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Dynamic behaviour of tantalum hydride supported on silica or MCM-41 in the metathesis of alkanes[†]

Sophie Soignier, Guillaume Saggio, Mostafa Taoufik, Jean-Marie Basset‡ and Jean Thivolle-Cazat*

The metathesis of ethane and propane catalysed by tantalum hydride supported on silica or MCM-41 was studied under static and dynamic conditions. During the reaction, the rate decreased over time, indicating deactivation of the catalyst. The evolution of the catalytic system and surface species over time was monitored by various physico-chemical methods: FTIR, ¹³C NMR spectroscopy, elemental analysis and chemical reactivity. A carbonaceous deposit composed of unsaturated hydrocarbyl species was observed by ¹³C NMR. This deposit was responsible for poisoning of the catalyst. The deactivation of the catalyst proved more severe at higher temperatures and under static rather than dynamic conditions. A partial regeneration of the catalyst could be achieved during a series of repeated runs. Mechanistically, the deconvolution of the products' distribution over time indicated the occurrence of hydrogenolysis in the early stages of the reaction, while pure metathesis dominated later on. The hydrogen was supplied by the dehydrogenation of hydrocarbyl surface species involved in the deactivation process.

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Introduction

The catalytic transformation of alkanes into valuable products remains an important challenge in chemistry considering the inertness of their C–H and C–C bonds and also the considerable application potential.^{1–5} We reported previously the discovery of the alkane metathesis reaction, where a highly electrophilic tantalum hydride supported on silica, $[(\equivSiO)_2Ta-H]/SiO_2$, 1,⁶ could catalytically transform at moderate temperatures any light alkane into its lower and higher homologues by both cleavage and formation of C–H and C–C bonds (eqn 1):^{7–9}

$$2C_{n}H_{2n+2} \rightleftharpoons C_{n-i}H_{2(n-i)+2} + C_{n+i}H_{2(n+i)+2}$$

$$n \ge 2, \ i = 1, 2...(n-1)$$
(1)

Kinetic studies performed at very low contact times showed that hydrogen and olefins were the primary products of the reaction suggesting that the same intermediates as those involved in olefin metathesis should be involved in this reaction. Further investigations revealed that the reaction occurred on a single site tantalum-carbene-hydride, Ta(=CHR)(H), and involved: (i) C-H activation on the metal

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 ‡ Present address: KAUST Catalysis Center (KCC), King Abdullah University of Science and Technology, Thuwal, Kingdom of Saudi Arabia hydride (Ta–H); (ii) α -H or β -H elimination on the tantalum– alkyl formed; (iii) olefin metathesis on the carbene moiety (Ta=CHR) with metallocyclobutane as a key intermediate, and (iv) hydrogenation of the new formed olefins on the metal hydride (Ta-H).8,10,11 Therefore, to support such a mechanism, a hydro-metathesis reaction was performed using an equimolar mixture of olefin and hydrogen with the same catalyst, which proved ten times more active than alkane metathesis.¹² The use of ¹³C-monolabelled ethane also showed the occurrence of degenerative processes besides the productive one, and the total scrambling of carbons in the various products.^{13,14} Surface complex 1 was obtained by treatment at 150 °C under hydrogen of the perhydrocarbyl surface tantalum complexes $[(\equiv SiO)Ta(=CHtBu)(CH_2tBu)_2]$ and [(=SiO)₂Ta(=CHtBu) (CH₂tBu)], resulting from the reaction of [Ta(=CHtBu)(CH₂tBu)₃],¹⁵ with the OH groups of a fumed silica (Evonik, Aerosil 200 m² g⁻¹) partially dehydroxylated at 500 °C.¹⁶⁻¹⁸ Surface complex [(=SiO)₂Ta-H]/MCM-41, 2, was obtained in a similar way on the mesoporous silica MCM-41 (800 m² g⁻¹).¹⁹ Complexes 1 and 2 were characterized by FTIR, elemental and mass balance analyses, chemical reactions and EXAFS.6,19

The latter technique indicated the presence of two σ -bonded oxygen atoms at 1.9 Å in the first coordination shell of tantalum, as well as several other surface oxygen atoms (probably from \equiv Si–O–Si \equiv bridges) in a close interaction between 2.6 and 2.9 Å for about 50 to 80% of the tantalum sites.^{6,19} Hence, surface tantalum hydride was likely to coexist with a trishydride on the sites free of interactions with donating oxygens.

Université de Lyon, ICL, C2P2 UMR 5265 (CNRS-CPE-Université Lyon 1) LCOMS-CPE-Lyon, 43 Boulevard du 11 Novembre 1918, F-69616, Villeurbanne, France. E-mail: thivolle@cpe.fr

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The reactions of 1 with cycloalkanes, or 2 with methane showed a decrease of the rate over time suggesting a heterogeneity of the surface tantalum sites^{6,19,20} as was also observed in the case of silica-supported zirconium hydride.²¹ Such a behaviour could be related to the presence of interacting surface oxygen atoms which would slow down the reactivity of tantalum hydride species, as did coordinating molecules such as PMe_3 .²² Similar observations have been mentioned in the literature regarding the use of silica-supported lanthanide centres^{23,24} or also a tungsten imido neopentylidene complex,²⁵ as well as reduced Cr(π) sites affording propagating species of various reactivity in polymerisation.^{26,27}

In addition, selective poisoning experiments with dry oxygen pulses on species 1 revealed that only 50% of the tantalum hydride sites were active in the alkane metathesis reaction; active species were assumed to be freed from interaction with the support surface.²⁸ Furthermore, during the alkane metathesis, the reaction rate decreased with time, indicating a deactivation process of the catalyst.⁷⁻⁹ Herein we wish to report a comparative study of the metathesis of ethane and propane on tantalum hydride, using both silica and MCM-41 as supports. The performances of the catalyst were evaluated at different temperatures and pressures under static or dynamic conditions in order to determine the optimal productivity during ethane metathesis. In addition, the deactivation of the catalyst needs to be understood in order to find ways to improve its stability. On-stream deactivation and evolution of the catalytic system and surface species were also monitored by various physico-chemical methods.

