Supplementary data for the paper in Chemical Communications

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"Improved hydrogen production from formic acid on a Pd/C catalyst doped by potassium"

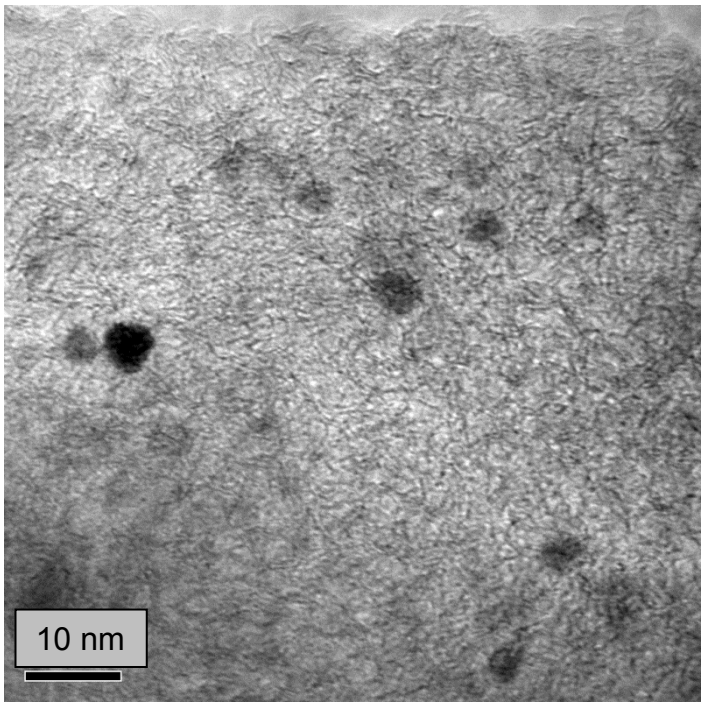
Chemicals, catalysts and activated carbon Darko were purchased from Sigma-Aldrich. Activated carbon Norit was purchased from Lancaster (Alfa Aesar).

BET surface areas were measured using a Micromeritics Gemini device after pretreatment of the samples in nitrogen for 2 h at 473 K. The BET surface area of the 1 wt.% Pt/C was 648 $m^2 g^{-1}$ before and 493 $m^2 g^{-1}$ after deposition of 10 wt.% K.

TEM images of the reduced (1 vol.% H_2/Ar, 1 h, 573 K) catalysts were taken with a JEOL JEM-2100F (200 kV) microscope. This instrument includes an EDAX X-ray energy dispersive spectrometer (EDX) and a JEOL high angle annular dark field (HAADF) detector. About 100 particles were used to calculate the mean particle size and the particle size distributions (Fig. S2). The catalysts were deposited on a TEM holder by dry spraying. For the line scanning EDS/TEM measurements of the physically mixed 1 wt.% Pd/C and 10 wt.% K/C samples before (Fig. S5) and after reaction/reduction (Fig. S6) the scanning started from the Pd containing part of the mixture which was identified by the presence of Pd particles seen by TEM.

The conversion was measured over a range of temperatures, from ca. 318 to 573 K, after the reduction of the catalyst in a 1 vol.% H_2/Ar mixture for 1 hour at 573 K. The catalyst was then cooled in He to the temperature of the reaction. The internal diameter of the reactor-tube used was 4 mm. Gas chromatographic analysis was utilised to determine the concentrations of formic acid and products. The carbon balances were in the frame 100±3%.

a)



b)

