

Greenhouse gas abatement

Impact of methane oxidation catalysis

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Secondary Pollutants : greenhouse gases

Gas	1900	1990	Increase
CO₂	280 ppm	353 ppm	+ 26%
CH₄	0.80 ppm	1.72 ppm	+115%
N₂O	0.28 ppm	0.30 ppm	+ 8%

World emissions/year

CO₂ : $6.5 \cdot 10^9$ Tons

CH₄ : $0.4 \cdot 10^9$ Tons

But GWP of methane: 21

Impact on greenhouse effect

CO₂ : 64%

CH₄ : 19%

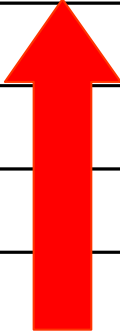
N₂O : 6%

A solution: the catalytic combustion of methane.

Comparison with other compounds

Light-off temperatures (50% conversion)

Catalyst: commercial Pt-Rh/CeO₂-Al₂O₃

n-alkanes	T50		Alkenes, alkyne	T50
Methane	515°C		Ethylene	205°C
Ethane	435°C		Propene	185°C
Propane	290°C		Acetylene	285°C
Hexane	195°C			

Aromatics	T50		Alcohols	T50
Benzene	205°C		Methanol	195°C
Toluene	220°C		Ethanol	200°C
O-Xylene	225°C		Propanol	205°C
			Butanol	210°C

Methane is by far the compound that is the most difficult to oxidize but...

Palladium is the most active CCM catalyst

Turnover frequencies (second⁻¹) on unsupported and alumina-supported metals.
Gas composition : 0.1%HC + 1%O₂ +N₂

HC		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
	Disp.% T°C	400	350	250	225
Pd	65	0.012	0.030	0.0045	0.0014
	16	0.31	0.093	0.0072	0.0042
	foil	5.4	3.6	0.25	0.19
Pt	87	-	-	0.16	1.75
	6	0.0095	0.31	1.5	5.2
	foil	0.017	0.93	10.0	10.4
Rh	57	0.0085	0.0095	0.0004	0.0004
	7	0.017	0.011	0.0006	0.0004
	foil	0.050	0.16	0.010	0.0076

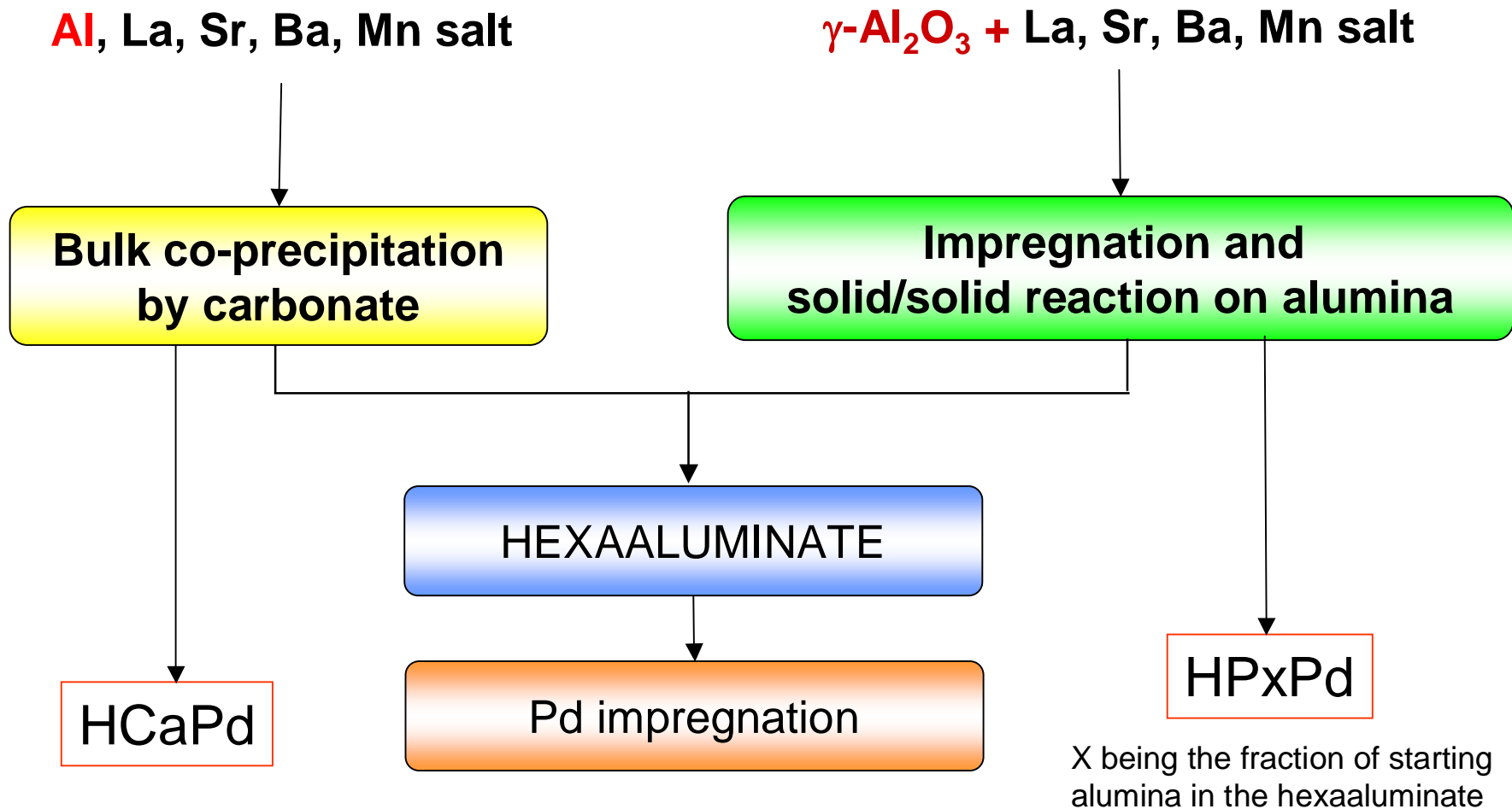
Pt is the best catalyst in the oxidation of C₂-C₄ alkanes

Pd is the best catalyst for CH₄ oxidation

Both are strongly structure-sensitive in light alkane oxidation

An efficient catalyst: Pd/hexaaluminate

A. Baylet, S. Royer, P. Marecot, JM Tatibouet, D. Duprez, Europacat 2007

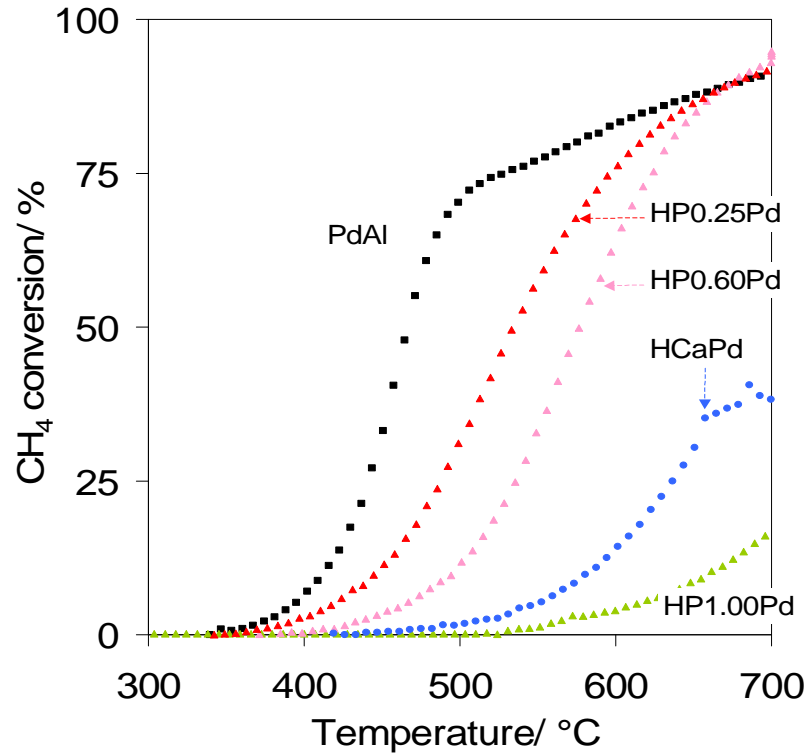


Theoretical composition: $(\text{La}_{0.2}\text{Sr}_{0.3}\text{Ba}_{0.5})(\text{MnAl}_{11})\text{O}_{19}$

