

Hafnium-Hydride Complexes Anchored to Silica. Catalysts of the Low Temperature Hydrogenolysis of Alkanes and Hydrogenation of Olefins

Lindora d' ORNELAS, Sheila REYES, Françoise QUIGNARD, Agnès CHOPLIN,*
and Jean- Marie BASSET^{†*}

*Institut de Recherches sur la Catalyse, EP0048, CNRS, 2, av. A. Einstein, 69 626 Villeurbanne Cedex, France

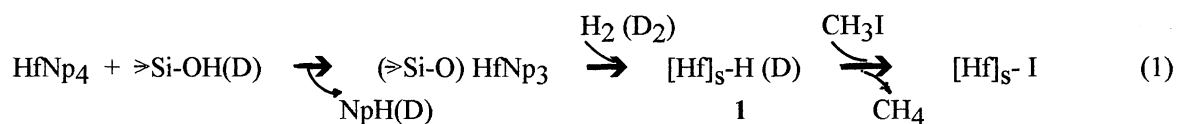
[†] Laboratoire de Chimie Organométallique de Surface, EP0048, CNRS,
2, av. A. Einstein, 69 626 Villeurbanne Cedex, France

Silica grafted hafnium hydride complexes were synthesized from tetra(neopentyl)hafnium and a partially dehydroxylated silica. These surface complexes are catalysts for hydrogenolysis of neopentane and butane and for hydrogenation of isobutene and propene, under mild conditions. Their catalytic properties are compared to the related supported Zr Hydride complexes.

Supported zirconium hydride complexes, synthesized via hydrogenolysis of tris(neopentyl)zirconium grafted at the surface of silica,¹⁾ activate stoichiometrically the σ C-H bond of alkanes, such as cyclooctane and even methane, at low to moderate temperatures.²⁾ They are active and selective catalysts for the hydrogenolysis of alkanes at temperatures below 423 K.³⁾ A possible mechanism was proposed including the following elementary steps: (i) electrophilic activation of a C-H bond of the alkane by the highly electrophilic Zr surface hydride (supposedly an $8e^-$ species) via a four center intermediate;⁴⁾ (ii) β -methyl migration with formation of a $[Zr]_5$ -methyl complex and liberation of the relevant olefin; (iii) restoration of the active $[Zr]_5$ -H centers via hydrogenolysis of this latter surface complex and liberation of methane. The olefin formed at step (ii) was assumed to be hydrogenated on the $[Zr]_5$ -H centers.

These findings lead us to search for other electrophilic supported complexes and to check some of the elementary steps of this hypothetical catalytic cycle. As a part of this project, we wish to report here the catalytic properties of silica supported hafnium hydride complexes for alkane hydrogenolysis and olefin hydrogenation.

The reaction between tetra(neopentyl)hafnium, $HfNp_4$, and silica dehydroxylated at 773 K, $SiO_2(773)$, results in the formation of a surface grafted neopentylhafnium complex, qualitatively characterized by its IR spectrum and the concomittant liberation of neopentane.⁵⁾ When this surface neopentylhafnium complex is heated under H_2 (400 torr) at temperatures between 423 and 473 K, surface hafnium hydride complexes, (**1**), are formed as qualitatively suggested by IR spectroscopy, chemical reactivity and deuterium exchange experiments (Eq. 1):⁶⁾



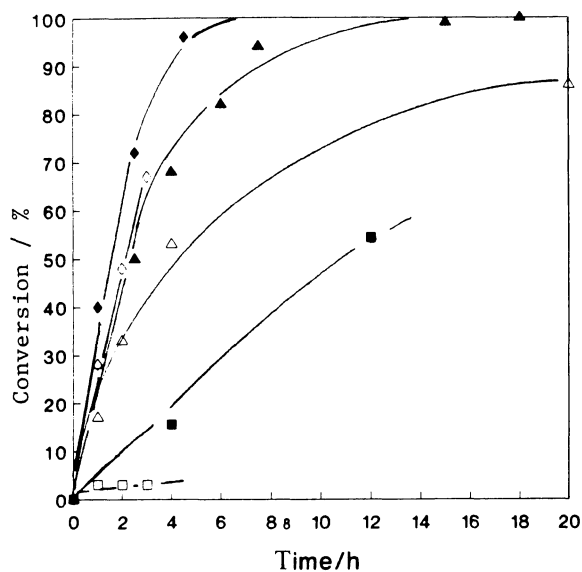


Fig. 1. Activity of $[\text{Hf}]_5\text{-H}$ (filled symbols) and $[\text{Zr}]_5\text{-H}$ (open symbols) for hydrogenolysis of neopentane. % wt: 3.1 (M=Hf); 1.5 (M=Zr); M/ H_2 / NpH: 1/ 300/ 60 (molar ratio); $\square, \blacksquare$ at 323 K; $\Delta, \blacktriangle$ at 373 K; $\diamond, \blacklozenge$ at 423 K

