

# A theoretical DFT study of the mechanism of C–C bond hydrogenolysis in alkanes on silica-supported zirconium hydrides

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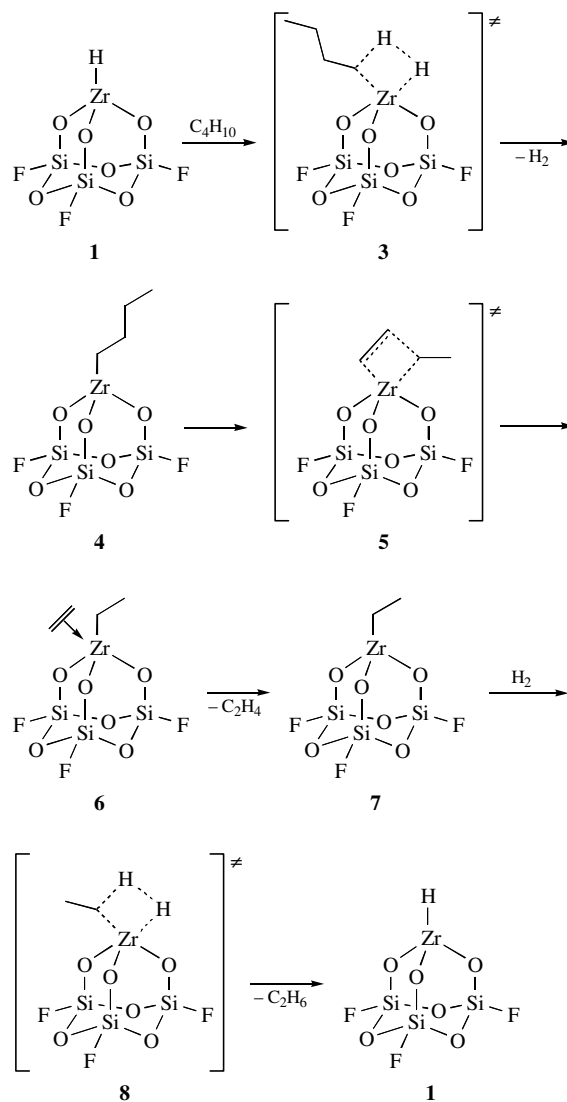
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A DFT study of C–C bond hydrogenolysis in alkanes on silica-supported zirconium monohydrides ( $\equiv\text{Si-O}$ )<sub>3</sub>ZrH and dihydrides ( $\equiv\text{Si-O}$ )<sub>2</sub>ZrH<sub>2</sub> shows that only the latter are capable of catalysing this process under mild conditions.

Silica-supported zirconium hydrides<sup>1–5</sup> draw recently much attention due to their ability to catalyse low-temperature olefin polymerization,<sup>1–2</sup> C–C bond hydrogenolysis in alkanes<sup>3</sup> and polyolefins<sup>4</sup> under mild conditions and H/D isotope exchange in alkanes.<sup>5–6</sup> Basset *et al.*<sup>3–6</sup> considered the catalytic sites of alkane hydrogenolysis to be grafted zirconium monohydrides ( $\equiv\text{Si-O}$ )<sub>3</sub>ZrH. On the other hand, Yermakov *et al.*<sup>1,2</sup> considered grafted zirconium dihydrides ( $\equiv\text{Si-O}$ )<sub>2</sub>ZrH<sub>2</sub> as the catalytic sites in this system. Earlier, we have performed DFT studies of the mechanisms of H/D isotope exchange in methane<sup>7</sup> and ethylene polymerization<sup>8</sup> catalysed by the Yermakov–Basset system. The catalytic activity of both types of supported zirconium hydrides was estimated to be quite proximal in respect to the polymerization of ethylene.<sup>8</sup> Zirconium dihydrides, however, were found to be much more active in the isotope exchange reaction.<sup>7</sup> Moreover, we calculated the activation parameters of H/D exchange for zirconium dihydrides, which are in a much better agreement with experimental data<sup>9</sup> than those for monohydrides.

