CO_2 hydrogenation at atmospheric pressure on ZnO supported Pd and Cu nanoparticles

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Introduction

The hydrogenation of CO_2 plays an important role in terms of environmental issues for the reduction of greenhouse gases and further on in chemical industry for production of valuable chemicals (e.g. methanol). For realisation of the utilisation of CO_2 via hydrogenation reactions catalysts are required. There are a lot of approaches to develop new catalysts for CO_2 hydrogenation but until now there are only a few solutions for industrial purposes.

In this work two ZnO supported Pd and Cu nanoparticle catalysts were prepared and characterized in view of chemical properties and structural information. Studies about the catalytic activity were carried out for the CO_2 hydrogenation reaction at atmospheric pressure.

Synthesis of the catalysts

- Nanoparticle catalysts:
  5 wt% Pd on ZnO support
  5 wt% Cu on ZnO support
- Preparation steps:
  1. Impregnation of a precursor salt (Pd^{2+}, Cu^{2+} in form of an acetate)
  2. Calcination (at 500°C in air)
  3. Reduction (10 vol% H_2; varied temperature: 200, 300, 500°C)

Temperature Programmed Reduction

- Gas composition: 10 vol% H_2 in Ar
- Temperature program: 25 to 500°C (ramp: 10°C/min)

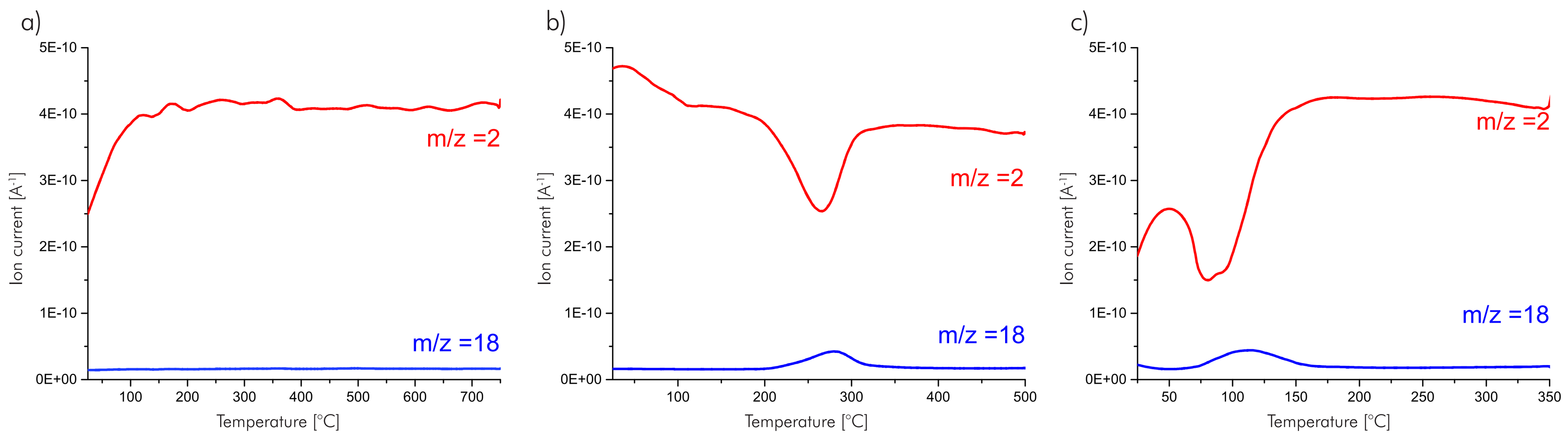


Fig.1: H_2-TPR of ZnO support (a), Cu/ZnO (b) and Pd/ZnO (c)