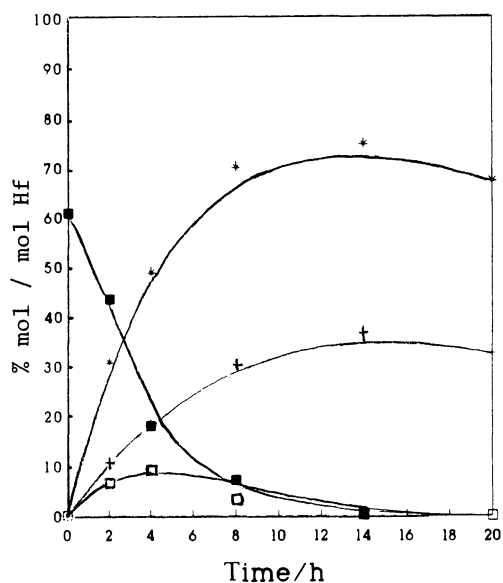


Fig. 3. Hydrogenolysis of butane on $[\text{Hf}]_5\text{-H}$ at 423 K. Concentration of the alkanes as a function of time
 $\blacksquare$ BuH; * C_2H_6 ; $\square$ C_3H_8 ; + CH_4

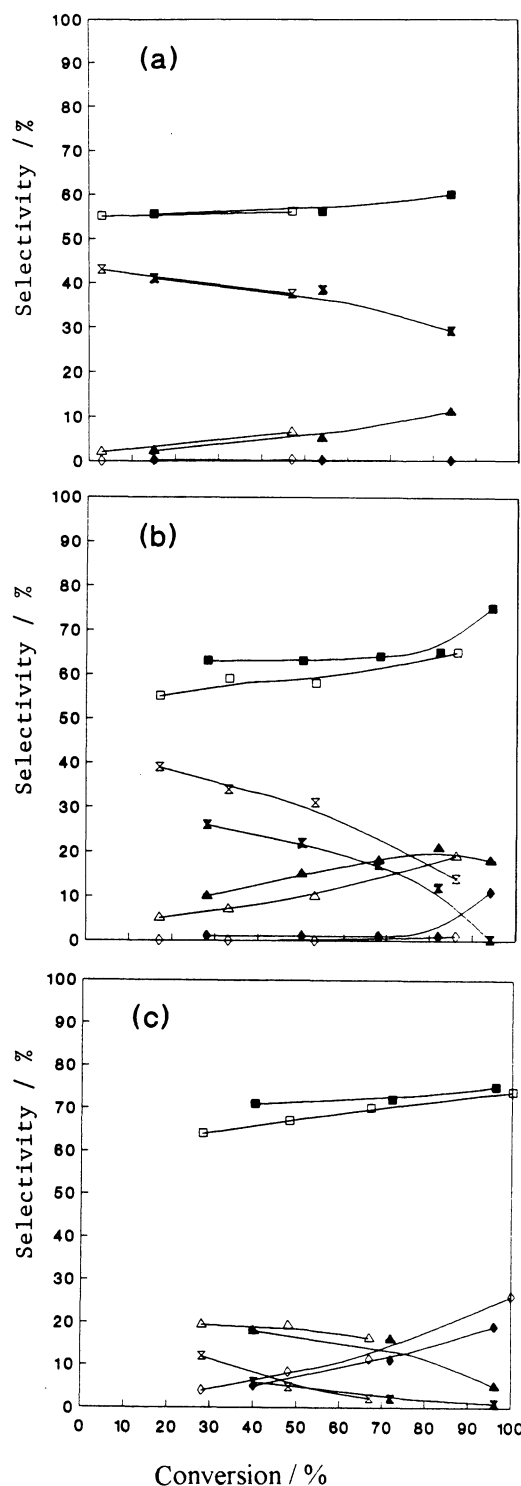
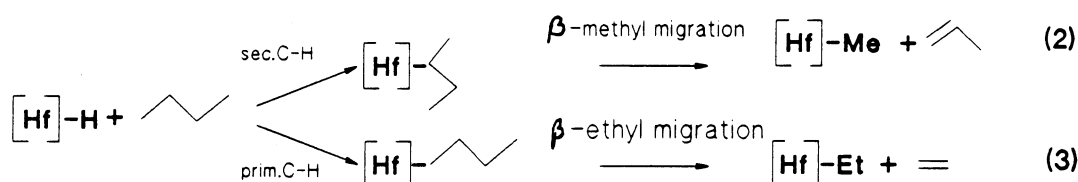


