2θ of 31.8° and 33.9° disappear during the reaction. According to Price and Kanazirev [12], this is due to a reduction of gallium oxide to gallium suboxide (Eq. (1)) and a further reaction of this suboxide with hydrogen to elemental gallium (Eq. (2a)) or with two acidic sites of the zeolite forming the gallium-exchanged form (Eq. (2b)).

$$Ga_2O_3 + 2\ H_2 \rightarrow Ga_2O + 2\ H_2O \quad (1)$$

$$Ga_2O + H_2 \rightarrow 2\ Ga + H_2O \quad (2a)$$

$$Ga_2O + 2H^+Z^- \rightarrow 2\ Ga^+Z^- + H_2O \quad (2b)$$

Compared to the unmodified zeolite H-ZSM-5, the decrease in the integral of the ^{1}H MAS NMR signal of bridging OH groups at 4.3 ppm of the resulting 4.9Ga/H-ZSM-5 catalyst is about 28%, indicating a partial introduction of gallium into the zeolite at cation positions. A remarkable decrease of the concentration of Brønsted acidic sites is also observed by FTIR spectroscopy with and without pyridine as a probe molecule, in agreement with earlier reports [13,14]. The bands at 3610 cm^{-1} in Fig. 1(A) are due to SiOHAl groups, and those at 1547 cm^{-1} in Fig. 1(B) are caused by adsorbed pyridinium ions. During temperature-programmed desorption of pyridine, we observed that the decline of the band at 1547 cm^{-1} is faster on 4.9Ga/H-ZSM-5 than on H-ZSM-5: only 15% of the pyridinium ions detected at 200°C remained after 1 h evacuation at 400°C compared to 37% on H-ZSM-5. From this we conclude that not only the concentration but also the strength of the Brønsted acidic sites is lower on 4.9Ga/H-ZSM-5.

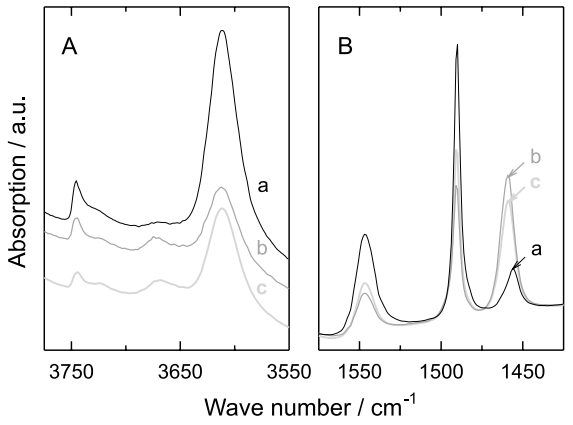

Fig. 1. FTIR spectra of the zeolites H-ZSM-5 (a) and 4.9Ga/H-ZSM-5 (before (b) and after (c) conversion of methylcyclohexane) without (A) and with (B) adsorbed pyridine.

On the other hand, the intensity of the bands attributed to pyridine adsorbed on Lewis acidic sites increases in a pronounced manner during the reaction with gallium oxide, and a shift from 1455 to 1459 cm^{-1} is observed. Additionally, a new weak vibration band at about 3670 cm^{-1} appears which we tentatively assign to OH groups on gallium oxide or Ga^{x+} ions [13]. No formation of extra-framework aluminum is observed with ^{27}Al MAS NMR spectroscopy.

The fact that there are still Brønsted acid sites observed on 4.9Ga/H-ZSM-5, even though a stoichiometric amount of gallium according to Eq. (2b) was used, can be explained by a competitive reaction according to Eqs. (2a) and (2b), by an incomplete reaction according to Eq. (2b), or by cluster formation (e.g., Ga_x^{n+} or $Ga_xO_y^{n+}$, with $n < x$) [15]. On 0.14Ga/H-ZSM-5, the gallium content is too low to observe equivalent results, but it is assumed that the same reactions proceed, though to a much lesser extent.

