

In Situ Monitoring of Ni-based Catalysts during the Synthesis of Propylene Carbonate

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Abstract. Three different nickel complexes were catalytically tested in the synthesis of propylene carbonate by carbon dioxide insertion. XAS measurements of the as prepared catalysts confirmed the differences in the structure which led to the varying catalytic activity. The structure of one of the active nickel-based catalysts was followed *in situ* by X-ray absorption spectroscopy using a specially designed batch reactor cell. The novel batch reactor allows *in situ* studies in dense carbon dioxide at elevated temperature and high pressure (up to 200 bar) even at the low energy of the nickel K-edge. Hence, important information on the fate of the ligands and structural changes under reaction conditions could be gained providing new insight into the reaction mechanism.

Keywords: *In situ* XAS, carbon dioxide, propylene carbonate, nickel catalysts.

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INTRODUCTION

The substitution of phosgene or carbon monoxide by non-toxic carbon dioxide as a safe and cheap C₁-building block is an attractive challenge toward “green chemistry” [1]. In the last decades, environmental aspects of energy and solvent saving processes have gained attention due to growing ecological awareness. For this reason, “solventless” processes are favored, which use the substrates also as solvent. A prominent example is the synthesis of propylene carbonate (PC) by carbon dioxide (CO₂) insertion in propylene oxide (PO), which needs no further solvent than the CO₂ itself. A broad range of different homogeneous catalysts exists for this reaction, but their activity is still quite low compared to other chemical syntheses and the heterogeneous catalysts known today are even less active. A better understanding of the reaction mechanism is a prerequisite for rational catalyst design and may pave the way to improved catalysts.

So far only little spectroscopic insight into catalysts acting in the synthesis of PC from CO₂ was gained. For this purpose XAS is a well-suited technique, because it provides element-specific information on the coordination sphere and *in situ* studies are possible even under high pressure conditions [2]. In a screening of various transition metal complexes, nickel-based catalysts were found to be catalytically active in the

solventless synthesis of PC in and with dense CO₂. Hence three different complexes were synthesized, catalytically tested, and analyzed by XAS measurements. More insight into the reaction has been gained by *in situ* studies during the insertion of carbon dioxide in propylene carbonate. An overview of the different Ni catalysts is given in Fig. 1.

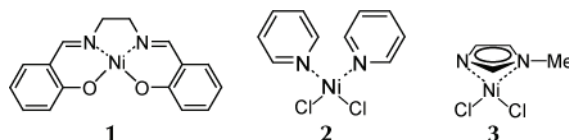


FIGURE 1. Overview of the different Ni-based catalysts.

EXPERIMENTAL

The catalytic synthesis of PC was carried out in a steel batch reactor with magnetic stirrer. Reaction conditions were 3 h reaction time at 140 °C and 45 bar. The catalysts **1** – **3** (Fig. 1) were pressed to pellets with additional polyethylene and measured at the ANKA-XAS beamline (Karlsruhe, Germany) with the corresponding pure metal as reference. *In situ* XAS measurements were carried out in a small stainless steel batch reactor with a total volume of 10 ml, equipped with two pairs of Be windows to monitor the solid/liquid interface in case of undissolved catalyst

present in the liquid phase. A similar setup has been reported in ref. [3]. Here we used a novel improved cell that was modified to measure also at the Ni K-edge. Therefore no PEEK inlet was used; this allowed a window distance of 3 mm (see Fig. 2). The reaction volume was similar to the previous reactor and the Be windows were protected by PTFE foils. The raw data were analyzed with the WINXAS 3.1 software [4]. For EXAFS analysis Fourier transformation was applied on the k^1 -weighted functions. Theoretical scattering amplitudes and phase functions were calculated using the FEFF code [5].

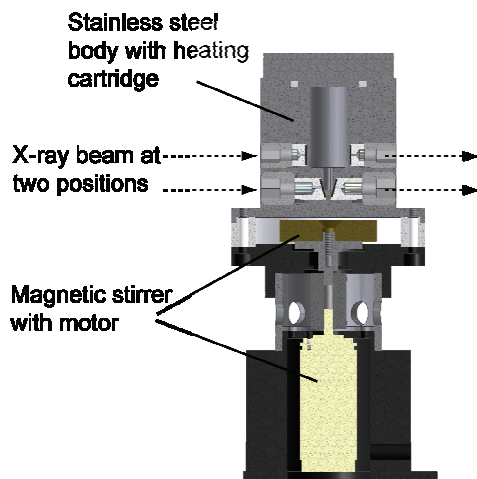


FIGURE 2. Batch reactor cell for *in situ* XAS measurements.

