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Dennis Dowden Commemoration

Catalysis - from Fundamentals to Application

Durham University

3-4 April 2013

Julian R.H. Ross

Some publications of D.A. Dowden

- Ralph A Beebe and Dennis A Dowden, J. Amer. Chem. Soc., 60 (1938) 2912-2922
“Heats of adsorption of gases on chromic oxide at low temperatures”
- D. A. Dowden, J.Chem.Soc., (1950) 242-265. "Heterogeneous Catalysis. I. Theoretical Basis." (Cited 277 times)
- Dennis Albert Dowden et al., US Patent No. 3222132 (1961)
“Steam reforming of hydrocarbons”

Dennis Dowden in Twente ca. 1987
– age about 70



0.35 coverage in an alloy \rightarrow very different of alloy
 \rightarrow poor choice of diff.

Hydrogenation of org acids
 $Ni \rightarrow CH_3$
 $Cu, + Cu_2O \rightarrow$ both selectivity (2nd better)
 but set of double bond
 $Pb \rightarrow$ unsaturated alcohol (Arrows to)

Pd/Ag - penta - butene \rightarrow butadiene.

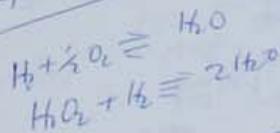
Poisons: ~~low~~ high ionisation potentials \rightarrow strong adsorption
 (Blocked)
 But microporous not adsorb

Fraser + Kilmer $2CO + 2NO \rightarrow 2CO_2 + N_2$

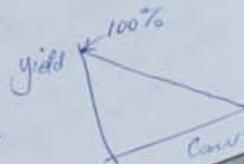


Selectivity of metals
 Small gas of C_2H_2 - Pd
 Large " " " Ni

Selectivity by inhibition
 Zn/Pd
 Pb/Pd
 Cu/Pd



DAD



$H_2 + O_2 \rightleftharpoons H_2O_2$
 Treat as hydrogen.
 Try Pd. Not Pd alone. Try poisons inhibited with CH_2
 Done in aq. solⁿ. Pd/PdO₂ hydrogenated with H_2
 O_2 in mol. form is hydrolyzed with H_2
 Once $[H_2O_2]$ is high, other rxns occur.



ROSS
 TECHNISCHE HOGESCHOOL TWENTE
 AFDELING DER CHEMISCHE TECHNOLOGIE

Probably 1987

DESIGN OF HETEROGENEOUS CATALYSTS

Prof. D.A. Dowden



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Lijun Jia, Dmitri A. Bulushev
Sergey Beloshapkin, Julian R. H. Ross

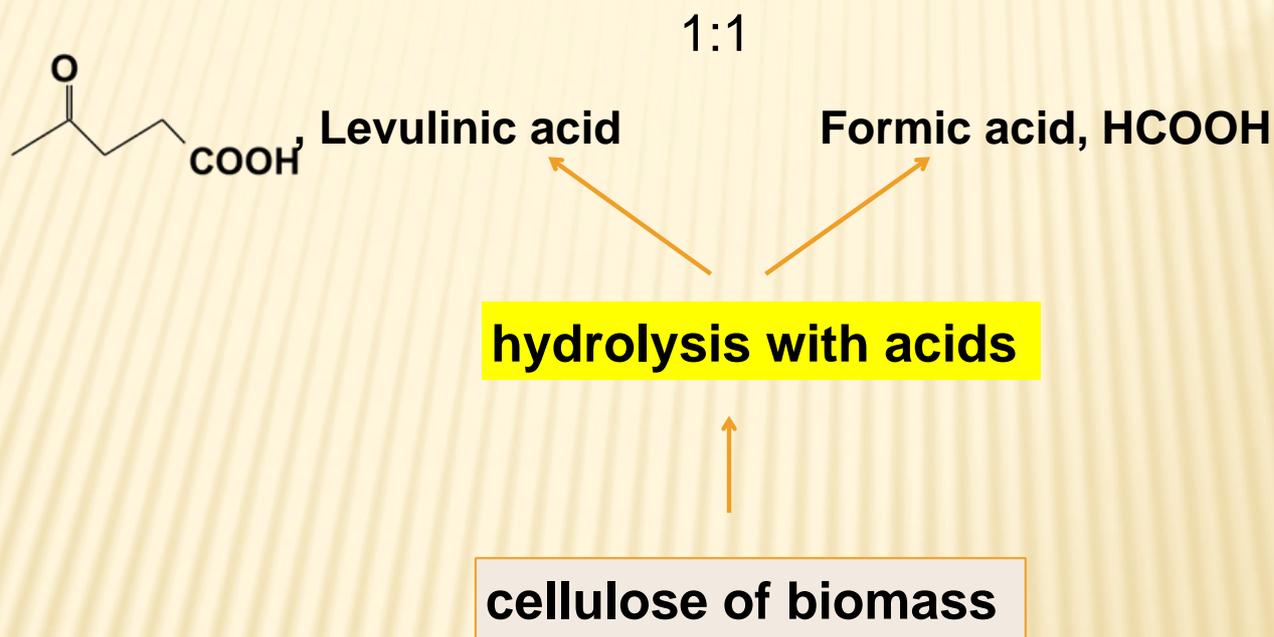
Formic Acid Decomposition over Pd/C Catalysts: Promotion and Change of Mechanism caused by Doping with Alkali Metal Ions

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Charles Parsons Initiative,
University of Limerick
Ireland*



Bishop's Island, Co. Clare

Why work with Formic Acid?

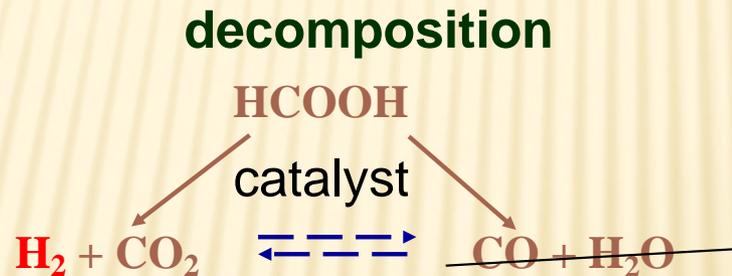


Formic acid for hydrogen storage

H_2 – clean fuel of the future



Gaseous H_2 at 220 bar – 9.8 mole H_2/L
Formic acid liquid – 26.5 mole H_2/L



It is easier to store formic acid than H_2 : no need for low temperatures and high pressures

Why Pd catalysts; why doping by alkali metal ions?