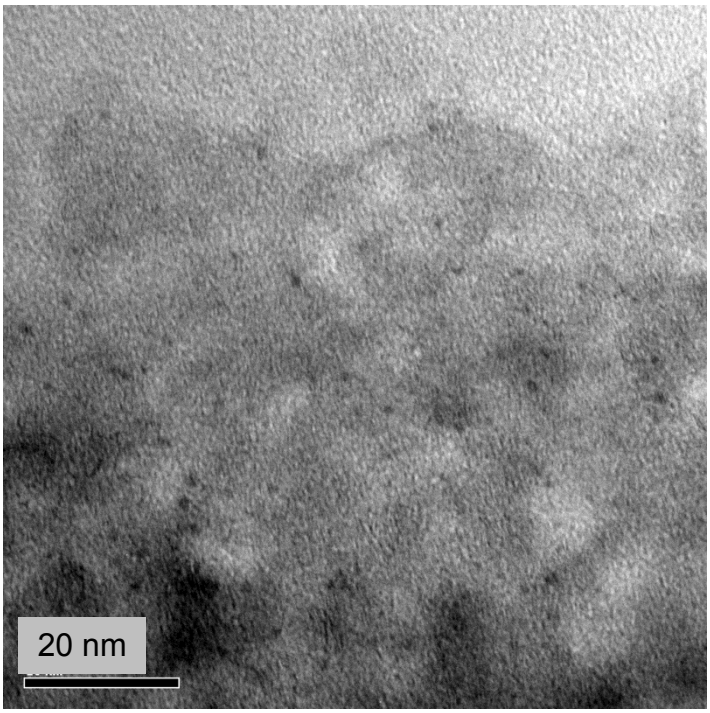


Fig. S1 TEM images of the undoped 1 wt.% Pd/C (a) and 1 wt.% Pt/C (b) catalysts after reduction in hydrogen.