As a continuation of these studies, we consider the probable mechanisms of C–C bond hydrogenolysis in alkanes on model species **1** and **2** (Schemes 1, 2) using butane as a model linear alkane. All the DFT calculations were performed under the same approach as previously<sup>7,8</sup> using the original PRIRODA program.<sup>10</sup> The replacement of the skeletal O–Si fragments by fluorine atoms when performing quantum-chemical calculations of the structure of silica-supported compounds was proposed and substantiated earlier.<sup>11</sup> The generalised gradient approximation (GGA) for the exchange-correlation functional by Perdew, Burke, and Ernzerhof<sup>12</sup> was employed. The 40 core electrons of Zr, 10 for Si and 2 for C, O and F were described by effective core potentials.<sup>13–15</sup> The orbital basis sets of contracted Gaussian-type functions of size (5s1p)/[3s1p] for H, (5s5p2d)/[3s3p2d] for C, O, F and Si, and (9s9p8d)/[5s5p4d] for Zr were used for the remaining electrons in conjunction with the density-fitting basis sets of uncontracted Gaussian-type functions of size (5s1p) for H, (6s3p3d1f) for C, O, F and Si, and (10s6p6d5f5g) for Zr. Full geometry optimization of all structures studied in this work was performed using analytical gradients followed by analytical calculations of the second derivatives of energy with respect to coordinates in order to



Scheme 1

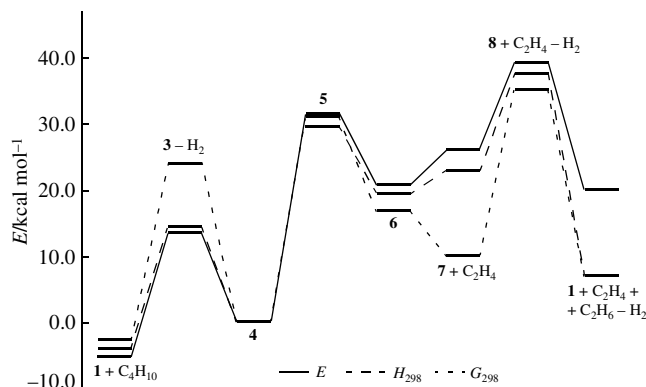
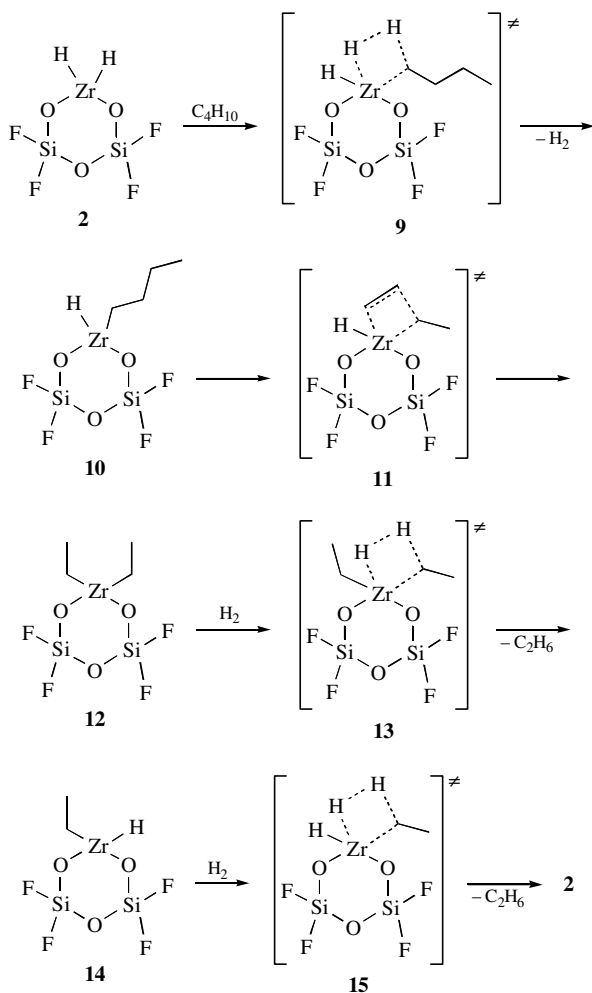


Figure 1 Energy profile for butane hydrogenolysis on zirconium monohydrides **1**.

characterise the nature of the resulting stationary points (minima or saddle points) on the potential energy surface (PES). Zero-point vibrational energies and thermodynamic data were calculated in the harmonic approximation.