- Pd based catalysts are among the best catalysts for formic acid decomposition
- Alkali metal ions improve the activity of such catalysts in the water-gas shift and methanol steam reforming reactions; both of these could have some similar mechanistic steps as formic acid decomposition

Objective: To examine the role of alkali metal ions in the production of H_2 from formic acid

Preparation of Pd/C catalysts doped by alkali metal ions; reaction conditions

- a) Impregnation of a 1 wt.% Pd/C catalyst (~3.6 nm, Sigma-Aldrich) with alkali metals carbonates or formates using ultrasonic agitation followed by drying at ambient temperature and then at 373 K
- b) Physical mixing of Pd/C and K/C samples using a pestle and mortar
- Reduction in 1% H₂/Ar at 573 K before the reaction
- 2 vol.% HCOOH/He, 51 ml/min, fixed bed reactor

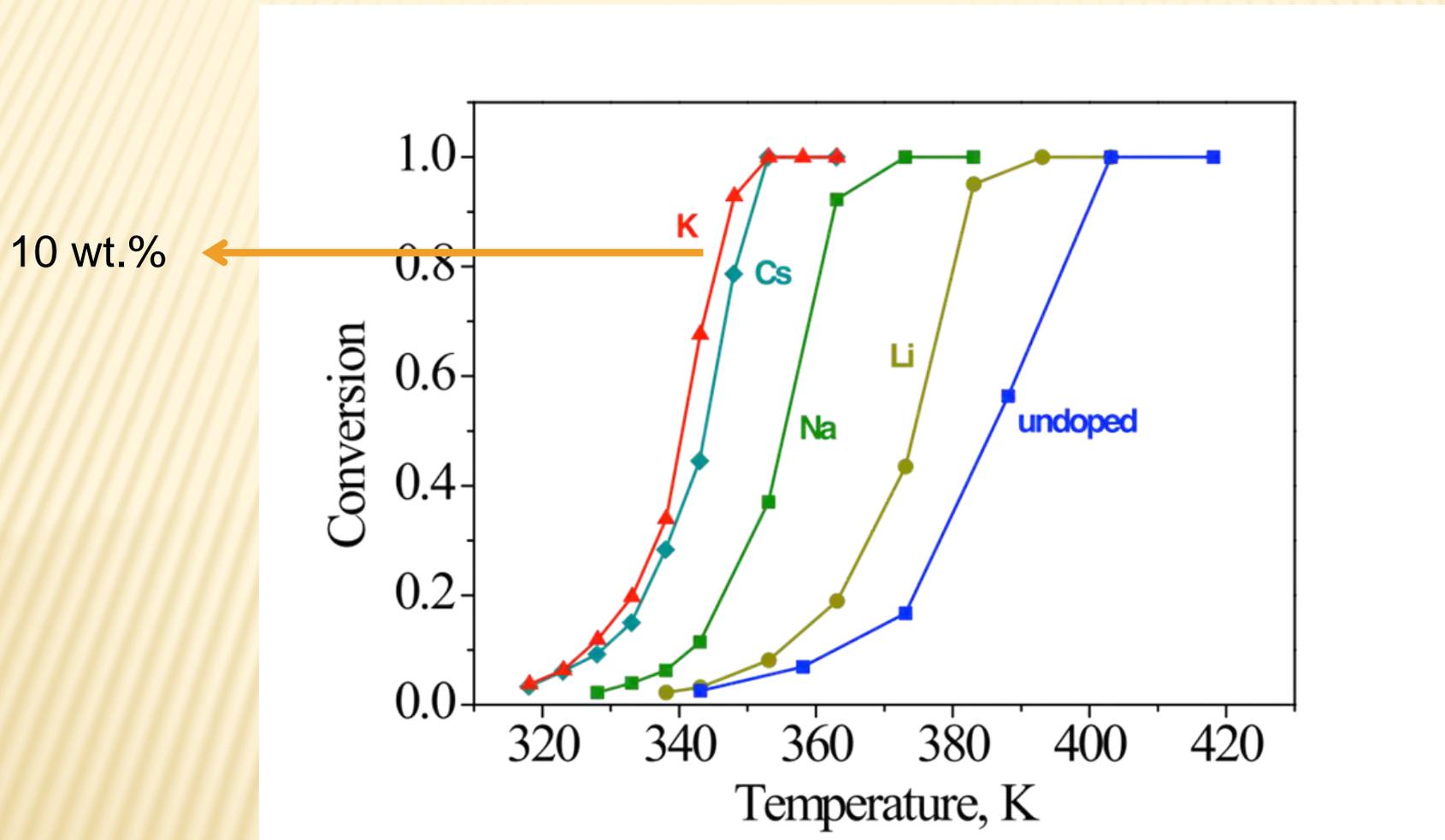
Steady-state activities

Activities of samples after reaction for ca. 1h.

(We return later to the behaviour during the first hour.)

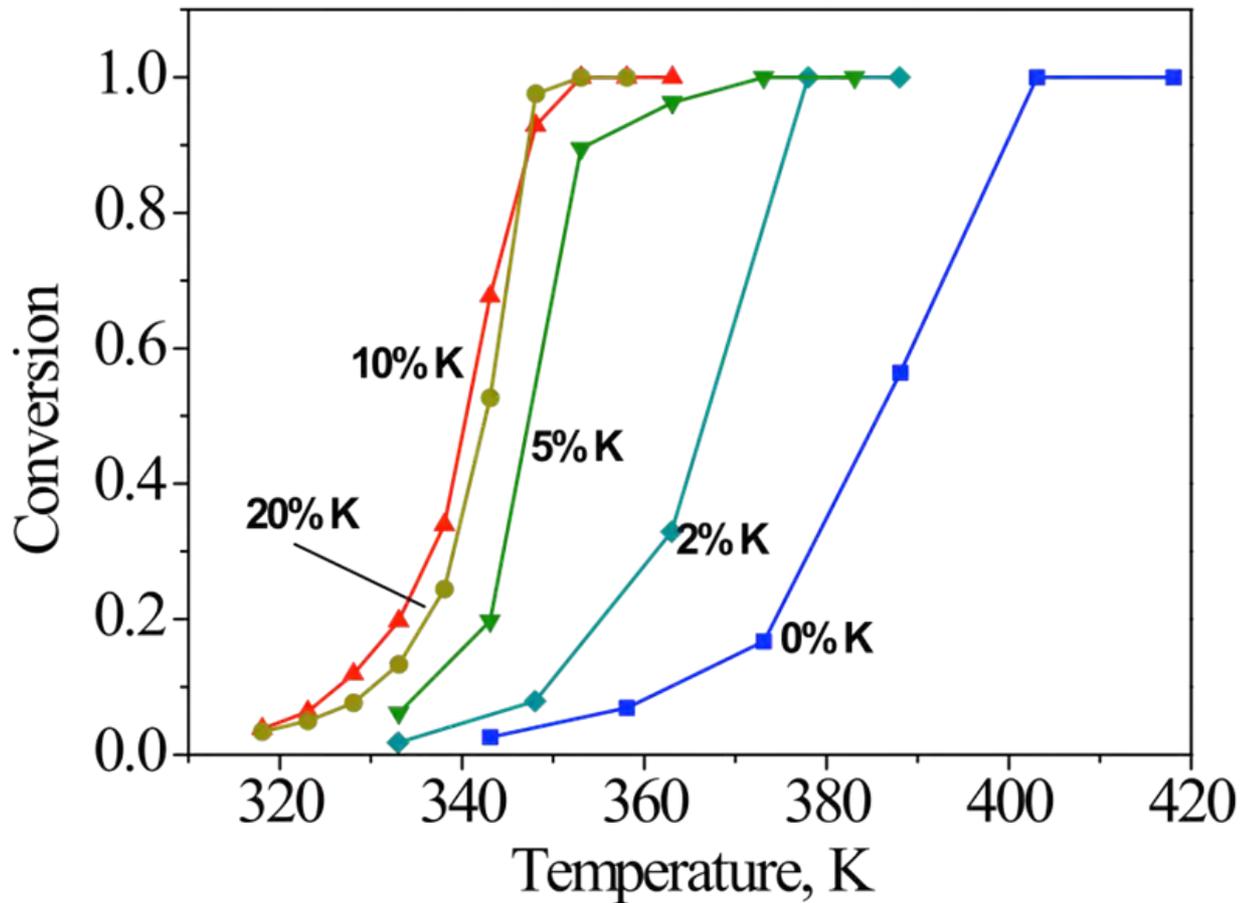
Effect of doping with various alkali metals