Results and discussion

I Study of the metathesis of ethane and propane in a continuous flow reactor

The metathesis of propane catalyzed by the silica-supported tantalum hydride $[(\equiv SiO)_2Ta-H]/SiO_2$, 1, in a continuous flow reactor has been reported previously.⁸ Tantalum hydride $[(\equiv SiO)_2Ta-H]/MCM-41$, 2, was also prepared on mesoporous silica in order to increase the metal content and improve the

characterization.¹⁹ It was used to study the metathesis of ethane and propane under static and dynamic conditions.

Ethane metathesis. The catalyst $[(\equiv SiO)_2Ta-H]/MCM-41,^{19}$ 2, (300 mg, wt% Ta = 11.7) was loaded directly into the continuous flow reactor. The metathesis of ethane was studied at 150 °C with a 3 Nml min⁻¹ flow rate under various pressures (1, 5 and 10 bar); conversions and turnover number (TON) are given in Fig. 1.

The conversions were found to increase rapidly up to maxima of 7, 12 and 17% as a function of pressure, before decreasing to pseudo steady states. Cumulated TON also increased with time and reached respective values of 90, 170 and 230 after 133 h. It turns out that both ethane conversion and TON increased with pressure (Fig. 1). Moreover, the catalyst deactivation appeared moderate when the pseudo steady state was reached. Mainly methane and propane were formed with smaller amounts of iso and *n*-butane. Whatever the pressure, the distribution of products at steady state proved very similar (Table 1).

Considering the product distribution of the reaction under 1 bar (Fig. 2-1), large quantities of methane were evolved initially, whereas a small amount of propane was formed; the curves then converged to reach a plateau after about 33 h (55% for methane and 39.4% for propane). Lower quantities of butane and isobutane were present throughout the reaction (2 and 3%, respectively) as well as traces of hydrogen (about 0.3%). According to the previously proposed mechanism,⁸ butanes necessarily arise from a secondary reaction.

As shown in the enlargement of Fig. 2-1 (0 to 16 h), only hydrogen can be observed initially (Fig. 2-2), while methane appeared during heating of the reactor (50 min). The propane formation started when the reactor temperature reached the plateau. The appearance of hydrogen corresponded to the initiation of the reaction during which the C–H bonds of ethane were activated by species 2; about 80% of species 2 was converted during the activation step after 6 hours according to the infrared study (*vide infra*). The amount of methane increased up to a maximum of 84%, while hydrogen decreased throughout from 100%. As ethane metathesis is expected to produce comparable amounts of methane and



Fig. 1 Conversion (1) and TON (2) *versus* time for ethane metathesis catalyzed by [\equiv SiO)₂Ta-H]/MCM-41, **2**, (300 mg, wt% Ta = 11.7) under 1 (\diamond), 5 (\Box) and 10 (\triangle) bar (150 °C, 3 Nml min⁻¹).

Table 1 Product distribution (%) after 116 h of ethane metathesis on $[(\equiv SiO)_2Ta-H]/MCM-41$, **2**, (300 mg, wt% Ta = 11.7) at different pressures in dynamic conditions (150 °C, 3 Nml min⁻¹)

P (bar)	CH_4	C_3H_8	$\mathrm{iC_4H_{10}}$	nC_4H_{10}	iC ₄ /nC ₄
1	55.3	39.6	3	2.1	1.43
5	54.8	39.5	3.3	2.4	1.37
10	55.5	38.2	3.4	3.4	1

propane, the observed excess of methane should result from another reaction, likely ethane hydrogenolysis.^{29,30} The origin of the hydrogen necessary for such a reaction probably does not arise from the C–H bond activation alone but should also involve other processes related to deactivation (*vide infra*). A similar evolution of products was observed under 5 or 10 bar of ethane.

Propane metathesis. The metathesis of propane was studied in a continuous flow reactor under 1 bar at 150 °C, with a 3 Nml min⁻¹ flow rate. The conversion increased rapidly up to a maximum of 40% (Fig. S1 in ESI†) before decreasing to a pseudo steady state affording a TON of 115 after 116 h.

Concerning the products of the reaction (Fig. 3), a mixture of lower and higher homologues was formed that included methane, ethane, butane, isobutane, pentane and isopentane; the amount of methane decreased progressively along the reaction time, whereas that of the other products reached a pseudo plateau after 40 h. Then after 116 h, the following values were obtained: ethane (49.5%) > butane (31.8%) > pentane (6.8%) > isobutane (4.5%) > methane (4.4%) > isopentane (2%) > hydrogen (0.9%). These data proved quite comparable to those obtained in the case of the Aerosil-silica as support.⁸

The enlargement of Fig. 3-1 at the beginning of the reaction (Fig. 3-2) shows firstly the sole presence of hydrogen, followed by the appearance of methane and ethane during heating of the reactor; both these products passed through maxima (47 and 43.1%, respectively) when the temperature reached the plateau. In parallel, the amount of hydrogen decreased. Again the formation of higher homologues, butane, isobutane, pentane and isopentane, started when the temperature reached the plateau.

The formation of hydrogen again corresponded to the initiation of the reaction during which the C–H bond activation of propane on species 2 took place; differing from ethane, this activation step proceeded rapidly since after 30 min about 90% of the v(Ta-H) bands were lost according to the infrared study (*vide infra*). The initial formation of methane and ethane was likely the result of propane hydrogenolysis.^{29,30} As for ethane, such a process is likely related to the deactivation process. Butane formation indicated that the metathesis reaction had started, which also contributed to the formation of methane and ethane.⁸

Deconvolution of hydrogenolysis and metathesis reactions during the whole process

Case of ethane. In order to evaluate to what extent the hydrogenolysis reaction can occur alongside the metathesis, some calculations were made using the products'



Fig. 2 Products distribution *versus* time for ethane metathesis under 1 bar, 3 Nml min⁻¹ and 150 °C, catalyzed by [$(=SiO)_2Ta-H]/MCM-41$, **2**, (300 mg, wt% Ta = 11.7): (1) alkanes and H₂ selectivities; (2) enlargement of the dashed region [0–16 h].