X-Ray Diffraction

- Cu K-α radiation (1,54060 Å)
- Quantification of Rietveld refinement

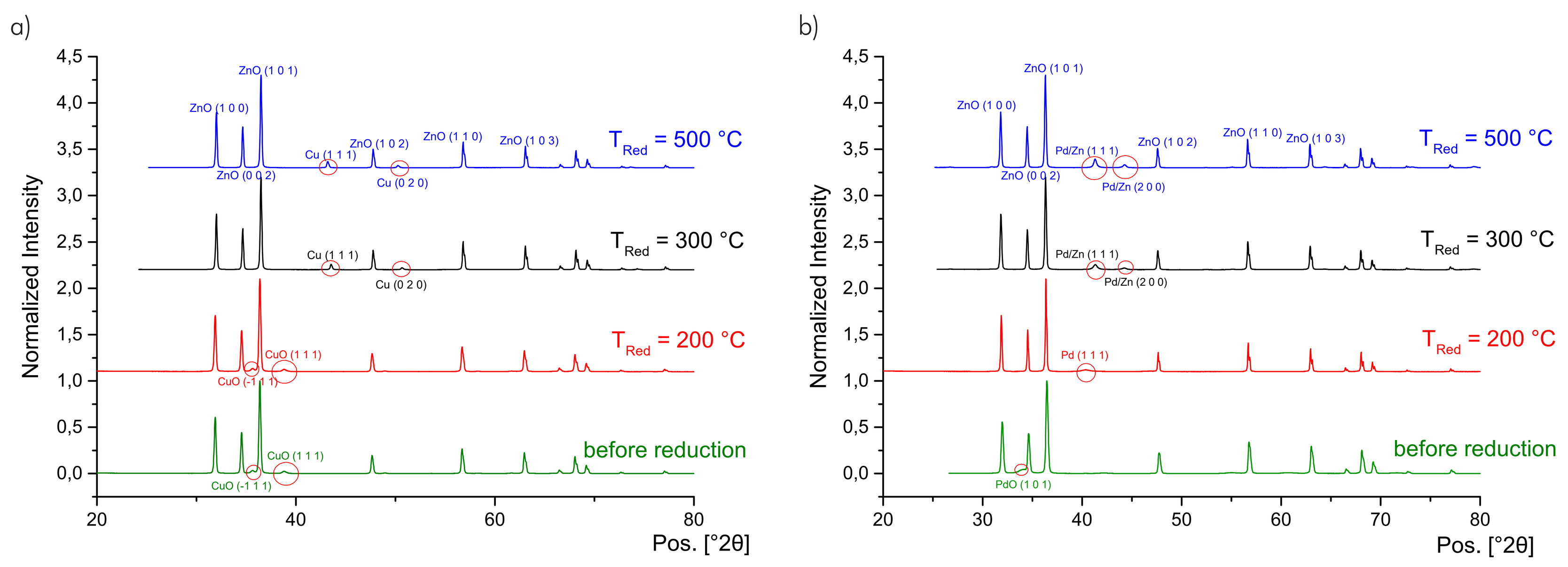


Fig. 2: XRD of Cu/ZnO (a) and Pd/ZnO (b) before reduction and after different reduction temperatures

Particle Size comparison

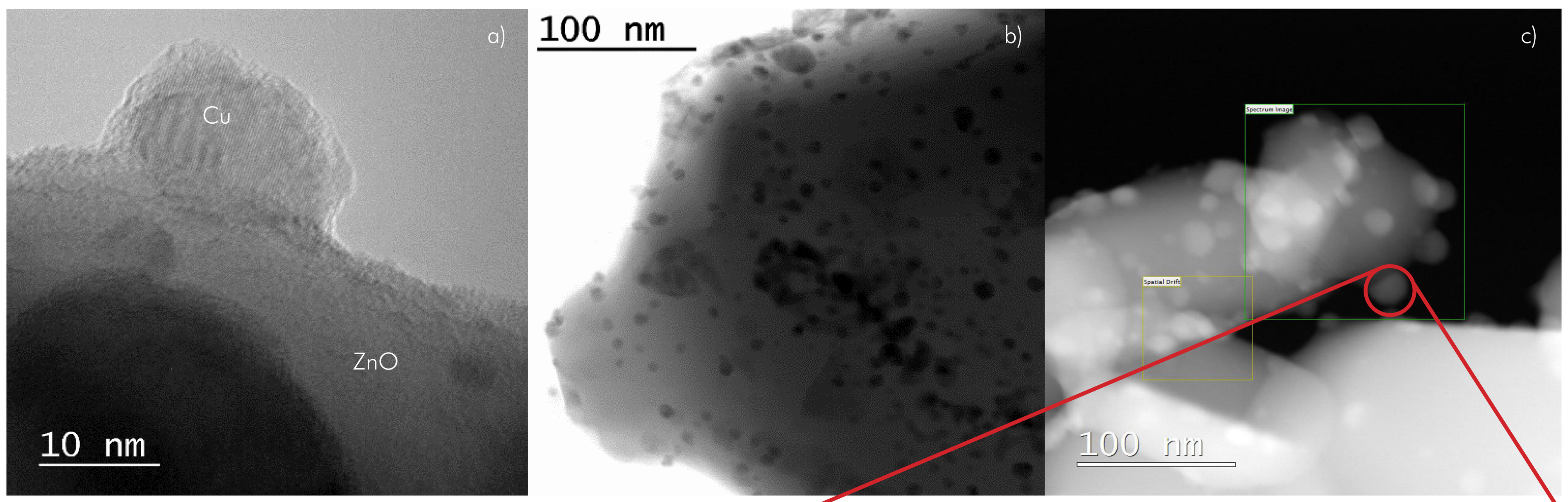
- Particle size analysis of TEM pictures