(Atomic ratio M+/Pd = 27; 0.68mg of Pd)



K ≥ Cs > Na > Li

Effect of K concentration; 1%Pd/C

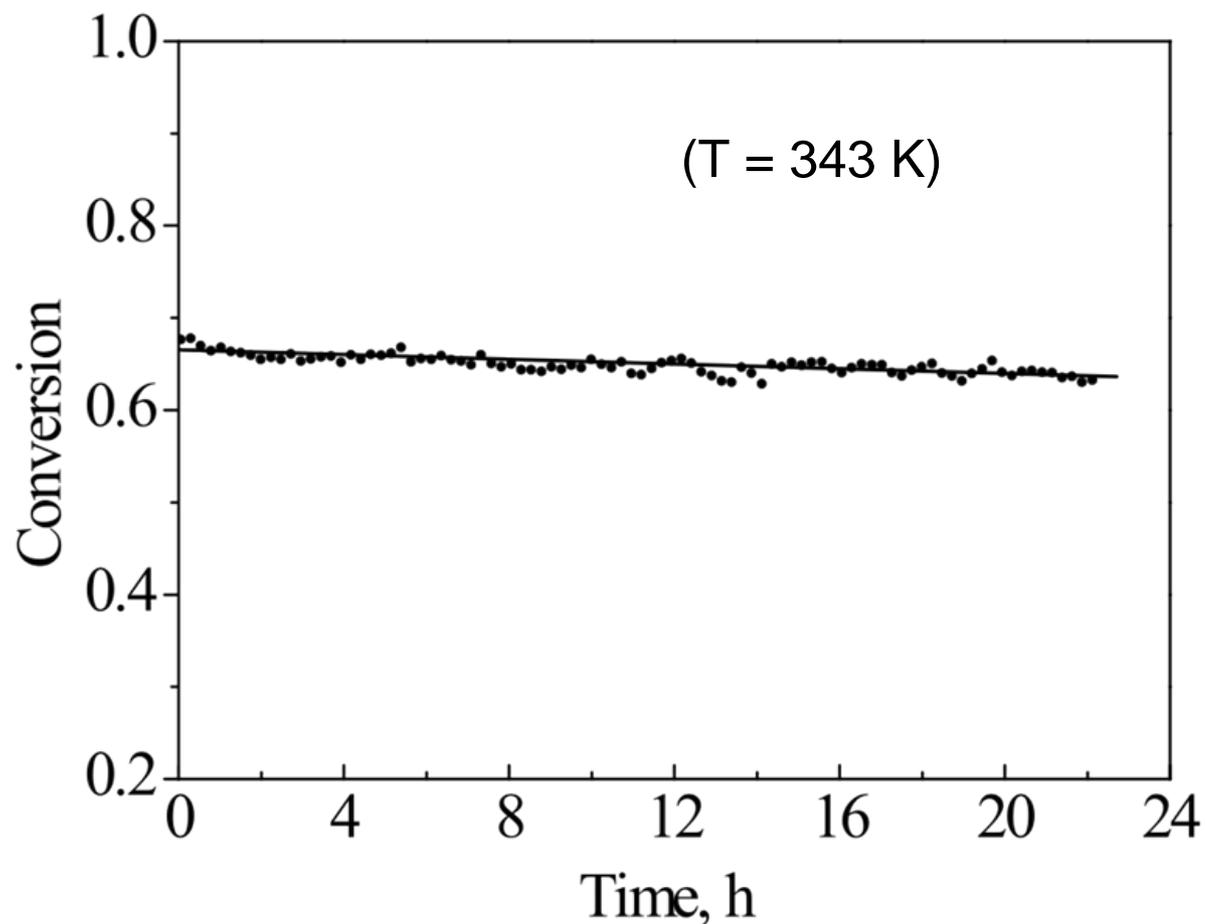


Pd weight 0.68 mg

H₂ selectivity for doped samples > 99%

**K improves the catalytic activity considerably
High K/Pd ratio is needed for optimal performance**

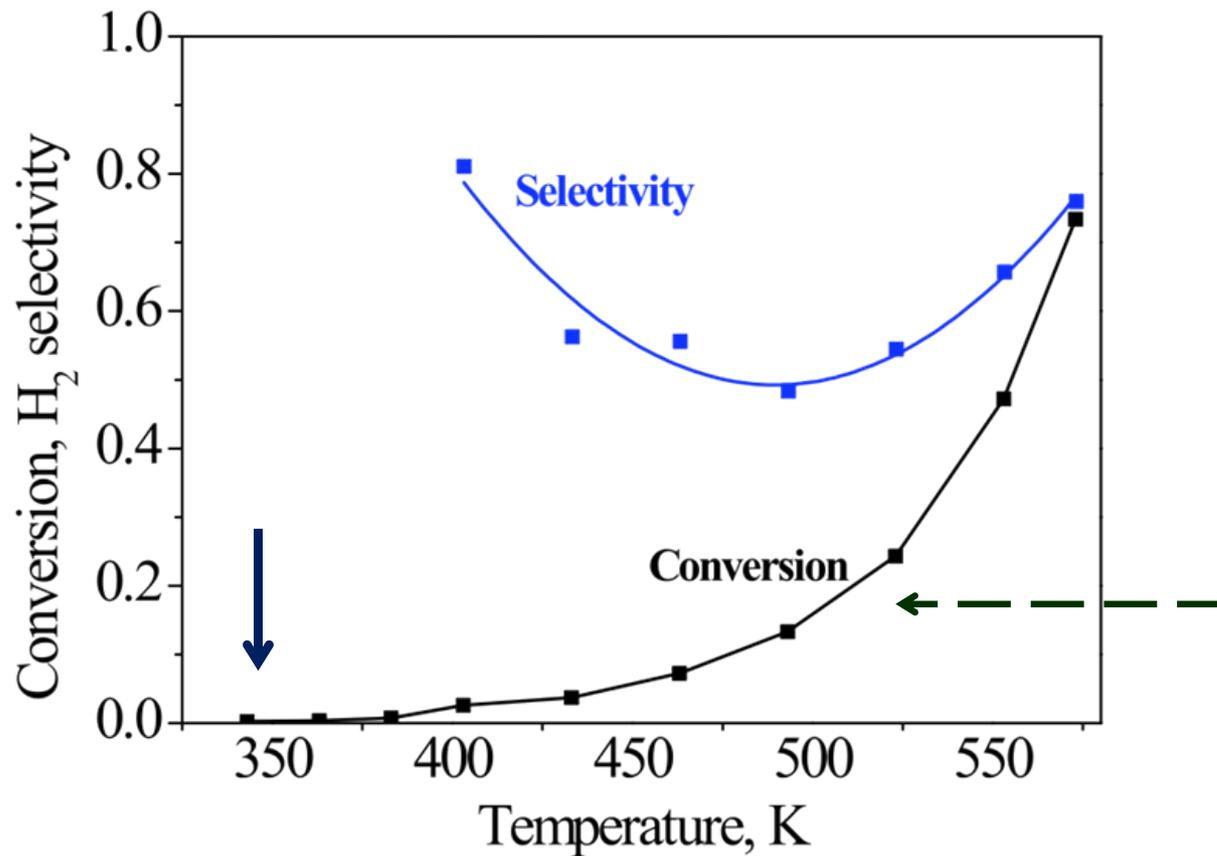