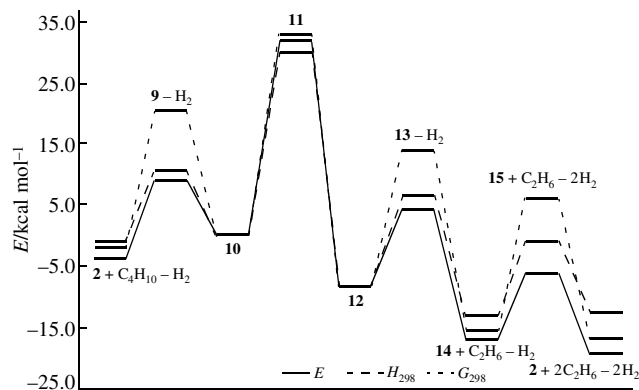
The catalytic cycle for the C<sub>2</sub>–C<sub>3</sub> bond hydrogenolysis in butane on supported zirconium monohydrides **1**, which is consistent with that proposed by Basset *et al.*,<sup>3–6</sup> is presented in Scheme 1. The energy profile is shown in Figure 1. The first stage of the hydrogenolysis, the transformation of the initial hydride into *n*-butyl derivative **4** with the elimination of a hydrogen molecule, proceeds by the  $\sigma$ -bond metathesis pathway via four-centered transition state **3** ( $\Delta E^\ddagger = 7.9$  kcal mol<sup>–1</sup>,  $\Delta G_{298}^\ddagger = 28.1$  kcal mol<sup>–1</sup> relative to **1** + C<sub>4</sub>H<sub>10</sub>). It was found to be endothermic ( $\Delta E = 5.3$  kcal mol<sup>–1</sup>,  $\Delta G_{298} = 4.0$  kcal mol<sup>–1</sup>). It is fol-



Scheme 2

lowed by C<sub>2</sub>–C<sub>3</sub> bond cleavage and the migration of a β-ethyl fragment to zirconium, which leads to the formation of zirconium alkyl-ethylene complex **6** via transition state **5**. The energy barrier for this transformation is rather high ( $\Delta E^\ddagger = 31.4$  kcal mol<sup>-1</sup>,  $\Delta G_{298}^\ddagger = 30.9$  kcal mol<sup>-1</sup>) and the process is extremely thermodynamically unfavourable ( $\Delta E = 20.6$  kcal mol<sup>-1</sup>,  $\Delta G_{298} = 17.2$  kcal mol<sup>-1</sup>). The equilibrium constant for the transformation **4** → **6** under the real experimental conditions ( $T = 150$  °C) was calculated to be  $1.3 \times 10^{-9}$ . The coordination sphere of the metal in **6** is saturated. Thus, it cannot coordinate an extra hydrogen molecule. Hence, the only way of its further transformations is the elimination of ethylene, as it is supposed by the Basset scheme. The corresponding transformation (**6** → **7**) leads to a further increase of the system energy ( $\Delta E = 5.4$  kcal mol<sup>-1</sup>), which is in part compensated by a considerable entropy gain ( $\Delta G_{298} = -7.0$  kcal mol<sup>-1</sup>). The last stage, allowing to repeat the catalytic cycle, is the hydrogenolysis of ethyl derivative **7** by the σ-bond metathesis pathway via transition state **8** ( $\Delta E^\ddagger = 13.2$  kcal mol<sup>-1</sup>,  $\Delta G_{298}^\ddagger = 24.7$  kcal mol<sup>-1</sup> relative to **7**). Effectively, the hydrogenolysis of butane using the Basset catalytic cycle describes the cleavage of butane into ethane and ethylene (C<sub>4</sub>H<sub>10</sub> → C<sub>2</sub>H<sub>6</sub> + C<sub>2</sub>H<sub>4</sub>). The calculated  $\Delta H_{298}$  and  $\Delta G_{298}$  values for this reaction are 22.7 and 11.0 kcal mol<sup>-1</sup>, respectively, which are in a good agreement with the tabulated  $\Delta H^0$  and  $\Delta F^0$  values of 22.4 and 12.5 kcal mol<sup>-1</sup>, calculated from the standard formation energies.<sup>16</sup> The data suggest that the hydrogenolysis of butane cannot proceed under mild conditions on supported zirconium monohydrides **1** by the Basset mechanism. The process is unfavourable from both kinetic and thermodynamic points of view.

