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Methane activation by silica-supported Zr(IV) hydrides: the dihydride [(≡SiO)$_2$ZrH$_2$] is much faster than the monohydride [(≡SiO)$_3$ZrH]

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The silica-supported Zr(IV) dihydride [(≡SiO)$_2$ZrH$_2$] reacts quickly and completely with methane to yield [(≡SiO)$_2$ZrMe$_2$] through the intermediate [(≡SiO)$_2$ZrHMe], while its monohydride analogue [(≡SiO)$_3$ZrH] yields the monomethylated product [(≡SiO)$_3$ZrMe] slowly and incompletely.

Metal hydride complexes play a key role in stoichiometric and catalytic alkane transformation chemistry[1] including the strategic field of methane activation.[1e,f] The silica-supported zirconium monohydride [(≡SiO)$_3$ZrH], **1a**,[2] which catalyses, *inter alia*, the low temperature hydrogen/deuterium exchange in saturated hydrocarbons,[2a,b] olefin polymerization[2c] as well as alkane or polyolefin hydrogenolysis,[2d,e] has been found to react stoichiometrically with methane under moderate conditions, to yield the supported zirconium methyl species [(≡SiO)$_3$ZrMe], **2a**, with liberation of hydrogen:[2f,g]

$$\underset{\mathbf{1a}}{[(\mathrm{SiO})_3\mathrm{ZrH}]} + \mathrm{CH_4} \rightarrow \underset{\mathbf{2a}}{[(\mathrm{SiO})_3\mathrm{ZrMe}]} + \mathrm{H_2}$$
$$\left(T = 423\ \mathrm{K},\ P_{\mathrm{CH_4}} = 440\ \mathrm{Torr},\ [\mathrm{CH_4}]:[\mathrm{Zr}]\ \text{ratio},\ R, = ca.\ 100\right) \quad (1)$$

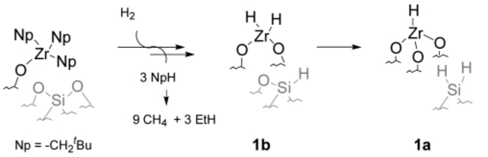
The synthesis of **1a** from the well-defined single-site precursor [(≡SiO)$_3$ZrNp$_3$],[3] also produces in smaller quantities [(≡SiO)$_2$ZrH$_2$], **1b** as was foreseen over 25 years ago.[2a,c,h] It is only very recently that **1b** was investigated theoretically,[4a] experimentally demonstrated and mechanistically rationalized (see Scheme 1).[4b–d]

This paper reports that the dihydride species [(≡SiO)$_2$ZrH$_2$], **1b**, produced in minor amount during the synthesis of **1a**, reacts with methane much faster than the major monohydride species **1a**, thus suggesting that surface "dihydrides" (and perhaps "polyhydrides" which are transient species during the synthesis of **1a**) could be much better candidates for catalytic reactions involving methane and or alkanes (*e.g.* hydrogenolysis of polyolefins, alkane metathesis, methanolysis of alkanes, …). While the reaction of **1a** with methane is incomplete at 150 °C, that of **1b** gives, by a stepwise process, a monomethyl and a dimethyl species by the following sequence of reactions already at room temperature:

$$\underset{\mathbf{1b}}{[(\mathrm{SiO})_2\mathrm{ZrH_2}]} + \mathrm{CH_4} \rightarrow \underset{\mathbf{2i}}{[(\mathrm{SiO})_2\mathrm{ZrHMe}]} + \mathrm{H_2} \quad (2a)$$

$$\underset{\mathbf{2i}}{[(\mathrm{SiO})_2\mathrm{ZrHMe}]} + \mathrm{CH_4} \rightarrow \underset{\mathbf{2b}}{[(\mathrm{SiO})_2\mathrm{ZrMe_2}]} + \mathrm{H_2} \quad (2b)$$

The reaction of **1** (obtained by hydrogenolysis of [(≡SiO)$_3$ZrNp$_3$], and typically containing **1a** and **1b** in a 3:1 ratio)† was experimentally investigated by ^{1}H and ^{13}C NMR, IR spectroscopy, surface and gas phase analyses, and theoretically studied by applying the B3-LYP functional.[5a] Three different experimental procedures were used: (i) batch reactor (molar ration between methane and Zr$_{\text{total}}$: R = 80); (ii) autoclave, (R = 1600); and (iii) continuous tubular reactor (R = 1600).‡



