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A DFT study of hydrogen–deuterium exchange over oxidized and reduced gallium species in Ga/HZSM-5 zeolite

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Quantum-chemical calculations give insight in the experimentally observed higher rate of hydrogen–deuterium exchange for oxidized Ga/HZSM-5 over reduced Ga/HZSM-5. The reaction is computed to be more facile over reduced (Ga^+) than over oxidized (GaO^+) cations. The difference lies in the difficult formation of active $GaH_2{}^+$ cations from Ga^+ compared to facile hydrogen dissociation over GaO^+ to give active $GaHOH^+$ cations. Neutral gallium oxide clusters are shown to have a lower intrinsic activity than GaO^+ cations.

KEY WORDS: DFT; gallium; zeolite; Ga/ZSM-5; hydrogen activation; isotopes; exchange.

1. Introduction

Gallium-containing ZSM-5 zeolite is an effective catalyst for the dehydrogenation of light alkanes to olefins and their subsequent aromatization [1]. This is commercially applied in the Cyclar process [2,3]. It is generally believed that gallium acts as a promoter to recombinative hydrogen removal during alkane dehydrogenation [1,4–9]. The nature of the active gallium species are still under debate and cationic species such as Ga^+ [8], $GaH_2{}^+$ and GaO^+ replacing the Brønsted acid protons to compensate the framework charge [10] as well as small neutral gallium oxide clusters are considered. Recently, GaH^{2+} cations were also proposed [11]. Experimentally, it was observed that an oxidized Ga/HZSM-5 shows a considerably higher hydrogen–deuterium exchange rate than its reduced counterpart [12]. From recent experimental works [13,14] it follows that gallium is present as Ga^+ or $GaH_2{}^+$ ions after reduction. The oxidized systems is characterized by GaO^+, $Ga(H)(OH)^+$ and $Ga(OH)_2{}^+$ ions.

Two pathways for the process$Z{-}GaH_2 + D_2 \rightarrow Z{-}GaHD + HD$ [15], where Z represents the zeolite are considered.

$$Z{-}GaH_2 + D_2 \leftrightarrows Z{-}GaHD + HD \quad (1)$$

$$Z{-}GaH_2 + D_2 \leftrightarrows ZD{-}GaH_2D \quad (2)$$

$$ZD{-}GaH_2D \leftrightarrows Z{-}GaHD + HD. \quad (3)$$

The first mechanism (equation (1)) is a concerted one and was shown to be improbable because of the computed high activation barrier. The alternative route involves the Lewis acid–base pair of Ga and the zeolitic oxygen anions and goes through the formation of a stable intermediate $Z(D)(Ga(H)_2(D))$ via equations (2) and (3).

Another mechanism included Z–Ga(H)(OH) and $Z{-}Ga(OH)_2$ species as intermediates to the elimination of water and successive oxidation by those water molecules. These processes were very slow in disagreement with experimental work [12]. In order to shed light on the differences in the hydrogen–deuterium exchange rates observed in Ref. [12], we computed the energies for several mechanisms using the cluster model of Bell and co-workers [15] as starting-point. Experimentally, reduced Ga^+ species can be oxidized to GaO^+ species by nitrous oxide at a temperature of 673 K [13]. On the other hand, oxidation by nitrous oxide at higher temperature or by oxygen leads to the partial regeneration of Brønsted acid protons and thus the formation of small extralattice gallium oxide species [12,14]. We will calculate the rates of hydrogen–deuterium exchange for the various species. Moreover, we will estimate the relative concentrations of active Ga species in both oxidized and reduced catalysts under typical reaction conditions.

2. Computational details

Similar to refs. [15–17], we chose a 1-T(UC) zeolite cluster model (figure 1), because it presents a simple and practical approximation of cation position structure, formed by a lattice aluminium ion. Comparative calculations for 1-T(UC) and 5-T(UC) clusters [15] have shown that the results obtained using these clusters are rather similar. Quantum-chemical computations have been carried out within the density functional theory (DFT) using the GAUSSIAN 98 program [18]. The hybrid B3LYP functional [19] was used involving a