Tab. 1: Particle size comparison before and after the hydrogenation reaction

Catalyst	Red. Temp. [°C]	Diameter after reduction [nm]	Diameter after reaction [nm]
Cu/ZnO	200	---*	27.1
Cu/ZnO	300	13.2	19.2
Cu/ZnO	500	15.0	18.1
Pd/ZnO	200	6.0	18.5
Pd/ZnO	300	6.5	20.3
Pd/ZnO	500	7.7	16.1

*at 200 °C reduction temperature CuO was still existing

HR-TEM and STEM-HAADF



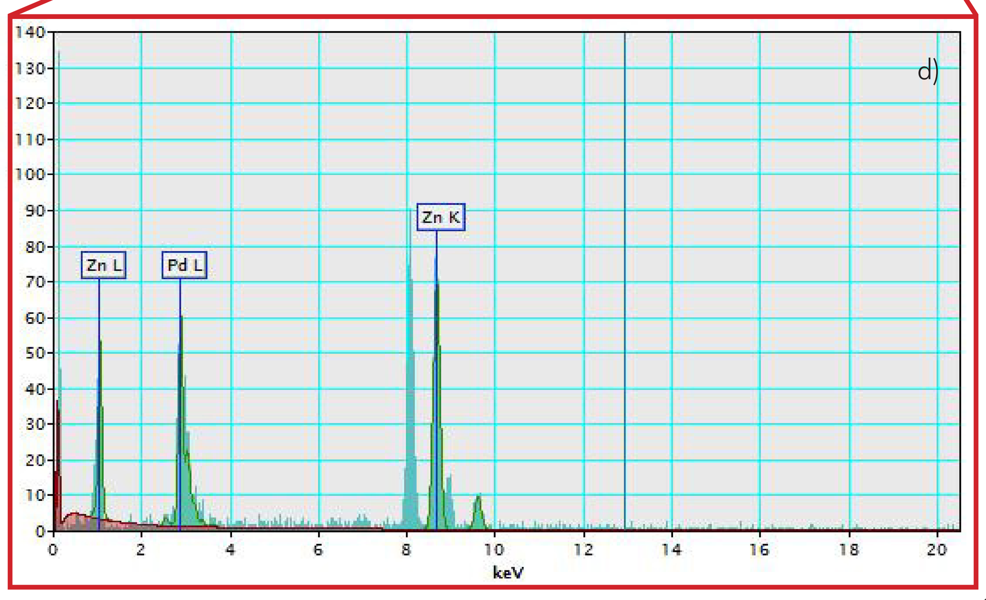


Fig.3:
HR-TEM of Cu/ZnO after 300°C reduction (a),
HAADF-BF TEM of Pd/ZnO after long term reaction (b),
HAADF-TEM of Pd/ZnO after 500°C reduction (c)
and EDX-spectra of Pd/Zn alloy (d)

Kinetic measurements

- Plug-flow fixed bed quartz tube reactor coupled to a micro-GC
- Pretreatment:
  1. 10 % O_2 in He at 500°C (cleaning step)
  2. 10 % H_2 in He at varied temperatures (reduction)
- Reaction: 5% CO_2 and 20% H_2 in He (total flow: 100 mL/min)
- Temperature range: 100 to 500°C, atmospheric pressure