Scheme 1

The ^{1}H NMR spectra of the reaction of **1** with methane in a batch reactor‡ showed the partial consumption of the signature resonance of **1a** (δ_{ZrH} = 10 ppm), and the complete disappearance of the signal of **1b** ($\delta_{\mathrm{ZrH_2}}$ = 12 ppm), indicating a different reactivity of the two hydrides **1a** and **1b**; a new resonance appeared in the 1 ppm region, consistent with the δ_{CH} resonances expected for the methylated products; no other changes with respect to the spectrum of starting **1** could be observed (Fig. 1(a)(i),(ii)). The ^{13}C CP-MAS NMR of the products showed a broad resonance at 35 ppm, with a shoulder at 25 ppm, consistent with the reported literature data for species **2a**, δ(CH$_3$) = 36 ppm (Fig. 1(b)).[2f]

The complete reaction of **1** with methane could not be achieved even under more vigorous experimental conditions, *viz.* a much larger CH$_4$:**1** ratio (*i.e.* R = 1600):‡ unreacted **1a** was still detectable in the ^{1}H NMR spectrum of the product (Fig. 1(a)(iii)).

The stepwise analysis of the IR spectra corroborated the NMR evidence, and allowed the novel identification of ν(ZrH) for **1a** (1633 cm^{-1}), **1b** (1649, 1622 cm^{-1}) and **2i** (1609 cm^{-1}). The *in-situ* IR spectroscopy of the batch-reaction experiment was carried out by means of three successive loadings of methane on a self-supporting silica disk.‡ The overall observation was a slow and incomplete decrease of the ν(Zr–H) bands clustered around 1630 cm^{-1} (Fig. 2). At the end of the first loading, *i.e.* after 15 min at 150 °C, an overall decrease by 10% of ν(ZrH) bands could be observed, due to the weakening of two lateral shoulders at 1645 and 1622 cm^{-1}, while the central band at 1633 cm^{-1} remained substantially unperturbed (Fig. 2(b)–(i)). The NMR experiments have shown that under these condition the species **1b** undergoes reaction with methane, therefore enabling the ν(ZrH$_2$) assignment for **1b** to these bands. By the end of the second and third loadings, the ν(ZrH) area further dropped (by 45 and 10%, respectively) for a total decrease by 75% of ν(ZrH) bands, indicating a partial consumption of the

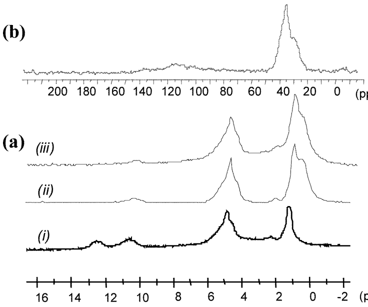


Fig. 1 (a) ^{1}H NMR spectra of the reaction of **1** with methane (addition at RT, heating at T = 150 °C for 720 min): (i) before addition; (ii) after addition ($P_{\mathrm{CH_4}}$ = 550 Torr, two loadings); (iii) after addition ($P_{\mathrm{CH_4}}$ = 30 bar, one loading). (b) ^{13}C CP-MAS NMR spectrum of the reaction product of **1** with ^{13}CH$_4$ ($P_{\mathrm{CH_4}}$ = 550 Torr).

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starting hydrides. The IR spectrum shows only one remaining band at 1633 cm^{-1} (Fig. 2(a)(v)), which is assigned to **1a**, given the NMR experimental data. Interestingly, the difference between the spectra taken at 30 and 15 min showed a transient band at 1609 cm^{-1} (Fig. 2(b)(ii)), assigned to ν(ZrH) of the proposed reaction intermediate **2i** (eqn. (2a)).