The thermodynamic restriction of the alkane hydrogenolysis could be overcome if the considerable energy loss for the C–C bond cleavage is compensated by the formation of two ethane molecules (in case of butane) in the catalytic cycle. The overall

Figure 2 Energy profile for butane hydrogenolysis on zirconium dihydrides **2**.

process described by this equation (C<sub>4</sub>H<sub>10</sub> + H<sub>2</sub> → 2C<sub>2</sub>H<sub>6</sub>) is thermodynamically favourable [ $\Delta H_{298} = -11.8$  kcal mol<sup>-1</sup>,  $\Delta G_{298} = -14.8$  kcal mol<sup>-1</sup>;  $\Delta H^0 = -10.3$  kcal mol<sup>-1</sup> (ref. 16),  $\Delta F^0 = -11.6$  kcal mol<sup>-1</sup> (ref. 16)]. This opportunity comes true if one considers the active catalytic sites to be zirconium dihydrides **2** (Scheme 2).

The process begins with the formation of *n*-butyl derivative **10** ( $\Delta E = 3.8$  kcal mol<sup>-1</sup>,  $\Delta G_{298} = 2.2$  kcal mol<sup>-1</sup>) via transition state **9** ( $\Delta E^\ddagger = 12.6$  kcal mol<sup>-1</sup>,  $\Delta G_{298}^\ddagger = 22.5$  kcal mol<sup>-1</sup> relative to free reagents). The equilibrium constant of this process is  $7.3 \times 10^{-2}$  at 150 °C. The cleavage of the C<sub>2</sub>–C<sub>3</sub> bond in the *n*-butyl fragment (**10** → **12**) requires the overcoming of the top-most energy barrier on the reaction path, transition state **11** ( $\Delta E^\ddagger = 31.9$  kcal mol<sup>-1</sup>,  $\Delta G_{298}^\ddagger = 33.0$  kcal mol<sup>-1</sup> relative to **10**, see Figure 2). The rate constant of this process at 150 °C was calculated to be  $1.7 \times 10^{-5}$  s<sup>-1</sup>, but this stage is exothermic ( $\Delta E = -8.4$  kcal mol<sup>-1</sup>,  $\Delta G_{298} = -8.5$  kcal mol<sup>-1</sup>) and thus the process may proceed under the experimental conditions described in ref. 3. It is noteworthy that the relaxation of transition state **11** leads directly to diethyl derivative **12** by-passing the stage of the intermediate η<sup>2</sup>-coordinated ethylene complex formation. Successive hydrogenolysis of **12** via standard pathway (**12** → **13** → **14** → **15** → **2**) requiring the overcome of two energy barriers and characterised by an overall energy gain of  $\Delta E = -11.1$  kcal mol<sup>-1</sup>,  $\Delta G_{298} = -8.5$  kcal mol<sup>-1</sup>. It finishes the overall thermodynamically favourable process and allows the catalytic cycle to restart.

Thus, we concluded that zirconium dihydrides **2**, which existence was postulated in 1977 by Yermakov *et al.*,<sup>2</sup> unlike zirconium monohydrides **1**, are capable to catalyse alkane hydrogenolysis under mild conditions. Basset *et al.*<sup>3</sup> undoubtedly proved that monohydrides **1** are mainly formed on the silica surface under conditions used for catalyst preparation.<sup>3</sup> Nevertheless, it is of no doubt that dihydrides **2** could coexist with monohydrides **1** on the silica surface. In our opinion, a more detailed experimental study has to be performed to determine the structure of real active centres in this catalytic system.

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