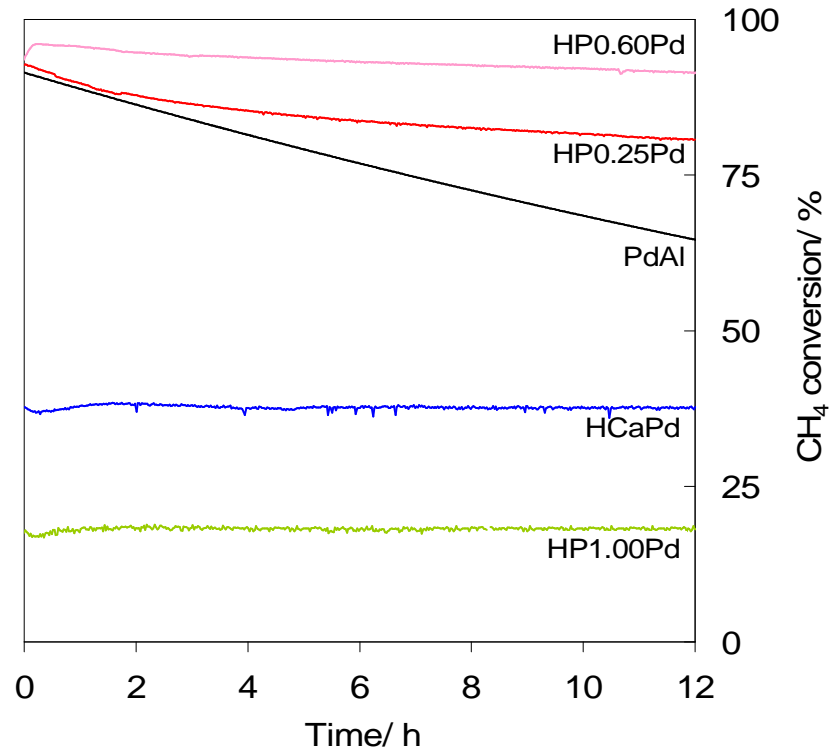
Pd catalysts: Activity tests

Starting Pd state: PdO

Activity (2nd run)



Stability at 700 °C

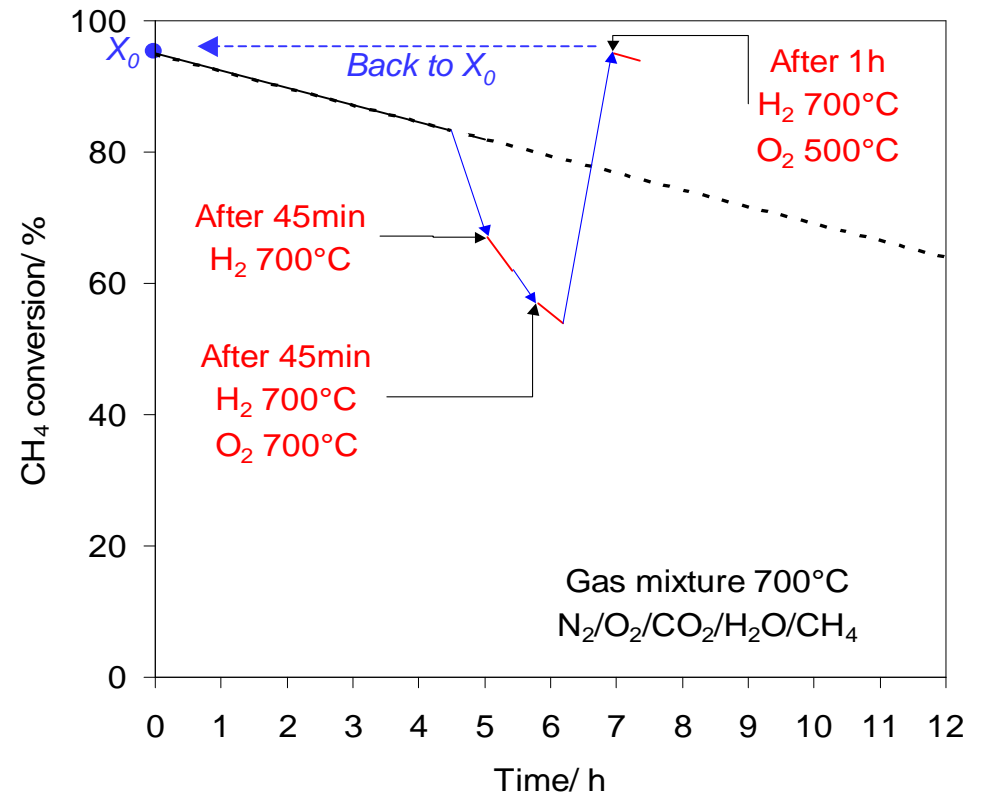
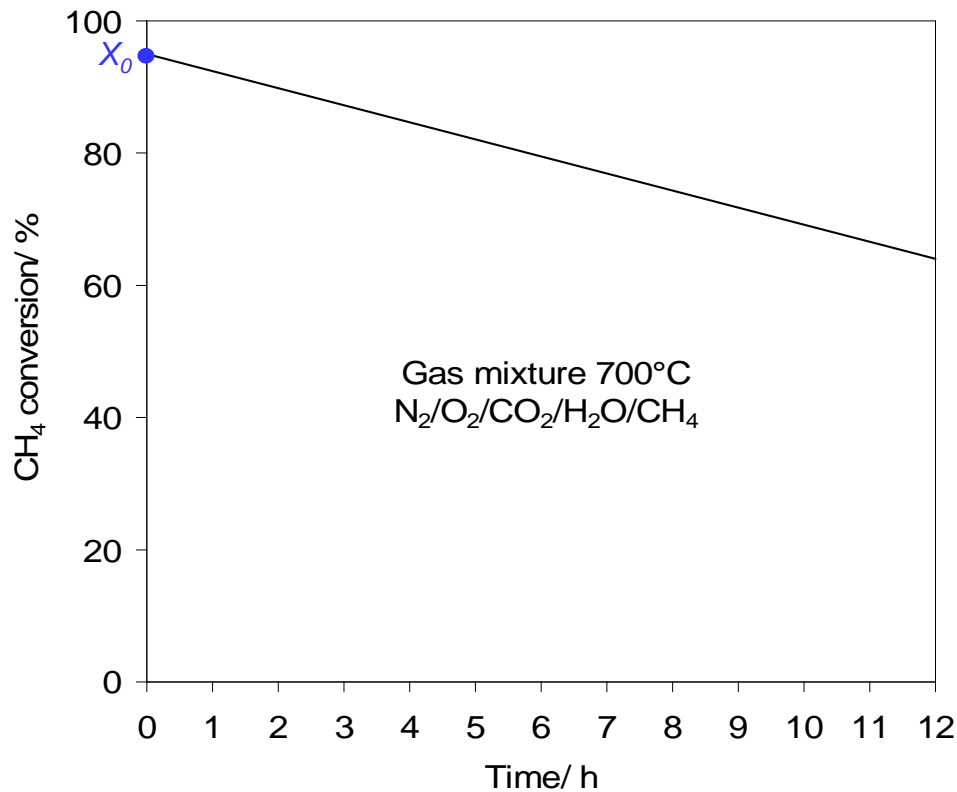


Deactivation: decrease of PdOx site number on γ -Al₂O₃ or sintering?

PdOx phase stabilised over doped Θ -Al₂O₃?

HP0.60 presents the best compromise between activity and stability

Pd/Al₂O₃: Stability after redox treatments



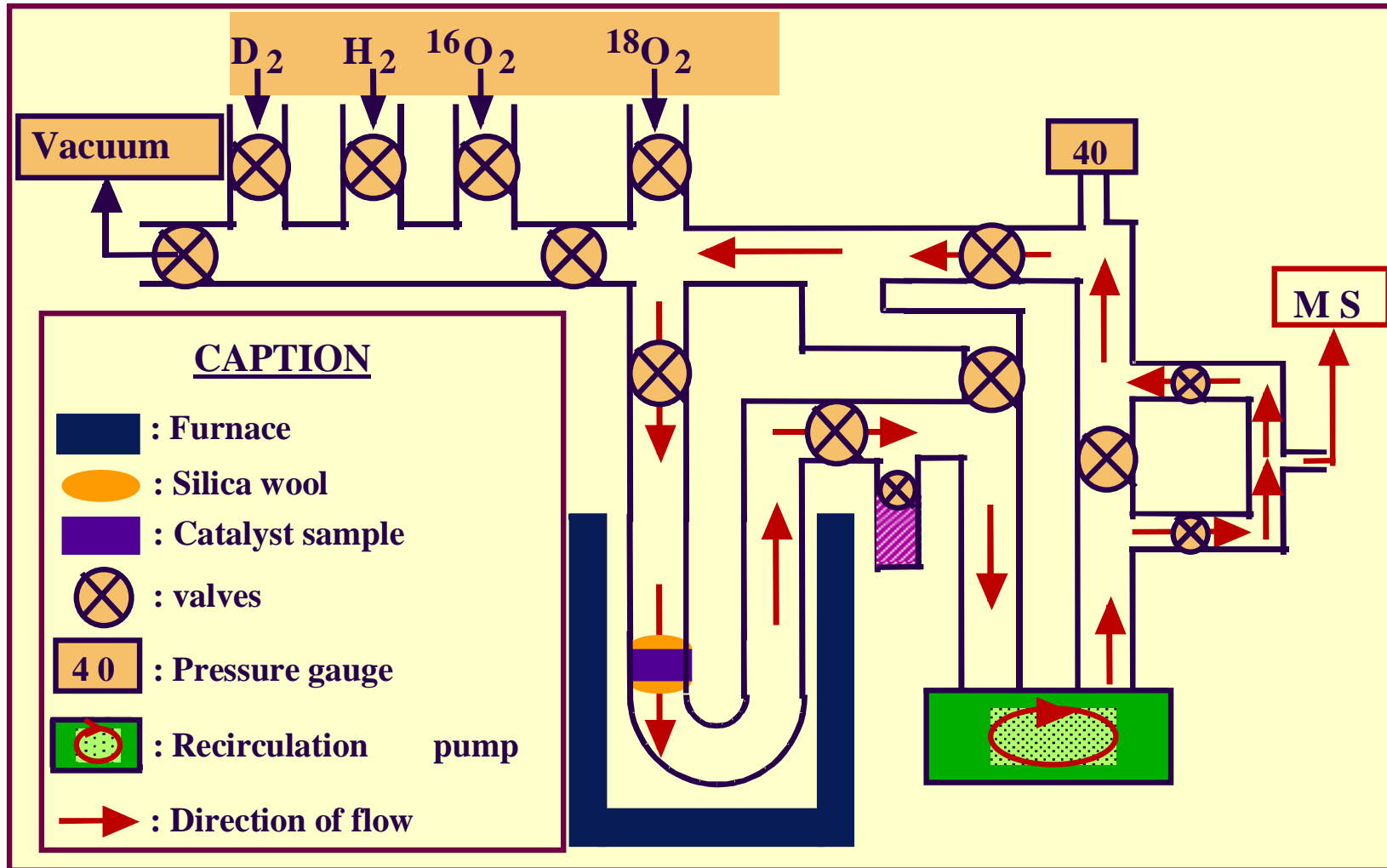
Deactivation linked to PdOx decomposition into metallic Pd and probably not due to sintering phenomena

How to explain the particular behaviour of Pd in methane oxidation ?