The proposed IR assignments were supported by calculation of ZrH stretching frequencies of computational models for the species involved in eqns. (1) and (2).[5] The computational models were based on a polyhedral oligomeric silsesquioxane (POSS) framework, for the known adequacy of POSS to mimic silica supported metallic complexes.[6] The selected cluster is derived from the existing Zr(IV) POSS derivative $[(c\text{-}C_6H_{11})_7Si_7O_9]O_3ZrCp^*$,[6c] where the metal centre is bonded by three siloxy bridges to the siliceous cage, and completes its coordination sphere by an anionic ligand, in close analogy with the structure of **1a**. For the calculations, the computationally expensive cyclohexyl group was replaced by fluorine atoms, to model silica's electronegativity: the clusters $[F_7Si_7O_9]O_3ZrH$, $\mathbf{1a_m}$, $[HF_7Si_7O_9]O_2ZrH_2$, $\mathbf{1b_m}$, and $[HF_7Si_7O_9]O_2ZrH(Me)$, $\mathbf{2i_m}$, were used as computational models for the monohydride **1a**, the dihydride **1b**, and the mixed hydride–methyl species **2i**, respectively. The optimized geometries are reported in Fig. 3, while the calculated frequencies and the corresponding observed ones are given in Table 1, showing a good to excellent agreement with the proposed assignments.‡

The partial reaction of **1** with methane was further proven by gas phase analyses. In all the batch-reactor experiments (R = 80, one loading; R = 80, three loadings; and R = 1600, one loading) the amount of dihydrogen evolved was substoichiometric with respect to the expected amount based on eqns. (1) and (2) (*viz.* 0.5, 0.7 and 0.7 H_2/Zr_{tot}, respectively, with respect to the expected 1.25 H_2/Zr_{tot}, **1a** and **1b** being present in a 3:1 ratio in **1**), thus corroborating a partial conversion of **1** to the reaction products.

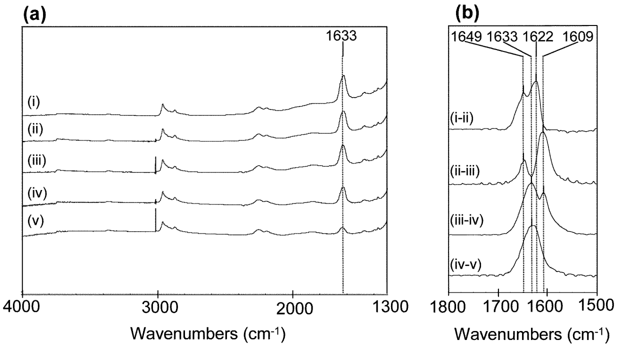
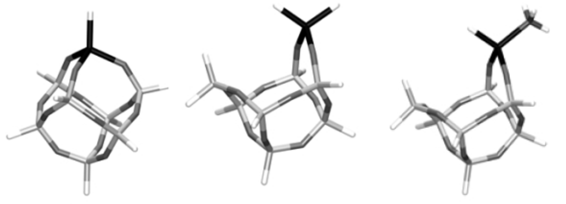


Fig. 2 (a) *In situ* IR-spectra (absorbance) of **1** exposed to CH_4 (550 Torr, three loadings): (i) before addition, (ii) immediately after addition (RT), (iii) at the end of the first loading (15 min at 150 °C), (iv) at the end of the second loading (45 min at 150 °C), (v) at the end of the third loading (500 min at 150 °C), in the 4000–1300 cm^{-1} region. (b) Difference spectra taken from (a): [(i) − (ii)]; [(ii) − (iii)]; [(iii) − (iv)]; [(iv) − (v)] in the 1800–1500 cm^{-1} region.



$\mathbf{1a_m}$ $\mathbf{1b_m}$ $\mathbf{2i_m}$

Fig. 3 Optimized geometries for cluster models of **1a**, **1b** and **2i**.

Table 1 Calculated ν(ZrH) stretching frequencies (cm^{-1}) for $\mathbf{1a_m}$, $\mathbf{1b_m}$ and $\mathbf{2i_m}$ and experimental ν(ZrH) stretching frequencies (cm^{-1}) for **1a**, **1b** and **2i**, with the proposed assignments

Mode	Calculated	Experimental
ν(ZrH)	1632	1633
$\nu_s(ZrH_2)$	1645	1649
$\nu_{as}(ZrH_2)$	1617	1622
ν(ZrHMe)	1614	1609

The Zr–Me bonds in **2a** and **2b** can be cleaved by hydrolysis, releasing methane in the phase gas as the only alkane (ethane and neopentane being released in hundred-fold less quantity), following the well known reactivity of metal alkyl species, see, for example, reaction (3). More interestingly, if such cleavage is carried out by dihydrogen, the starting hydrides are regenerated, therefore proving that reactions (1) and (2) are reversible.

$$\underset{\mathbf{2a}}{[(SiO)_3ZrMe]} + H_2O \rightarrow [(SiO)_3ZrOH] + MeH \qquad (3)$$

As expected, the quantity of methane released during these reactions matched in all cases the dihydrogen that had been released during the synthesis of **2a** and **2b**. The hydrolysis of the methanation product also evolved dihydrogen in the expected quantities, as is consistent with the presence of unreacted **1a** at the end of the reaction.

