

Water-Promoted Hydrocarbon Activation Catalyzed by Binuclear Gallium Sites in ZSM-5 Zeolite**

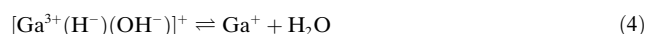
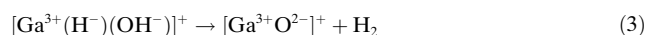
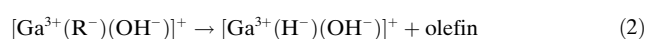
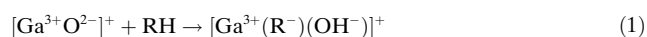
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Dedicated to Süd-Chemie on the occasion of its 150th anniversary

Catalytic reactions of hydrocarbons in zeolites can be profoundly affected by extraframework transition-metal cationic clusters. MFI zeolites containing dehydrogenating species such as gallium, zinc, and platinum form the basis for light alkane aromatization (Cyclar, Aroforming, Z-forming) processes.^[1,2] Combining partial alkane dehydrogenation with subsequent olefin conversion is another option.^[3] An additional appealing example is the incorporation of methane into gasoline products in the MTG process over Ga/HZSM-5.^[4] A catalytic issue relates to the nature of the cationic clusters. Are the alkanes activated by isolated cations, or do the extraframework oxygen atoms also play a role? Current literature on Zn- and Ga-promoted catalysis in zeolites mainly refers to systems in which the state of the cationic cluster is not well-defined.^[1,2] As a starting point for this study, a zeolitic material has been chosen in which Ga³⁺ ions can be considered as single-site catalysts. The water-induced enhancement in the rate of alkane activation by Ga/ZSM-5, as discussed herein, relates to transformation of these single Ga³⁺ centers to binuclear cationic Ga complexes involving a Ga₂O₂²⁺ core.

Recent experimental^[5–8] and computational^[9–13] studies have contributed to our understanding of the mechanism of alkane activation by single Ga Lewis acid sites. As candidate active sites, various mononuclear Ga-containing cations (Ga³⁺, GaH₂⁺, GaH²⁺, GaO⁺) have been considered.^[8–13] Quantum-chemical calculations^[13] showed that C–H bond activation by reduced Ga/ZSM-5 proceeds over the Lewis acid–base pair formed by the Ga³⁺ ion and a zeolite-framework basic oxygen anion (Ga³⁺⋯ZO[−]). The experimentally observed increase in activity of Ga³⁺ species in ZSM-5 upon oxidation at 473 K by nitrous oxide was ascribed to formation of gallyl (GaO⁺) ions.^[8] Their higher reactivity is derived from more facile C–H bond cleavage catalyzed by the stronger Lewis acid–base

pair formed by a Ga³⁺ ion and the extraframework oxygen atom. The following elementary reaction steps [Eqs. (1)–(4)] may be proposed for alkane (RH) dehydrogenation by the gallyl ion.



Earlier studies^[6,10] have shown that H₂O formation [Eq. (4)] is energetically favored over H₂ desorption [Eq. (3)] catalyzed by these mononuclear GaO⁺ species. Indeed, oxidized Ga/ZSM-5 rapidly loses its high initial activity in propane conversion because of Ga³⁺ reduction to Ga⁺.^[8] According to this reaction scheme, GaO⁺ can be stabilized by addition of steam. Herein, we report experimental results showing that addition of steam indeed substantially increases the rate of alkane dehydrogenation over Ga/ZSM-5 and results in stable operation. A mechanistic model is proposed, which is supported by DFT calculations of the stability of various possible cationic Ga-containing species formed upon hydroxylation. Also, energy barriers associated with H₂ recombination are reported.

The results of catalytic activity measurements of propane conversion as a function of the steam partial pressure over initial Ga³⁺ ions in ZSM-5 are summarized in Table 1. Clearly,

Table 1: Conversion (X) and molar hydrocarbon product distribution during reaction of propane over Ga/ZSM-5 as a function of the steam partial pressure and over parent HZSM-5.^[a]

P _{H₂O} [kPa]	X [%]	CH ₄ [%]	C ₂ H ₄ [%]	C ₃ H ₆ [%]	C ₄ H ₈ [%]	BTX ^[b] [%]	H ₂ ^[c]
Ga/ZSM-5							
0.00	7	5	9	80	2	3	1.06
0.01	14	7	15	65	4	7	1.10
0.05	16	8	16	63	3	7	1.16
0.3	19	10	19	58	2	7	1.19
0.5	16	11	19	61	2	4	1.11
1	14	11	19	62	2	4	1.08
4	11	11	21	65	1	2	0.98
HZSM-5							
0.00	5	42	42	14	–	–	0.24

[a] 50 mg catalyst, atmospheric pressure, T = 823 K, WHSV = 11.8 g_{propane} g_{catalyst}^{−1} h^{−1} (WHSV = weight-hourly space velocity); [b] benzene, toluene, xylenes; [c] moles of H₂ per mole converted C₃H₈.