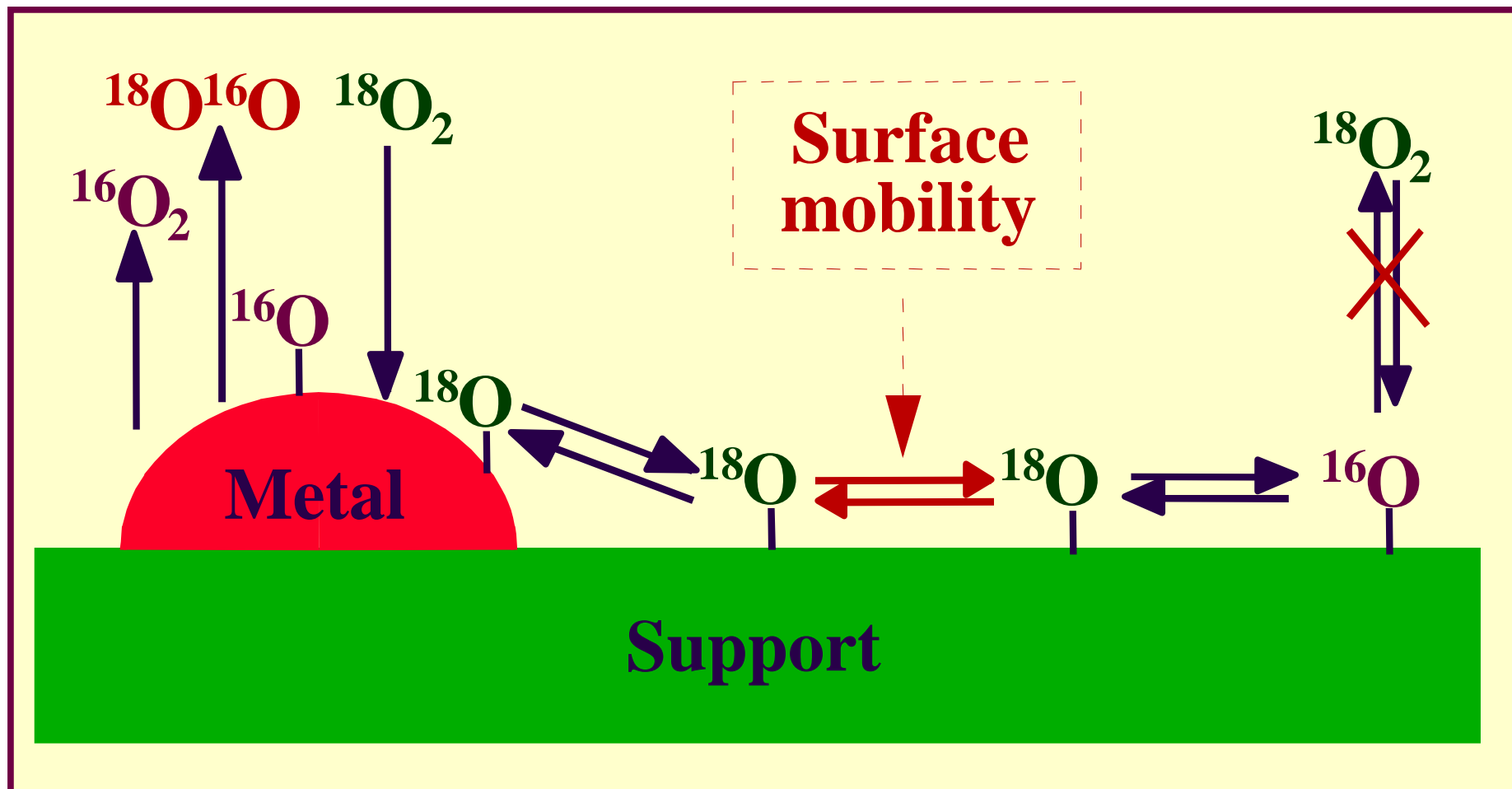
- Oxygen activation on Pd or PdO
- CH₄ activation on Pd or PdO
- O₂-CH₄ activation on Pd or PdO
- Role of CO₂