The data presented hereto point to the existence of thermodynamic and/or kinetic limitations for the reaction of **1** with methane to yield the methylated species $[(\equiv SiO)_2ZrMe_2]$, **2b** (through the mixed species, $[(\equiv SiO)_2ZrHMe]$, **2i**) and $[(\equiv SiO)_3ZrMe]$, **2a**. The computational data, IR data and new experiments carried out under dynamic conditions‡ proved that such limitations are substantially kinetic. Computationally, the slight difference in endothermicity between reactions (2a), (2b) and (1) shows that the reason for the observed difference is not essentially thermodynamic (ΔH_0 = 7.9, 13.5 and 11.7 kJ mol^{-1}, respectively).‡ Ongoing calculations suggest that the reactivity differences are due to different energy barriers, in agreement with existing similar reports.[2i,4a] Deeper insight will be possible upon completion of these preliminary studies, which will be published in due course.

The IR study presented above also shows site heterogeneity in **1**. Fig. 4 reports the plot of the area, A, of the IR ν(ZrH) band *vs.* time, during the three successive methane loadings and the initial slopes in drop in A calculated for each loading (normalized to A = 100 at each methane addition). Such slope represents the overall apparent initial kinetic rate of the reaction(s) occurring on the surface, given the pseudo-first-order condition of the reaction with respect to **1** (*viz.* at the start of each loading the dihydrogen is absent from the gas phase and methane is present in very large excess with respect to **1**). The difference between these initial rates (0.8, 0.6 and 0.3 min^{-1}, respectively) indicates site heterogeneity in **1**, given that the presence of one unique reacting site in **1** would yield equal initial rates.

To further assess the kinetic nature of the limitations at hand on reaction of **1** with methane, an experiment was carried out in a tubular reactor, thus removing thermodynamic limitations by displacement of one of the products, *viz.* dihydrogen. The quantities of dihydrogen evolved remained substoichiometric (0.85 H_2/Zr). Closer inspection of the plot of hydrogen release over time also indicated the existence of roughly three phenomena: a peak in the hydrogen release was observed very rapidly (within the first 50 min, when the reactor is still substantially at RT), a second peak was

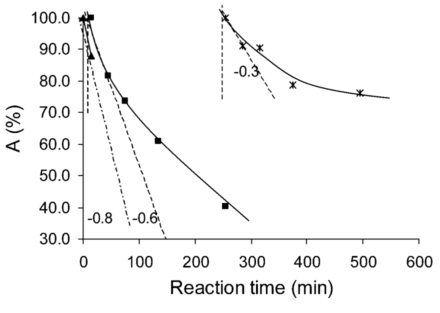


Fig. 4 Plot of the ν(ZrH) area, A (integration limits: 1750–1550 cm^{-1}) *vs.* time (min), during the three successive methane loadings (area normalized to A = 100 at each methane addition).

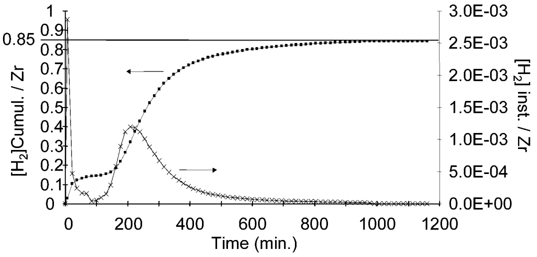


Fig. 5 Plot of hydrogen evolved (mol H_2/mol Zr) *vs.* time (min) during the reaction of **1** with methane in tubular reactor: instantaneous (crosses) and cumulated (squares) quantity of H_2 evolved (P_{CH_4} = 30 bar, 3 N mL min^{-1}, $T_{addition}$ = 298 K, T_{final} = 423 K, ramp 250 °C h^{-1}, 1200 min).

observed within the first 300 min, and finally the hydrogen release died out, and was substantially over after 1000 min (Fig. 5). These data are consistent with the proposed reactions (2a), (2b) and (1), respectively, as they indicate the existence of (at least) three species reacting at different rates with methane under dynamic condition, the latter being the inert monohydride **1a**.