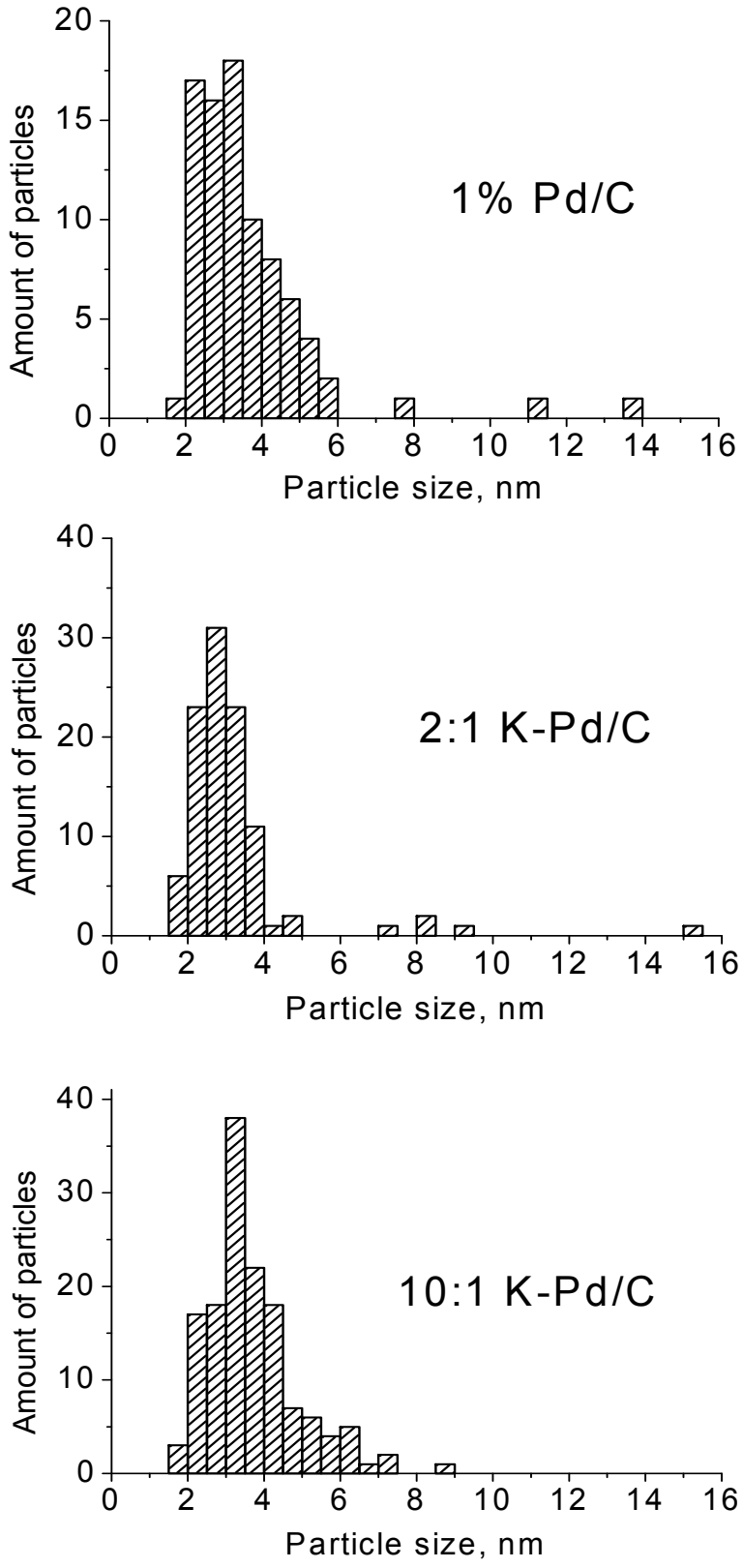


Fig. S2 Particle size distributions over the undoped and K-doped 1 wt.% Pd/C catalysts after reduction in hydrogen

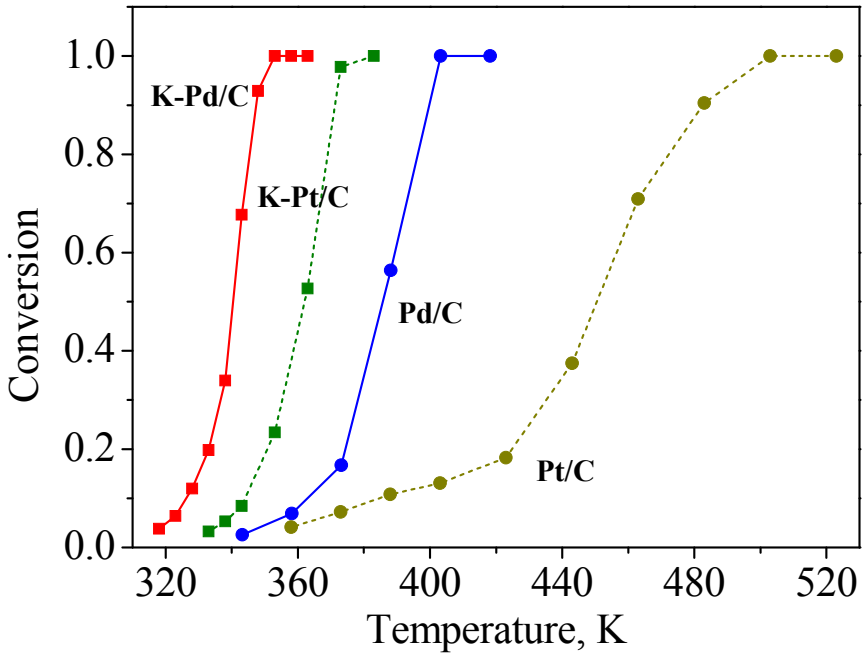


Fig. S3 Conversion in the decomposition of formic acid on the 1 wt.% Pd/C and 1 wt.% Pt/C catalysts with and without addition of 10 wt.% of K. Catalyst weight - 0.068 g for the undoped and 0.075 g for the doped samples.