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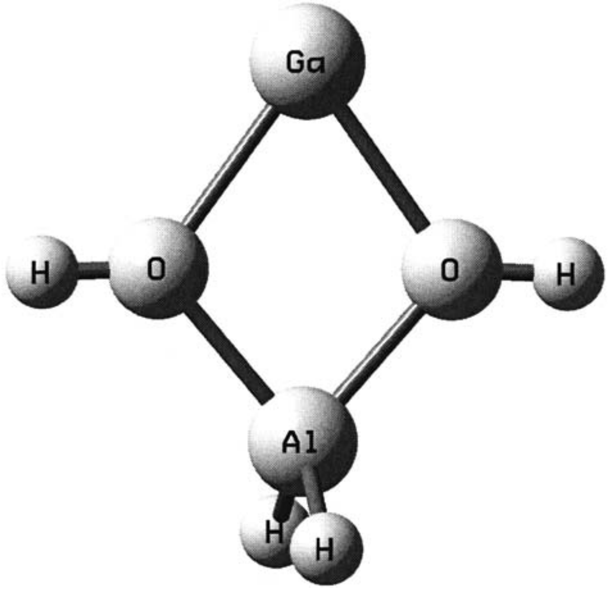

Figure 1. Structural model of the zeolite 1-T(UC) cluster.

6-311 + G* basis set for all the atoms. This method accounts for the Hartree–Fock exchange, for a mixture of exchange and correlation functionals including gradient corrections of the electron density and includes carefully chosen empirical parameters obtained from fitting of calculated values to accurate experimental data. Earlier, the hybrid B3LYP method has been reported to provide good descriptions of various reaction profiles, particularly of geometries, the heats of reactions, the barrier heights and of vibrational analyses [20].

All calculations were performed with full geometry optimization. Stationary points were checked by frequency calculations. Local minima were identified by the absence of imaginary frequencies, whilst transition states were characterized by one imaginary frequency for the saddle point. Gibbs free energy differences were computed for two sets of conditions. The first one was at a temperature of 800 K at atmospheric pressure of hydrogen. The second one describes the experimental conditions in ref. 12 closely ($T = 573$ K at a hydrogen pressure of 3 kPa). Rate constants were calculated from these energy differences, applying

$$k = (k_\mathrm{B}T/h)\exp(-\Delta G^{*}/RT),$$

where k_B stands for Boltzmann's constant, T for temperature (K), h for Plank's constant and R is the universal gas constant.

3. Results and discussion

Two main reaction pathways were considered for reduced gallium species in line with earlier work [15]. In the first one, hydrogen–deuterium exchange takes place via an Eley–Rideal-type mechanism in which a gas-phase deuterium molecule interacts with one of the hydrides of GaH_2^+ and forms HD (equation (1)). The other deuterium atom remains at the Ga site forming a $GaHD^+$ species. In the alternative case, deuterium dissociates over GaH_2^+ forming an intermediate where one deuterium is added to Ga and the other to the basic oxygen site of the zeolite lattice. After H/D is desorbed from the catalytic surface (equations (2) and (3)). The activation energies for these two mechanisms are listed in table 1. In agreement with the work of Bell and co-workers [15], the activation barrier for the first mechanism is relatively high. The decomposition of deuterium in the second mechanism yields two deuterium atoms pointing towards each other. The acitvation barrier for the addition of D_2 is about 23 kcal/mol. The barrier for the subsequent decomposition of the complex is much lower (~6 kcal/mol). The decomposition product results from deuterium adsorbed to the basic oxygen site and the nearest deuterium or hydrogen of the GaH_2D fragment closest. Hydrogen–deuterium exchange therefore requires rotating the GaH_2D fragment along the Ga–O bond by 120°. This rotation presents a small barrier of about 5 kcal/mol. Hence, we replace equations (2) and (3) by equations (4)–(6) to include the rotation in the kinetic scheme.

$$\mathrm{Z{-}GaH_2 + D_2 \leftrightarrows Z(D){-}GaH_2[D]} \qquad (4)$$

$$\mathrm{Z(D){-}GaH_2[D] \leftrightarrows Z(D){-}GaHD[H]} \qquad (5)$$

$$\mathrm{Z(D){-}GaH_2[D] \leftrightarrows Z{-}GaHD + HD.} \qquad (6)$$

The forward rate constants of the various pathways are listed in table 2, assuming that the amounts of the intermediates is at steady state. The activation energy of the GaH_2D group rotation is of the same magnitude as the activation energy of the intermediate decomposition, inclusion of the rotation decreases the rate constant for the overall reaction only by 20%. This does not provide an explanation for that is not enough to concurrent with water oxidation mechanism proposed in [15].

