New insights into the precursor chemistry of Cu/ZnO/Al_2O_3 catalysts – Decoupling precipitation and aging

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Introduction / Motivation

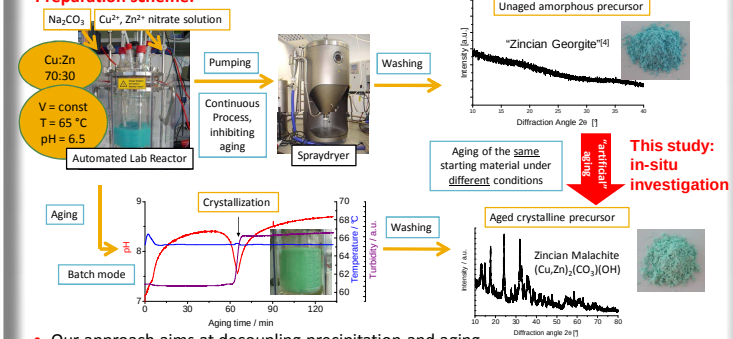
Cu/ZnO/Al_2O_3 catalysts:

- Have been optimized in the last 40 years of industrial application, e. g. methanol synthesis
- Precursors are formed by controlled co-precipitation (pH, T = const.)[1]
- Subsequently, the precipitate is aged in the mother liquor, filtrated, washed, dried, calcined to yield a dark oxide powder and finally reduced for activation

Effect of Aging:[1-3]

- Step is very crucial and has been reported to be essential for a successful catalyst
- During this period a pH-minimum occurs indicating crystallization of the initially amorphous precursor (color change from blue to bluish green)

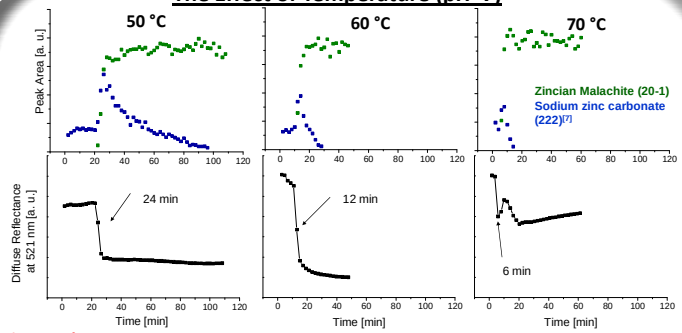
Preparation scheme:



- Our approach aims at decoupling precipitation and aging
- Continuously prepared "unaged" sample as starting material for aging in mother liquor-analogous media ("stepmother liquor": A_2CO_3, HNO_3, H_2O, A = Na, K)
- Allows systematic variation of aging conditions (T, pH, additives, …) without affecting the co-precipitation process and vice versa
- Both events, precipitation and aging, can be studied separately and possibly optimized independently

[1] D. Waller, D. Stirling, F. S. Stone, M. S. Spencer, *Faraday Discuss. Chem. Soc.* 87 (1989) 107.
[2] D. M. Whittle, A. A. Mirzaei, J. S. J. Hargreaves, R. W. Joyner, C. J. Kiely, S. H. Taylor, G. J. Hutchings, *Phys. Chem. Chem. Phys.* 4 (2002) 5915.
[3] B. L. Kniep, T. Ressler, A. Rabis, F. Girgsdies, M. Baenitz, F. Steglich, R. Schlögl, *Angew. Chem Intern. Ed.* 43 (2003) 112.
[4] A. M. Pollard, M. S. Spencer, R. G. Thomas, P. A. Williams, J. Holt, J. R. Jennings, *Appl. Catal. A* 85 (1992) 1.

The Effect of Temperature (pH=7)



Aging results:

- Aging in artificial media ("stepmother liquor") yields crystalline **zincian malachite $(Cu,Zn)_2(CO_3)(OH)_2$**
- An intermediate, **sodium zinc carbonate, $Na_2Zn_3(CO_3)_4 \cdot 3\ H_2O$,** was observed when the amorphous co-precipitate crystallizes
- Sodium zinc carbonate has been mentioned in literature in this context[6]
- This is the first in-situ observation of the appearance during the crystallization process of the initial amorphous co-precipitate into the zincian malachite precursor phase
- Sodium zinc carbonate salt is transformed into zincian malachite within 15 – 80 min, depending on T
- Final aging product is phase pure zincian malachite,
- No aurichalcite, residual intermediate or other by-phase are detected after 120 min of aging
- Change of color within few minutes tracked by UV-Vis-setup and assigned to beginning formation of crystalline zincian malachite
- Color change is no suitable probe for the end of the aging process
- Increasing T changes kinetics of aging and leads to earlier onset and faster reaction
- No effect of temperature on the final degree of Zn incorporation in zincian malchite is observed (similar $d_{(20\text{-}1)}$-spacing at all three temperatures)

