Non-oxidative methane aromatization in a catalytic membrane reactor

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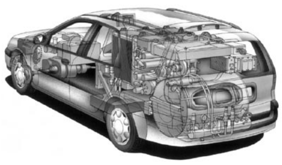
Production of H_2 : growing interests

§ Demand in ecofriendly fuels and processes

§ Fuel-cell technology development



F ideal energy carrier

Major source of H_2

§ Natural gas

- Abundance of methane reserves

- Canada is the 3rd world largest producer
  the 2nd world exporter

F Economic significance of CH_4 conversion into H_2

H_2 production from CH_4

Main industrial processes :

§ Gas steam reforming

§ Catalytic methane decomposition

§ Methane pyrolysis

Disadvantages :

à energy intensive and costly

à low H_2 purity

à greenhouse gas emissions

F non-oxidative process

Non-oxidative methane conversion into H_2 and hydrocarbons

x CH_4 ó y H_2 + z C_nH_m

C_nH_m = alkanes, alcenes (C_2 to C_8)

<u>1- or 2- step processes :</u> Garnier et al.,1997, Smith et al.,1995, Cheikhi et al.,1994

C_nH_m = aromatics (benzene, toluene,...)

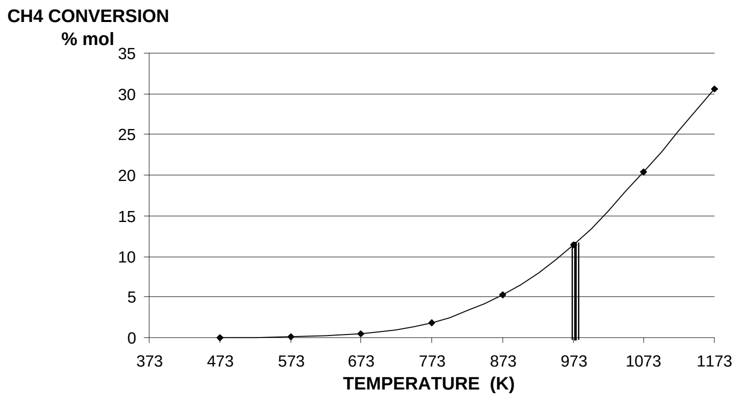
<u>1- or 2-step processes:</u> Iglesia et al., 1999, Shu et al., 1999, Weckhuysen et al.,1998

F low yield , complexity

Aromatization:

Equilibrium-limited conversion

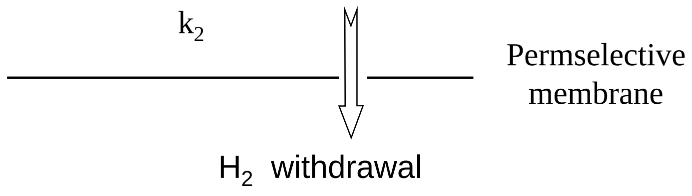
6 CH_4 ó 9 H_2 + C_6H_6



F Limitation: 11.3% at 973K

Shift of the thermodynamic equilibrium using permselective membrane

$$6\ CH_4 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 9\ H_2 + C_6H_6$$



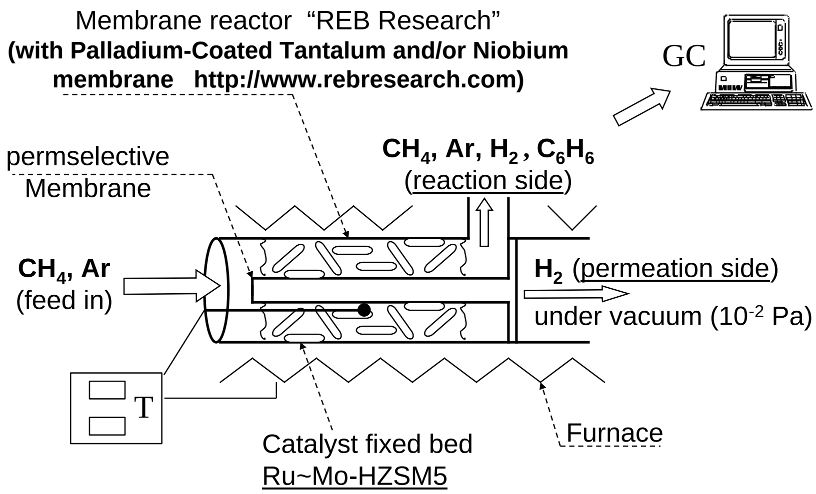
F lower temperature, higher yield separation in situ