3.2. Hydroconversion of methylcyclohexane

During the conversion of methylcyclohexane over 0.14Ga/H-ZSM-5 at 250°C, isomers (ethyl- and dimethylcyclopentanes), heptane isomers and secondary cracking products (propane, *iso*- and *n*-butane) are formed in similar amounts at a conversion of 1.5%. With increasing temperature the conversion increases very fast. While the yield of *n*-alkanes with two and more carbon atoms (C_{2+}-*n*-alkanes) and the yield of methane increase monotonously, the yields of cycloalkanes and *iso*-alkanes pass through maxima at 275°C and 320°C, respectively (see Fig. 2). In comparison with zeolite H-ZSM-5, on 0.14Ga/H-ZSM-5 at 300°C a remarkably higher conversion accompanied by higher yields of all cracking products and lower yields of cycloalkanes is observed (see Table 1). Upon further increasing the temperature, the yield of *iso*-alkanes declines significantly faster on 0.14Ga/H-ZSM-5, and, therefore, at 400°C a higher yield of the desired C_{2+}-*n*-alkanes of 75.1% is achieved compared to 72.4% on H-ZSM-5. This is due to considerably higher yields of ethane and propane and unfortunately accompanied by an increased formation of methane (see Table 2). With increasing gallium content this trend continues, and on 4.9Ga/H-ZSM-5 the yield of C_{2+}-*n*-alkanes is 77.6%. This value is similar to the one achieved on zeolite H-ZSM-5 containing extremely low amounts of palladium (e.g., 100 wt-ppm in 0.01Pd/H-ZSM-5), which we refer to as Haag-Dessau catalysts [16], but very different from the one on typically bifunctional catalysts such as 0.2Pd/H-ZSM-5 (see Table 2).

The respective catalytic properties of zeolite H-ZSM-5 with various palladium contents [16] have been related to different contributions of classical cracking via adsorbed carbenium ions and non-

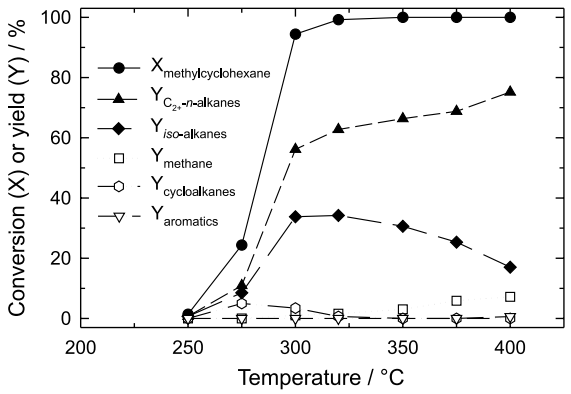

Fig. 2. Conversion of methylcyclohexane on zeolite 0.14Ga/H-ZSM-5 after 30 min time-on-stream.

Table 1
Conversion of methylcyclohexane on zeolite H-ZSM-5 with and without modification with gallium at 300°C after 30 min time-on-stream

Ga content (wt%)	$X_{\text{methylcyclohexane}}$/ (%)	Y_{methane}/ (%)	$Y_{C_{2+}\text{-}n\text{-alkanes}}$/ (%)	$Y_{iso\text{-alkanes}}$/ (%)	$Y_{\text{cycloalkanes}}$/ (%)	$Y_{\text{aromatics}}$/ (%)
0.00	65.0	0.3	34.7	19.9	10.1	0.0
0.14	94.0	1.0	56.2	33.2	3.6	0.0

Table 2
Conversion of methylcyclohexane on zeolite H-ZSM-5 containing gallium or palladium at 400°C after 30 min time-on-stream (the data for Pd/H-ZSM-5 are taken from [16])

	—	0.14 wt% Ga	4.9 wt% Ga	0.01 wt% Pd	0.20 wt% Pd
$X_{\text{methylcyclohexane}}/(\%)$	100	100	100	99.8	100
$Y_{\text{methane}}/(\%)$	3.9	7.0	11.5	3.5	3.5
$Y_{\text{ethane}}/(\%)$	10.4	14.3	9.4	12.3	6.1
$Y_{\text{propane}}/(\%)$	48.6	51.7	57.1	51.5	47.8
$Y_{n\text{-butane}}/(\%)$	12.4	8.8	11.0	13.7	12.6
$Y_{n\text{-pentane}}/(\%)$	1.0	0.3	0.1	0.9	0.2
$Y_{C_{2+}\text{-}n\text{-alkanes}}/(\%)$	72.4	75.1	77.6	78.4	66.7
$Y_{iso\text{-alkanes}}/(\%)$	22.4	17.3	10.9	17.7	29.8
$Y_{\text{cycloalkanes}}/(\%)$	0.0	0.0	0.0	0.1	0.0
$Y_{\text{aromatics}}/(\%)$	1.3	0.6	0.0	0.3	0.0
CMR[a]	0.86	1.37	1.95	1.44	0.33
$Y_{n\text{-butane}}/Y_{\text{butanes}}$	0.43	0.36	0.51	0.50	0.30

[a] Cracking mechanism ratio (CMR $\equiv (Y_{\text{methane}} + Y_{C_2\text{hydrocarbons}})/Y_{iso\text{-butane}}$, after Wielers et al. [21]).