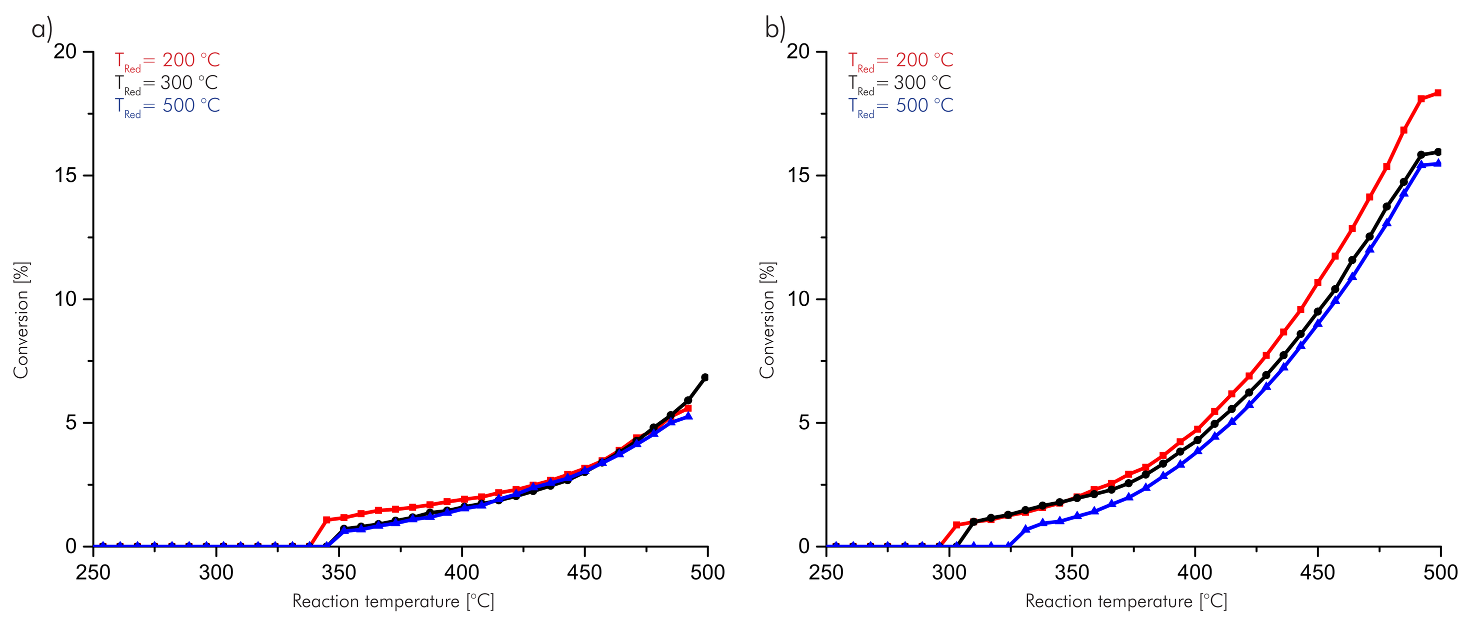


Fig.4: Conversion in CO of Cu/ZnO (a) and Pd/ZnO (b) at varied reduction temperature

Conclusion

- Reduction temperature of PdO (100°C) lower than CuO (300°C) (Fig. 1)
- Different phases present during reduction (Pd or Pd/Zn alloy) (Fig. 2b)
- No alloy formation of Cu/ZnO (Fig. 2a)
- Nanoparticle size growth due to sintering effects and alloy forming (Tab.1)
- Main hydrogenation product: CO via reversed Water-Gas Shift at atmospheric pressure
- Increasing reaction temperature leads to higher conversion for both catalysts
- Pd/ZnO higher conversions ~ 20% (Fig. 4)

References

[1] K. Föttinger and G. Rupprechter, "In situ spectroscopy of complex surface reactions on supported Pd-Zn, Pd-Ga, and Pd(Pt)-Cu nanoparticles," Acc. Chem. Res., vol. 47, no. 10, pp. 3071–3079, 2014.