Study by isotopic exchange and labeling using ¹⁸O₂

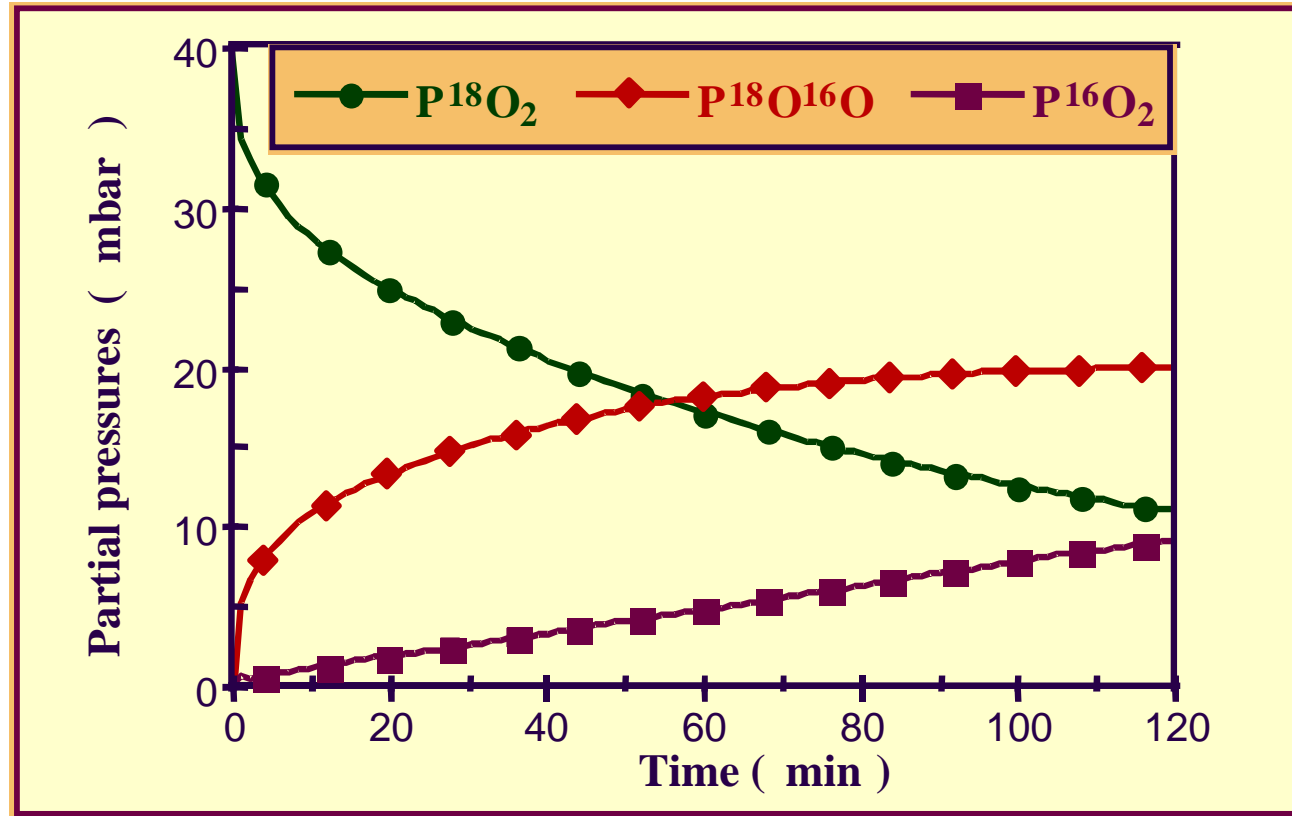
ISOTOPIC EXCHANGE: Close loop reactor



ISOTOPIC EXCHANGE: Mechanism on supported metal catalyst

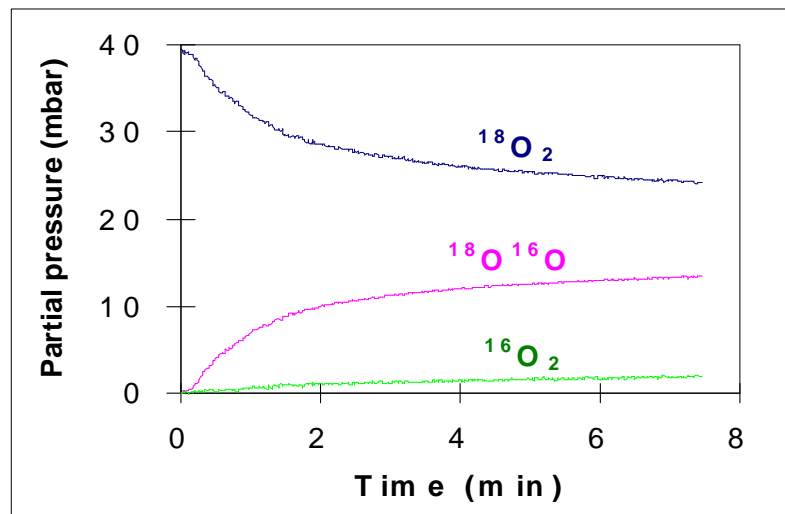
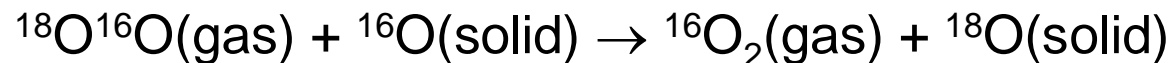
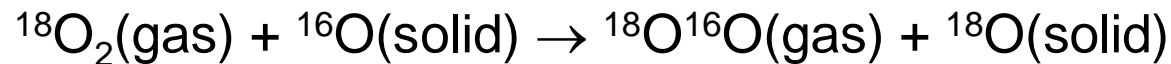


ISOTOPIC EXCHANGE: Mass spectrometry analysis



Kinetic parameters of exchange

The reaction is carried out with pure $^{18}\text{O}_2$ at $t=0$:



Fraction of ^{18}O in gas phase

$$\alpha_g = \frac{\frac{1}{2} P_{34} + P_{36}}{P_0}$$

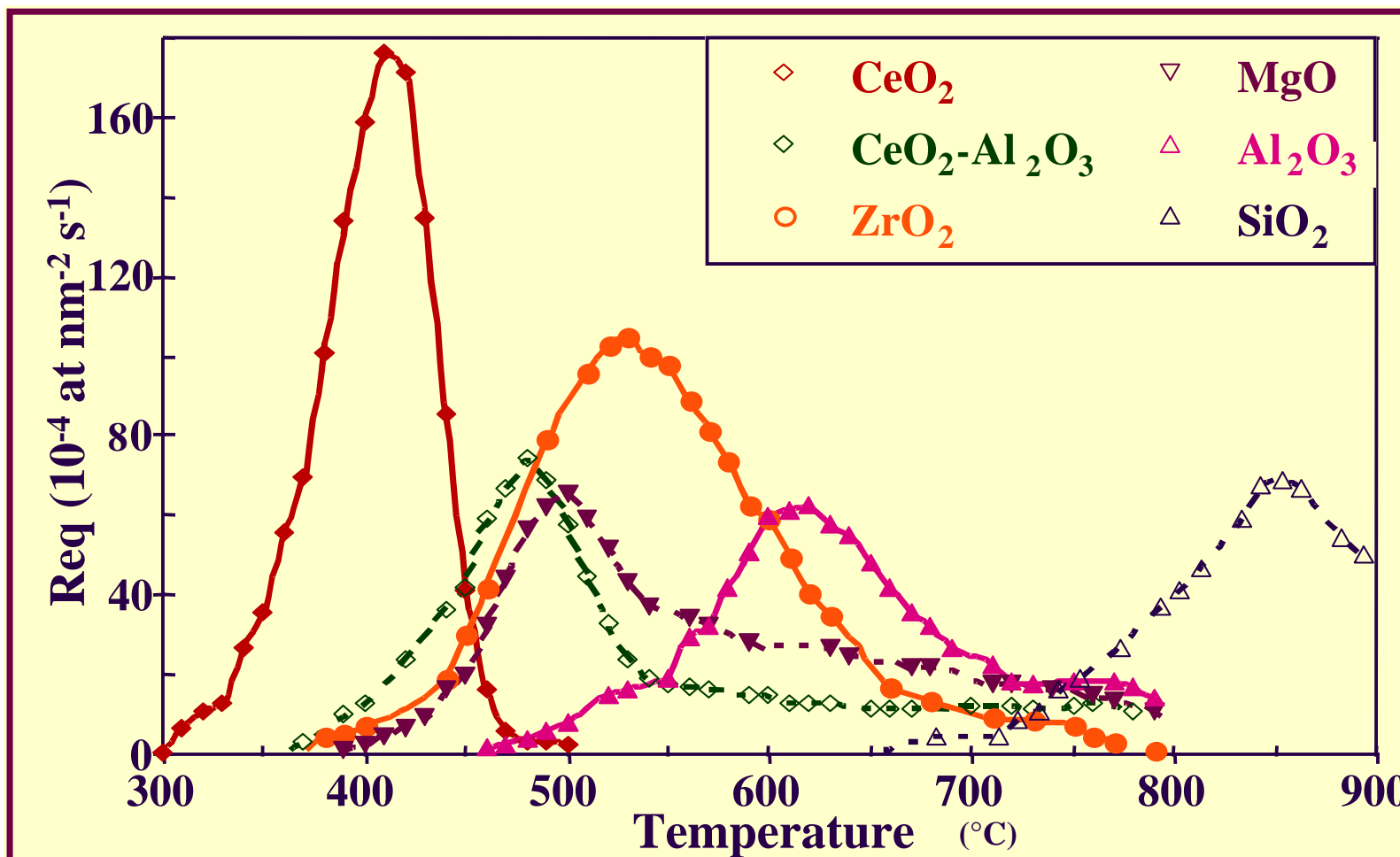
$$\text{with } P_0 = P_{32} + P_{34} + P_{36}$$

From the variations of α_g with time, it is possible to calculate:

- The number of exchanged atoms in the solid at time t
- The number of exchangeable atoms (at $t \rightarrow \infty$)
- The initial rate of exchange

More sophisticated models allow to calculate coefficients of diffusion of O ON the solid (surface diffusion) and IN the solid (bulk diffusion)

Temperature-programmed exchange over support oxides

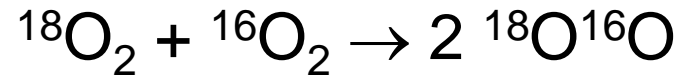


Exchange on ceria occurs at low temperature

Exchange on alumina is very slow at 500°C. TPIE has a maximum at 620°C.

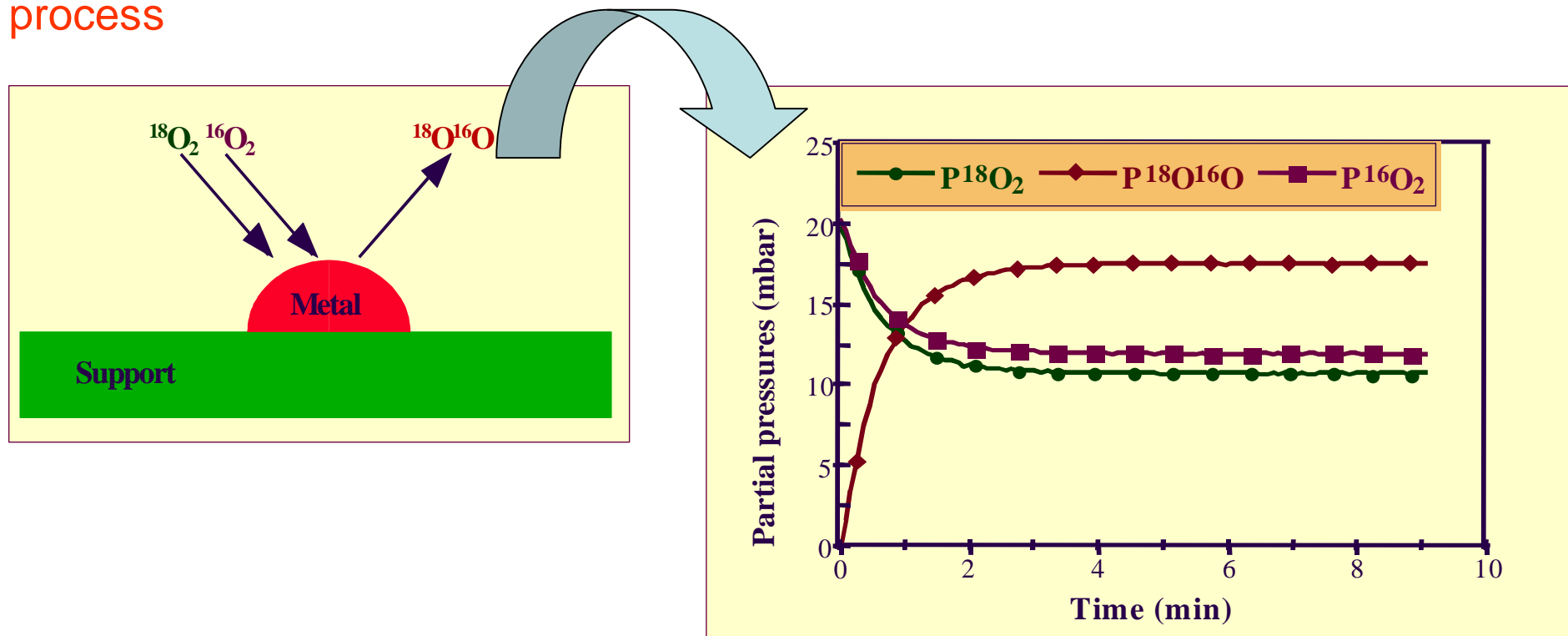
ISOTOPIC EQUILIBRATION

The reaction is carried out with equimolar mixtures of $^{18}\text{O}_2$ and $^{16}\text{O}_2$