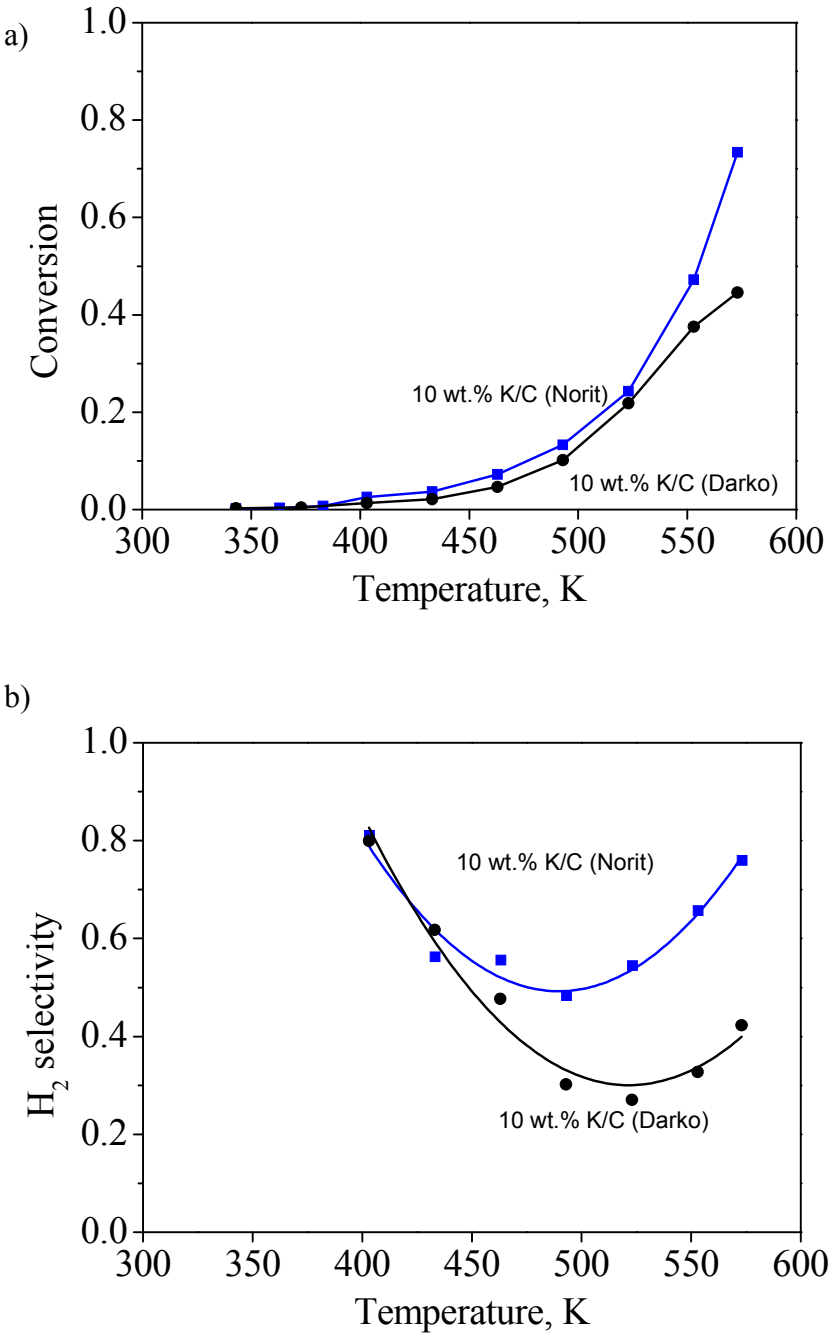


Fig. S4 Conversion (a) and H_2 selectivity (b) in the formic acid decomposition over the 10 wt.% K/C (Norit, S_{BET}=580 m^2 g^{-1}) and 10 wt.% K/C (Darko, S_{BET}=534 m^2 g^{-1}) samples. Sample weight - 0.068 g.