Table 1
Activation energies for reactions of hydrogen–deuterium exchange on $ZGaH_2$ (kcal/mol)

Reaction	Ea_f	Ea_r
$\mathrm{Z{-}GaH_2 + D_2Z{-}GaHD + HD}$	51.58	51.58
$\mathrm{Z{-}GaH_2 + D_2Z(D){-}GaH_2[D]}$	22.50	5.98
$\mathrm{Z(D){-}GaH_2[D]Z(D){-}GaHD[H]}$	5.35	5.35
$\mathrm{Z(D){-}GaH_2[D]Z{-}GaHD + HD}$	5.98	22.50

Table 2
Reaction rate constants (T = 800 K, $p = 1$ atm)

Pathway	Rate constant
Concerted	1.23×10^{-6}
With intermediate	2.92
With intermediate and rotation	2.42

Considering oxidized gallium species, Bell and coworkers [15] proposed a scheme that was thought to proceed through Z–Ga(H)(OH) and Z–Ga$(OH)_2$ species through pathways involving HDO elimination and addition reactions (equations (7)–(11)), and a concerted mechanism, shown in equation (11) (figure 2).

$$\text{Z—Ga—(H)(OH)} + D_2 \leftrightarrows \text{Z—Ga—(D)(OH)} + \text{HD} \tag{7}$$

$$\text{Z—Ga—(H)(OH)} + D_2 \leftrightarrows \text{Z—Ga—(H)(D)} + \text{HDO} \tag{8}$$

$$\text{Z—Ga—(H)(D)} + \text{HDO} \leftrightarrows \text{Z—Ga—(H)(OD)} + \text{HD} \tag{9}$$

$$\text{Z—Ga—}(OH)_2 + D_2 \leftrightarrows \text{Z—Ga—(D)(OH)} + \text{HDO} \tag{10}$$

$$\text{Z—Ga—(D)(OH)} + \text{HDO} \leftrightarrows \text{Z—Ga—(OH)(OD)} + \text{HD}. \tag{11}$$

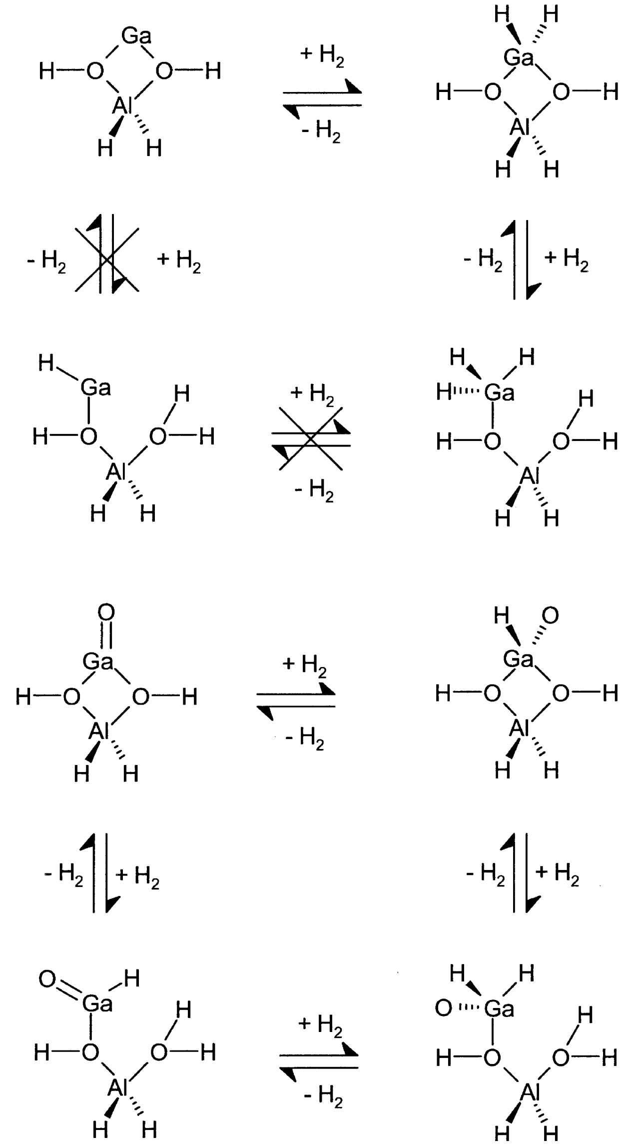

Figure 2. A scheme of consecutive hydrogen addition and removal used to describe hydrogen-deuterium exchange in reduced and oxidized forms of gallium-containing zeolite.