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cofeeding of water leads to a substantial increase of the propane conversion. The conversion passes a maximum at $p_{\text{H}_2\text{O}}$ of 0.3 kPa. Catalyst performance in the presence of steam (0.3 kPa) was found to be stable over a period of at least 4 h. The very different product composition between $\text{Ga}^+/\text{ZSM-5}$ in the absence of steam and HZSM-5 points to a change in the mechanism from protolytic hydrocarbon activation involving C–H and C–C bond cleavage for HZSM-5 to dominant C–H activation by the Lewis acidic Ga cations.^[8]

Addition of water to the feed strongly increases the activity. The main product remains propylene, although with increasing water content slightly increased amounts of methane and ethylene are formed. The formation of methane and ethylene is due to protolytic cracking of propane. This finding indicates some regeneration of Brønsted acid protons, which are formed upon hydrolysis of gallium species.^[6] More ethylene than methane is formed because of additional proton-catalyzed oligomerization/cracking reactions of propylene. The carbon selectivity to dehydrogenated products remains well over 85 %. The increased dehydrogenation activity of Ga/ZSM-5 compared to HZSM-5 is obvious from the increased amount of hydrogen formed. No carbon oxides were detected in the reactor effluent. The activity decrease at higher $p_{\text{H}_2\text{O}}$ is likely due to more complete hydrolysis of the active intrazeolitic Ga sites. ²⁷Al NMR spectroscopy measurements indicate that prolonged steam exposure does not lead to massive redistribution of tetrahedral aluminium species (see the Supporting Information).

The promoting effect of water is due to the formation of reactive partly hydrolyzed gallium species. For mononuclear gallium sites, the catalytic cycle is initiated by desorption of H_2 from $[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+$ to form the GaO^+ ion. However, Table 2 shows that the energy barrier for hydrogen recombina-

tion is prohibitively high (305 kJ mol⁻¹), which is due to the very low acidity of the hydrogen atom attached to the oxygen atom. In agreement with earlier computations,^[11] water formation is strongly favored. We propose that multinuclear Ga sites are formed. To clarify whether such species can be generated upon water adsorption and whether their formation facilitates hydrogen desorption, we studied the interaction of two distantly placed Ga^+ ions with H_2O by quantum-chemical cluster calculations in the DFT formalism. The Ga^+ ions are stabilized by two negatively charged Al-containing oxygen tetrahedra embedded in a cluster of 14 T atoms (T = Si, Al) representing the elongated eight-membered ring of the wall of the sinusoidal channel of MFI zeolite. The cluster approach was chosen, because modeling of the unit cell of MFI zeolite with 96 T atoms is computationally prohibitive. On the other hand, the cluster with 14 T atoms is large enough to account for all significant interactions between the cationic species and the zeolite framework as well as to describe activation of small molecules such as H_2 and H_2O . This conclusion is supported by recent quantum-chemical calculations with this cluster.^[12] Water dissociation at cluster I is exothermic ($\Delta E = -102 \text{ kJ mol}^{-1}$, Figure 1) and

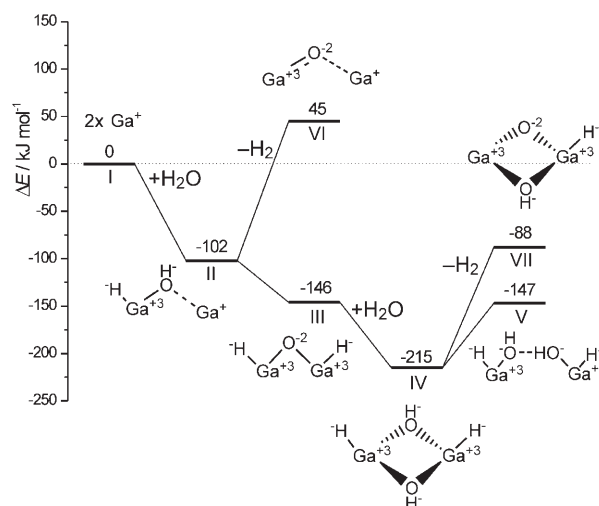


Figure 1. Relative stability of binuclear cationic Ga species stabilized by the eight-membered ring of ZSM-5 zeolite. For clarity, the zeolite clusters are not included in the depicted structures. All of the structures involve bidentate coordination of each Ga cation to two zeolite-framework oxygen anions of the 14-T-atom zeolite cluster (see the Supporting Information).