[6] S.-i. Fujita, A. M. Satriyo, G. C. Shen, N. Takezawa; *Catalysis Letters* 34 (1995); 85-92
[7] T. E. Gier, X. Bu, S.-L. Wang, G. D. Stucky; *J. Am. Chem. Soc.* 118 (1996) 3039-40

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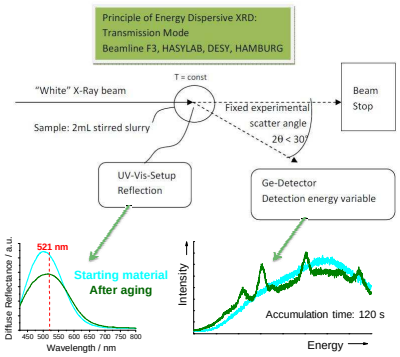
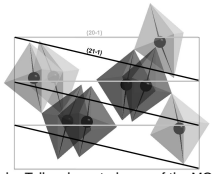
Experimental Setup of the in-situ-Measurement



Crystal Chemistry of Zincian Malachite[5]



Jahn-Teller elongated axes of the MO_6 octahedra in zincian malachite are oriented perpendicular to the (20-1) and (21-1) netplanes

Average Jahn-Teller distortion decreases as Zn^{2+} (d^{10}) replaces Cu^{2+} (d^9)

The $d_{20\text{-}1}$-spacing of zincian malachite is a measure for Zn^{2+} incorporation. High Zn-levels are beneficial for Cu dispersion

[5] M. Behrens, F. Girgsdies, A. Trunschke, R.Schlögl, *Eur. J. Inorg. Chem.* 10 (2009) 1347.

The Effect of Acidity (T = 60°C)

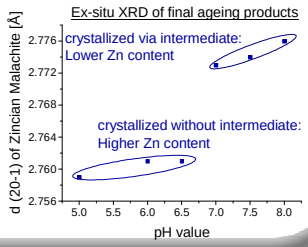
pH	5	6	6.5	7	7.5	8
Na-Intermediate	-	-	-	x	x	x
$d_{20\text{-}1}$-spacing [Å]	2,759	2,761	2,761	2,773	2,773	2,776
Onset [min]	20	34	36	12	12	14

Aging results:

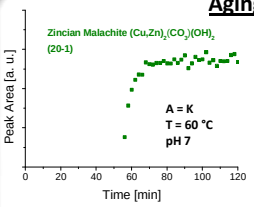
- Changes in Acidity strongly affect the mechanism of aging
- Low pH (pH ≤ 6.5) inhibits formation of intermediate, delay of crystallization
- Sodium zinc carbonate was only formed for pH ≥ 7
- Significantly higher degree of Zn-incorporation for absence of sodium zinc carbonate (based on ex-situ measured $d_{20\text{-}1}$-spacings of zincian malachite)

Ex-situ XRD of recovered samples:

- In-situ samples were recovered for XRD
- Accurate measurement of $d_{20\text{-}1}$-spacings (being qualitatively consistent with those obtained from EDXRD spectra) suggests presence of two groups of precursors
- Higher degree of Zn-incorporation in zincian malachite, if crystallized without intermediate (at low pH)



Aging in A_2CO_3 (A = Na, K)



	A = K pH 7 60°C	A = K pH 7 70°C	A = Na pH 7 60°C	A = Na pH 7 70°C
Intermediate	-	-	x	x
$d_{20\text{-}1}$-spacing [Å]	2,772	2,774	2,773	2,773
Onset [min]	56	18	12	6

Aging in K_2CO_3:

- As expected, no sodium zinc carbonate were formed when using K_2CO_3 instead of Na_2CO_3
- Accordingly, crystallization of zincian malachite was delayed
- Although preventing the intermediate, the $d_{20\text{-}1}$-spacings were comparable to those in Na_2CO_3 highlighting the importance of pH for the Zn-incorporation in the precursor

Summary

- **The aging process of CuZn-precursors was decoupled from the precipitation and studied independently using in-situ EDXRD**
- **Crystalline zincian malachite was successfully formed from the amorphous starting material in all experiments by aging in "stepmother liquor"**
- **Under certain conditions a crystalline intermediate, sodium zinc carbonate $Na_2Zn_3(CO_3)_4 \cdot 3\ H_2O$, was formed leading to accelerated crystallization, but low Zn-content in the product**
- **Low pH values inhibit formation of the intermediate and led to higher Zn-contents**