Fig. 3 Products distribution *versus* time for propane metathesis under 1 bar, 3 Nml min⁻¹ and 150 °C, catalyzed by [(\equiv SiO)₂Ta–H]/MCM-41, **2**, (300 mg, wt% Ta = 11.7): (1) alkanes and H₂ selectivities; (2) enlargement of the dashed region [0–16 h].

distribution previously obtained, to deconvolute both processes; as metathesis is assumed to produce equimolar quantities of higher and lower homologues, any excess of the latter was ascribed to hydrogenolysis (see ESI† for the calculation method).

The total TOF (turnover frequency) of the reaction was first plotted versus reaction time for the various experiments performed under 1, 5 and 10 bar of ethane (Fig. 4-1). As observed for the conversion of ethane, the TOF presented maxima which increased with pressure; the following pseudo plateau for each of them was also situated at a higher value when the pressure was higher. Under 1 and 5 bar, two maxima were observed, whereas under 10 bar they coalesced, probably because of the contact time which increased with the pressure. Starting from the distribution of the various deconvoluted products, this TOF was between the hydrogenolysis and the metathesis reactions.

Fig. 4-2 shows ethane hydrogenolysis TOF. As in the previous case, the TOF over time presented two maxima under 1 bar, which progressively coalesced when the pressure reached 10 bar. Again, the height of these maxima increased with the pressure; the maximal rates of the pure hydrogenolysis obtained under 10, 5 and 1 bar corresponded to the following values: 4.3, 3.24 and 2.16 mol of ethane (mol Ta)⁻¹ h⁻¹, respectively. After 8 h, this TOF became very small and close to 0. The presence of the first maximum corresponded to the temperature plateau accompanied by the C–H bond activation step on species 2; the second peak is assigned to a dehydrogenation process during the start of the metathesis reaction, involving also the deactivation of the catalyst. Fig. 4-3 corresponds to the TOF of the pure ethane metathesis which presented only one maximum for each

pressure and pseudo plateau situated at different values according to the pressure; the values of the maxima and of the pseudo plateau increased with the pressure. The maximal rates of the pure metathesis obtained under 10, 5 and 1 bar corresponded to the following values: 3.4, 2.48 and 1.48 mol of ethane (mol Ta)⁻¹ h⁻¹; from these maxima a decrease of the rates was observed indicating the deactivation of the catalyst. In the range of 16-41 h, corresponding to the pseudo plateau, the TOF of pure metathesis decreased twice as fast under 10 bar than under 1 bar. This deactivation process could lead to the formation of hydrogen, explaining the presence of a second peak in the figures related to the hydrogenolysis or the total TOF (Fig. 4-1 and 4-2). From Fig. 4-2 and 4-3, the contribution of the metathesis reaction in the global process during the reaction time was deduced (Fig. 4-4). Independently from the pressure, the evolution of the various curves appears very close, which indicates that the effect of pressure on the rates of hydrogenolysis and metathesis was comparable. For each experiment, it clearly appears that the contribution of the hydrogenolysis was high at the beginning, whereas that of the metathesis reaction increased rapidly afterwards; after 33 h, the contribution of this latter ranged between 97 to 100% for the various pressures employed.

Again, the occurrence of a hydrogenolysis reaction at the beginning of the process raised the question of the source of the hydrogen. First of all, in each experiment a hydrogen release was detected at the beginning of the reaction; Fig. 5-1 showed a first peak at room temperature giving the same amount of hydrogen evolved per tantalum (about $0.25 H_2$ per Ta) for each experiment; this value can correspond to the liberation of hydrogen from a tantalum trishydride species (about



Fig. 4 Ethane metathesis (at 150 °C, 3 Nml min⁻¹) catalyzed by [$(\equiv SiO)_2Ta-H]/MCM-41$, **2**, (300 mg, wt% Ta = 11.7) under 1 (\diamond), 5 (\Box) and 10 (\triangle) bar: (1) total TOF; (2) TOF of hydrogenolysis reaction; (3) TOF of metathesis reaction and (4) percentage of metathesis contribution *versus* time.

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25%) since the activation of ethane cannot take place significantly under these conditions. As reported in the literature, the formation of a σ -alkane complex can be envisaged which would help with the hydrogen release.³¹ When the temperature was raised, a second peak appeared, corresponding to the C–H bond activation of ethane. This peak decreased faster under pressure, probably because the space velocity of the reactant gas decreased inside the reactor when the pressure increased, thus raising the contact time (Fig. 5-1).

Then, the hydrogen corresponding to the C-H bond activation of ethane would react and be consumed more significantly under pressure to perform hydrogenolysis. Thus, the cumulated amounts of hydrogen liberated per tantalum varied from 0.6 to 1.2 when the pressure decreased from 10 to 1 bar (cf. Table 2). Naturally, this hydrogen detected by GC was not consumed in hydrogenolysis. Therefore, the distribution of the various products was also used to evaluate the amount of hydrogen responsible for the excess of lower homologues, *i.e.* methane, resulting from hydrogenolysis (see ESI[†] for the details of the calculations). Fig. 5-2 shows that the amount of hydrogen increased with pressure and the reaction time. After 41 h, 3.9 (1 bar), 5.2 (5 bar) and 7.9 (10 bar) mol H₂ per mol Ta were determined. Table 2 sums up the various data concerning (i) the hydrogen detected, (ii) the hydrogen which participated in the hydrogenolysis and (iii) that arising from the deactivation process, deduced from (i) and (ii) (see the details of the calculations in Table 2). It turns out that the amounts of the last two types of hydrogen increased with the pressure. Since the pressure increased the contact time and

the surface concentration of the reactants and products, this could favour the dehydrogenation process.