Table 2: Comparison of reaction energies (ΔE) and activation barrier energies ($\Delta E^\ddagger$) for H_2 and H_2O desorption over various Ga clusters.

Reaction ^[a]	ΔE [kJ mol ⁻¹]	$\Delta E^\ddagger$ [kJ mol ⁻¹]
II $\rightarrow$ VI + H_2	147	263
II $\rightarrow$ I + H_2O	102	230
IV $\rightarrow$ VII + H_2	127	211
IV $\rightarrow$ II + H_2O	113	142
$[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+ \rightarrow \text{GaO}^+ + \text{H}_2$ ^[b]	242	305
$[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+ \rightarrow \text{Ga}^+ + \text{H}_2\text{O}$ ^[b]	128	259

[a] Roman letters refer to structures in Figure 1; [b] reference [10].

nation is prohibitively high (305 kJ mol⁻¹), which is due to the very low acidity of the hydrogen atom attached to the oxygen atom. In agreement with earlier computations,^[11] water formation is strongly favored. We propose that multinuclear Ga sites are formed. To clarify whether such species can be generated upon water adsorption and whether their formation facilitates hydrogen desorption, we studied the interaction of two distantly placed Ga^+ ions with H_2O by quantum-chemical cluster calculations in the DFT formalism. The Ga^+ ions are stabilized by two negatively charged Al-containing oxygen tetrahedra embedded in a cluster of 14 T atoms (T = Si, Al) representing the elongated eight-membered

leads to formation of structure II, which contains a $[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+$ ion in which the hydroxyl group coordinates to the neighboring Ga^+ ion. This structure can rearrange by migration of the hydroxyl H atom to the Ga^+ ion to give structure III, an oxygen-bridged binuclear $[(\text{Ga}^{3+}(\text{H}^-))_2\text{O}]^{2+}$ ion. The latter rearrangement allows an additional stabilization energy of 44 kJ mol⁻¹. Reaction of a second water molecule with structure III results in further stabilization of the extraframework gallium dimer by 69 kJ mol⁻¹ and gives structure IV (Figure 1). Structure IV contains an almost square and planar Ga_2O_2 core with hydride ions and protons bound to the extraframework Ga cations and O anions, respectively. Rearrangement of structure IV to the conventional situation with two isolated $[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+$ ions (structure V) interacting through a hydrogen bond costs 68 kJ mol⁻¹.

Since hydrogen-atom recombination at the hydroxylated structures II and IV is required to initiate alkane dehydrogenation, the corresponding energetics were evaluated. Reaction energies and activation barriers are listed in Table 2. Coordination of the hydroxyl group of the $[\text{Ga}(\text{H}^-)(\text{OH}^-)]^+$ ion to the neighboring gallium cation results in a significant decrease of the reaction energy for H_2 recombination (147 kJ mol⁻¹)

compared to that from the isolated $[\text{Ga}(\text{H}^-)(\text{OH}^-)]^+$ ion (242 kJ mol⁻¹).

In contrast, the effect on H₂O desorption is much smaller. Very similar trends are noted for H₂ and H₂O desorption from structure IV. The strong decrease in the activation energy for H₂ recombination on the Ga dimer is due to the increased acidity of the OH group. Compared to the $[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+$ ion, the O–H bond is weaker in the dimer, which can be understood from the bond-order conservation principle.^[14] Moreover, for the dimer complex, H₂ recombination does not result in complete decomposition of the stable tetrahedral arrangement around the Ga cations. Hydrogen recombination from the isolated $[\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+$ ion results in less stable three-fold coordinated Ga.

These theoretical insights imply that H₂ desorption should be facile from hydroxylated Ga clusters in ZSM-5. To verify this assertion, we carried out a temperature-programmed experiment over Ga⁺/ZSM-5 in an atmosphere of 0.3 vol % H₂O in He. Hydrogen evolution is observed around 600 K (see the Supporting Information). In a similar experiment with HZSM-5, no hydrogen was formed. The desorption energy estimated from the H₂ desorption maximum gives a value of 140 ± 12 kJ mol⁻¹. This result agrees well with the computed value for H₂ recombination from the fully hydroxylated cluster (IV → VII, $\Delta E = 127$ kJ mol⁻¹, Table 2). Structural information about the Ga species in Ga/ZSM-5 was obtained by extended X-ray absorption fine structure (EXAFS) spectra at the Ga K edge. Table 3 lists the