This is a measurement of the adsorption/desorption rates of oxygen on metals

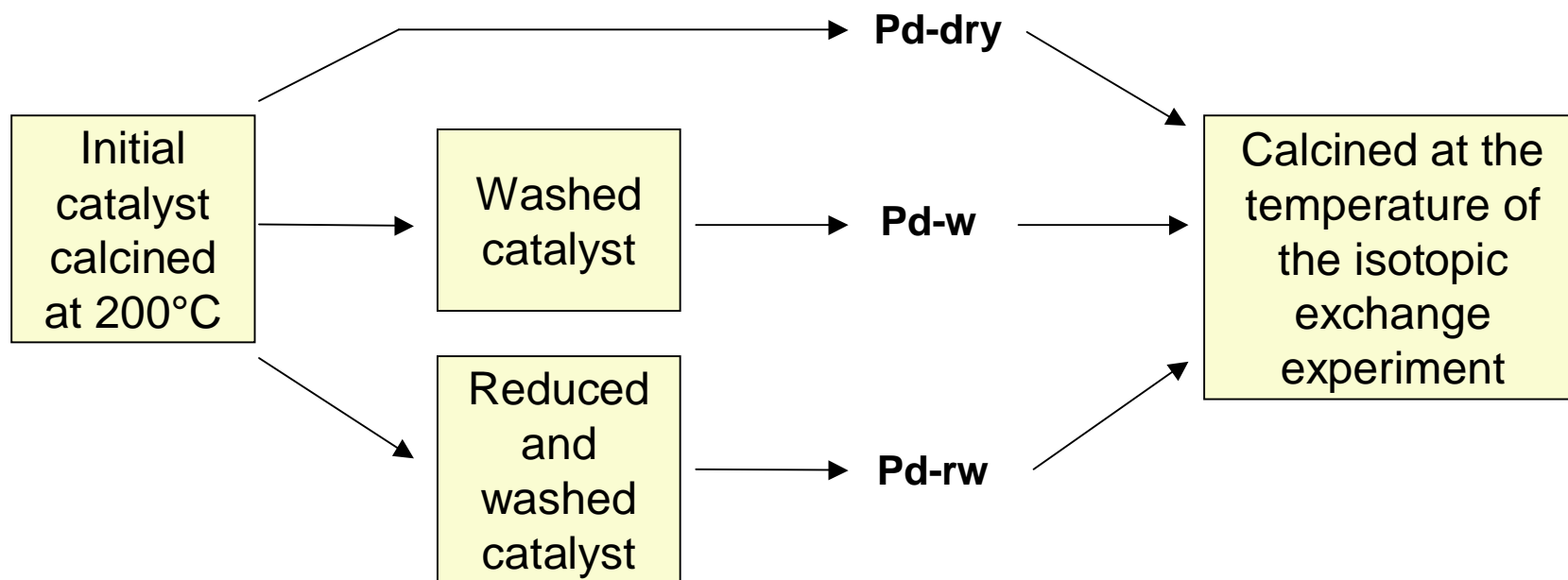
The fraction of ^{18}O atoms in gas phase (α_g) does not change in a pure equilibration process



PREPARATION OF THE SAMPLES

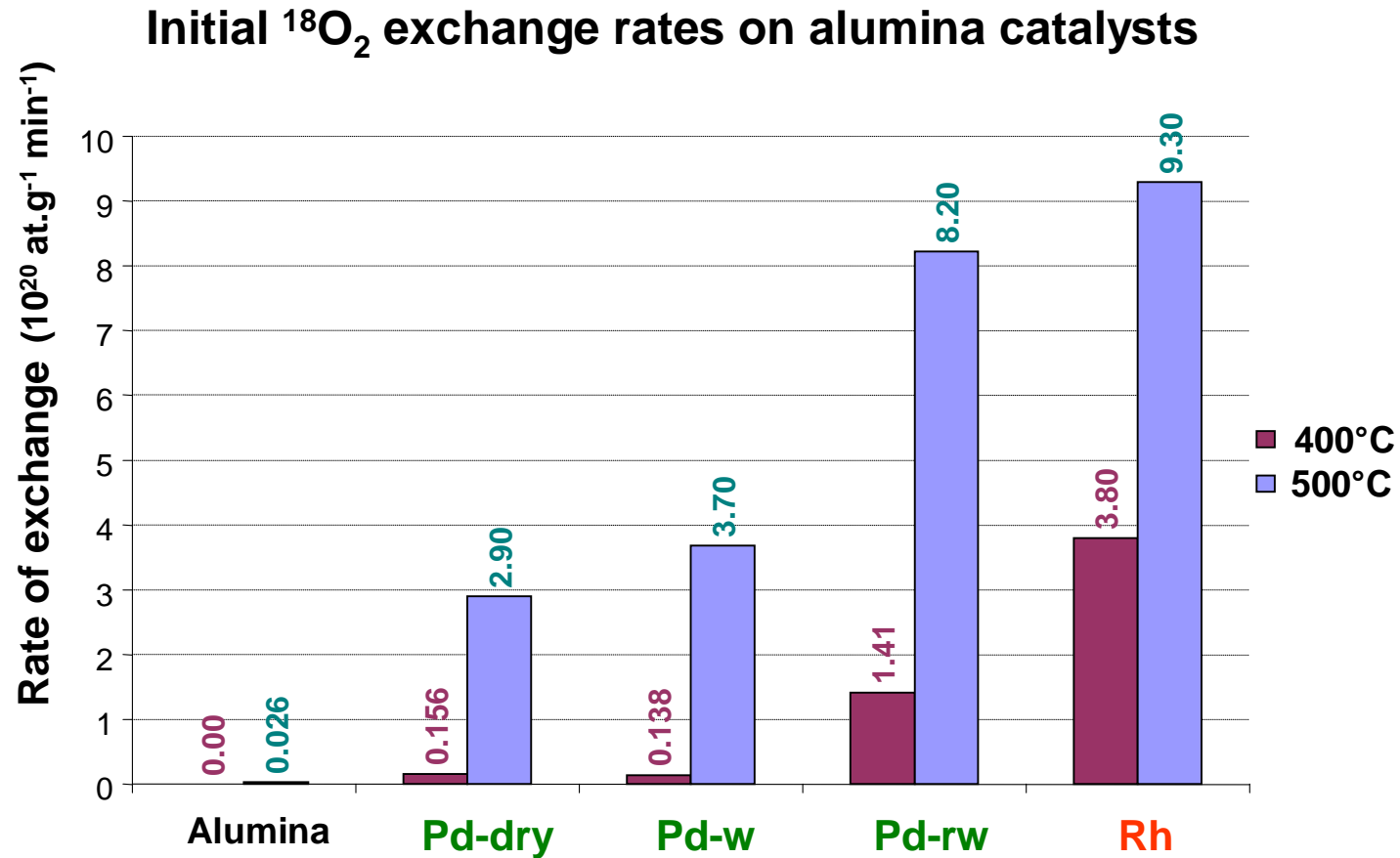
Pd/Al₂O₃

Incipient wetness impregnation on γ -Alumina with **Pd-nitrite** complex formation from **NaNO₂** and **Pd-nitrate**



Catalysts	Pd (wt %)	Na (wt %)	S _{BET} (m ² /g); 400°C	S _{BET} (m ² /g); 500°C
Pd-dry	0.86	1.10	185	193
Pd-w	0.86	0.38	189	197
Pd-rw	0.87	0.62	225	247

Isothermal isotopic exchange on Pd/Al₂O₃.