RESULTS AND DISCUSSION

The catalytic results are shown in Table 1. Catalyst **1** was strikingly less active than catalysts **2** and **3**. In the corresponding XANES spectra (Fig. 3) at the Ni K-edge of these Ni catalysts the spectrum of catalyst **1** differs from the others. A pre-edge and a decreased whiteline indicate a square planar structure if compared to previous XAS studies on Ni complexes in literature [6].

TABLE 1. Summary of catalytic results of the nickel catalysts.

Catalyst	Yield ^a / %	TOF / h ⁻¹	PO / cat. ratio
1	10.0	15	455
2	59.3	80	400
3	57.2	60	300

^aYield of PC based on PO; the reaction was carried out in 10 ml (140 mmol) of PO, 100 mg catalyst, CO₂ (480 – 550 mmol, 3.4 – 3.9 eq.), reaction time was 3 h at 140 °C.

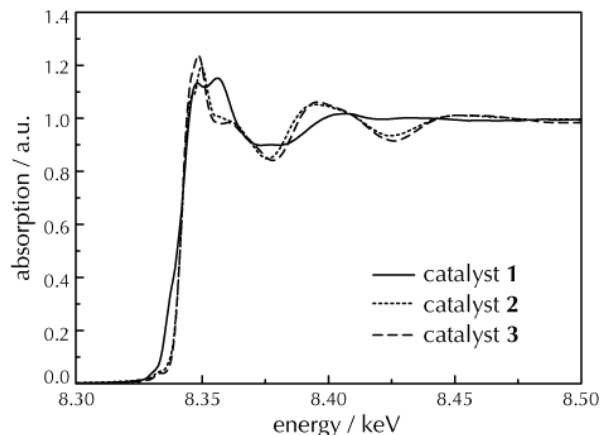


FIGURE 3. XANES spectra of the Ni catalysts.

In the EXAFS region oscillations are less pronounced at higher k -value due to the lack of heavier backscatters such as the chloride neighbors of catalysts **2** and **3**. The expansion of the coordination sphere of the Ni center atom resulted in a higher catalytic activity.

The *in situ* XAS measurements with the Ni catalyst **3** showed no changes in the spectra during the addition of PO and CO₂. At the reaction temperature of 120 °C a pre-edge appeared in the XANES spectrum accompanied by a decrease in the oscillation in the far k -space (Fig. 4).

TABLE 2. Structural parameters determined from the Ni K-edge EXAFS spectra of catalyst **3**.

	A–B ^a	$r^b / \text{\AA}$	N^c	$\sigma^2^d / \text{\AA}^2$	$\Delta E_0^e / \text{eV}$	Residual ^f	$k\text{-range} / \text{\AA}^{-1}$
Before reaction	Ni–N	2.14 ± 0.01	2.4 ± 0.5	0.008	–5.5	14.4	3.0 – 12.0
	Ni–Cl	2.50 ± 0.01	4.0 ± 0.5	0.010	9.2		
After reaction	Ni–N	2.05 ± 0.01	4.9 ± 0.5	0.008	–3.0	7.2	3.0 – 12.0

^aAbsorber–backscatterer pair. ^bDistance. ^cCoordination number. ^dDebye–Waller factor. ^eShift of the energy threshold. ^fResidual indicates the quality of fit [3].

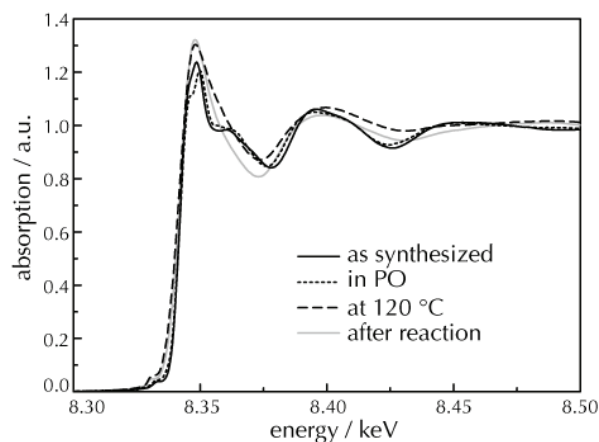


FIGURE 4. XANES spectra of the *in situ* measurements of catalyst **3** at the Ni K-edge.