The barrier energies were higher for these processes than those over reduced Ga species. In view of the discrepancy with the experimental results, we have considered a different pathway, involving basic oxygen sites of the zeolite framework similar to the case for reduced Ga species.

We start with considering hydrogen–deuterium exchange over Z–Ga = O species. Hydrogen dissociation over this structure leads to a Z–Ga–H(OH) species which can undergo hydrogen–deuterium exchange in a similar fashion as GaH_2^+ species (equations (12) and (13)).

$$\text{Z—Ga—H(OH)} + D_2 \leftrightarrows \text{Z(D)—Ga—H(D)(OH)} \tag{12}$$

$$\text{Z(D)—Ga—H(D)(OH)} \leftrightarrows \text{Z—Ga—D(OH)} + \text{HD}. \tag{13}$$

Hydrogen adsorption to Z–Ga = O may also result in Z(H)–GaHO which can be involved in the hydrogen–deuterium exchange by deuterium introduction (equations (14) and (15)).

$$\text{Z(H)—Ga—H(O)} + D_2 \leftrightarrows \text{Z(H)—Ga—H(D)(OD)} \tag{14}$$

$$\text{Z(H)—Ga—H(D)(OD)} \leftrightarrows \text{Z(H)—Ga—D(O)} + \text{HD}. \tag{15}$$

The energy barrier for the decomposition of the oxidized intermediate in equation (10) is computed to be 73 kcal/mol (table 3) and is much higher than the barrier for the decomposition via recombination of a proton connected to the basic oxygen atom and a hydride attached to Ga (equation (8)). Therefore, we conclude that the catalytic cycle for hydrogen–deuterium exchange over Z–Ga = O may start via two different pathways but will continue only by the route presented in equation (8). A comparison of the activation energies for the various routes learns that the barriers for hydrogen–deuterium exchange over the oxidized species (21.3 and 23.7 kcal/mol for Z(H)–GaHO and Z–Ga–H(OH), respectively) are similar to those for the reduced species (22.5 kcal/mol for Z–GaH_2).

In principle, one also should take into account hydrogen–deuterium exchange over neutral gallium oxide species which may be formed upon oxidation [12]. To this end, we have calculated various reaction steps over neutral $HGa(OH)_2$ moieties (equations (16) and (17)) which are very similar to equations (7) and (8).

$$HGa(OH)_2 + D_2 \leftrightarrows HGaD(OH) + HDO \tag{16}$$

$$HGaD(OH) + HDO \leftrightarrows HGa(OH)(OD) + HD. \tag{17}$$

The activation barrier of reaction (16) is computed to be 27.45 kcal/mol which is higher than for the corresponding reactions (4) (reduced species, 22.5 kcal/mol) and (7) (oxidized cationic species, 23.5 kcal/mol). The

Table 3

Energetics for hydrogen adsorption reaction involved in H/D-exchange (kcal/mol)

Reaction	Ea_f	Ea_r	ΔE	ΔG^a
Z—Ga=O + H_2Z—Ga—H(OH)	19.9	75.6	55.6	83.1
Z—Ga—H(OH) + H_2Z(H)—GaHH(OH)	23.7	8.1	−15.6	−37.8
Z—Ga=O + H_2Z(H)—Ga—H(O)	31.7	20.5	−11.1	20.2
Z(H)—Ga—H(O) + H_2Z(H)—GaHH(OH)	21.3	72.5	51.2	25.1
Z—Ga + H_2Z—GaH_2	69.2	73.5	4.3	−19.1

[a] T = 573 K, $p = 3$ kPa.

next step (17) also presents a higher barrier (17.53 kcal/mol) than for reduced and oxidized species. Accordingly, the exchange reaction proceeds at a lower rate of neutral gallium oxide species than over cationic GaO^+ species. This appears to be in accord by experimental data [12], showing that the formation of neutral gallium oxide moieties at the expense of cationic GaO^+ ones leads to a decrease of the reaction rate.