Case of propane. The deconvolution between hydrogenolysis and metathesis was also applied to the case of propane. In general, under 1 bar at 150 °C, propane behaved similarly to ethane with the particularity of showing a sharp and unique initial maximum for the total TOF of hydrogenolysis and metathesis, as well as for the TOF of each reaction (Fig. S2[†]). IR analysis indicated that the C-H activation of propane was faster than that of ethane (v(Ta-H)) bands disappeared within 30 min) and the deactivation proved to be more rapid. This data explains why no separation of peaks corresponding to these two processes was observed. Therefore, the percentage of metathesis reached a plateau faster, with a value of about 95.5%, slightly lower than in the case of ethane (96.5 to 99.5%). Even with some experimental error, it seems that some hydrogenolysis was occurring during the reaction due to some possible residual deactivation. In fact, in the range of 16-41 h corresponding to the pseudo plateau, the TOF of the pure metathesis of propane decreased 2.5 times faster than in the case of ethane. The propane metathesis maximum TOF appeared to be about 3 times higher than that of ethane with a value of 5.17 mol of propane (mol Ta)⁻¹ h⁻¹, instead of 1.48 mol of ethane $(mol Ta)^{-1} h^{-1}$.

Regarding the detected hydrogen per tantalum (Fig. S3-1†), the first peak evolved at room temperature corresponded to an amount (0.29 H₂ per Ta) comparable to the case of ethane (0.25 H₂ per Ta), The second peak, previously assigned to

Table 2 Estimate of hydrogen produced by a dehydrogenation process of surface species in ethane metathesis after 39 h						
Pressure	Total H ₂ detected	Total H ₂ needed for hydrogenolysis	Total H_2 coming from deactivation ^{<i>a</i>}			
(bar)	(mol per mol Ta)	(mol per mol Ta)	(mol per mol Ta)			
1	1.1	3.85	2.7			
5	0.7	5.2	3.65			
10	0.6	7.9	6.25			

^{*a*} H₂ coming from deactivation was determined as the sum of the second and third columns, to which an amount of 2.25 H₂ arising from a mixture of 25% (TaH₃) and 75% (Ta–H) was subtracted. Indeed, H₂ needed for hydrogenolysis = H₂ arising from deactivation + H₂ coming from Ta–hydrides – H₂ detected. From ref. 19 (EXAFS) and 28, it was deduced that the tantalum hydrides were a mixture of 25% (TaH₃) and 75% (Ta–H) which contributed to H₂ release and C–H bond activation for a total amount of 2.25 H₂ produced per Ta when a trisalkyl–tantalum complex was formed.

C-H activation, was smaller because the propane is expected to have been consumed more rapidly by the hydrogenolysis. The amount of hydrogen necessary for the hydrogenolysis reaction grew continuously over time (Fig. S3-2†). This suggests a continuous residual deactivation process supplying this hydrogen throughout the reaction. After 41 h, the hydrogen coming from the deactivation process was estimated to be 8.35 H₂ per Ta (Fig. S3-2†: 10 H₂ per Ta needed for hydrogenolysis + 0.6 H₂ per Ta detected – 2.25 H₂ per Ta coming from Ta-hydrides). By comparison with the value obtained in similar conditions with ethane (2.7 H₂ per Ta), this amount of hydrogen indicated a stronger deactivation in the case of propane.

II Effect of reaction conditions on the deactivation of the catalyst

Comparison of alkane metathesis performed under batch or dynamic conditions. In the light of the previous discussion, it was interesting to compare the evolution of the metathesis reaction performed in a batch or in a continuous flow reactor for ethane and for propane as illustrated in Fig. 6. It appears that for both gases a higher TON was reached in the continuous flow reactor; for instance, after 100 h, TONs of 73 and 105 (dynamic) instead of 31.5 and 50.5 (batch) were respectively obtained for ethane or propane. Conversely, the catalyst underwent a higher deactivation in the batch conditions. Furthermore, the selectivity proved better in the case of the continuous flow reactor since in the batch conditions a higher amount of lower homologues was observed (Table S1[†]). Indeed, under the latter conditions, neither hydrogen nor the reaction products could be eliminated by the gas flow; the products can then undergo further reactions, hydrogenolysis and dehydrogenation on the catalyst surface, which can progressively inhibit the active sites.

Effect of the reaction temperature on the deactivation process. The possible effect of the reaction temperature on the deactivation was also studied. Fig. S4 (ESI[†]) represents the evolution of TON *versus* time for different reaction

temperatures (150, 200 and 250 °C) in the metathesis of ethane. It turns out that the initial rate increases with temperature and the evolutions of the TON at 200 and 250 °C are very close and somewhat homothetic to the curve at 150 °C (Fig. S4†). Concerning the product distribution, it appears that at higher temperatures, methane was favoured relatively to the higher products (Table S2†). A possible explanation is that the dehydrogenation reactions were favoured by the temperature which increases the deactivation and the resulting hydrogen supply; similarly, the hydrogenolysis was also favoured.

Study of the regeneration of the catalyst under hydrogen. The regeneration of the catalyst was checked in the case of the silica-supported tantalum hydride $[(\equiv SiO)_2Ta-H]/SiO_2, 1$, during a series of catalytic runs of propane metathesis performed on the same catalyst in a batch reactor (Fig. 7). After each run performed at 150 °C, the catalyst was treated under hydrogen at 150 °C for 15 h, in order to hydrogenolyse the hydrocarbyl species which could have formed on the surface. Indeed, during such a treatment, an evolution of methane was observed.

