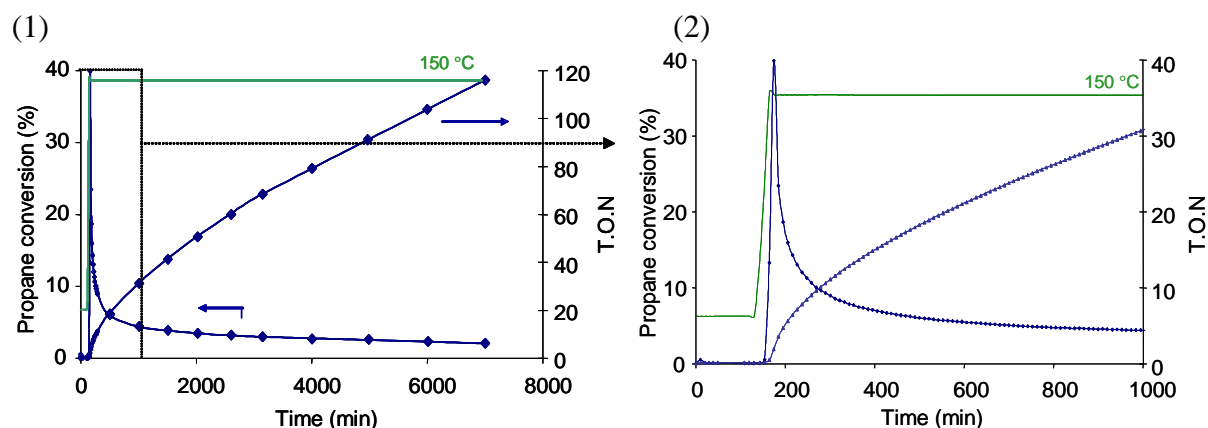**Dynamic Behaviour of the Tantalum Hydride Supported on Silica or MCM-41 in the Metathesis of Alkanes.**

Sophie Soignier,[a] Guillaume Saggio,[a] Mostafa Taoufik,[a] Jean-Marie Basset,[b] Jean Thivolle-Cazat.[a]*

Figure S1: Propane metathesis under 1 bar, at 150 °C and 3 Nml/min, catalysed by [(≡SiO)$_2$Ta-H]/MCM-41, **2**, (300 mg, wt% Ta = 11.7): (1) propane conversion and T.O.N versus time. (2) Enlargement of the region [0-1000 min].

Principle of the calculation of the T.O.F. of hydrogenolysis and metathesis reactions:

Case of ethane:

The total T.O.F of the reaction is the sum of the T.O.F. of the hydrogenolysis and of that of metathesis calculated from the quantification of products observed in the gas phase.

To calculate the T.O.F. of metathesis the following equations were considered:

(1) $C_2 + C_2 \longrightarrow C_1 + C_3$

(2) $C_2 + C_3 \longrightarrow C_1 + C_4$

(3) $C_2 + C_4 \longrightarrow C_1 + C_5$
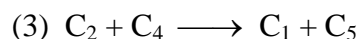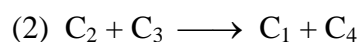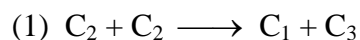
Thus, for each higher homologue formed (Sup) the lower one (Inf) that is methane was obtained. **The T.O.F. of metathesis** was calculated in carbon equivalent and given by the formula:

T.O.F. = $1/2 \times [\sum(\text{number of carbons of Sup}) + \sum(\text{number of carbons of Inf})]/(\text{mol of Ta})$

$= 1/2 \times [(3 \times F_{C3} + 4 \times F_{C4} + 5 \times F_{C5}) + (F_{C3} + 2 \times F_{C4} + 3 \times F_{C5})]/(\text{mol of Ta})$, where the molar flow rate, F_{Ci}, was determined by GC analysis.

Indeed, since the hydrogenolysis occurs, to determine the amount of the lower homologues (methane) coming from metathesis only we have to consider the higher homologues formed concomitantly with methane. Then, when propane, butane and pentane were formed, one, two or three methane molecules should be respectively obtained in parallel.

