H/D exchange between CH_4 and CD_4 catalysed by a silica supported tantalum hydride, $(\equiv SiO)_2Ta–H$

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The silica supported tantalum hydride $(\equiv SiO)_2Ta–H$ 1, catalyses the H/D exchange reaction between CH_4 and CD_4 at 150 °C producing the statistical distribution of all methane isotopomers.

Methane is the most thermodynamically stable alkane. Its activation necessarily requires the cleavage of a C–H bond and, for example, the H/D exchange reaction between CH_4 and a deuterium source (D_2, D_2O or a deuterated alkane or arene) is a typical process involving C–H bond activation.[1] Some of the first examples were observed in the 1930s and 1940s using metal surfaces.[2] Numerous examples have appeared since in heterogeneous catalysis,[3] while only few homogeneous systems are known to perform the catalytic H/D exchange with CH_4.[4]

Surface OrganoMetallic Chemistry (SOMC) lies at the interface between homogeneous and heterogeneous catalysis and consists in grafting a molecular organometallic complex onto an oxide or metal surface to generate ultimately single site catalysts.[5] This strategy has led to the synthesis and the characterization of a silica supported tantalum hydride, $(\equiv SiO)_2Ta–H$ **1**, a highly electrophilic complex (formally a eight electron complex).[6] It can activate the C–H bond of cyclic alkanes, to form a tantalum cycloalkyl species, $(\equiv SiO)_2Ta–C_nH_{2n-1}$.[7] It also catalyses both the low temperature hydrogenolysis of alkanes[8] and the new reaction of alkane metathesis,[9] which transforms acyclic alkanes into their higher and lower homologues. Here, we report that **1** also catalyses the H/D exchange reaction between CH_4 and CD_4, leading to the statistical formation of all possible isotopomers.

When a 55:45 mixture of CH_4/CD_4 was contacted with **1** at 150 °C for 10 h, it was converted into a mixture of all the isotopomers of methane as a statistical distribution (Fig. 1).† At low conversion, d_1- and d_3-methanes were formed faster than d_2-methane, suggesting that the H/D exchange was stepwise *via* the exchange of one H/D atom at a time [Fig. 1(a)]. This initial CH_4/CD_4 mixture gave a mixture of methane isotopomers, of which CD_2H_2 was the major product. If a 65:35 mixture of CH_4/CD_4 was contacted with **1** under identical conditions, the evolution toward a different statistical distribution of all isotopomers was observed. The composition of the equilibrated mixture according to GC–MS was 24, 40, 24, 12, 0% of d_0-, d_1-, d_2-, d_3- and d_4-methanes, respectively, in good agreement with the calculated statistical distribution (18, 38, 31, 11, 1.5%), which was no longer centered on CD_2H_2 since there was an excess of H- over D-atoms in the initial mixture.

The number of turnovers for this exchange reaction can be estimated according to eqn. (1) if considering that (a) the formation of CDH_3 and CD_3H requires at least one C–H(D) bond cleavage and formation from CH_4 and CD_4, respectively, and that (b) the formation of CD_2H_2 necessitates at least two C–H bond cleavages and formations from either CH_4 or CD_4

$$\mathrm{TON} = [Q(\mathrm{CDH_3}) + Q(\mathrm{CD_3H}) + 2\,Q(\mathrm{CD_2H_2})]/Q(\mathrm{Ta}) \quad (1)$$

$Q(X)$ represents the amount (in mol) of the compound X.

The number of turnovers as defined in eqn. (1) is underestimated since it does not take into account degenerate processes such as the exchange of a D atom with another D atom. The calculated TON for the H/D exchange is therefore *ca.* 200 after 6 h of reaction. For a comparison, the metathesis of ethane catalysed by the same surface complex **1** under similar experimental conditions has reached a TON of *ca.* 4 after 6 h.[9] The higher activity of **1** for H/D exchange reaction is however not surprising since this process involves C–H in place of C–C bond cleavage for alkane metathesis.