It turns out that after each regeneration treatment under hydrogen, the catalytic activity was partially restored but a decrease in TON of about 15% was observed; however, a prolonged treatment under hydrogen (run 5) resulted in a better activity recovery. An average of 1.6 \pm 0.3 mol CH₄ per mol Ta was evolved at each regeneration and 2.9 mol after 36 h. The deactivation of the catalyst can have different origins: formation of unsaturated tantalum species and/or blocking of active sites by coke or polymers, as reported for different supported olefin metathesis catalysts. Two approaches were used to elucidate this point. The first one was to study at a molecular level the evolution of the surface species during the metathesis reaction by infra-red and solid state NMR spectroscopy. The second one consisted of the determination of the nature of hydrocarbyl-tantalum species by hydrolysis of the catalyst at different reaction times.



Fig. 6 Comparison of alkane metathesis catalyzed at 150 °C by $[(=SiO)_2Ta-H]/MCM-41$, **2**, and performed under batch (empty symbols, P = 0.8 bar) or dynamic conditions (full symbols, 3 Nml min⁻¹, 1 bar) for ethane (\mathbf{v} , ∇) or propane (\mathbf{u} , \Box).

Fig. 7 Propane metathesis catalyzed by [(\equiv SiO)₂Ta–H]/SiO₂, **1**, in a batch reactor (P = 0.8 bar, T = 150 °C): evolution of the TON *versus* time, obtained during a series of alternate run and regeneration processes ($P_{H_2} = 0.8$ bar, T = 150 °C, t = 15 h); run 5 was performed after a regeneration time of 36 h.

III Study of the evolution of surface species during the metathesis reaction

Monitoring of C-H bond activation of alkanes and metathesis reaction by IR spectroscopy. The study by IR spectroscopy of the C-H bond activation of methane at 150 °C by tantalum hydride supported on MCM-41, 2, has been reported previously; it showed a decrease of the ν (Ta-H) bands but the reaction rate decreased with time, indicating the presence of less reactive tantalum sites.¹⁹

Case of ethane. Similarly, in the case of ethane, the evolution of the tantalum hydride [(=SiO)₂Ta-H] supported both on silica or MCM-41 was monitored by IR spectroscopy during the metathesis performed at 150 °C in a batch reactor. Several spectra were recorded at various reaction times. At the beginning of the reaction, the v(Ta-H) bands centred at 1830 cm⁻¹ decreased rapidly, but again the reactivity of tantalum hydride slowed down over time as observed in the case of methane. The curves differed slightly according to the support but showed the same trend (Fig. 8). Different behaviour for the species supported on Aerosil and MCM-41 was also mentioned previously in the case of zirconium.³² In parallel, v(C-H) and δ (C-H) vibration modes corresponding to alkyl groups increased progressively to reach a plateau of intensity in the same period of time (Fig. S5[†]). More precisely, the v(C-H) bands at wavenumbers of 2956, 2905, 2864, and 2815 cm⁻¹ were assigned to $v_{as}(CH_3)$, $v_{as}(CH_2)$, $v_s(CH_3)$, and $v_{\rm s}({\rm CH}_2)$ vibration modes. Concerning $\delta({\rm CH})$ bands, mainly two peaks at wavenumbers of 1466 cm⁻¹, corresponding to $\delta_{as}(CH_3)$ and $\delta_{s}(CH_2)$, and 1364 cm⁻¹ corresponding to $\delta_{\rm s}({\rm CH}_3)$ were observed. These bands showed no significant evolution after 5-6 hours, which means that the IR technique did not prove sensitive enough to perceive any change in the surface species.

Case of propane. In the same way, the evolution of tantalum hydride supported on MCM-41 was also monitored by IR spectroscopy during the metathesis of propane performed at 150 °C in a batch reactor. The C-H bond



Fig. 8 Evolution of the intensity of ν (Ta–H) bands *versus* time during the activation at 150 °C of methane (\blacksquare), ethane (▲, \triangle) and propane (\blacklozenge , \diamond) ($P_{C_n,H_{2m+2}} = 0.8$ bar), on tantalum hydride supported on MCM-41 (full symbols) or Aerosil silica (empty symbols).

activation step was more rapid in this case, since the intensity of the v(Ta-H) bands decreased rapidly and, after 1.5 h at 150 °C, only a very small band remained apparent on the IR spectrum (Fig. 8). The higher reactivity of propane compared to ethane can be related to a stronger adsorption of the gas on the catalyst surface, as it was shown that the latter increased with the molecular weight of the alkane.²⁰ Conversely, methane was seen to react even more slowly than ethane, as shown in Fig. 8. Moreover, the C–H bond energy decreases in the order CH₄ (104.9 kcal mol⁻¹) > C₂H₆ (101.1 kcal mol⁻¹) > n-C₃H₈ (100.4 kcal mol⁻¹) > i-C₃H₈ (98.6 kcal mol⁻¹),³³ which could influence the reactivity with [(\equiv SiO)₂Ta–H] in the same direction.

As observed with ethane, v(C-H) and $\delta(C-H)$ bands appeared progressively, the intensities of which rapidly reached a plateau. They correspond to wavenumbers situated at 2962, 2938, 2911 and 2873 cm⁻¹, and 1463 and 1369 cm⁻¹, somewhat similar to those obtained with ethane (Fig. S6†).