This indicates a loss of chloride in the coordination sphere of the Ni. In the Fourier transformed $k^1\chi(k)$ function of the EXAFS spectrum taken during reaction (Fig. 5), the signal of the first neighboring shell shifted from 2.0 Å to 1.6 Å in accordance to the loss of the chloride (Table 2). Also the extracted $k^1\chi(k)$ functions of the catalyst before and after reaction corroborate the loss of chloride and indicate the change from octahedral to tetrahedral coordination of the Ni center.

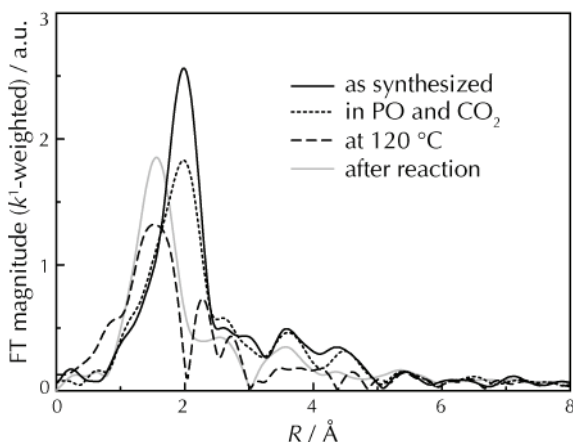


FIGURE 5. *In situ* EXAFS spectra. Fourier transformed $k^1\chi(k)$ function of catalyst **3**.

Hence this evidences the relatively low stability of the Ni–Cl bond and explains, why the octahedral coordination of Ni did not hinder the substrates to interact with the active center. Due to the weaker binding of the chloride, the center atom of catalyst **3** was more easily accessible than the center of the

chelate salen complex **1** despite the lower coordination number of the Ni atom in the latter catalyst. A similar effect was recently observed in the case of Zn-based catalysts [7].

CONCLUSIONS

In situ X-ray absorption spectroscopy proved to be a well-suited technique for monitoring the structure of the catalyst under real reaction conditions, even at high pressure. Changes in the coordination sphere of the nickel and detachment of the chloride under reaction conditions were observed. Obviously, the mechanisms have to be modified in a way that chloride is not attached to the complex.

This study showed that the modified *in situ* XAS batch reactor cell is even applicable at lower energies such as the Ni K-edge at 8.333 keV. At synchrotron facilities with high intensity and a critical energy of about 6 keV, this setup should even allow *in situ* measurements for Cr-based catalysts (Cr K-edge at 5.989 keV), another important class of catalysts for the synthesis of PC from PO and CO₂ [8].

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REFERENCES

1. M. Aresta and E. Quaranta, *Chemtech* **27**, 32-40 (2004).
2. J.-D. Grunwaldt and A. Baiker, *Phys. Chem. Chem. Phys.* **7**, 3526-3539 (2005).
3. J.-D. Grunwaldt, M. Ramin, M. Rohr, A. Michailovski, G. R. Patzke and A. Baiker, *Rev. Sci. Instr.* **76** 054104 1-7 (2005).
4. T. Ressler, *J. Synchrotron Rad.* **5**, 118-122 (1998).
5. S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers and M. J. Eller, *Phys. Rev. B: Condens. Matter Mater. Phys.* **52**, 2995-3009 (1995).
6. M. P. Feth, A. Klein and H. Bertagnolli, *Eur. J. Inorg. Chem.*, 839-852 (2003).
7. M. Ramin, J.-D. Grunwaldt and A. Baiker, *J. Catal.* **234**, 256-267 (2005).
8. M. Ramin, F. Jutz, J.-D. Grunwaldt and A. Baiker, *J. Mol. Catal. A: Chem.* **242**, 32-39 (2005).