Stability test for 10%K/1%Pd/C



**Selectivity >99.8%,
CO content <30 ppm**

The catalyst provides very stable activity with a high selectivity to CO₂

Activity and H₂ selectivity of 10%K/C sample

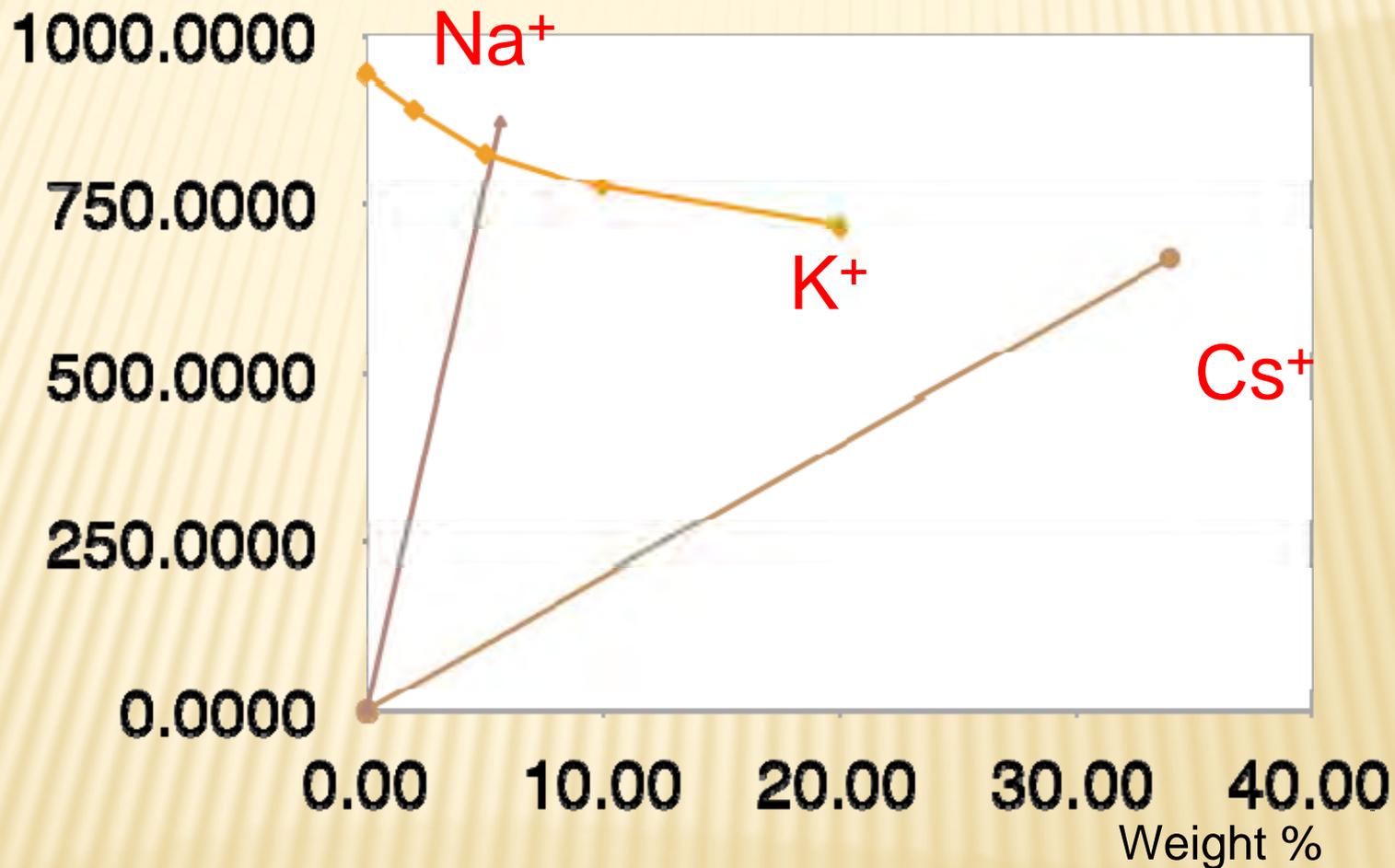


190 K is higher than for the K/Pd/C catalyst

K/C is not active or selective in the reaction when compared with K/Pd/C