Characterization of surface species by hydrolysis of the catalyst at different reaction times. Several alkyl, alkylidene or alkylidyne compounds of early transition metals are known to react with water affording the liberation of the corresponding alkane. This method has been widely used in surface organometallic chemistry to characterize the perhydrocarbyl-complexes of Ti, Zr, Hf, Ta and W present at the surface after grafting on oxide supports, via the GC analysis of the liberated alkanes.³⁴ It was also used to titrate the alkyl ligands issued from a C-H bond activation of an alkane on a supported metal-hydride.^{6,20,34,35} Thus, the analysis by GC of alkanes liberated by the hydrolysis of surface species with different conversions should account for the distribution of the hydrocarbyl groups linked to the tantalum during alkane metathesis. Fig. 9 presents the distribution of alkanes evolved after different reaction times for the metathesis of ethane or propane performed at 150 °C in a batch reactor with $[(\equiv SiO)_2Ta-H]/SiO_2, 1.$

The results obtained in Fig. 9 show that in each case, the main gas liberated by hydrolysis was the reagent ethane or propane, representing around 65 and 45% respectively; a certain quantity of methane was also present. A significant amount of neopentane was also released at any reaction time, around 25%, suggesting that some low-reactive tantalum centres bearing neopentyl or neopentylidene groups have not undergone hydrogenolysis during the preparation of the hydride from the tantalum-hydrocarbyl precursor. The other compounds correspond to the products of metathesis and appear in weaker amounts in both cases (total 6–15%). After a period of 48 h, some olefins were detected.

After a short reaction time, the amount of alkanes evolved ranged between 1.4 to 1.8 mol per Ta, depending on the precise reaction time, the reagent or the temperature, whereas hydrogen varied between 0.4 to 0.6 mol per Ta (Fig. 10). These values decreased during the reaction time to stabilize below unity for the alkanes and close to zero for hydrogen when the reaction was conducted at 150 $^{\circ}$ C; this indicates that non hydrolysable species were growing on some



Fig. 9 Distribution of hydrocarbons liberated by hydrolysis of the catalyst at different reaction times during ethane (1) or propane (2) metathesis performed at 150 °C on [(=SiO)₂Ta-H]/SiO₂, **1**, in batch conditions (0.8 bar).



Fig. 10 Number of mol of alkanes and hydrogen per Ta, liberated by hydrolysis of surface species at various reaction times of alkane metathesis performed in batch: ■, □ alkanes; ◆, ◇ hydrogen: (1) metathesis of ethane on [(=SiO)₂Ta–H]/SiO₂, 1, at 150 °C (full symbols), or [(=SiO)₂Ta–H]/MCM-41, 2, at 200 °C (empty symbols); (2) metathesis of propane on [(=SiO)₂Ta–H]/SiO₂, 1, at 150 °C.

tantalum sites which were poisoned. Moreover, the curves decreased more rapidly in the case of propane (Fig. 10-2) compared to ethane, showing a stronger deactivation. Similarly, the curve decrease was quicker for ethane metathesis conducted at 200 °C versus 150 °C, again in relation with a faster deactivation. Interestingly, the curves tend to extrapolate to a value of two for alkanes and one for hydrogen at reaction time zero; this would correspond to an average formula $[(\equiv SiO)_2Ta(H)(R)_2]$ which may be looked at as the precursor of the active form of the catalyst, the alkyl-alkylidene tantalum species [(=SiO)₂Ta(=CH-R')(R)].⁸ If we consider that the remaining active Ta species keep the same structure, it can be deduced that 50 to 65% of tantalum sites and probably the most active ones were poisoned after about 50 h at 150 °C. Some remaining neopentyl groups were also displaced from tantalum during the metathesis reaction since the total amount of alkanes evolved decreased with time and the proportion of neopentane stayed rather constant (Fig. 9).

In order to get further information, the deuterolysis of these surface species in the case of propane was performed using CD_3OD . The products were analyzed by GC–MS and the same distribution of alkanes as in the case of water (Fig. 9) was obtained with various deuteration degrees and a

proportion of isotopomers slightly changing with reaction time. In a global observation, d_0 and d_1 alkanes tended to decrease with reaction time, from around 40 to 20% and 55 to 40%, respectively. Conversely, d_2 and d_3 alkanes tended to increase from 8 to 25% and 5 to 15%, respectively. The presence of d_0 alkanes can be explained by the occurrence of α -H elimination processes between alkyl ligands,¹⁵ whereas that of d_2 and d_3 alkanes suggests the formation of alkylidene and unexpected alkylidyne tantalum species.

Study of the evolution of surface species during alkane metathesis by solid state NMR. In order to get more information about the surface species which form during alkane metathesis, ¹³C NMR spectra of the catalyst were recorded at the end of each run of ethane metathesis performed at 150 °C under the various pressures in the continuous flow reactor (*cf.* Fig. 1). They all showed a series of peaks at 12, 20 and 30 ppm and other broad peaks around 110 and 130 ppm (Fig. S7†). The first series of peaks likely corresponds to alkyl chains; particularly the peak at 30 ppm may be assigned to the methyl groups of tantalum-bonded neopentyl fragments evidenced by hydrolysis (*vide supra*). The second series should be related to unsaturated products, responsible for the liberation of hydrogen and of the catalyst deactivation at the same time. The pressure proved to slightly

favour the formation of these carbonaceous species as confirmed by the elemental analysis performed in parallel (4.8 C per Ta under 1 bar and 6.1 C per Ta under 10 bar). Indeed, the pressure raises the contact time; thus, the reactant stream was less able to sweep off the products which could dehydrogenate more significantly and become poisons.

Furthermore, the formation of unsaturated products proved higher at 200 °C under static conditions than at 150 °C, as the NMR spectra showed better resolved peaks, particularly at 110 and 120 ppm (Fig. S8†). Elemental analysis confirmed a higher amount of deposited carbon with 7.3 C per Ta at 200 °C instead of 4.8 C per Ta at 150 °C. This is also in agreement with the stronger deactivation observed in catalysis at higher temperatures (Fig. S4†).

In the same way, a 13 C NMR spectrum recorded at the end of propane metathesis (Fig. S9†) performed at 200 °C and 1 bar showed similarly, two series of peaks around 20 ppm and 110–130 ppm with a high intensity. The elemental analysis of carbon also indicated a higher accumulation of carbonaceous deposit in the case of propane compared to ethane with a ratio C/Ta = 8.8 *versus* 7.3 for ethane.