Consequently, **the T.O.F. of hydrogenolysis** was obtained by the formula:

T.O.F. $= 1/2 \times [\sum(\text{number of carbons of Inf measured}) - \sum(\text{number of carbons of Inf from metathesis})]/(\text{mol of Ta})$

$\qquad = 1/2 \times [(F_{C1}) - (F_{C3} + 2 \times F_{C4} + 3 \times F_{C5})]/(\text{mol of Ta})$

To quantify the hydrogen necessary to the hydrogenolysis reaction according to the equation $C_2 + H_2 \longrightarrow 2\,C_1$, we have integrated versus time: $nH_2 = nC_1/2 = 1/2 \times [(F_{C1}) - (F_{C3} + 2 \times F_{C4} + 3 \times F_{C5})]/(\text{mol of Ta})$ to cumulate this hydrogen during all the reaction (Cf Figure 5-2).

Case of propane:

To calculate the T.O.F. of metathesis the following equations were considered:
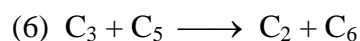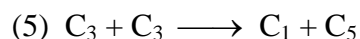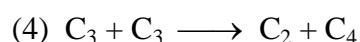
(4) $C_3 + C_3 \longrightarrow C_2 + C_4$

(5) $C_3 + C_3 \longrightarrow C_1 + C_5$

(6) $C_3 + C_5 \longrightarrow C_2 + C_6$

The T.O.F. of metathesis was calculated in carbon equivalent and given by the formula:

T.O.F. $= 1/3 \times [\sum(\text{number of carbons of Sup}) + \sum(\text{number of carbons of Inf})]/(\text{mol of Ta})$

$\qquad = 1/3 \times [(4 \times F_{C4} + 5 \times F_{C5} + 6 \times F_{C6}) + (F_{C5} + F_{C6}) + 2 \times (F_{C4} + F_{C6})]/(\text{mol of Ta})$

$\qquad = [(2 \times F_{C4} + 2 \times F_{C5} + 3 \times F_{C6})]/(\text{mol of Ta})$, where the molar flow rate, F_{Ci}, was determined by GC analysis.

Since the hydrogenolysis occurs, to determine the amount of the lower homologues (methane and ethane) coming from metathesis we have to consider the higher homologues formed concomitantly with methane and ethane. Then, when butane and pentane were formed (equation (4) and (5)), one ethane and one methane were obtained respectively. Moreover, when hexane was formed (equation (6)) one pentane was consumed (implying the previous formation of one methane) and one ethane was obtained; therefore $F_{C1} = (F_{C5} + F_{C6})$ and $F_{C2} = (F_{C4} + F_{C6})$.

Consequently, **the T.O.F. of hydrogenolysis** was obtained by the formula:

T.O.F. = $1/3 \times [\sum$(number of carbons of Inf measured) - $\sum$(number of carbons of Inf from metathesis)]/(mol of Ta)

$= 1/3 \times [(F_{C1} + 2 \times F_{C2}) - ((F_{C5} + F_{C6}) + 2 \times (F_{C4} + F_{C6}))]/$(mol of Ta)

To quantify the hydrogen necessary to the hydrogenolysis reaction according to the equation $C_3 + 2\ H_2 \longrightarrow 3\ C_1$, we have integrated versus time: $nH_2 = nC_1 \times (2/3) = 2/3 \times [(F_{C1} + 2 \times F_{C2}) - ((F_{C5} + F_{C6}) + 2 \times (F_{C4} + F_{C6}))]/$(mol of Ta) to cumulate this hydrogen during all the reaction.

(1)   (2)