Objective of this study

Investigation of methane aromatization

in a catalytic membrane reactor

Experimental set-up

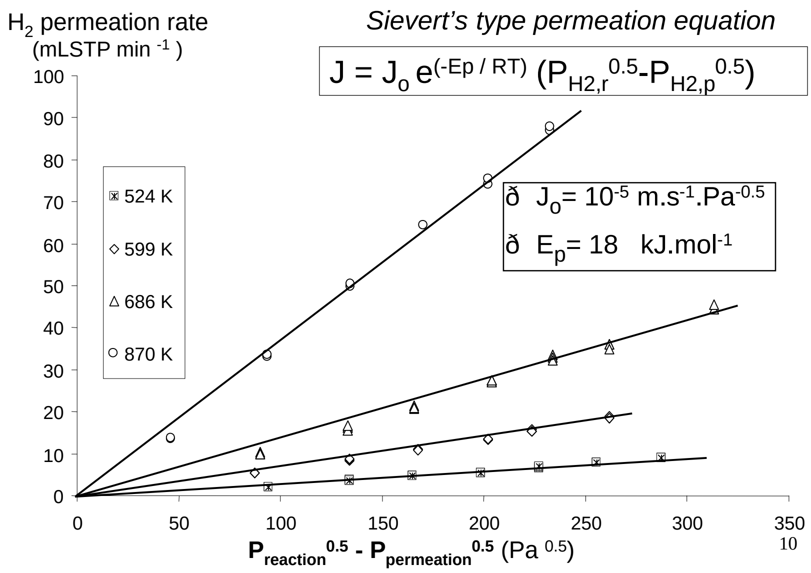


prepared by wet impregnation

Test on H_2 permeation through REB-Research Membrane

Sievert's type permeation equation

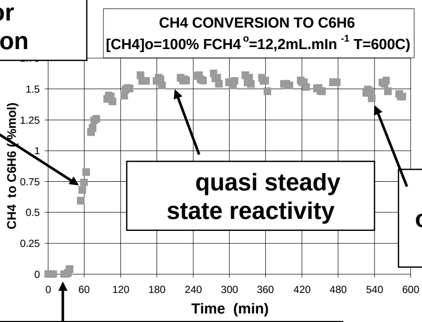
$$J = J_o\, e^{(-Ep / RT)} \left(P_{H2,r}^{0.5} - P_{H2,p}^{0.5}\right)$$



Test on catalytic activity without hydrogen permeation

1) Catalyst is 100% selective in benzene

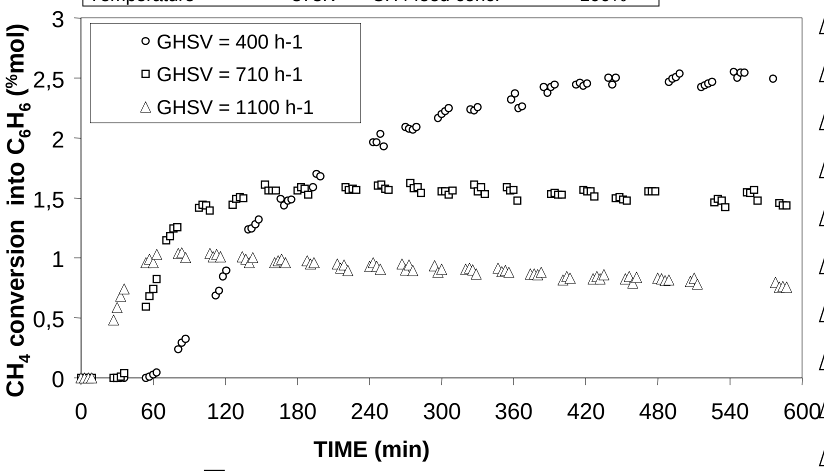
2) Catalyst activity: complex pattern



Residence time effect on methane conversion (without hydrogen permeation)