classical Haag-Dessau cracking with carbonium ions in the transition state [17,18]. On bifunctional catalysts such as 0.2Pd/H-ZSM-5, hydrocracking of alkanes [19] or ring opening of cycloalkanes [20] proceed via a route sketched in the upper part of Fig. 3(a): Methylcyclohexane is dehydrogenated on metal sites and then protonated and adsorbed on acidic sites. Usually, isomerization into highly branched isomers occurs, whereupon classical β-scission (via carbenium ions) can proceed. Finally, the diene formed is hydrogenated on metal sites. On acidic catalysts, two different mechanisms are operative [17,18]. On the one hand, classical β-scission is possible, but the adsorbed carbenium ion has to form via a bimolecular hydride transfer (see lower part of Fig. 3(a)). On the other hand, methylcyclohexane can be directly protonated forming a non-classical carbonium ion in the transition state (Haag-Dessau cracking, see Fig. 3(b)). If ring opening is accompanied by consecutive secondary and tertiary cracking steps, *iso*-alkanes (no methane and ethane due to the instability of primary carbenium ions) will be formed predominantly in the first case due to the preceding isomerization, while *n*-alkanes will be the dominating products in the second case.

Fig. 4 shows the temperature dependence of the cracking mechanism ratio (CMR $\equiv (Y_{\text{methane}} + Y_{C_2\text{ hydrocarbons}})/Y_{iso\text{-butane}}$) as defined by Wielers et al. [21] as a measure of the contribution of non-classical cracking versus classical cracking. On 0.2Pd/H-ZSM-5, the CMR is relatively small, whereas on acidic zeolites, the CMR increases considerably with increasing temperature due to the high activation energy of Haag-Dessau cracking. An even higher CMR is reported for 0.01Pd/H-ZSM-5 [16], and this is also the case for gallium-containing zeolites H-ZSM-5 (see Fig. 4 and Table 2). Obviously, relatively high contents of metals with a low hydrogenation/dehydrogenation activity, such as gallium, have a similar effect as very low contents of metals with a high hydrogenation/dehydrogenation activity (e.g., palladium or platinum). In [16], the high CMR observed on such

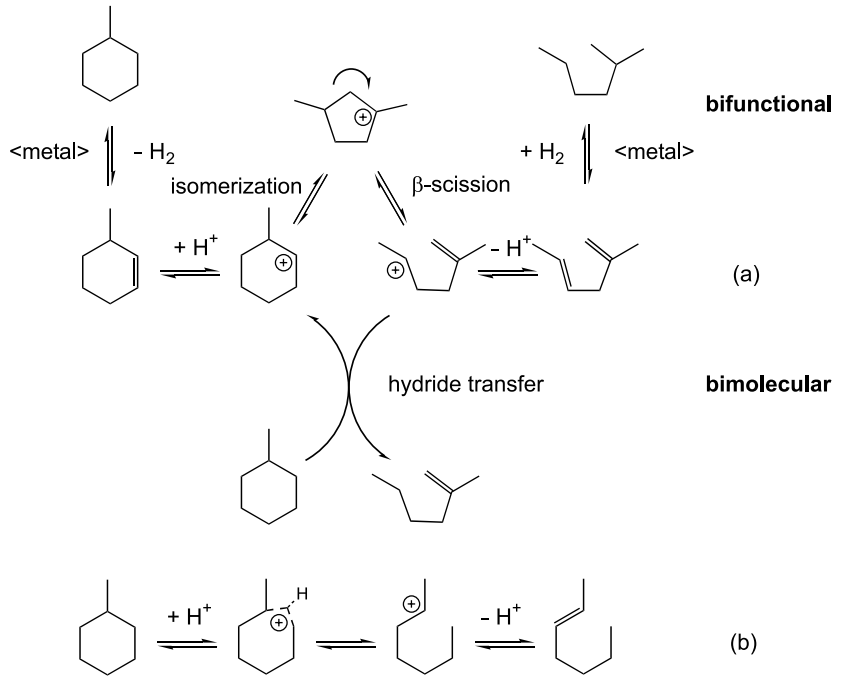

Fig. 3. Mechanisms of ring opening of cycloalkanes: (a) classical (bifunctional and bimolecular) and (b) non-classical Haag-Dessau cracking according to [16].

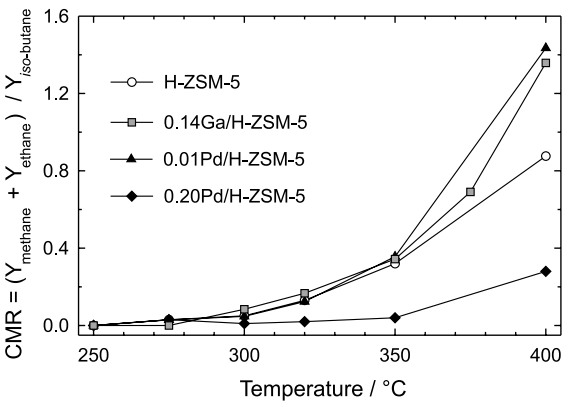

Fig. 4. Temperature dependence of the cracking mechanism ratio (CMR, [21]) during the conversion of methylcyclohexane on metal-free, gallium- and palladium-containing [16] zeolite H-ZSM-5 after 30 min time-on-stream.