Use of ¹³C bi-labelled ethane. To improve the observation of surface species formed during the metathesis reaction, ¹³C bi-labelled ethane was used. As previously, the metathesis with the ¹³C bi-labelled ethane was performed on [(=SiO)₂Ta-H]/MCM-41, 2, at 200 °C under 0.8 bar during 30 min, 2 h and 50 h (Fig. 11). The ¹³C CP MAS NMR spectrum after 30 min of reaction presented five main peaks centred at 9, 20, 33, 56 and 65 ppm with shoulders at 75 and 88 ppm. As observed in the case of methane, two weak peaks were present at 220 and 305 ppm, which can be assigned respectively to carbene and carbyne species.³⁶ With increasing reaction time, the spectrum evolved significantly; in particular the broad peak centred at 60 ppm (corresponding reasonably to tantalum-alkyl species) decreased notably for the benefit of new peaks at 110 and 130 ppm which increased (Fig. 11b). After 50 h (Fig. 11c), the spectrum obtained was fairly similar to that found with non-labelled ethane (Fig. S7[†]) with peaks corresponding to methyl groups (12-20 ppm) and unsaturated species (110-130 ppm). The peak at 130 ppm

 $\begin{array}{c} 110 & 20 \\ 130 & 88 & 56 \\ (b) & & & & & & \\ (a) & 305 & 220 \\ \hline & & & & & & & \\ 330 & & & & & & \\ (a) & 305 & 220 \\ \hline & & & & & & & \\ 350 & 300 & 250 & 200 & 150 & 100 & 50 & 0 & -50 \\ ppm \end{array}$

Fig. 11 ¹³C CP MAS NMR spectra of surface species obtained after metathesis of ¹³C bi-labelled ethane (0.8 bar) on $[(=SiO)_2Ta-H]/MCM-41$, **2**, at 200 °C in batch conditions, during 30 min (a); 2 h (b); 50 h (c).

corresponds to a range of aromatic species. The peak at 110 ppm was previously observed when tantalum hydrides interacted with cyclopentane leading to tantalum-cyclopentadienyl species.^{28,37}

In order to establish a parallel with the hydrolysis experiments (vide supra), the last sample (Fig. 11c) was treated with a vapour of acetic acid and the corresponding NMR spectrum was recorded (Fig. 12). It appears that the peaks at 110-130 ppm were not much affected by this treatment; only the peaks at 12-20 ppm decreased comparatively and the small peaks between 50 and 100 ppm disappeared. The former species (110-130 ppm) then appeared strongly bonded to tantalum and capable of withstanding hydrolysis; reasonably, they should be responsible for the catalyst deactivation during alkane metathesis. On the contrary, the other peaks which disappeared would correspond to species affording the liberation of hydrocarbons during hydrolysis (Fig. 9 and 10). Indeed, the treatment with acetic acid liberated $0.34 C_n$ per Ta (0.3 C_n per Ta in the case of H_2O) corresponding to 0.57 equiv. C₁ per Ta (0.6 equiv. C₁ per Ta in the case of H₂O); the distribution of alkanes and alkenes was comparable to that obtained with water vapour.

In order to investigate the possibility of regeneration of the catalyst, the surface species also underwent treatment under H₂ at 150 and 200 °C for various periods of time (Fig. 13). The treatment at 150 °C for 15 h did not modify the NMR spectrum significantly (Fig. 13b); however some alkanes were evolved in the gas phase (0.62 C₁, 0.33 C₂, 0.11 C₃ per Ta or 1.61 equiv. C₁ per Ta). After 15 h at 200 °C, only the peak at 50 ppm disappeared and, if the treatment was prolonged for 24 h more, the peaks became thinner but remained at 12, 22, 30, 115 and 130 ppm. At the end, a mixture of C₁ to C₃ alkanes (corresponding to 3.6 total equiv. C₁ per Ta) was liberated in the gas phase, whereas 1.9 C per Ta remained on the solid according to elemental analysis. It is interesting to note that the treatment under hydrogen at 150 °C and 200 °C allows the elimination of more carbon (3.6 total equiv. C_1 per Ta) from the surface than the hydrolysis (0.6 total equiv. C1 per Ta with water or acetic acid). This is a reason why a partial regeneration could be achieved as observed above (Fig. 7). It is likely that hydrolysis only cleaves the Ta-C bonds of Ta-alkyl and Ta-alkylidene species, while



Fig. 12 ¹³C CP MAS NMR spectra of surface species obtained after metathesis of ¹³C bi-labelled ethane (0.8 bar) on [$(=SiO)_2Ta-H]/MCM-41$, **2**, at 200 °C in batch conditions, 50 h (a); then treatment of (a) under a vapour of acetic acid (b).



Fig. 13 ¹³C CP MAS NMR spectra of surface species obtained after metathesis of ¹³C bi-labelled ethane (0.8 bar) on $[(\Longrightarrow SiO)_2Ta-H]/MCM-41$, **2**, at 200 °C in batch conditions, 50 h (a); treatment of (a) under 0.8 bar of H₂ at 150 °C, 15 h (b); treatment of (b) under 0.8 bar of H₂ at 200 °C, 15 h (c); treatment of (c) under 0.8 bar of H₂ at 200 °C, 24 h (d).

hydrogenolysis should be able to also cleave the C–C bonds of the strongly bonded species. It is surprising that the presence of part of the peaks at 12, 22 and 30 ppm assigned to methyl or methylene groups indicates resistance to the treatment by acetic acid or by hydrogenolysis at 200 °C. These peaks seem to be associated with those at 115 and 130 ppm, which also remained after these treatments. These various peaks could correspond to strongly bonded cyclic or linear olefinic species (115 and 130 ppm) with possible alkyl substituent (12, 22 and 30 ppm); particularly, tantalumcyclopentadienyl species giving a peak at 115 ppm were seen to totally poison the catalyst during the hydrogenolysis of cycloalkanes.³⁷

In summary, the evolution of the catalyst during the alkane metathesis reaction was studied using the harsher conditions which favoured the deactivation, that is in a batch reactor and at higher temperatures. The deactivation proved moderate under dynamic conditions and mild temperature. IR spectroscopy allowed us to follow the evolution of the tantalum hydride at the beginning of the reaction but did not yield precise information on the nature of the resulting surface species. The hydrolysis of surface species at different times of reaction revealed the presence of a Ta-hydrocarbyl species likely related to the metathesis catalytic process itself, whereas ¹³C NMR showed the strongly bonded surface species to be responsible for the deactivation of the catalyst.