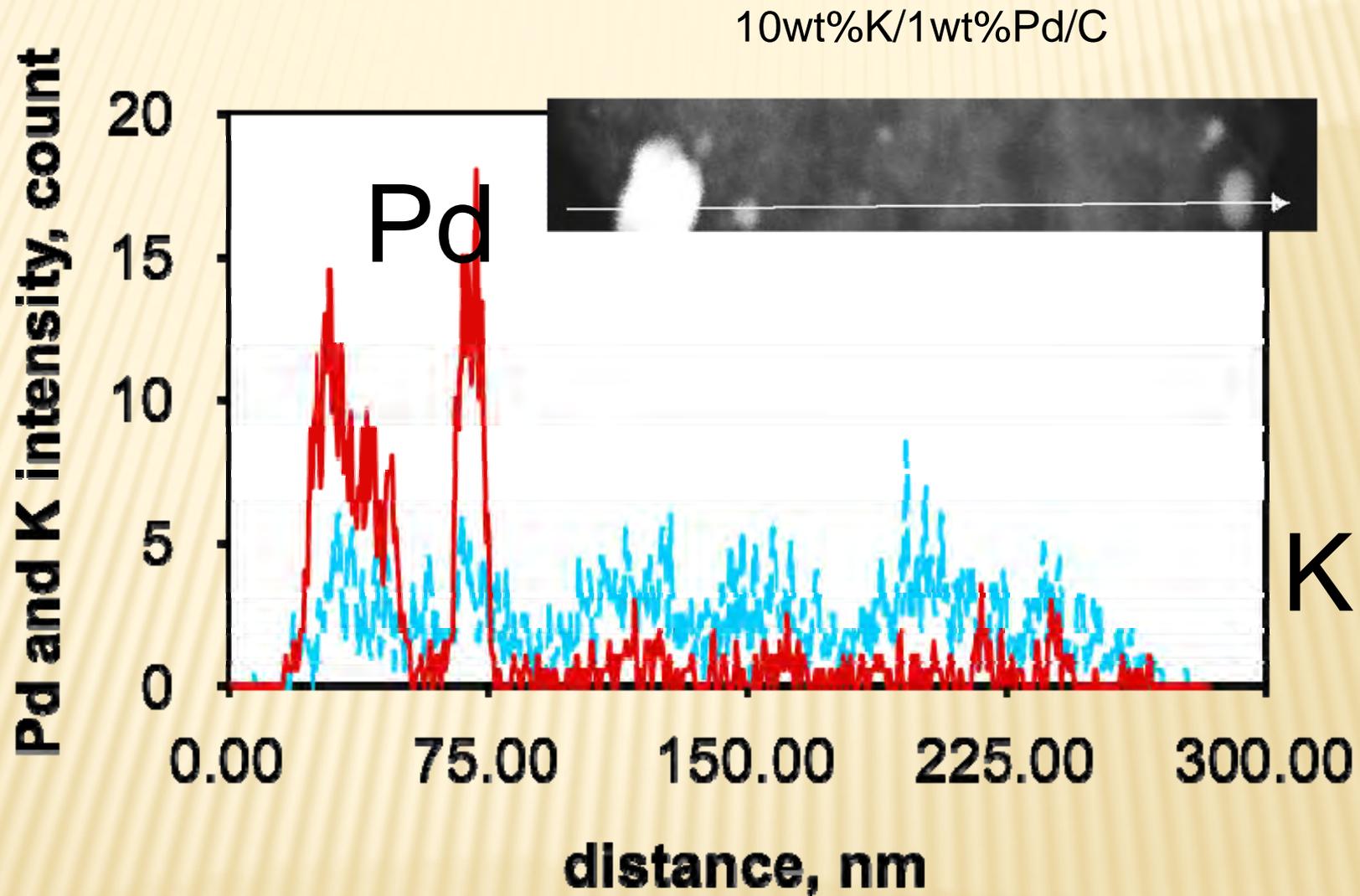
Characterisation

BET surface areas of the doped samples



The BET surface area decreases, probably due to pore blockage

EDS/TEM Line Scanning to determine the position of the K



K covers the surface evenly

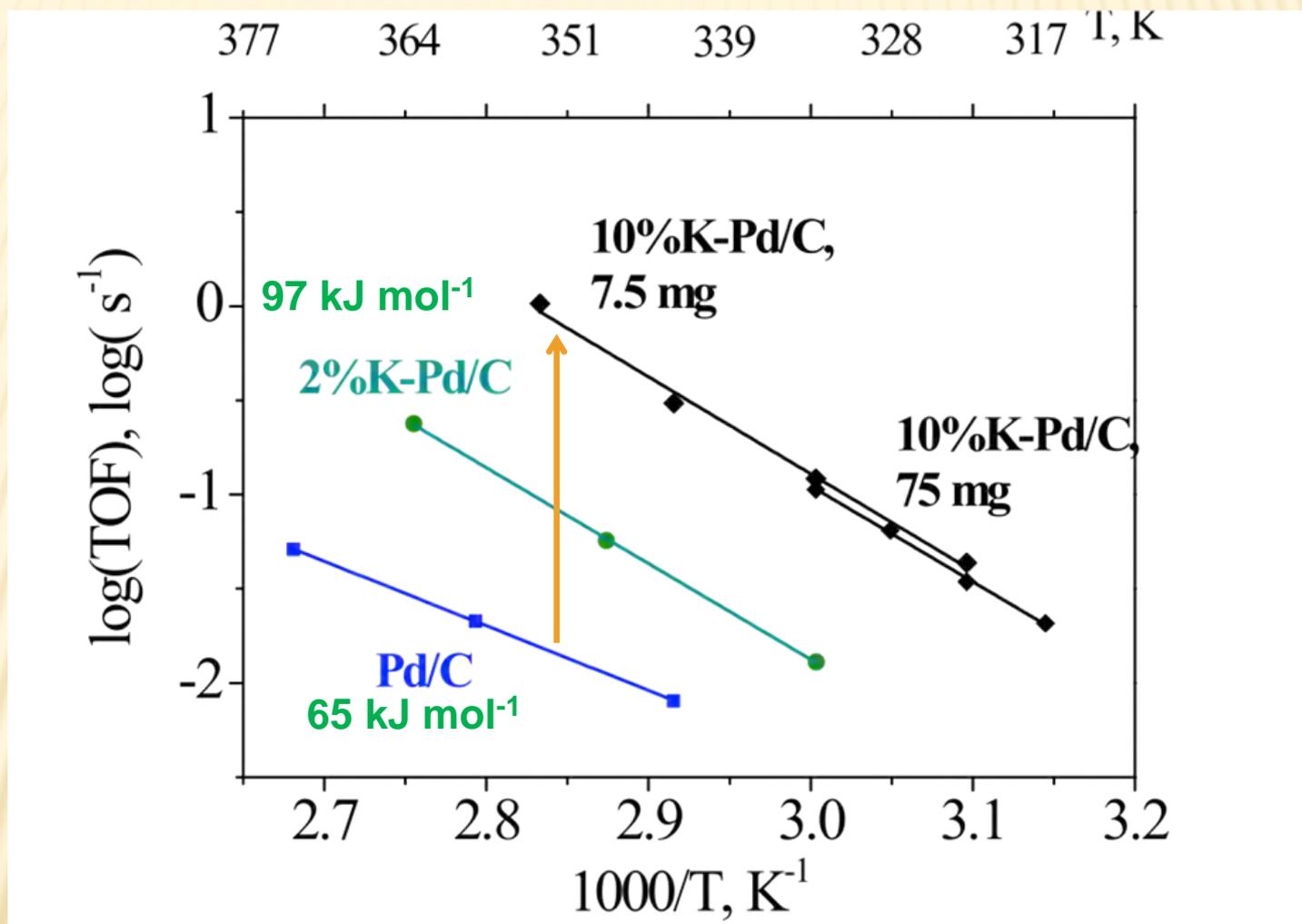
CHARACTERIZATION : TEM, XPS and CO adsorption