We have computed reaction rates constants (table 4) using transition-state theory for conditions similar to those for hydrogen–deuterium exchange reactions described in ref. 12. Under these conditions, the rate of hydrogen–deuterium exchange for the reduced species ${GaH_2}^+$ is predicted to be higher than for oxidized species. This is deviant from the experimental findings (table 5) that gave a higher exchange rate for the oxidized catalyst. The difference is believed to be due to the concentration of catalytically active species. Activation of hydrogen over Ga^+ cations to form ${GaH_2}^+$ is very slow compared to the formation of Z–Ga–H(OH). The slow formation of ${GaH_2}^+$ species is corroborated by a recent experimental study [13], which showed that the number of ${GaH_2}^+$ species increases only slowly upon cooling of Ga^+ in hydrogen. Moreover, a lower cooling rate increased the number of ${GaH_2}^+$ species indicating that their formation is kinetically controlled. Desorption of hydrogen is also slow and only proceeds at appreciable rates at high temperatures [13]. The catalyst in ref. 12 was prepared by reduction of a dimethylgallium/ZSM-5 precursor. The alkyl ligands are removed at high temperature via

$$\mathrm{Z{-}Ga(CH_3)_2 + 2H_2 \rightarrow Z{-}GaH_2^+ + 2CH_4},$$

giving methane and ${GaH_2}^+$ species. These ${GaH_2}^+$ species decompose above 773 K slowly in the absence of hydrogen. Thus, during cooling in inert atmosphere [12], part of the ${GaH_2}^+$ species decompose to Ga^+. It is thus likely that the reduced Ga/ZSM-5 sample contains a mixture of Ga^+ and ${GaH_2}^+$ species. During the isotopic exchange reaction the amount of ${GaH_2}^+$ species probably does not increase significantly because the rate of formation is very low. Thus, the exchange reaction takes place over a relatively small number of ${GaH_2}^+$ species. In contrast, the equilibrium between Z–Ga = O and Z–Ga–H(OH) is favoring the hydrogenated product. This implies that the number of catalytically active sites in the oxidized catalyst is much higher than in the reduced catalyst.

The difference in the isotopic exchange rate between reduced and oxidized Ga/HZSM-5 species is thus not due to the difference in intrinsic reaction rate but to the difference in the number of catalytically active sites.

4. Conclusions

The experimentally observed higher rate of isotopic hydrogen–deuterium exchange for oxidized Ga/ZSM-5 compared to reduced Ga/ZSM-5 is due to a lower number of active species in the reduced catalyst (${GaH_2}^+$ species). DFT calculations show that the reaction pathway over ${GaH_2}^+$ species is more favorable than over GaO^+ species. The reaction over neutral gallium oxide species is found to be even less favorable in accordance with experimental data. The reaction over the reduced species proceeds via dissociation of hydrogen over a Lewis acid–base pair formed by the

Table 4

Hydrogen adsorption rates constants (T = 573 K, $p = 3$ kPa)

Reaction	k_f	k_r
Z—Ga + H_2 ⇔ Z—GaH_2	4.2×10^{-22}	8.3×10^{-15}
Z—GaH_2 + H_2 ⇔ Z(H)—GaH_3	0.00045	1.5×10^{11}
Z—Ga=O + H_2 ⇔ Z—Ga—H(OH)	2.8×10^{17}	5.4×10^{-15}
Z—Ga—H(OH) + H_2 ⇔ Z(H)—GaHH(OH)	0.00017	4.5×10^{10}
Z—Ga=O + H_2 ⇔ Z(H)—Ga—H(O)	1.3×10^{14}	2.6×10^{6}
Z(H)—Ga—H(O) + H_2 ⇔ Z(H)—GaHH(OH)	0.0012	3.2×10^{-13}

Table 5

Hydrogen–deuterium activities (initial HD formation rate) (initial H_2 and D_2 and N_2 partial pressures: 1 kPa; total pressure 3 kPa; T = 573 K [12])

Catalyst	Pretreatment	Rate (g HD/g cat h)	Rate (mol HD/mol Ga h)
TMG/ZSM-5	Reduced	9.9	0.6
TMG/ZSM-5	Oxidized	30	1.6
TMG/ZSM-5	Red. + Ox.	15	3.3

charge-compensating species and the basic oxygen atom of the zeolite lattice. Rotation of the GaH_2D fragment preceding desorption is included in the kinetic scheme. Under reaction conditions, the concentration of GaH_2^+ species is much lower than that of $GaHOH^+$ ones, because the formation of GaH_2^+ from Ga^+ and hydrogen is a very slow reaction. On the contrary, GaO^+ cations react readily to $GaHOH^+$ species that can catalyze the hydrogen–deuterium exchange.

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