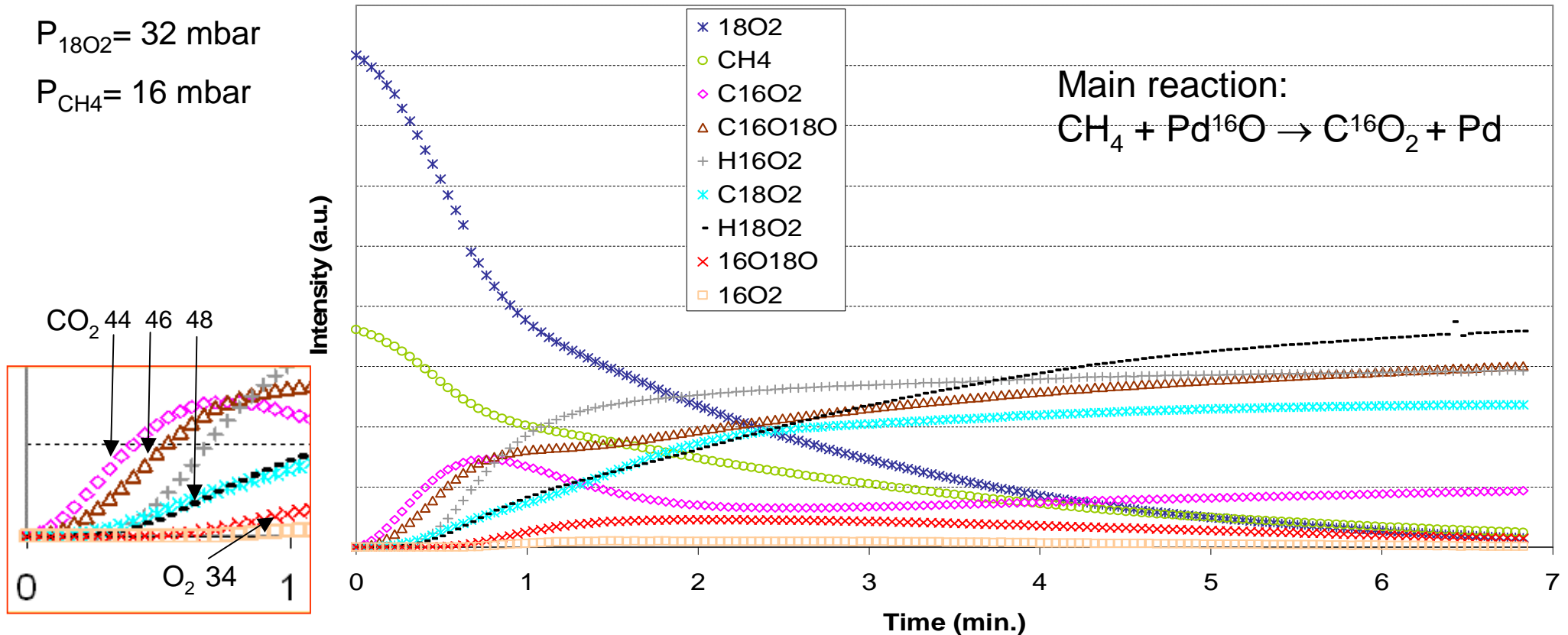
- Rh exchanges oxygen much more rapidly than Pd at 400°C
- The presence of Na does not affect the mobility of oxygen
- Important beneficial effect of the reduction step before the washing of the catalyst

Isothermal isotopic exchange on PdO/Al₂O₃ in the presence of methane: CH₄ + ¹⁸O₂ on Pd¹⁶O/Al₂O₃

¹⁸O₂ exchange at 500°C on Pd-rw in presence of CH₄

P_{18O₂} = 32 mbar

P_{CH₄} = 16 mbar

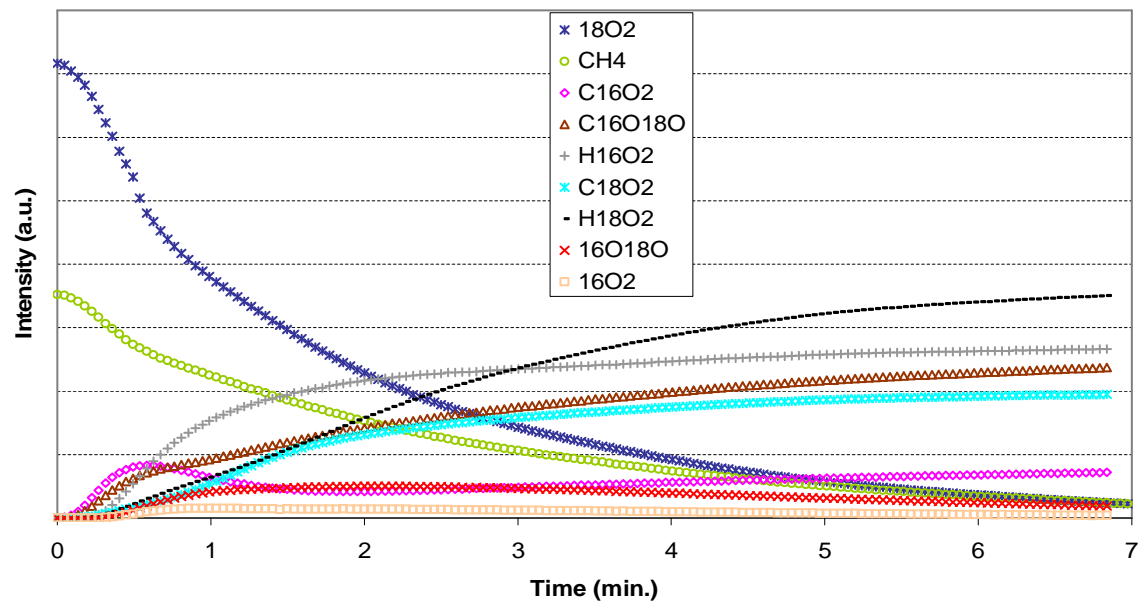


- ❑ The presence of methane intensifies the ¹⁸O₂ disappearance
- ❑ Immediate formation of C¹⁶O₂ before C¹⁶O¹⁸O. ¹⁶O₂ and ¹⁶O¹⁸O appear later
- ❑ Oxidation of CH₄ with O from PdO

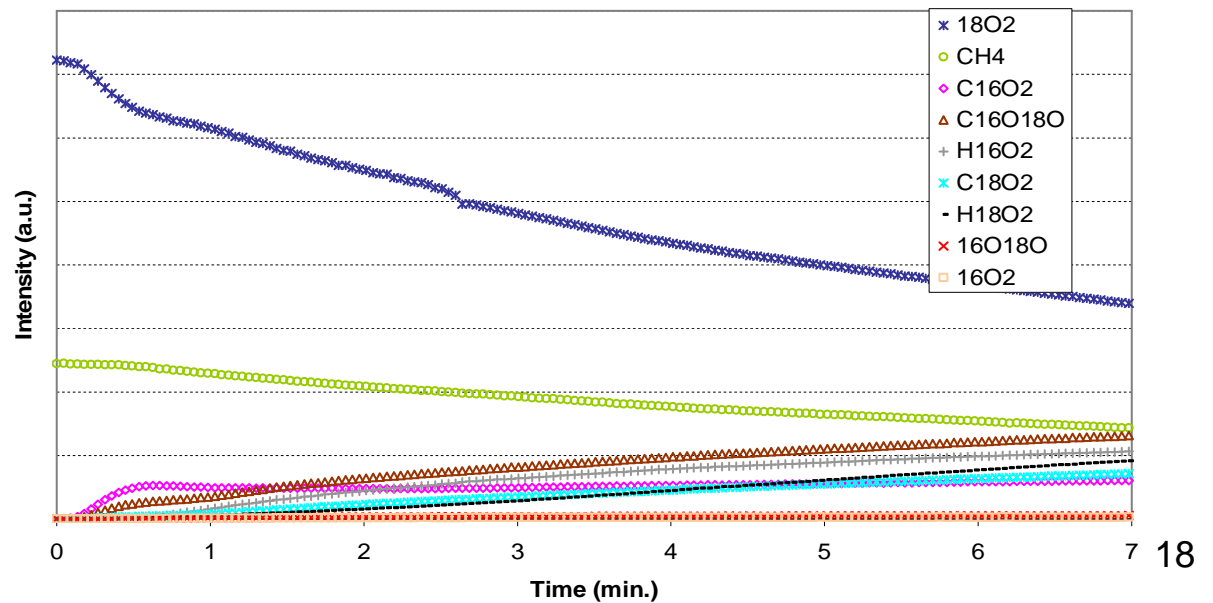
Comparison between isotopic exchange at 500°C and 400°C in the presence of methane

The same evolution is observed but the kinetics are different

$^{18}\text{O}_2$ exchange at 500°C on Pd-w in presence of CH_4



$^{18}\text{O}_2$ exchange at 400°C on Pd-w in presence of CH_4



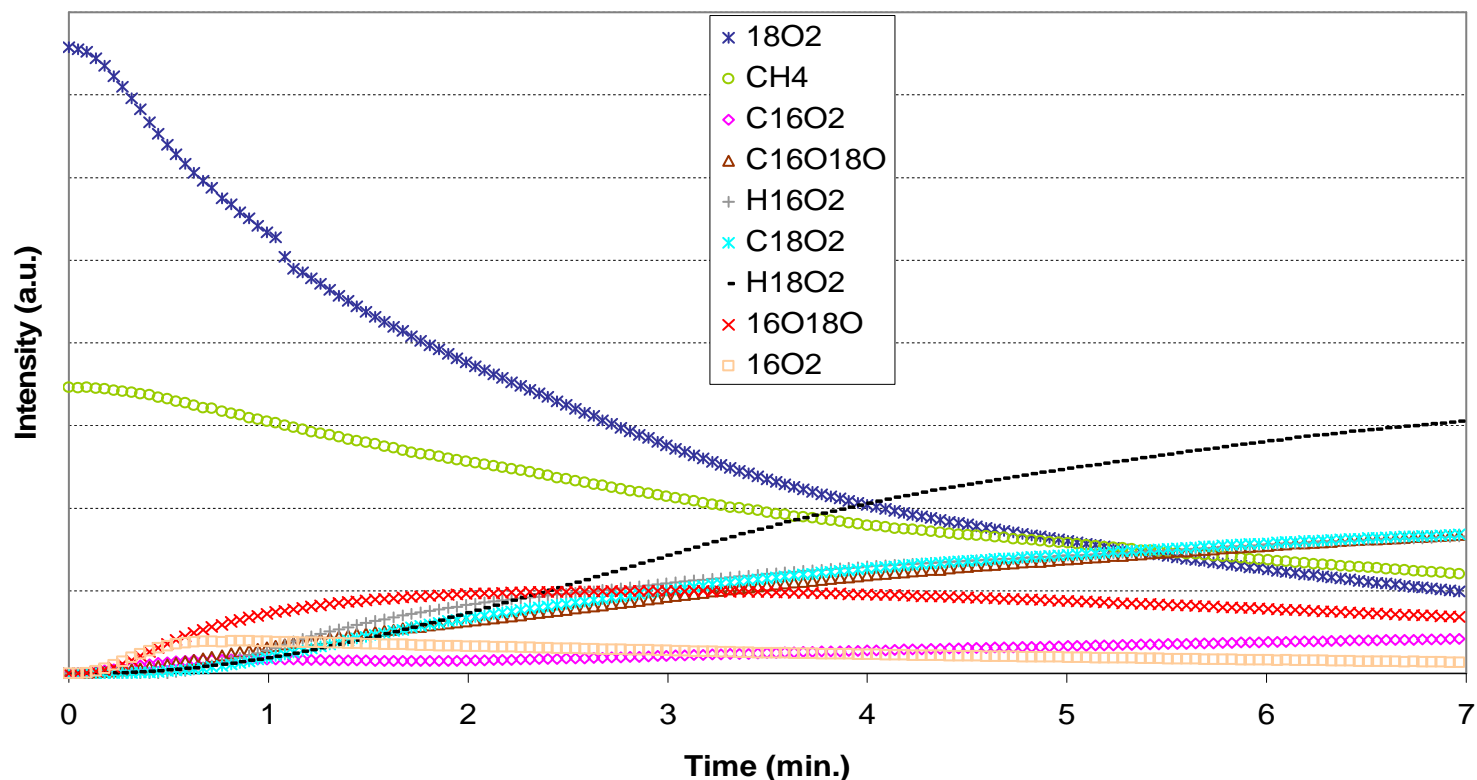
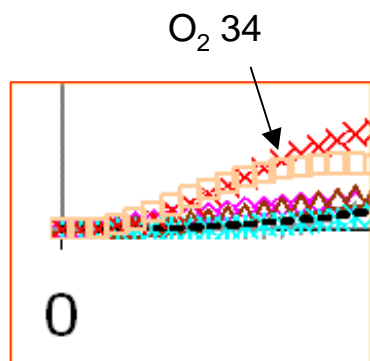
Isothermal isotopic exchange on Pd⁰/Al₂O₃ in the presence of methane: CH₄ + ¹⁸O₂ on Pd⁰/Al₂O₃