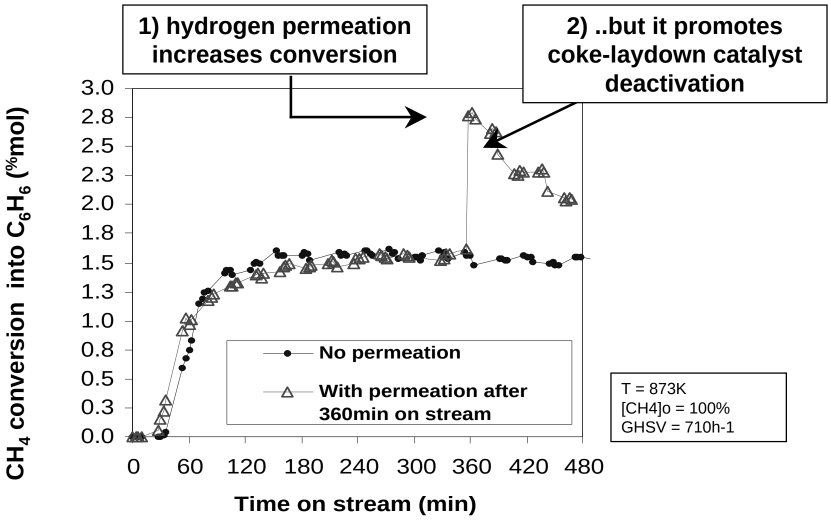
Experimental Conditions

No permeation		P reaction side	= 101 kPa
Temperature	= 873K	CH4 feed conc.	= 100%



F still under kinetics control

Effect of hydrogen permeation on conversion



Results on CH_4 conversion:

H_2 withdrawal (permeation)	Temperature K	CH_4 feed dilution % mol	G.H.S.V. h^{-1}	CH_4 conversion [b,c] % mol	Thermodynamic CH_4 conversion % mol
No	773	100	350	0.20	1.8
Yes [a]	773	100	350	0.36	1.8
No	823	100	380	0.76	3.2
No	873	100	400	2.5	5.2
Yes [a]	873	100	400	5.8	5.2
No	873	100	710	1.6	5.2
Yes [a]	873	100	710	2.8	5.2
No	873	100	1100	1.0	5.2
No	873	43	800	2.2	7.2
No	873	24	1500	2.8	8.9

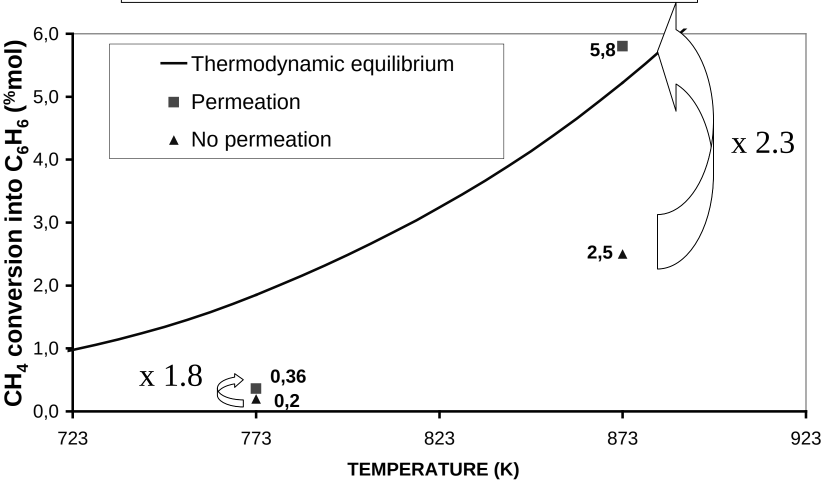
a = $P_{TOTAL\ permeation}$ = 0.2 Pa b = calculated on a benzene basis
c without permeation, quasi steady state conversion is reported
with permeation, initial conversion is reported

Permeation effect on methane conversion

Experimental Conditions

P permeation side = 0,2 Pa P reaction side = 101 kPa

G.H.S.V. = **350-400** h^{-1} CH4 feed conc. = 100%



Literature comparison

- Best yield in C_6H_6 at 873K:
  - **2.6** %mol

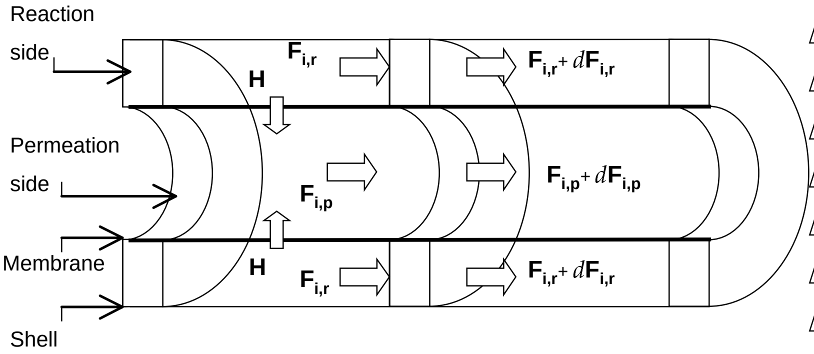
  (G.H.S.V.= **50**h^{-1}, Pt-HZSM-5, Marczewski et al., 1994)