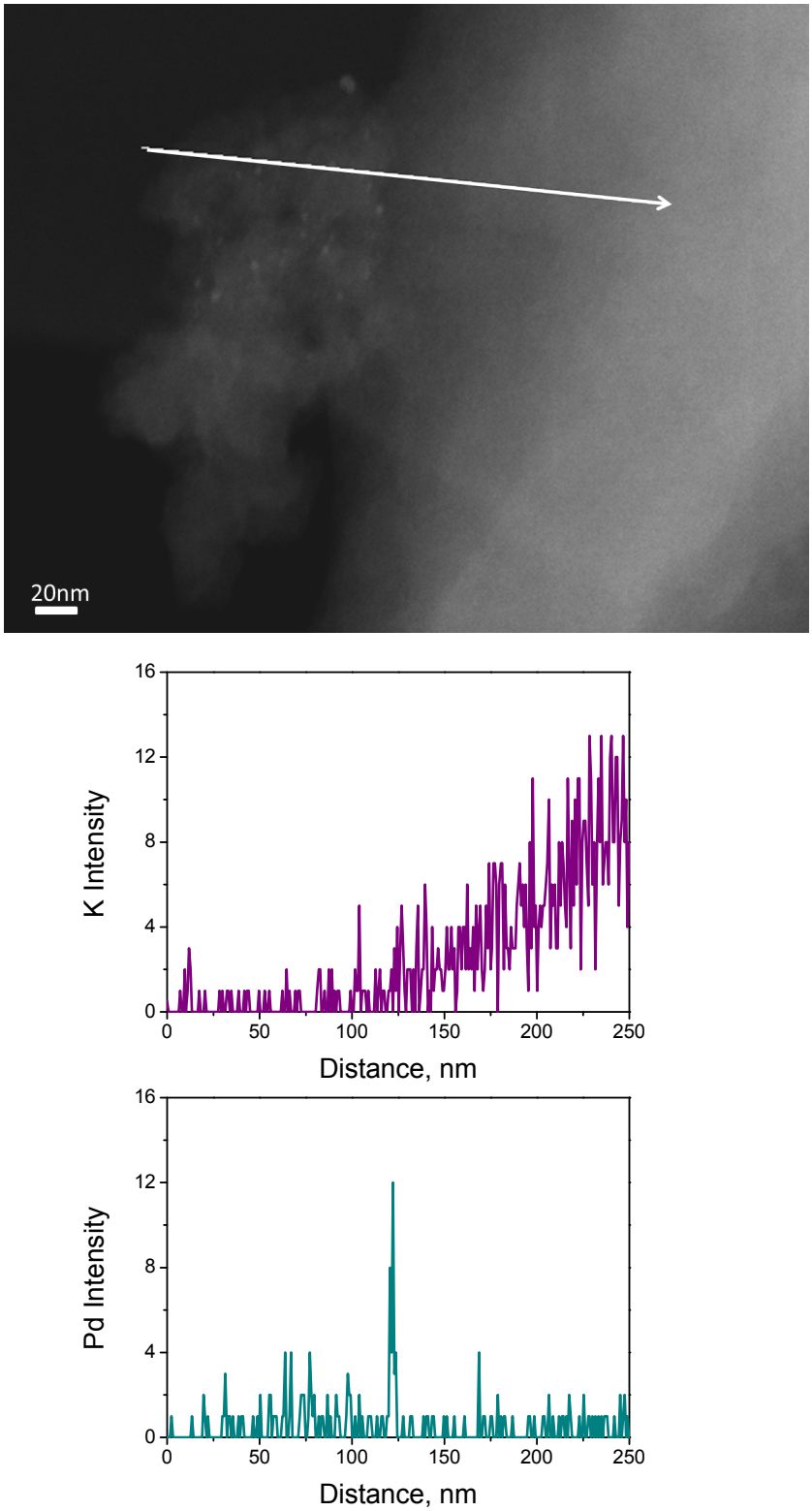


Fig. S5 Line scanning EDS/TEM measurements of the physically mixed 1 wt.% Pd/C and 10 wt.% K/C (Norit) samples before reaction and reduction (Pd particles are clearly seen on the TEM picture).