	Mean particle size (TEM), nm	Binding energies Pd 3d _{5/2} (XPS), eV (Pd ⁰ and Pd ²⁺)	CO/Pd ratio Chemisorption
no doping	3.6 ± 1.7	335.7, 337.6	0.229
with 2 wt.% K	3.2 ± 1.8	335.6, 337.3	0.154
with 10 wt.% K	3.7 ± 1.3	335.6, 337.7	0.147

**Mean Pd particle size and electronic state of Pd do not change
CO chemisorption decreases 1.5 times and does not depend on K content**

K ions may be located partially on the Pd particles

Arrhenius Plots



**K doping leads to an increase of activity by 10-100 times.
The value of E_a for all the doped samples is constant
and higher than for the undoped sample**

Different reactor conformations and mixed samples

*Catalyst bed
in a tubular
fixed bed
reactor*

Pd/C
impregnated
with K ions



Pd/C
mixed
10%K/C



Pd/C



10%K/C

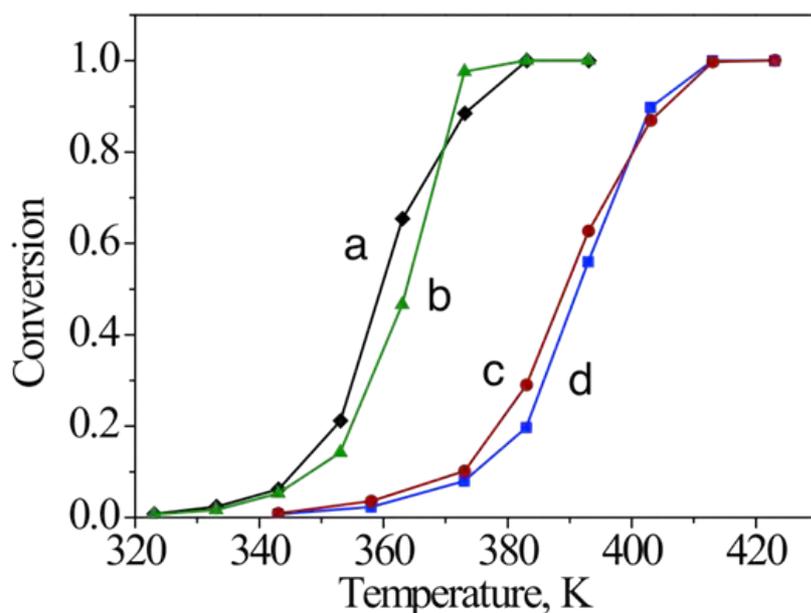


Pd/C

10%K/C

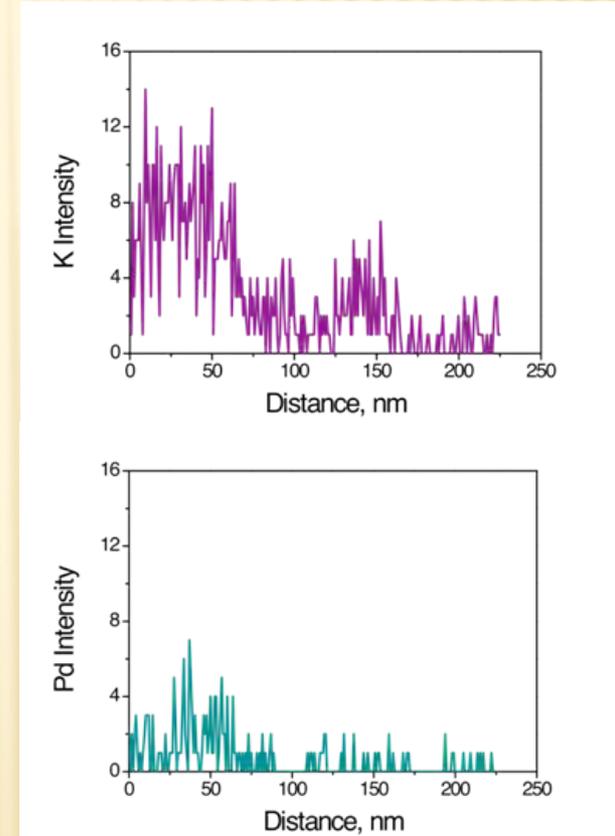
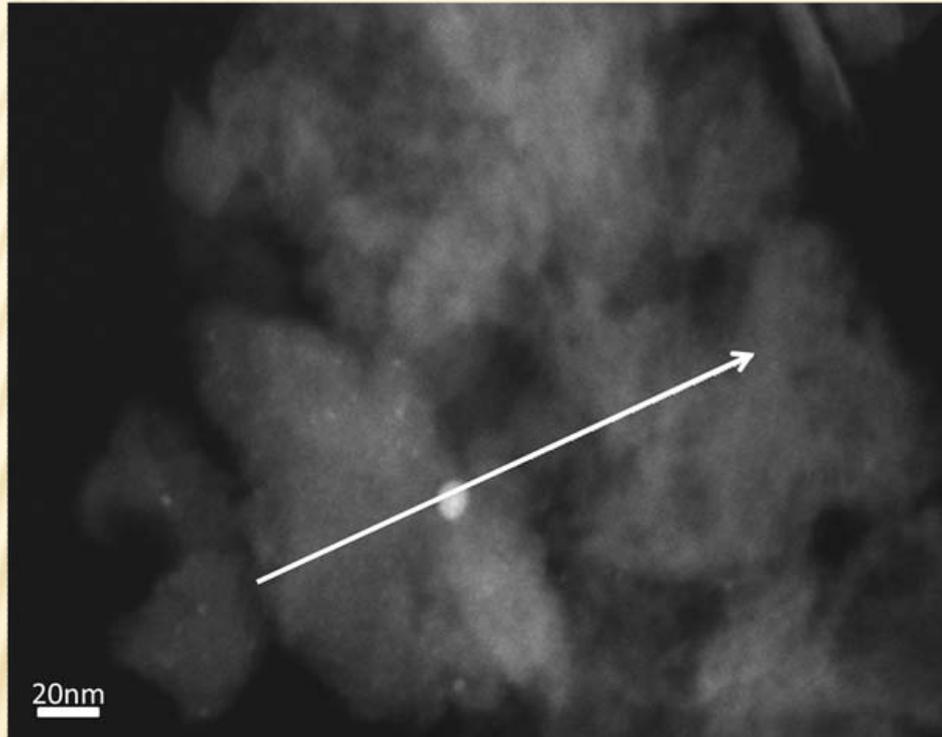
← quartz wool