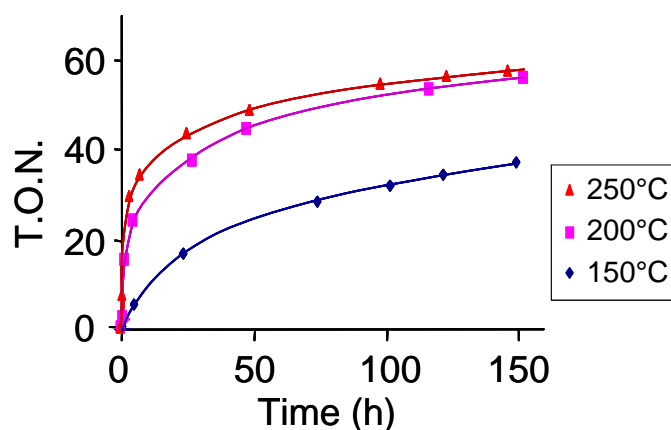(3)   (4)
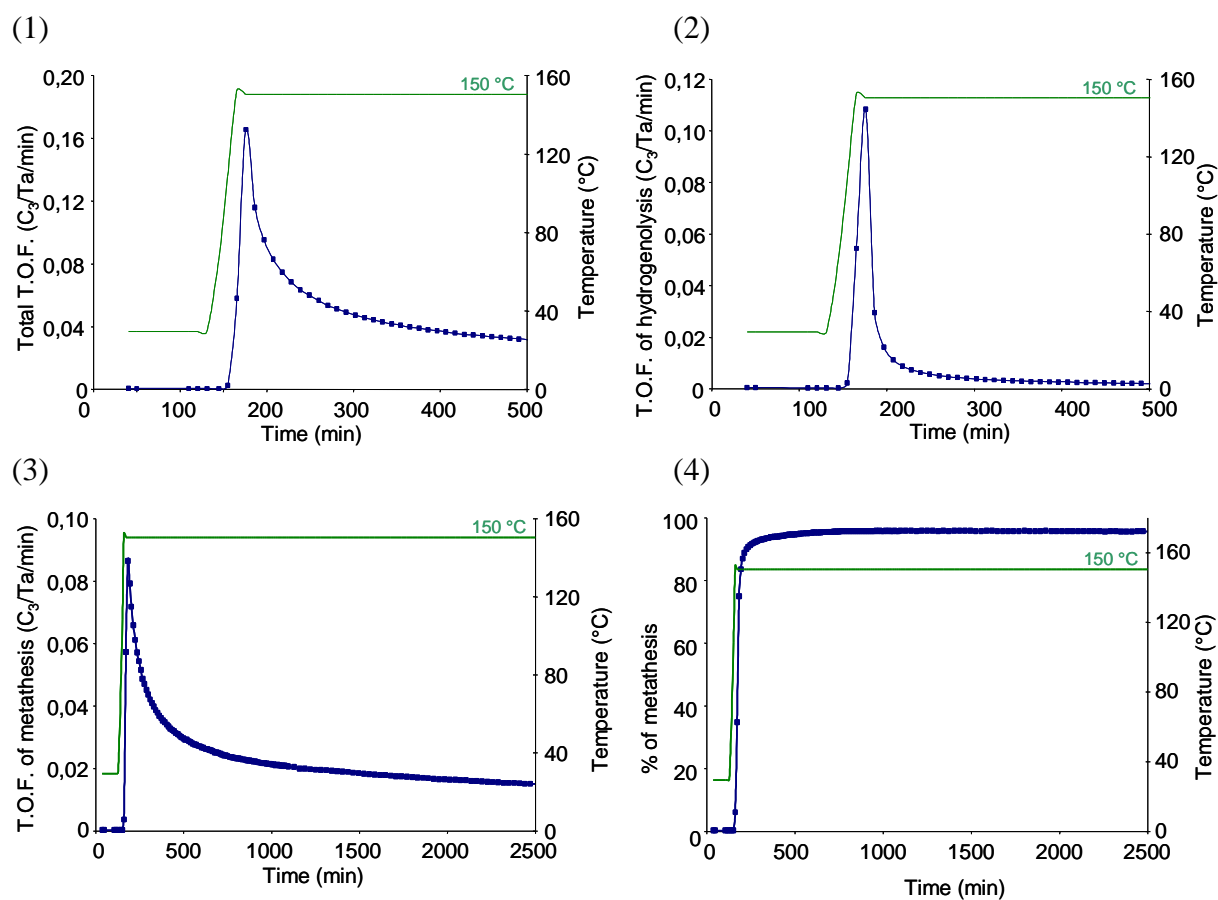
Figure S2: Propane metathesis (at 150 °C, 3 Nml/min, 1 bar) catalyzed by [(≡SiO)$_2$Ta-H]/MCM-41, **2,** (300 mg, wt% Ta = 11.7); (1): total T.O.F., (2): T.O.F. of hydrogenolysis, (3): T.O.F. of metathesis and (4): percentage of metathesis contribution versus time.