catalysts has been tentatively attributed to a lack of an efficient formation mechanism for carbenium ions. On gallium-containing zeolites, the hydrogenation/dehydrogenation sites are not active enough to dehydrogenate methylcyclohexane at a sufficiently high rate for the bifunctional mechanism to proceed; however, the activity of these same sites does suffice for the hydrogenation of the unsaturated reaction products. This hinders the hydride transfer and, therefore, the bimolecular mechanism. Thus, less carbenium ions are adsorbed, and a larger number of acid sites are available for adsorption of methylcyclohexane. As a net effect, the Haag-Dessau mechanism is favored.

Another point which should be addressed is the formation of methane: Studies of aromatization reactions on gallium-containing catalysts suggest that the formation of light alkanes, in particular of methane, occurs predominantly on acidic sites [1,10], possibly on Lewis acid sites such as Ga^{+} cations [15]. Comparing the yield of methane on gallium-free catalysts with or without palladium (ca. 4%) with the one on 0.14Ga/H-ZSM-5 and 4.9Ga/H-ZSM-5 (7.0% and 11.5%, respectively), a contribution of such gallium species to the methane formation seems likely. Considering that 4.9Ga/H-ZSM-5 is the catalyst with the lowest

density and, probably, the lowest strength of Brønsted acidic sites (cf. Section 3.1), this becomes even more likely. A formation of methane through hydrogenolysis on gallium appears unlikely, because there is almost no conversion on a Ga_2O_3/silicalite-1 catalyst.

3.3. Catalyst deactivation

During the conversion of methylcyclohexane on H-ZSM-5, 0.14Ga/H-ZSM-5 or palladium-containing catalysts, the yields are constant with time-on-stream [16]. In contrast, on 4.9Ga/H-ZSM-5 the yields of C_{2+}-*n*-alkanes and methane decrease steadily, while the yield of *iso*-alkanes increases (see Fig. 5). Accordingly, the CMR decreases from 1.95 after 30 min time-on-stream to 0.53 after 530 min. With FTIR spectroscopy, an increase of the number of Brønsted acidic sites (see bands at 3610 cm^{-1} due to SiOHAl groups in Fig. 1(A) and bands at 1547 cm^{-1} due to adsorbed pyridinium ions in Fig. 1(B)) and a decrease of the number of Lewis acidic sites (see bands at 1459 cm^{-1} in Fig. 1(B)) is simultaneously detected. This is tentatively attributed to some sintering of gallium species as reported earlier by Chang and Lee [15]. Speculating that the sintered species could have an enhanced hydrogenation/dehydrogenation activity, a higher concentration of methylcyclohexenes in the steady state can be invoked, which would favor classical cracking over Haag-Dessau cracking. An additional effect of pore blocking by sintered species [15] cannot be excluded. Deactivation by coke formation, however, can be ruled out, since the coke content of the used catalyst is below the detection limit of 0.1 wt%, and its color is white.

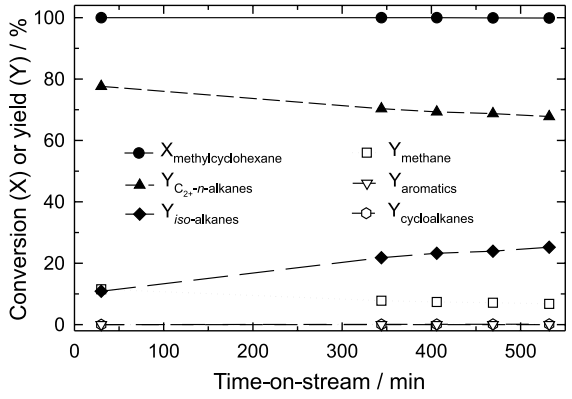

Fig. 5. Conversion of methylcyclohexane on zeolite 4.9Ga/H-ZSM-5 at 400°C.

4. Conclusions

It has been shown previously [7] that cycloalkanes such as methylcyclohexane can be converted on zeolite H-ZSM-5 into a high-quality steam-cracker feedstock with a yield of the desired C_{2+}-*n*-alkanes of 72%. It is now demonstrated that this yield can be further increased to 75% and 78% on zeolite H-ZSM-5 containing 0.14 and 4.9 wt% gallium, respectively. We interpret this as a higher contribution of the non-classical Haag-Dessau cracking vis-à-vis the classical cracking. Similar effects were reported earlier for the conversion of methylcyclohexane on H-ZSM-5 catalysts containing very small amounts of palladium [16]. For such catalysts, the term Haag-Dessau catalyst has been coined [16], and on the basis of the present communication, we find it justified to extend it to zeolites of the type described here.

Acknowledgements

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