The same amounts of Pd and K were placed in the reactor in each case:
K/Pd = 27; weight of Pd = 0.068 mg



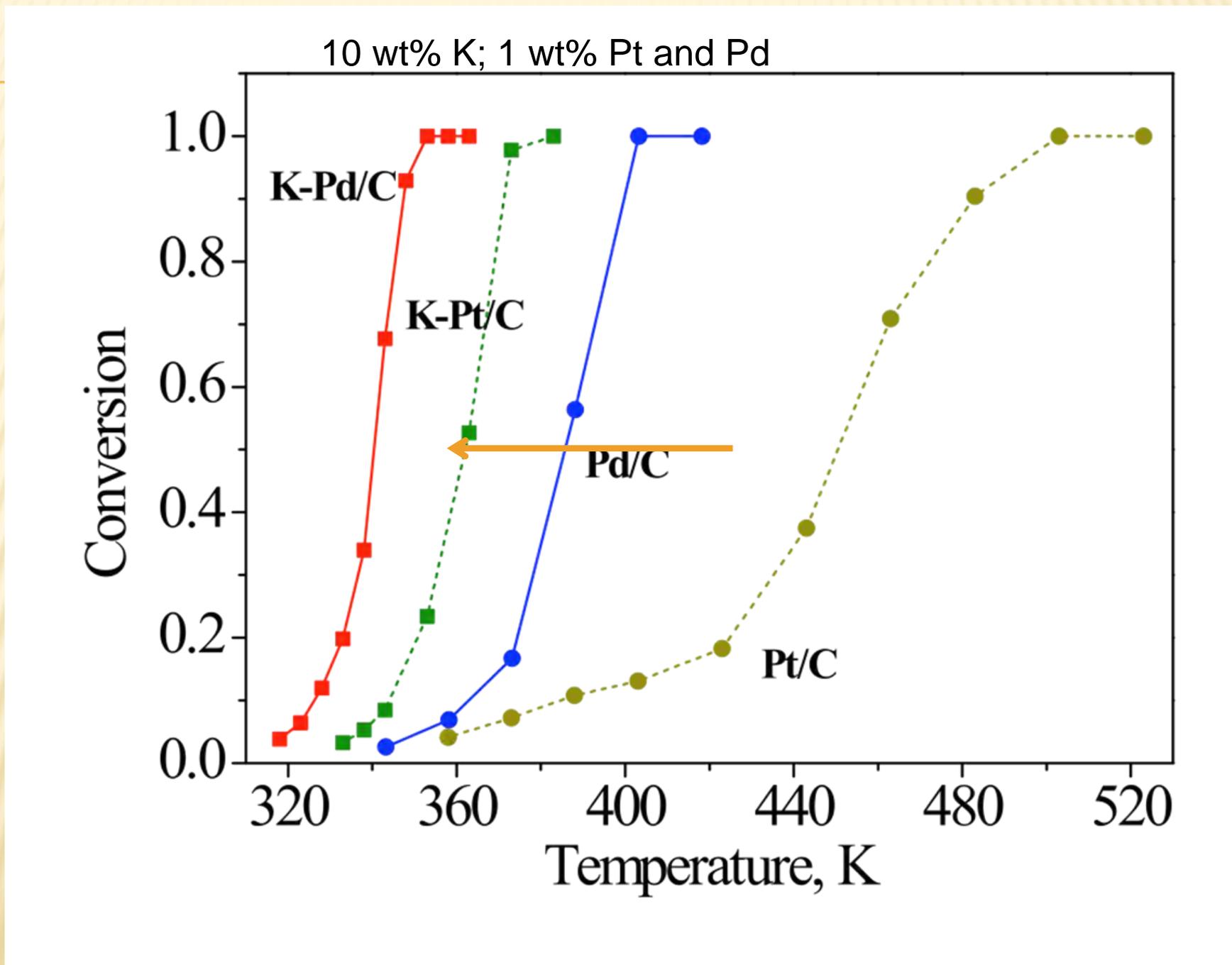
Pd/C physically mixed with K/C gives the same considerable improvement in activity