(1) (2)
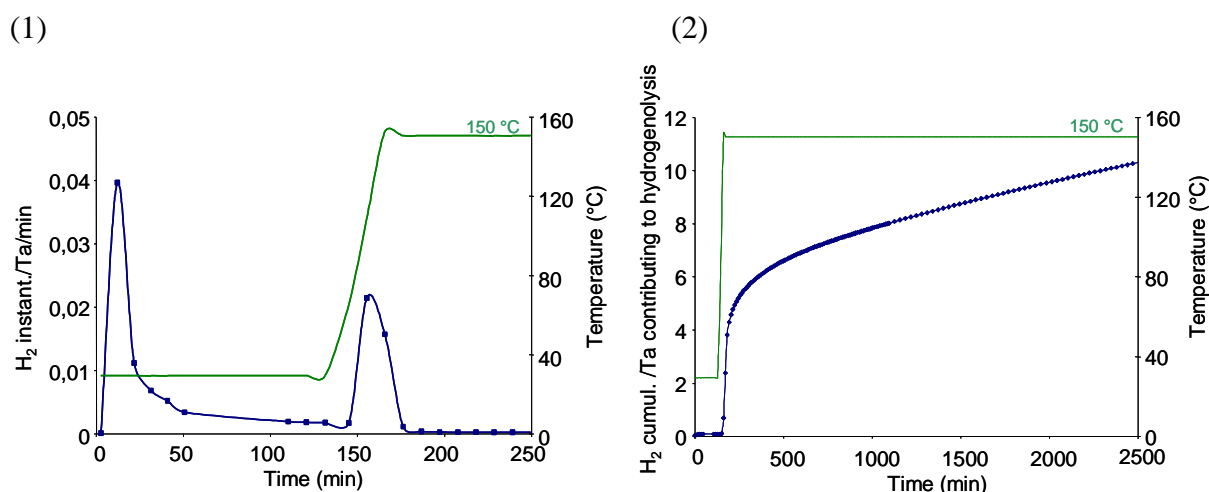
Figure S3: Propane metathesis (at 150 °C, 3 Nml/min, 1 bar) catalyzed by [(≡SiO)$_2$Ta-H]/MCM-41, **2,** (300 mg, wt% Ta = 11.7); (1): detected hydrogen: mol.H$_2$/mol.Ta/min and (2): calculated amount of hydrogen contributing to hydrogenolysis: cumulated mol.H$_2$/mol.Ta versus time.

Table S1: Products selectivity (%) after 120 h of alkane metathesis on [(≡SiO)$_2$Ta-H]/MCM-41, **2,** (wt% Ta = 11.7), at 150 °C under batch or dynamic conditions.

| Conditions	CH$_4$	C$_2$H$_6$	C$_3$H$_8$	n C$_4$H$_{10}$	i C$_4$H$_{10}$	C$_5$H$_{12}$	C$_6$H$_{14}$
C2 batch	63		32.7	1.9	2.5		
C2 dyn	55,3		39,6	2,1	3		
C3 batch	14.7	45		24.2	8.2	7	1.15
C3 dyn	4.5	48		32	4.5	9	0.9

Figure S4: T.O.N. of ethane metathesis obtained at 150, 200 and 250 °C on [(≡SiO)$_2$Ta-H]/MCM-41, **2,** (wt% Ta = 11.7); in batch conditions (150 °C, 0.8 bar, R = 600).

Table S2: Products selectivity (%) after 120 h of ethane metathesis on $[(\equiv SiO)_2Ta-H]/MCM-41$, **2,** (wt% Ta = 11.7), at different temperatures, 150, 200, 250 °C in batch conditions (0,8 bar, R = 600).