Conclusion

The origin of the deactivation of the catalyst during the metathesis reaction of ethane and propane under static and dynamic conditions was discussed. In the early stages of the reaction, a dehydrogenation of the hydrocarbyl surface species was shown to take place leading to the formation of an unsaturated poisoning carbonaceous deposit. In parallel, the hydrogen produced by this process led to an alkane hydrogenolysis side-reaction, which became rapidly limited in the time. Studies are in progress to improve the reaction conditions as well as the catalyst formulation in order to avoid the occurrence of such deactivation.

Experimental section

General procedures

All experiments regarding the handling of air sensitive compounds were carried out under a dry argon atmosphere using standard Schlenk and glove-box techniques. For the synthesis and treatment of the surface species, high-vacuum lines (1.34 Pa) and glove-box techniques were used. Diethyl ether and pentane were used directly from the solvent dispenser mBRAUN MB SPS-800. All gaseous alkanes and hydrogen (N25, Air Liquide) were purified over freshly regenerated X-11 BASF catalyst/molecular sieves (4 Å) prior to use. $[Ta(=CHtBu)(CH_2tBu)_3]$ was prepared as described in the literature.¹⁹ $[(=SiO)_2Ta-H]/SiO_2$, 1,⁶ and $[(=SiO)_2Ta-H]/MCM-41$, 2,¹⁹ were prepared as reported previously.

Elemental analyses were performed at the University of Bourgogne in Dijon for carbon, and at the Service Central d'Analyse in Solaize (France) for tantalum.

Transmission IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer, using an airtight glass cell equipped with CaF_2 windows.

¹H MAS and ¹³C CP-MAS solid-state NMR spectra were recorded on a Bruker Avance-500 spectrometer with a conventional double-resonance 4 mm CP-MAS probe at the Laboratoire de Chimie Organométallique de Surface in Ecole Supérieure de Chimie Physique Electronique de Lyon (ESCPE). The samples were introduced under argon in a glove-box into a 4 mm zirconia rotor, which was then tightly closed. The spinning frequency was set to 10 kHz for all the experiments reported herein. Chemical shifts were given with respect to TMS as the external reference for the ¹H and ¹³C-NMR. The ¹³C CP NMR spectra were recorded under proton decoupling TPPM-15. The contact time for CP was 2 ms. An exponential line broadening of 50 Hz was applied before Fourier transformation.

Monitoring of the metathesis reaction in an infrared cell

Silica or MCM-41 (50 mg) were pressed into a 17 mm selfsupporting disk and put into the IR glass cell, then treated at 500 °C under vacuum (1.34 Pa) for 15 h. The $[Ta(=CHtBu)(CH_2tBu)_3]$ complex was sublimed at 80 °C onto the silica disk; the excess of physisorbed complex was removed by a reverse sublimation at 80 °C and trapped in liquid nitrogen. After evacuation of argon, dry hydrogen (80 kPa) was introduced into the cell and the disk was heated at 150 °C to form the supported tantalum hydride. After evacuation of the gas phase, ethane or propane was introduced (0.8 bar) through a molecular sieve and deoxo-catalyst trap and the cell was heated to 150 °C. From time to time, the cell was cooled and the gas phase trapped in liquid nitrogen in order to record IR spectra. In parallel, the gas phase was analyzed by expanding aliquots in a small volume for injection in GC. Alkanes were titrated on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an Al₂O₃-KCl on fused silica column (50 m × 0.32 mm).

Metathesis of alkanes in a batch reactor

 $[(\equiv SiO)_2Ta-H]/SiO_2$, 1, (300 mg; 5.95 wt% Ta) or $[(\equiv SiO)_2Ta-H]/MCM-41$, 2, (150 mg; 11.7 wt% Ta) were charged within a glove-box into a glass reactor (500 ml). After evacuation of argon, the reactor was filled again with ethane or propane (0.8 bar) through a molecular sieve and deoxo-catalyst trap then heated to 150 °C in an oven. The reaction products were analyzed periodically by GC as was done from the IR cell.

Monitoring of the surface species by hydrolysis after alkane metathesis

The catalyst was introduced into a batch reactor as described above and the metathesis reaction run for a given time. After stopping, the gas phase of the reactor was evacuated and a vapor of water (18 Torr) was introduced. Alkanes were analyzed as above and hydrogen on an Intersmat IGC 120MB gas chromatograph equipped with a katharometer detector and a filled molecular sieves column (3 m \times 3.2 mm).

Metathesis of alkanes in a continuous flow reactor

[(\equiv SiO)₂Ta-H]/MCM-41, 2, (250 mg; 11.7 wt% Ta) was charged within a glove-box into a stainless steel 0.5 inch diameter continuous flow reactor fitted with a fourchannels isolating valve. After connection to the rack, all the tubing was purged under a flow (3 ml min⁻¹) of the desired alkane. The four-channel valve was then switched on and the alkane was sent through the catalytic bed with a flow rate (3 ml min⁻¹) maintained constant using a mass flow controller, then the oven was heated to 150 °C within 50 min. The gas products, alkanes and hydrogen were analyzed on line with a Varian micro-GC CP-4900 using capillary columns (10 m PPU; 6 m 5CB; 10 m Al2) and katharometer detectors.

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