The catalyst Pd-dry has been heated at 700°C under vacuum to try to decomposed Pd-O

¹⁸O₂ exchange at 500°C in presence of CH₄ on Pd-dry
decomposed at 700°C

P_{18O₂} = 32.8 mbar

P_{CH₄} = 19.5 mbar



- Immediate appearance of ¹⁶O₂ and ¹⁶O¹⁸O
- On Pd⁰, ¹⁸O₂ is directly exchanged (Carbonate species formation are not needed)
- Oxidation of CH₄ with O from PdO is confirmed by the presence of C¹⁶O¹⁸O and C¹⁸O₂

ISOTHERMAL EQUILIBRATION

Kinetic parameters

CO₂ effect on the isotopic equilibration rate

Experiments of isotopic equilibration at 500°C in presence of **25mbar ¹⁸O₂ + 25mbar ¹⁶O₂**
or **25mbar ¹⁸O₂ + 25mbar C¹⁶O₂**

Calculation of the initial isotopic equilibration rate:

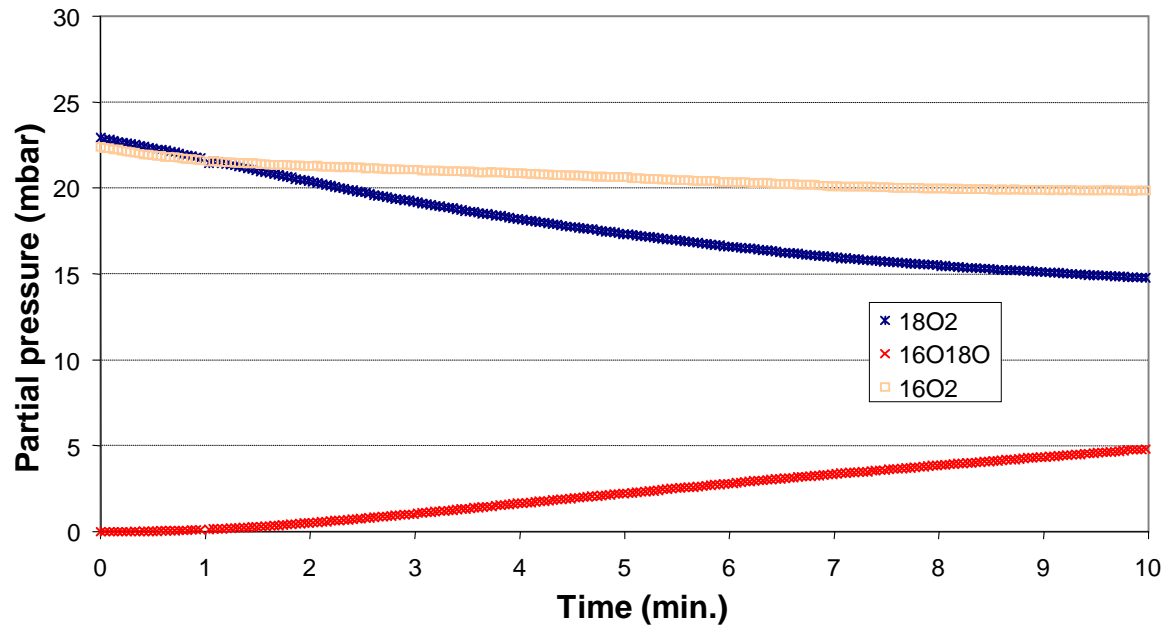
- without CO₂ :

$$r_{\text{equilibration}} = \frac{2 * N_g}{P_o} * \left[\frac{dP_{34}}{dt} \right]_{t=0}$$

- with CO₂:

$$r_{\text{equilibration}} = \frac{2 * N_g}{P_o} * \left[\frac{dP_{34}}{dt} + \frac{dP_{46}}{dt} + 2 \frac{dP_{32}}{dt} + 2 \frac{dP_{48}}{dt} \right]_{t=0}$$

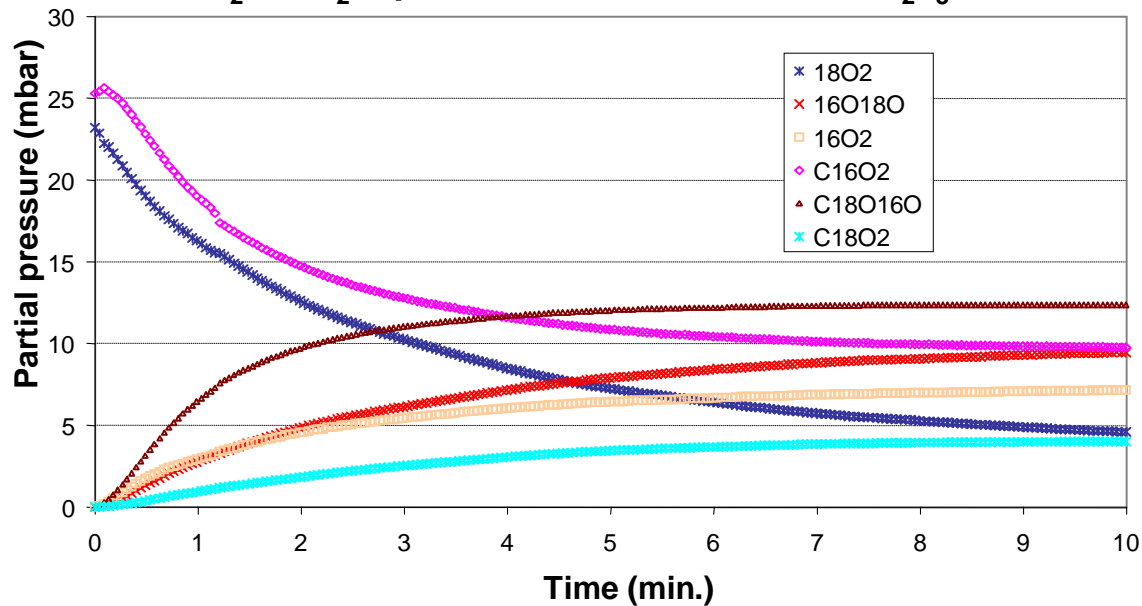
$^{18}\text{O}_2/^{16}\text{O}_2$ equilibration at 500°C on Pd/Al₂O₃-w



$r_{\text{equilibration}} = 18.5 \cdot 10^{18} \text{ at. g}^{-1} \text{ min}^{-1}$

On Pd/Al₂O₃, oxygen equilibration is faster in the presence of CO₂ (x25)