A similar H/D-exchange also occurs between deuterated methane and hydrogen. When a 1:2 mixture of CD_4/H_2 (P_{tot} = 200 Torr) was contacted with **1** (52 mg, 5.2 wt% Ta) at 150 °C, the formation of d_0-, d_1-, d_2-, d_3-methanes could be detected after 40 min by IR spectroscopy. A new stable composition of the gas mixture, containing all the deuterated methanes, was reached after several hours, which corresponded to the statistical distribution of all H/D atoms (7.6, 15.8, 35.8, 26.6, 14.2% of d_0-, d_1-, d_2-, d_3- and d_4-methanes, respectively, *cf.* the calculated theoretical composition of 6, 25, 37.5, 25, 6%). The initial rates obtained in the exchange of CH_4/CD_4 and CD_4/H_2 do not appear to be significantly different, which is in agreement with the cleavage of the C–H bond being the rate-determining step for both transformations.

During the reaction with CH_4/CD_4 mixtures, the evolution of **1** could be followed by *in situ* IR spectroscopy. The addition at room temperature of a mixture of d_0- and d_4-methanes to **1** did not lead to a significant decrease in intensity of the ν(Ta–H) band, centered at 1825 cm^{-1}.[6] However, after 45 min at 150 °C, the ν(Ta–H) band was reduced to about half its initial intensity, and a new band at 1323 cm^{-1} was observed, which corre-

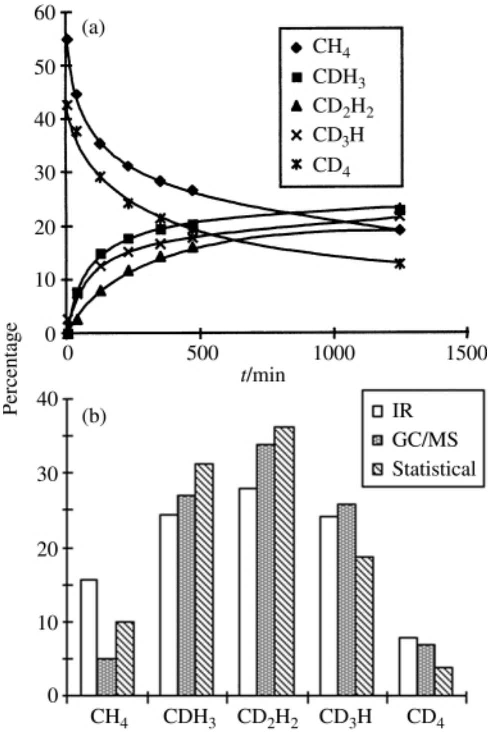

Fig. 1 CH_4/CD_4 exchange reaction (CH_4/CD_4 = 55:45; P_{tot} = 200 Torr; 150 °C, 36 mg of **1** (6.1 wt% Ta)). (a) Isotopomeric composition of the gas phase *vs.* time. (b) Distributions of the different isotopomers at the end of the reaction (2500 min).

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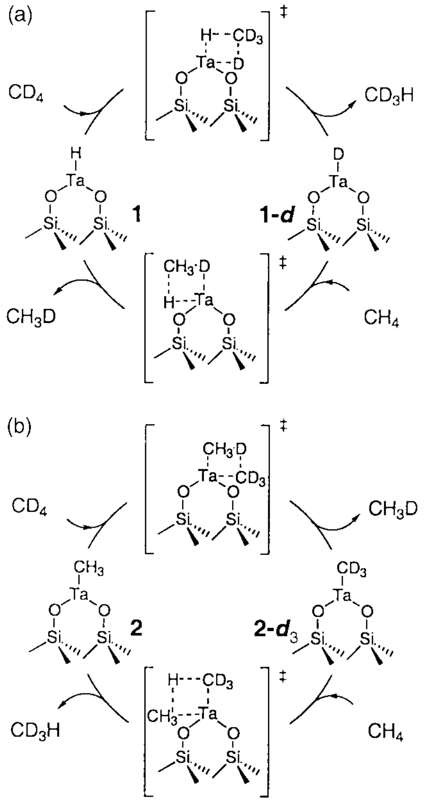
sponded to a ν(Ta–D) vibration.‡ No peaks associated with Ta–CH_3 or Ta–CD_3 were detected, but these types of surface species are usually difficult to observe by IR spectroscopy.[7] In fact, independent experiments showed that hydrolysing the surface species formed after reacting **1** with CH_4 (P = 200 Torr, T = 150 °C, 2 days) gave methane in the gas phase, which probably arose from the hydrolysis of a surface tantalum methyl, $(\equiv SiO)_2Ta–CH_3$ **2**. This consequently shows that **1** can be converted into **2** under the H/D exchange experimental conditions although the complete disappearance of both the Ta–H and Ta–D vibration bands has never been observed.