EDS/TEM of the physically mixed sample: after reduction and reaction



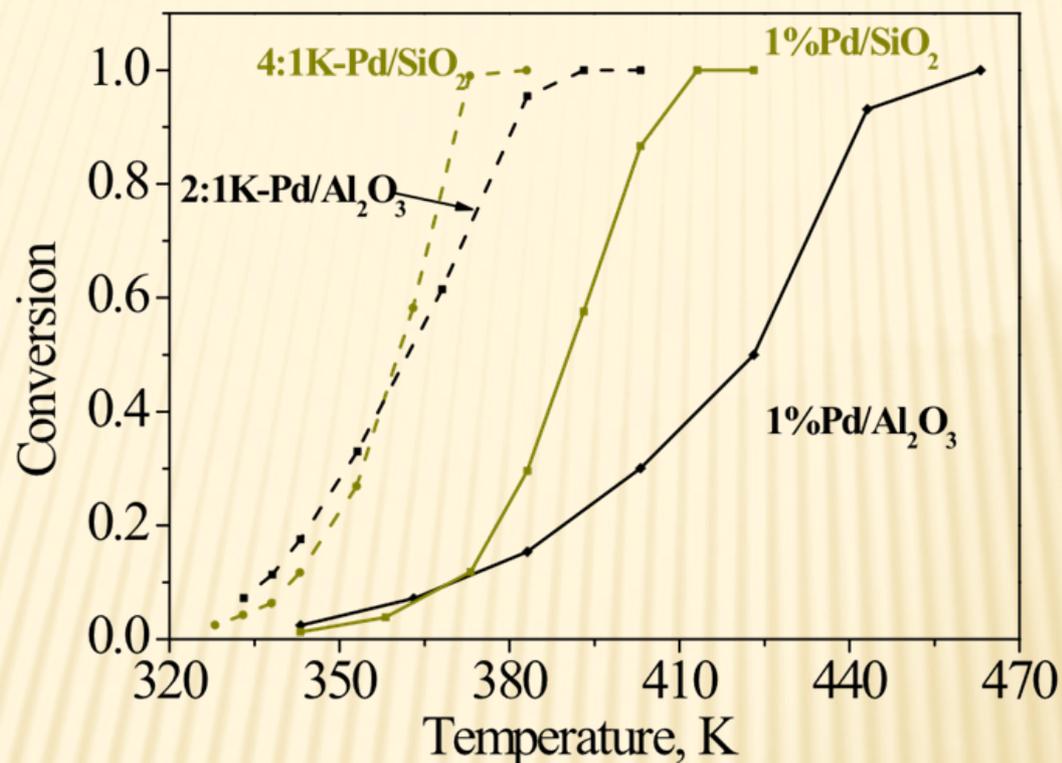
K ions diffuse to the Pd-containing part of the sample.
K should be located in the proximity of Pd particles for the catalytic effect

Comparison of the effects of K-doping of Pt/C and Pd/C



Promotion of the reaction by K ions is also observed for Pt/C (1.6 nm)

Similar promotion by K⁺ with silica or alumina supports



Catalysts

Activation energy, kJ/mol

1 % Pd on Al₂O₃ 68mg

49

1 % Pd on SiO₂ 68mg

78

2K-Pd on Al₂O₃ 68mg

84

4K- Pd on SiO₂ 70m

95

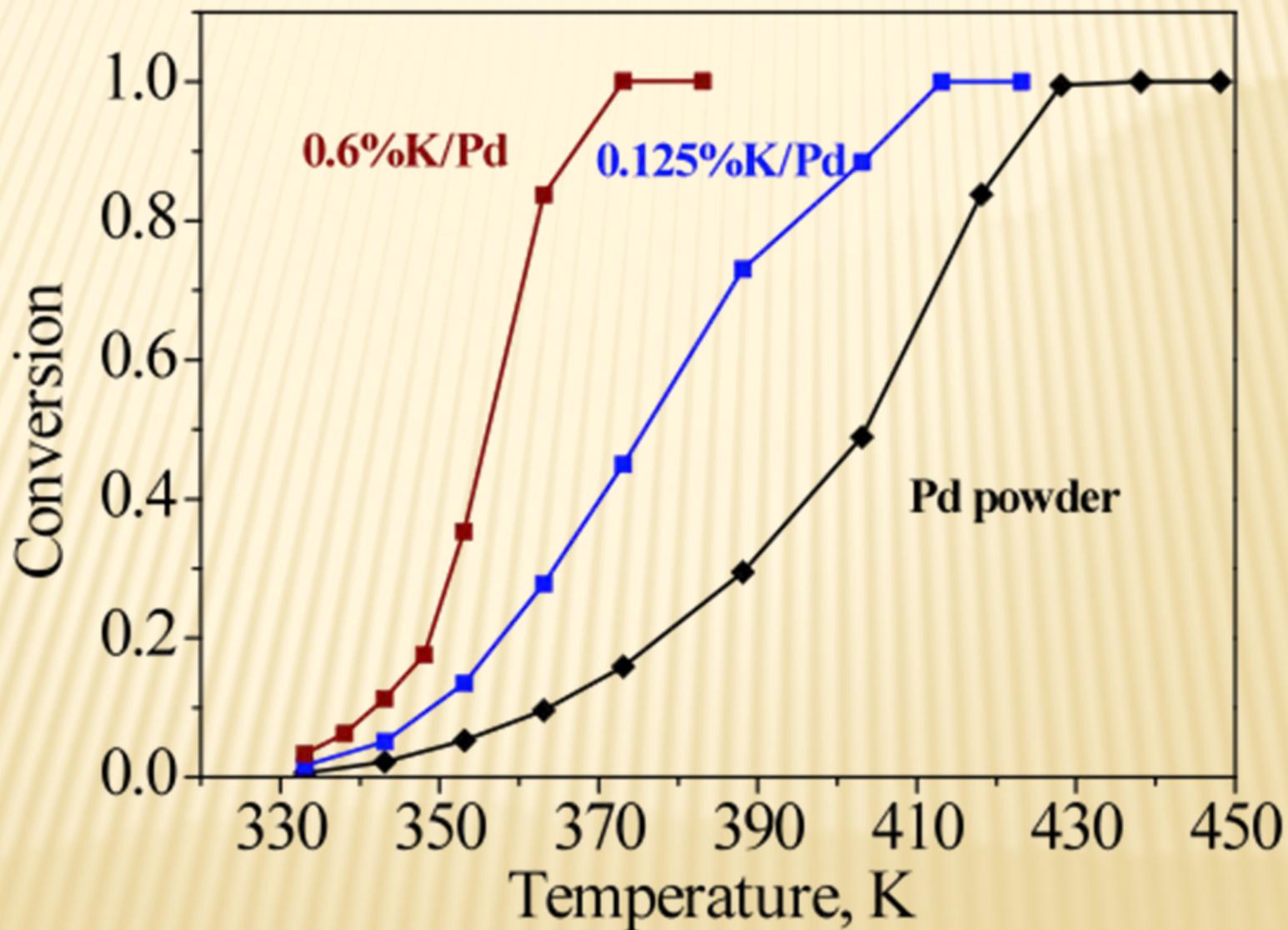
1%Pd/C 68 mg

65

10K-Pd/C 75 mg

97

Effect of K on the behaviour of a Pd powder



Possible explanation



Standard free energy change for first reaction
with gaseous water as product = - 39 kJ/mol

The interface of the Pd particles appears to be critical

Conclusions

- Pd/K/C catalysts give formic acid conversion at low temperature
- K covers both Pd and C
- Formation of K formate species occurs
- Pd is essential for this to occur
- Similar results are obtained with silica or alumina as a support
- Further work is in progress or planned
- Potential use as hydrogen storage material?

Acknowledgements

- Science Foundation Ireland
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- Dr. F. Cardenas (EPFL, Switzerland)

- Bulushev, D.A., Jia, L., Beloshapkin, S., Ross, J.R.H.
“Improved hydrogen production from formic acid on a Pd/C catalyst doped by potassium”, *Chemical Communications*, 2012, v. 48, pp. 4184-4186.