Table 3: EXAFS fit parameters for Ga⁺/ZSM-5 oxidized by nitrous oxide at 473 K.^[a]

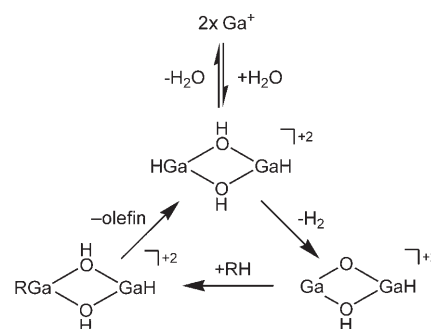
Backscatterer	N	R [Å]	$\Delta\sigma^2 [\times 10^{-3} \text{ Å}^2]$	ΔE_0 [eV]
Ga–O	4.05	1.84	8.48	8.3
Ga–O (VII) ^[b]	4	1.799–2.250		
Ga–Ga	1.09	2.98	14.2	–12.3
Ga–Ga (VII) ^[b]	1	2.816		
Ga–Al	1.11	2.72	12.5	9.8
Ga–Al (VII) ^[b]	1	2.772–2.998		

[a] Estimated accuracies: $N \pm 20\%$, $R \pm 0.04 \text{ Å}$, $\Delta\sigma^2 \pm 20\%$, $\Delta E_0 \pm 10\%$; [b] from DFT calculations.

EXAFS fit parameters for a model catalyst obtained by oxidation of Ga⁺/ZSM-5 by nitrous oxide at 473 K that shows a high initial activity in propane conversion.^[8] Four O atoms are detected at a distance of 1.84 Å. A Ga–Ga coordination is identified at an interatomic distance of 2.98 Å with a coordination number close to one. A Ga–Al backscatterer at a distance of 2.72 Å with a coordination number of 1.1 is included. These structural data attest to the presence of a Ga₂O₂ core structure coordinating to the zeolite oxygen anions with a structure in reasonable agreement with the DFT calculations. While EXAFS analysis provides averaged structural data, we note that the computations have been carried out for one specific ring structure. A detailed study of the sites of bivalent cations has shown a preference for the occurrence

of Al pairs in the ring structures of ZSM-5 zeolite for Si/Al ratios up to 22.^[15]

In summary, addition of water to reduced Ga cations stabilizes binuclear hydroxyl-bridged Ga-containing cationic reaction intermediates. The increased acidity of the bridging hydroxyl bond and the stable tetrahedral configuration around Ga³⁺ ions facilitate H₂ desorption. In essence, the result that H₂ recombination is facilitated at Ga sites is in agreement with earlier kinetic studies over reduced Ga/HZSM-5.^[16] The higher activity of dimeric oxygen-bridged Ga species compared to single-site Ga⁺ species is in line with the lower energy for H₂ recombination.^[13] Dehydrogenation of an alkane over the Ga₂O₂ dimer proceeds by initial heterolytic dissociation by the Lewis acid pair formed by Ga³⁺ and the basic extraframework oxygen atom (Scheme 1) with



Scheme 1. Proposed reaction cycle for alkane dehydrogenation over binuclear Ga-containing cations in the presence of water.

subsequent olefin desorption and hydrogen recombination. Similar to earlier findings for the single-site Ga⁺ catalyst,^[13] the last two steps may take place in a concerted manner. Continuous addition of water is required to maintain a high steady-state concentration of the hydroxylated reaction intermediate.

Experimental Section

Ga/ZSM-5 was prepared according to reference [8]. In Ga/ZSM-5 the Brønsted protons have been quantitatively replaced by Ga⁺ ions. Propane conversion was carried out in a single-pass atmospheric quartz reactor by passing a mixture of C₃H₈ (5 kPa) in He with WHSV = 11.8 g_{propane} g_{catalyst}⁻¹ h⁻¹ at 823 K. Water was added via a well-thermostated saturator. X-ray absorption spectroscopic measurements were carried out at the Ga K edge (Duble, ESRF). Structural information was extracted from the *k*⁻¹- and *k*³-weighted EXAFS functions by multiple-shell fitting in *R* space. Quantum-chemical cluster calculations at the DFT level were carried out to compute the relative stability of various Ga cationic species coordinating to a zeolite cluster. A zeolite cluster representative of the elongated eight-membered ring of the sinusoidal channel of MFI zeolite and containing two framework substitutions (Al³⁺ for Si⁴⁺) was employed. Further experimental and computational details are given in the Supporting Information.

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