| Temperature	CH_4	C_3H_8	n C_4H_{10}	i C_4H_{10}
150 °C	63	32.7	1.9	2.5
200 °C	63.5	32.1	1.7	1.9
250 °C	65	31	1.5	1.7
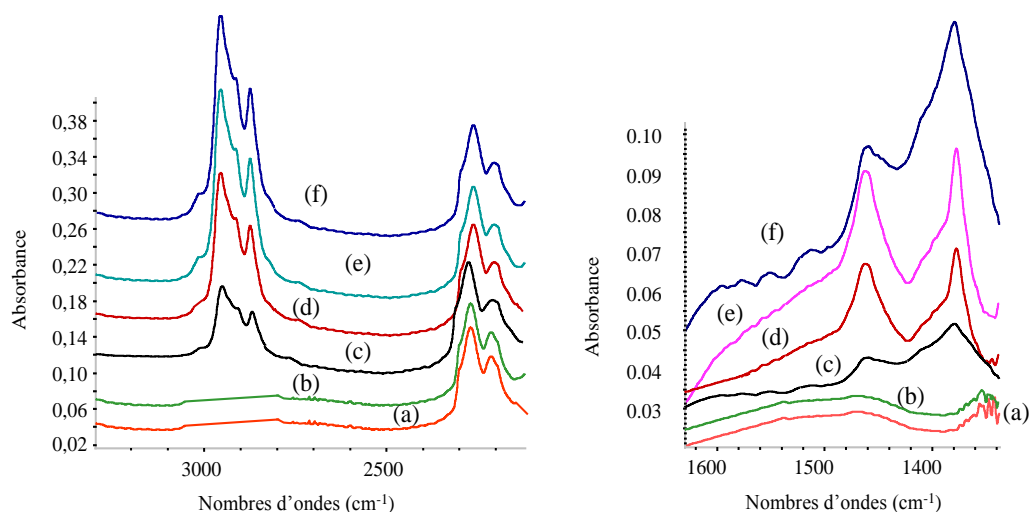


Figure S5: FTIR spectra of the catalyst during ethane metathesis catalyzed by $[(\equiv SiO)_2TaH]/SiO_2$, **1**, (silica spectrum subtracted and gas phase trapped in liquid N_2): (a) complex $[(\equiv SiO)_2TaH]/SiO_2$, **1**. (b): (a) + 0.8 bar of ethane at 25 °C. (c): (b) + heating to 150 °C for 1 h. (d): (c) + heating to 150 °C for 2 h. (e): (d) + heating to 150 °C for 2 h. (f): (e) + heating to 150 °C for 85 h.
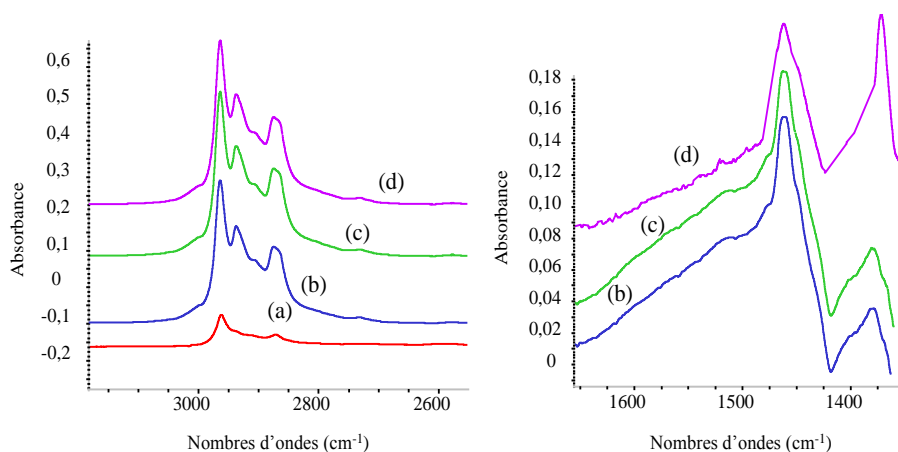