Two mechanisms for the H/D exchange reaction between CH_4 and CD_4 can be proposed. Both rely on a σ-bond metathesis C–H activation step and involve different active species, *i.e.* **1** or **2** (Scheme 1).



Scheme 1

A two-step experiment, in which **1** is first contacted with CD_4 (step 1) and then with CH_4 (step 2) under the same conditions, should provide a different isotopomeric distribution depending on the reaction mechanism (Scheme 2).

Mechanism (a) : Ta-H + CD_4 ⟶ Ta-D + CD_3H *Step (1)*

Ta-D + CH_4 ⟶ Ta-H + CDH_3 *Step (2)*

Mechanism (b) : Ta-H + CD_4 ⟶ Ta-CD_3 + HD *Step (1)*

Ta-CD_3 + CH_4 ⟶ Ta-CH_3 + CD_3H *Step (2)*

Scheme 2

Therefore, the reaction of CD_4 (30 Torr) with **1** at 150 °C for 3 h (step 1) led to the formation of CD_3H as the sole methane isotopomer in the gas phase. After removing the gas phase, the addition of 20 Torr of CH_4 (step 2) followed by a 3 h reaction at 150 °C gave CDH_3 as the only deuterated product present in the gas phase. This shows that despite the probable formation of Ta–CD_3 species in step 1 (*vide supra*), it does not participate efficiently in the H/D exchange process since CD_3H has not been observed [mechanism (b), step 2]. Consequently, mechanism (a) which only involves Ta–H bonds instead of Ta–C bonds [mechanism (b)] appears to be the most consistent to describe the H/D exchange between methanes. This observation also agrees with previous data relative to the stability of four-center intermediates, in which a carbon atom opposite to the metal [Scheme 1(a)] instead of a hydrogen/deuterium atom [Scheme 1(b)] is preferred.[4e]

In summary, the silica supported tantalum hydride **1** catalyses the H/D exchange reaction in CH_4/CD_4 mixtures. This reaction proceeds under mild conditions and leads to the formation of the statistical distribution of all isotopomers of methane. Its rate is approximately two orders of magnitude faster than that of the alkane metathesis reaction. A mechanism in which the tantalum hydride species is the active intermediate in the catalytic cycle rather than the Ta–CH_3 species is consistent with the experimental observations.

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Notes and references

† A statistical distribution corresponds to a random distribution of all hydrogen and deuterium atoms among the five possible isotopomers of methane and can be calculated by the coefficients of the polynom: $(d_0 + d_4)^4$, where d_0 and d_4 represent the initial amount of non-deuterated and perdeuterated methane, respectively. The consumption of CH_4 and CD_4 as well as the formation of the different isotopomers of methane (d_1, d_2, d_3) were monitored by IR spectroscopy. CH_4, CDH_3, CD_2H_2, CD_3H and CD_4 show characteristic IR bands at 1347 cm^{-1} (CH_4), 1156 cm^{-1}, (CDH_3), 1090 cm^{-1} (CD_2H_2), 1034 cm^{-1} (CD_3H) and 994 cm^{-1} (CD_4). The isotopomeric composition of the gas phase was also measured by GC–MS at the end of the reaction. The determination of the isotopomeric distribution was evaluated by minimizing the sum of the square difference of the respective peaks of calculated theoretical and experimental spectra. The calculated theoretical spectra were generated by incrementing the selectivity of various relative amounts of d_0-, d_1-, d_2-, d_3- and d_4-methanes, which fragmentation patterns were taken from *Compilation of mass spectral data*, ed. A. Cornu and R. Massot, Heyden & Son Limited, London, 1966. The mass spectrum of a mixture of variously labelled methanes was considered according to a peak distribution in the range m/z 13–20.

‡ Changes in the intensity of the Ta–D vibration band are not easily observed since this band appears at the border of the spectral window of silica and is partially truncated.

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