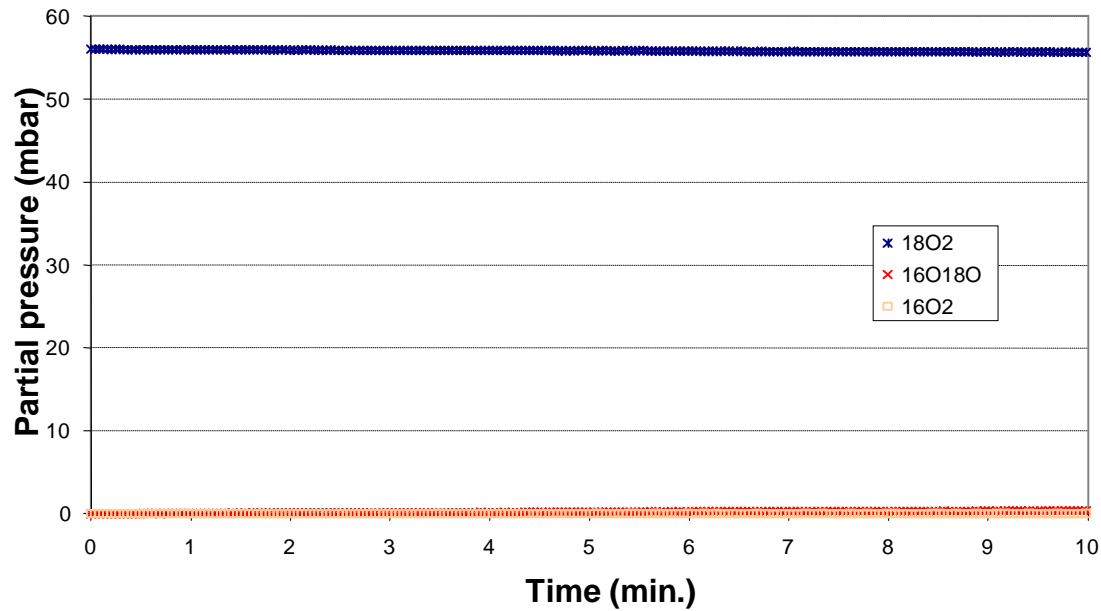
$^{18}\text{O}_2/\text{C}^{16}\text{O}_2$ equilibration at 500°C on Pd/Al₂O₃-w



$r_{\text{equilibration}} = 4,5 \cdot 10^{20} \text{ at. g}^{-1} \text{ min}^{-1}$

$^{16}\text{O}_2$ seems to be produced at the same time as C¹⁶O¹⁸O and before $^{16}\text{O}^{18}\text{O}$

$^{18}\text{O}_2/^{16}\text{O}_2$ equilibration at 500°C on Al_2O_3

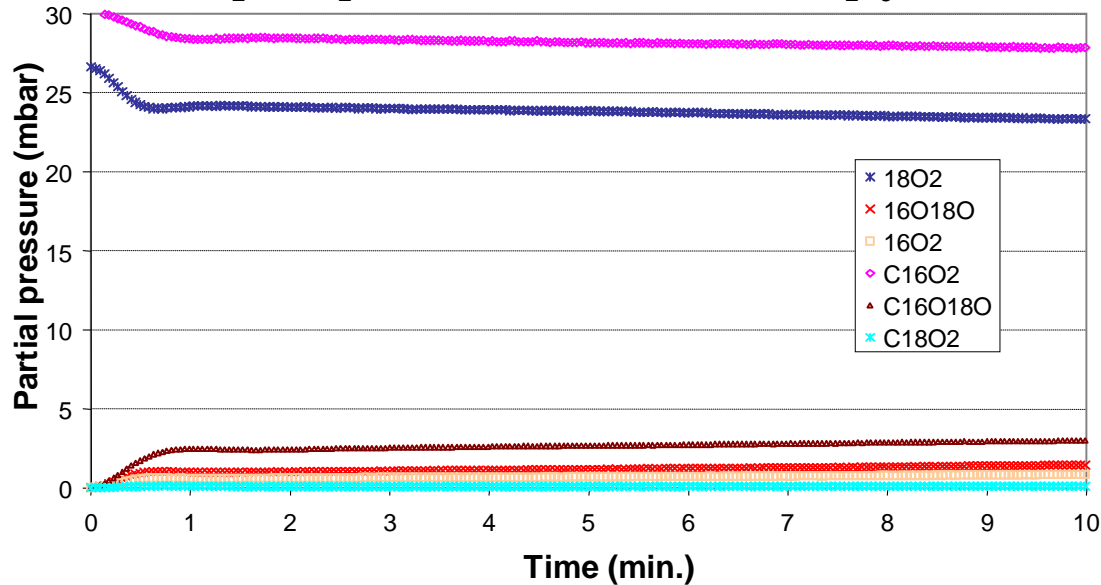


$$r_{\text{equilibration}} = 2.28 \cdot 10^{18} \text{ at.g}^{-1}.\text{min}^{-1}$$

On alumina:

- extremely slow oxygen equilibration.
- Fast but small equilibration between CO_2 and O_2

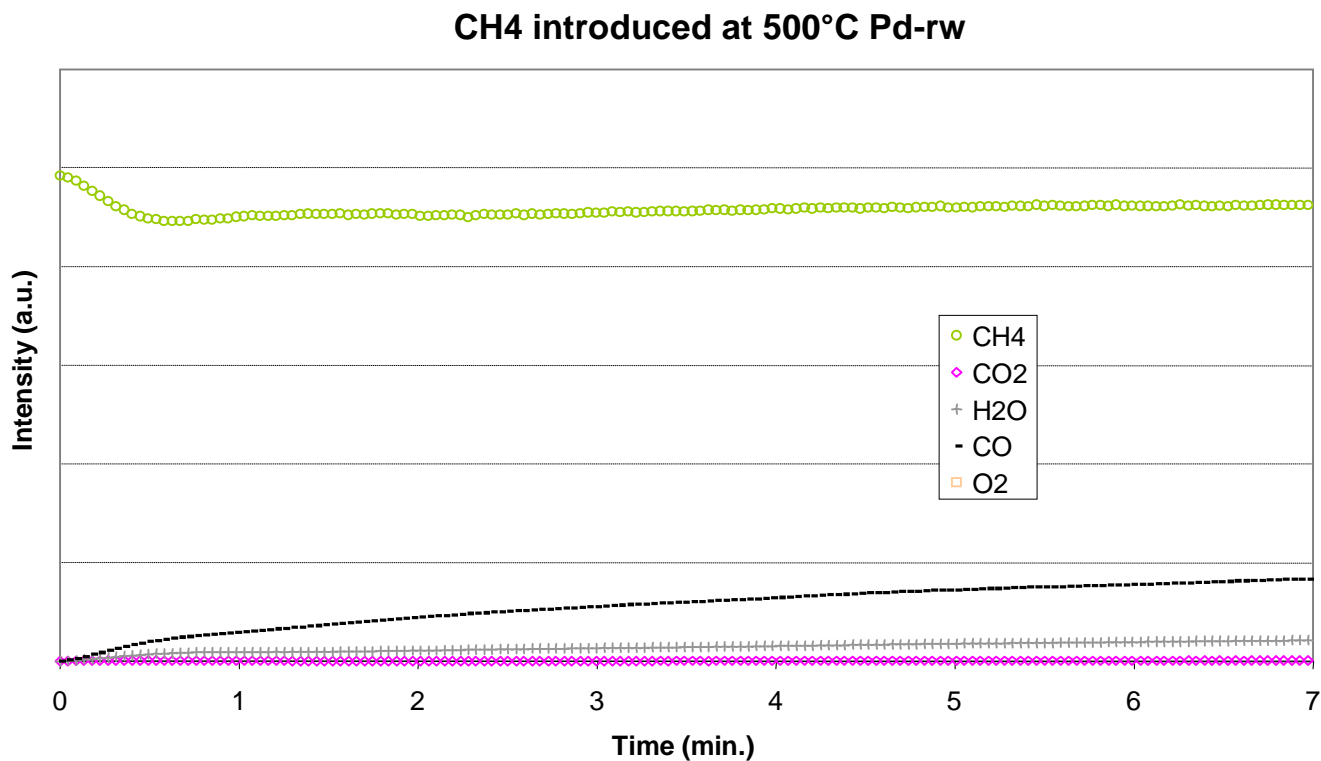
$^{18}\text{O}_2/\text{C}^{16}\text{O}_2$ equilibration at 500°C on Al_2O_3



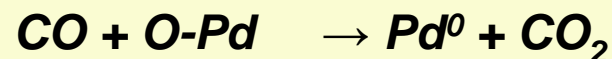
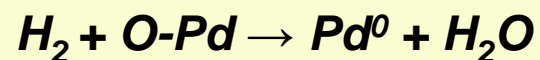
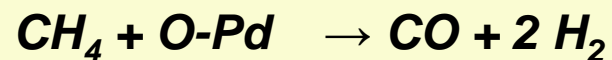
$$r_{\text{equilibration}} = 1.1 \cdot 10^{20} \text{ at.g}^{-1}.\text{min}^{-1}$$

Reaction of CH₄ over Pd⁰/Al₂O₃

When only CH₄ is sent on a Pd/Al₂O₃ catalyst reduced at 500°C, the total pressure in the closed system increases and we observe **only CO by mass spectrometry (no CO₂)**. Reforming of CH₄ is supposed but the mass corresponding to H₂ was not collected to confirm.



These steps are proposed :



Conclusions

- Pd/Al₂O₃ is a very active catalyst for methane oxidation.
- But it is not stable at high temperature. This is due to a slow decomposition of palladium oxide, the active Pd phase in oxidation.
- Other supports can stabilize PdO, specially certain hexaaluminates.

Conclusions from the studies with ¹⁸O:

- Pd can hardly activate the gaseous oxygen (slow ¹⁸O₂ + ¹⁶O₂ isotopic equilibration, very sensitive to the catalyst preparation and activation).
- On PdO, CH₄ is oxidized first with the O of PdO.
- On Pd^o, CH₄ is first reformed into CO (and probably H₂)
- CO₂ seems to be a good vector for O₂ in oxidation (acceleration of the equilibration). Its exact role should be clarified.