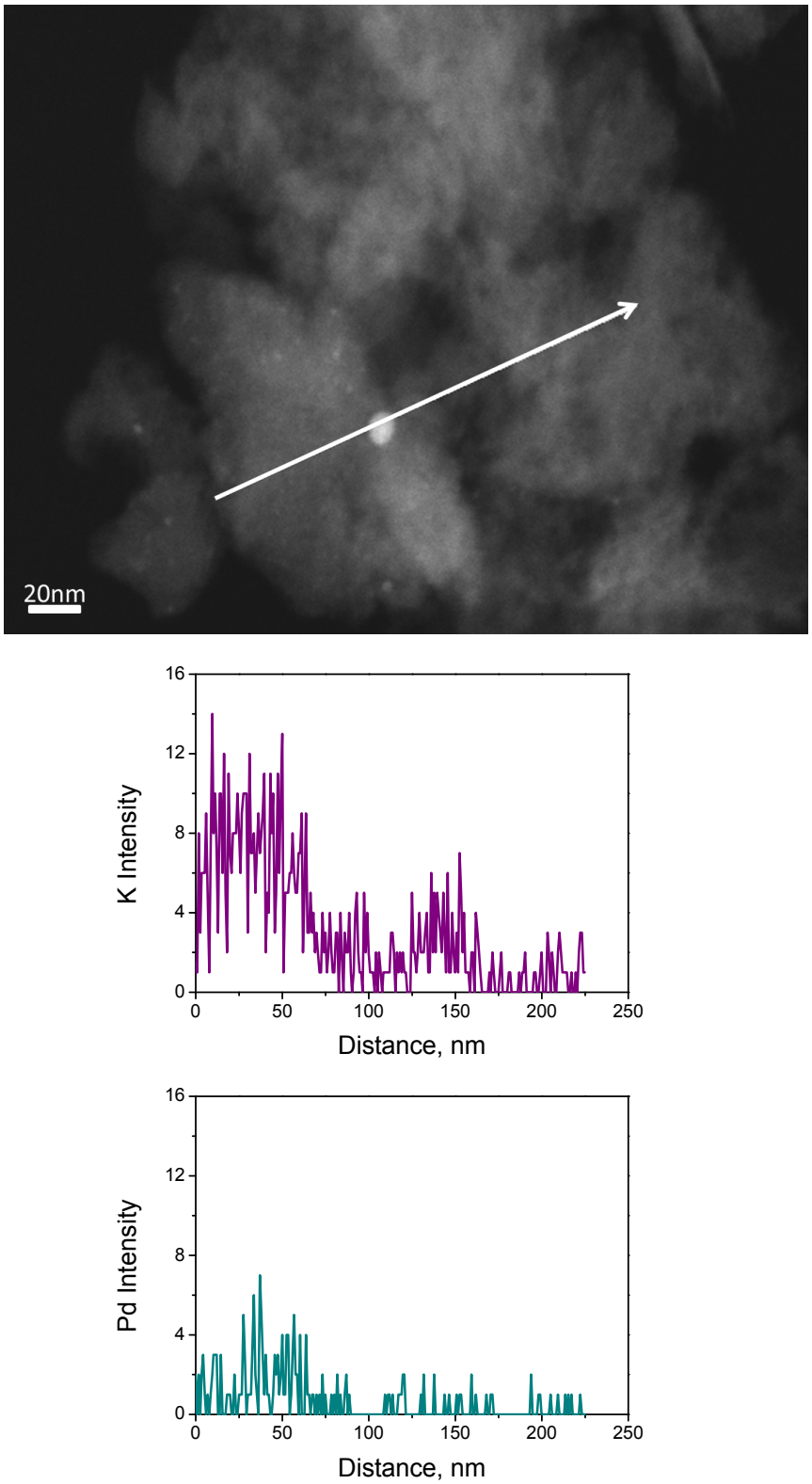


Fig. S6 Line scanning EDS/TEM of the physically mixed 1 wt.% Pd/C and 10 wt.% K/C (Norit) samples after reaction and reduction.