Fig. 2. Product selectivities versus conversion for hydrogenolysis of neopentane on $[\text{Hf}]_5\text{-H}$ (filled symbols) and $[\text{Zr}]_5\text{-H}$ (open symbols) at (a): 323 K; (b): 373 K and (c) at 423 K. Experimental conditions see Fig. 1. (Data for $[\text{Zr}]_5\text{-H}$, ref. 3). $\square, \blacksquare$ CH_4 ; $\diamond, \blacklozenge$ C_2H_6 ; $\Delta, \blacktriangle$ C_3H_8 ; $\text{X}, \blacktext{X}$ $i\text{-C}_4\text{H}_{10}$

Thus, the surface organometallic chemistry of Hf and Zr seem to be very similar.⁷⁾ The catalytic properties of **1** towards hydrogenolysis of neopentane were determined for three temperatures: 323, 373 and 423 K, which are all lower than the temperature of formation of **1**.

Complex **1** is already active at 323 K (Fig. 1), although its performances are rather poor: total neopentane conversion is only achieved after ca. 50 h. Initially, only methane and isobutane are formed in close amounts (Fig. 2a). Selectivity remains high as long as conversion is lower than 50%: it is then close to 50% CH₄ and 50% iso-C₄. Above ca. 50% conversion, formation of propane occurs, indicating the occurrence of successive reactions. At higher temperatures, activity of **1** increases sharply (Fig. 1), but selectivity at iso-conversion decreases (Fig. 2b,c). At 100% conversion, mainly methane and ethane are obtained, with a molar ratio close to 3/1 (Fig. 2c). These results compare qualitatively well with those obtained for the related [Zr]_S-H catalysts.³⁾ Although the complexes [Hf]_S-H seem a little more active (Fig. 1), a true comparison is not relevant here: the number and the precise nature of the active sites are not well known.

Hydrogenolysis of butane at 423 K is slow: total conversion of n-butane is achieved within ca. 14 h (Fig. 3). Thus activity of the catalyst seems to be lower for n-butane than for neopentane hydrogenolysis. Interestingly, methane, ethane and propane are formed already at low conversion in relative amounts close to 1/3/1. At 100% conversion, mainly ethane and methane are formed, their relative molar ratio being close to 2/1. As already observed previously, ethane is not hydrogenolyzed, a fact certainly related to the absence of a β -methyl group in the [Hf]_S-ethyl complex. Finally, an overall loss of C among the gaseous products is observed, suggesting the formation of polymerization products. Initial formation of ethane could result from activation of a primary C-H bond, followed by a β -ethyl migration (Eq. 3). Hydrogenolysis of the [Hf]_S-ethyl surface complex or hydrogenation of the liberated ethylene produce ethane. Simultaneous initial formation of propane and methane may result from activation of a secondary C-H bond (Eq. 2), followed by β -methyl migration. This hypothesis is currently under investigation.



Activity of **1** for olefin hydrogenation was studied with isobutene and propene. At 423 K, quasi-total conversion of isobutene is reached within ca. 2 h; isobutane, propane and methane (36%, 24%, 32%) are the major products. These results suggest that isobutene is more rapidly hydrogenated than isobutane is hydrogenolyzed to propane and methane. Propene is hydrogenated to propane at 423 K: 98% conversion is obtained within 4.5 h with a high selectivity for propane (89%). No significant amounts of methane and ethane are formed, even after 40 h, but simultaneously, only approximately 70% of the initial C (reactants) is recovered

among the gaseous products. This strongly suggests that polymerization of propene occurs on the $[\text{Hf}]_S\text{-H}$ sites.⁸⁾

These studies confirm that hydrogenolysis of silica anchored homoleptic alkyl d^0 complexes of elements of group 4 (Zr, Hf) is an efficient method for synthesizing highly electrophilic hydride complexes of these elements: they are formally $8e^-$ species. Thus, hafnium and zirconium hydrides anchored to partially dehydroxylated silica catalyze under mild conditions the hydrogenolysis of alkanes such as neopentane and butane: the initial formation of isobutane and ethane respectively is explained by a step involving a β -alkyl migration⁹⁾, respectively methyl or ethyl. The ability of $[\text{Hf}]_S\text{-H}$ to catalyze the hydrogenation of olefins is confirmed. Polymerization must simultaneously be considered.

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- 5) experimental conditions as described in Ref 7), $\nu(\text{C-H})/\text{cm}^{-1}$: 2953, 2864, 1464, 1359.
- 6) $\nu(\text{Hf-H})/\text{cm}^{-1}$: 1702, 1676; **1** reacts with water and liberates gaseous hydrogen; **1** reacts with CH_3I and liberates methane.
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