In summary, the reaction of methane with the silica-supported species [(≡SiO)$_3$ZrH], **1a**, and [(≡SiO)$_2$ZrH$_2$], **1b**, obtained simultaneously during the hydrogenolysis of single-site [(≡SiO)ZrNp$_3$], was studied by NMR, IR and GC analysis in batch, autoclave and dynamic reactor conditions. The data indicate that the minor species [(≡SiO)$_2$ZrH$_2$], **1b**, is extremely reactive and completely converted to the dimethyl species [(≡SiO)$_2$ZrMe$_2$], **2b**, through a stepwise H–Me exchange. In contrast, the major species [(≡SiO)$_3$ZrH], **1a** is rather inert: the monohydride is slowly and partly converted to the monomethylated species [(≡SiO)$_3$ZrMe], **2a**, and as many as half of the **1a** sites cannot be converted to the Zr–Me species, even under high pressures (P_{CH_4} = 30 bar), and under dynamic conditions. These experimental data are in good agreement with the conclusions of the theoretical investigations performed on the system.

In conclusion, despite the heterogeneity of the sites, it is has been possible to offer a molecular description of some of the C–H activation pathways of methane on silica-supported Zr-hydrides, differentiating between poorly and highly reactive species toward C–H bond activation of methane (*i.e.* [(≡SiO)$_3$ZrH] and [(≡SiO)$_2$ZrH$_2$], respectively). The lability of the dihydride and the inertness of the monohydride is particularly relevant in the context of the catalytic ability of **1** species to activate alkanes.

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Notes and references

† Typical synthesis of **1** consists in the reaction of H_2 (550 Torr, 150 °C, 12 h) with [(≡SiO)ZrNp$_3$], obtained by impregnation of ZrNp$_4$ on silica previously dehydroxylated at 500 °C.[3] Under these conditions, the average relative ratio of **1a** : **1b** in **1** is 3:1, as confirmed, *inter alia*, by the release of 1.25 mol H_2/mol Zr$_{total}$ during the hydrolysis.[4b–d] The ^{1}H NMR and IR spectra of **1** are reported in Fig. 1(a)(i) and Fig. 2(a), respectively.

‡ Experiments were carried out as follows: (i) *NMR data*: powder of **1** (32 mg, 2.9 wt% Zr), P_{CH_4} = 550 Torr, T = 423 K, 720 min, two loadings, gas phase analysis after each loading (0.5 H_2/Zr and 0.1 H_2/Zr released, respectively); *IR data*: self-supporting silica disk of **1** (10 mg, 2.9 wt% Zr-estimated) pre-treated under vacuum (100 °C, 3 h and 150 °C 30 min, < 0.1 H_2/Zr evolved), P_{CH_4} = 550 Torr, added at RT (three loadings at t = 0, 15, 250 min, gas phase analysis monitored over time for each loading, vacuum at RT before each loading), T = 423 K, t(total) = 500 min; (ii) powder of **1** (749 mg, 2.9 wt% Zr), P_{CH_4} = 30 bar, T = 423 K, 720 min; (iii) powder of **1** (300 mg, 2.9 wt% Zr), P_{CH_4} = 30 bar, 3.0 N mL min^{-1}, T = 423 K, 1200 min; (iv) structure optimizations with Turbomole 5.6, hybrid functional B3-LYP; triple zeta quality basis set (TZVP), with effective core potential approach (ECP) approach for core orbitals of Zr; vibrational frequencies calculated through analytical second derivatives on optimized structures (absence of imaginary frequencies checked). Frequency analysis was performed with a artificial fluorine mass of 100 u in order to suppress spurious coupling with Si–F stretch modes. The calculated frequencies for the Zr–H stretching vibrations, that are in the harmonic approximation, have been scaled by 0.9614 as suggested by Scott and Radom for results obtained with the B3-LYP functional.[5c] The calculated enthalpy differences include ZPE.

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