Figure S6: FTIR spectra of the catalyst during propane metathesis catalyzed by $[(\equiv SiO)_2TaH]/SiO_2$, **1**, (silica spectrum subtracted and gas phase trapped in liquid N_2): (a) complex $[(\equiv SiO)_2TaH]/SiO_2$, **1**. (b): (a) + 0.8 bar of propane and heating to 150 °C for 1 h. (c): (b) + heating to 150 °C for 5 h. (d): (c) + heating to 150 °C for 20 h.
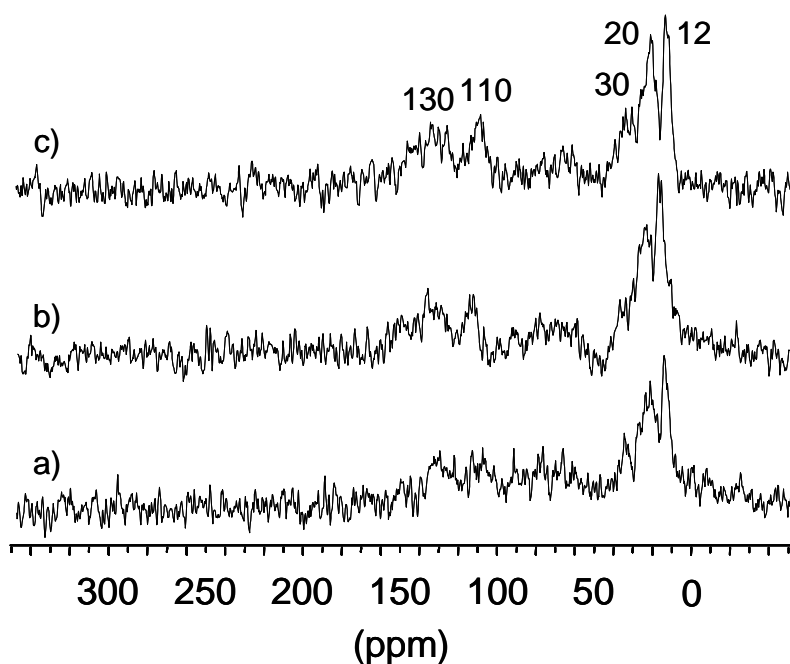
Figure S7: ^{13}C CP MAS NMR spectra of the catalyst, recorded at the end of ethane metathesis reaction catalyzed by [($\equiv$SiO)$_2$Ta-H]/MCM-41, **2,** in dynamic conditions (300 mg, wt% Ta = 11.7; at 150 °C, 3 Nml/min) under (a): 1, (b): 5, (c): 10 bar.
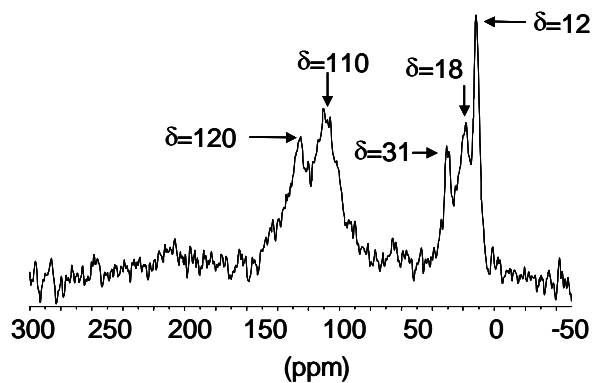
Figure S8: ^{13}C CP MAS NMR of surface species obtained by ethane metathesis catalyzed by [($\equiv$SiO)$_2$Ta-H]/MCM-41, **2,** in batch conditions (300 mg, wt% Ta = 11.7) at 200 °C under 0.8 bar during 48 h.
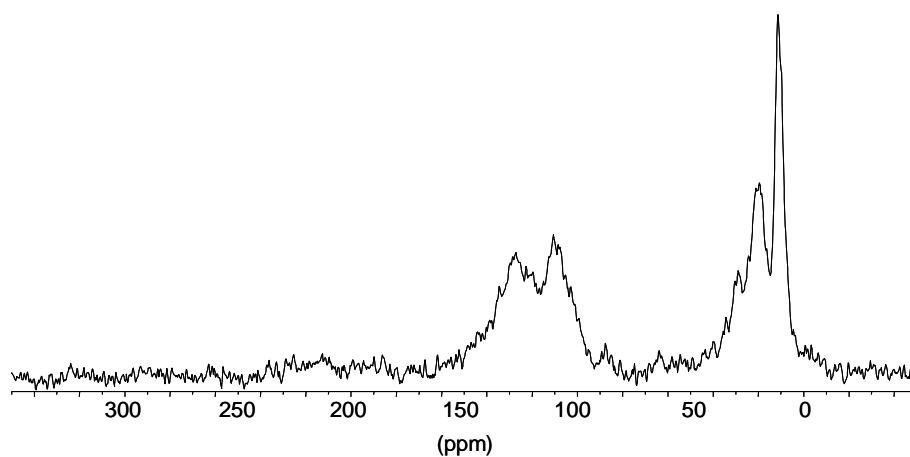
Figure S9: ^{13}C CP MAS NMR of surface species obtained by propane metathesis catalyzed by [($\equiv$SiO)$_2$Ta-H]/MCM-41, **2,** (300 mg, wt% Ta = 11.7) at 200 °C under 0.8 bar during 48 h.