- Permeation effect :
  - Conversion of propane into aromatics is increased by a factor **2** in a membrane reactor

  (Uemiya et al., 1990)

Membrane Reactor Modelling:

- Schematic of the membrane reactor (plug-flow)



- Simplified reaction rate

$$r_{CH_4} = k_1 \left(\frac{P_{CH_4}}{R.T}\right)^{\alpha} - k_2 \left(\frac{P_{C_6H_6}}{R.T}\right)^{\beta} \left(\frac{P_{H_2,r}}{R.T}\right)^{\gamma}$$

Membrane Reactor Modelling:

- CH_4 balance:

$$r_{CH_4} = \frac{d\,X_{CH_4}}{d\left(\frac{W}{F_{CH_4}}\right)}$$

- Permeation rate:

$$d\,F_{H_2,p} = J\,dA$$

$$J = J_o\, e^{(-Ep/RT)} \left(P_{H_2,r}^{0.5} - P_{H_2,p}^{0.5}\right)$$

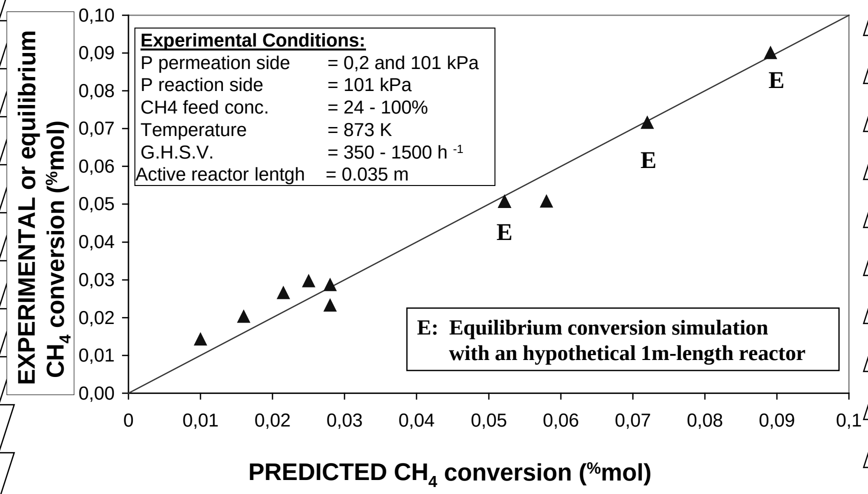
- H_2 balance:

$$P_{H_2,r} = P_{t,r} \left(\frac{{}^3/_2\, X_{CH_4} F_{CH_4} - F_{H_2,p}}{(1 + {}^2/_3)\, X_{CH_4} F_{CH_4} + F^o_{Ar} - F_{H_2,p}}\right)$$

- Fitting of kinetic parameters using Powell algorithm:

$\alpha = 0.41$ | $\beta = 0.41$ | $\gamma = 0.31$ | $k_1 = 6.10^{-5}$ | $k_2 = 4.10^{-4}$

Modelling results (at 873 K)



Conclusions

•Ru~Mo-HZSM5 catalyst was prepared

•Methane aromatization with 100% benzene selectivity was observed

•REB-Research membrane reactor has been tested:
Hydrogen permeation:
ð J improves the conversion rate (by a factor 2)
at 600 ºC, conversion of 5.8 % vs 2.5% without permeation
ð L contributes to catalyst deactivation

•Membrane reactor model has been proposed and validated

Future work

§ Enhancement of catalyst performances:
Æ X_{CH_4}, â coking, Æ stability
ð adding small amounts of CO, CO_2 (Ichikawa et al.,1999)

Boudouart:

CO ⇔ $[C]_{active}$ + CO_2

carbide species formation (promoting effect)

$[C]_{actif}$ + $^{x}/_{2}$ H_2 ⇔ CH_x

« Decokefaction » and regeneration (stabilizing effect)

$[C]_{inert}$ + CO_2 ⇔ CO

(coke)

ex:

{+1.8% CO during 100h} ð 2x 4% = 8% conv. of CH_4 with a selectivity in C_6H_6 alm. cste (# 67%)

(Ichikawa et al., 1999)