ACTCO2

Activation of CO_2 on ZnO surfaces and subsequent reactions with nucleophilic coadsorbates

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Goals

- ✓ Synthesis of Cu/ZnO and Au/ZnO with small particle size (only the results on Cu/ZnO are presented here)
- ✓ Characterization of CO_2 interaction with the support and the final materials
- ✓ Evaluation of catalytic properties in CO_2 activation (to be done in germany)

Preparation and characterisation of Cu/ZnO catalysts (1 wt% Cu on ZnO Kadox-911, 8 m^2/g)

Deposition-Precipitation with urea (DPU)

H_2O + ZnO +$Cu(NO_3)_2$ + NH_2CONH_2 → stirring 80° C → washing H_2O → drying RT → As-prepared DPU-Cu

Incipient wetness impregnation (IWI) of different copper precursors

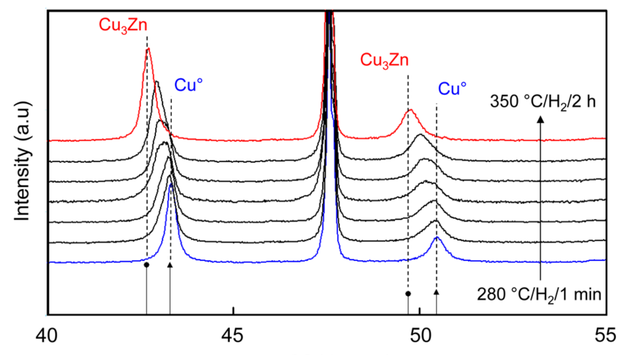
- copper nitrate ($[Cu(NO_3)_2$)
- copper tetraamine ($[Cu(NH_3)_4(H_2O)_2](NO_3)_2$),
- copper bis-ethylenediamine ($[Cu(en)_2(H_2O)_2](NO_3)_2$)
- copper acetylacetonate ($Cu[CH(COCH_3)_2]_2$

+ ZnO → stirring RT → drying RT → **As-prepared**
IWI-CuNit
IWI-$CuNH_3$
IWI-CuEN
IWI-CuAcAc

Characterisation of Cu/ZnO catalysts by XRD, UV and TEM

Samples	As-prepared		Calcined O_2/400 °C		Calc./400 °C + red. 350 °C	
	XRD	UV	XRD	UV	XRD	TEM
DPU-Cu	CuO	Edge at 900 nm (CuO)	CuO	Edge at 900 nm (CuO)	Cu_3Zn (20 nm)	20-30 nm
IWI-CuNit	—	Cu(II) d-d band at 765 nm	CuO	Edge at 900 nm (CuO)	Cu_3Zn (20 nm)	20-30 nm
IWI-$CuNH_3$	—	Cu(II) d-d band at 765 nm	CuO	Edge at 900 nm (CuO)	Cu_3Zn (14 nm)	10 nm
IWI-CuAcAc	—	Cu(II) d-d band at 660 nm	—	Edge at 900 nm (CuO)	—	3-4 nm (1-10)
IWI-CuEN	—	Cu(II) d-d band at 545 nm	—	Edge at 900 nm (CuO)	—	3-4 nm (1-17)

Evolution of the XRD as a function of the reduction conditions



Cu_3Zn (350 °C/2 h)

$Cu_{1-x}Zn_x$ (0 <x <0.25)

Cu^0 (280 °C/1 min to 2 h)

IWI-CuNit (higher Cu loading : 10 wt%) calcined in air at 400° C for 2 h

- **Depending on the nature of copper precursor, copper particle sizes can be controlled. The smallest (4 nm) comes from strong chelating ligand (Acac or EN)**
- **Formation of Cu_3Zn is evidenced for the first time in such materials and can be tuned by controlling the reduction temperature**

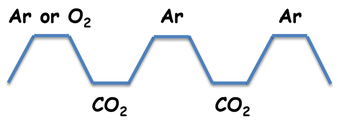
S. Derrouiche, H. Lauron-Pernot, C. louis, Chem. Mater. 2012, *24*, 2282-2291

CO_2 interaction with ZnO and Cu/ZnO (followed by DRIFTS and by quantitative analysis)

Influence of pretreatment atmosphere (role of ZnO vacancies)

Pretreatment

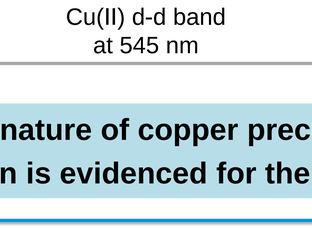
- Thermal treatment at 450° C under Ar or O_2 during 2 h
- Elimination of H_2O and CO_2



Adsorption of CO_2

- Pulse of CO_2 (chemisorption)

1.5 mL of CO_2 (at 150° C)



- Flow of CO_2 (DRIFTS study)

3 mL/min during 10 min

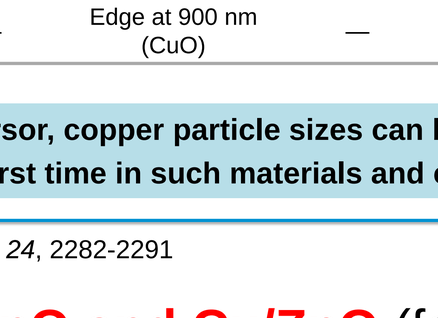
Recording of spectra every 2 min

Desorption

Thermal treatment at 450° C under Ar during 2 h

Results

	Pretreatment under Ar	Pretreatment under O_2	Pretreatment under O_2, then Ar
Amount of CO_2 adsorbed per 500 mg of ZnO	1.00 x 10^{-2} mmol	1.44 x 10^{-2} mmol	1.40 x 10^{-2} mmol



Identified species	Wavelength cm^{-1}
Monodentates carbonates	1543; 1313
Bidentates carbonates	1615; 1293
	1595; 1339; 1000; 848
Tridentates carbonates	1609;1329; 994; 839
Hydrogenocarbonates	3605; 1635; 1424; 1229; 835
Polydentates carbonates	1466; 1386
	1522; 1327; 1030; 876; 720; 660

Summary

- **Correlation between DRIFTS and chemisorption analysis**
- **O_2 treatment restructures irreversibly the materials, fills oxygen vacancies and favours CO_2 adsorption**
- **Polydentate species are the more stable on the surface**

Study of Cu/ZnO calcined catalysts

Influence of calcination conditions and mass % of Cu ex nitrate

	Cu/ZnO (1% wt) calcined at 450 °C under O_2	Cu/ZnO (1% wt) calcined at 450 °C under air	Cu/ZnO (10% wt) calcined at 450 °C under air
Amount of CO_2 adsorbed per 500 mg of catalyst	1.12 x 10^{-2} mmol	0.70 x 10^{-2} mmol	0.22 x 10^{-2} mmol

Influence of precursor

	Cu/ZnO (1% wt) calcined at 450 °C under air	Cu/ZnO (1% wt) calcined at 450 °C under air
Precursor	**copper acetylacetonate**	**copper nitrate**
Amount of CO_2 adsorbed per 500 mg of catalyst	1.10 x 10^{-2} mmol	0.70 x 10^{-2} mmol

Summary

The amount of CO_2 adsorbed is favoured by :

- **Oxidative calcination atmosphere**
- **Low amount of copper**
- **Highly chelating ligand precursors**

Perspectives

- ✓ Study of the supported metallic materials, and role of hydrogen as a reductant
- ✓ Calorimetric study of the CO_2 adsorption (*in situ* conditions)
- ✓ Study of the reactivity of CO_2 towards nucleophilic compounds (alkenes or alkynes in LRS and amines or alcohols in germany)

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