Metal-Organic-Framework Mediated Single-Atom Dispersed Co@NC and Fe@NC Catalysts In Hydrogenation Of Nitroarenes To Their Substitute Anilines

In April 2017 we have performed a successful and productive session of XAS measurements at BM26A DUBBLE beamline. Due to the synthetic problems the Fe-based catalysts were not prepared properly and were not analysed, but all cobalt-containing samples were synthesized and investigated according to the planning. The obtained results were used in a recent publication (X. Sun et al., Single Cobalt Sites in Mesoporous N-Doped Carbon Matrix for Selective Catalytic Hydrogenation of Nitroarenes. *J. Catal. (2018), 357, 20*). For the series of Co@NC catalysts XANES and EXAFS spectra were measured at Co K-edge in transmission mode.

Several types of samples were analysed:

1) Co@NC catalysts, prepared from metal organic framework ZIF-67 (cobalt 2-methylimidazolate) by 8 h pyrolysis at different temperatures (600, 700, 800^{o}C);
2) Co@NC catalysts after acid leaching in HCl for 24 h (prepared by 4 h pyrolysis of ZIF-67 at 700, 800 and 900 ^{o}C);
3) Co,Zn@NC catalysts, prepared by 4 h pyrolysis of bimetallic framework BIMZIF(Co,Zn) with different Zn:Co ratio, resulting in cobalt content of 1.5, 2.5, 3.5 and 4.7 wt%;
4) Co,Zn@mesoNC catalysts, prepared by pyrolysis of BIMZIF@SiO2 composite with consequent leaching of SiO2; samples with cobalt content of 1.5, 2.5 and 3.5 wt% were measured after 2 h and 4 h pyrolysis time;
5) ZIF-67, BIMZIF, cobalt phthalocyanine (CoPc) and other cobalt references.

XAS characterization of Co@NC catalysts, prepared from ZIF-67, shows that even at the lowest pyrolysis temperature (600^{o}C) most of cobalt(II) converts into metallic cobalt nanoparticles (Fig. 1). Acid leaching does not change the coordination environment of cobalt in these samples, indicating that most of cobalt is covered by the carbon shell and remains unaffected during the leaching.

In contrast to Co@NC catalysts, cobalt in Co,Zn@NC and Co,Zn@mesoNC remains oxidized regardless the cobalt content and pyrolysis time (Fig. 2). In the fitting of EXAFS spectra for Co,Zn@NC and Co,Zn@mesoNC it was not possible to include any Co-Co scattering paths with reasonable parameters even in case of the sample with the highest cobalt loading of 4.7 wt%. Comparison of the edge and pre-edge features in XANES spectra of BIMZIF(Co,Zn), Co,Zn@NC and Co,Zn@mesoNC shows that cobalt in the catalysts does not adopt the tetrahedral coordination environment, typical for the parent BIMZIF(Co,Zn) material (Fig. 2A). In order to reveal how the cobalt sites change during the high-temperature pyrolysis process we performed the fitting of EXAFS spectra for these catalysts. The best fit for all samples was obtained using the model of square-planar CoN_4 complexes with additional O-containing species (e.g. H_2O) coordinated to Co in the axial position (Fig. 3). These results agree well with TEM, XRD and XPS characterization of these samples and give insight into the

actual active site structure in these catalysts. XAS experiments performed in April 2017 have a core value for understanding the nature of catalytic activity of Co,Zn@NC materials and are important for further development of this catalytic system.

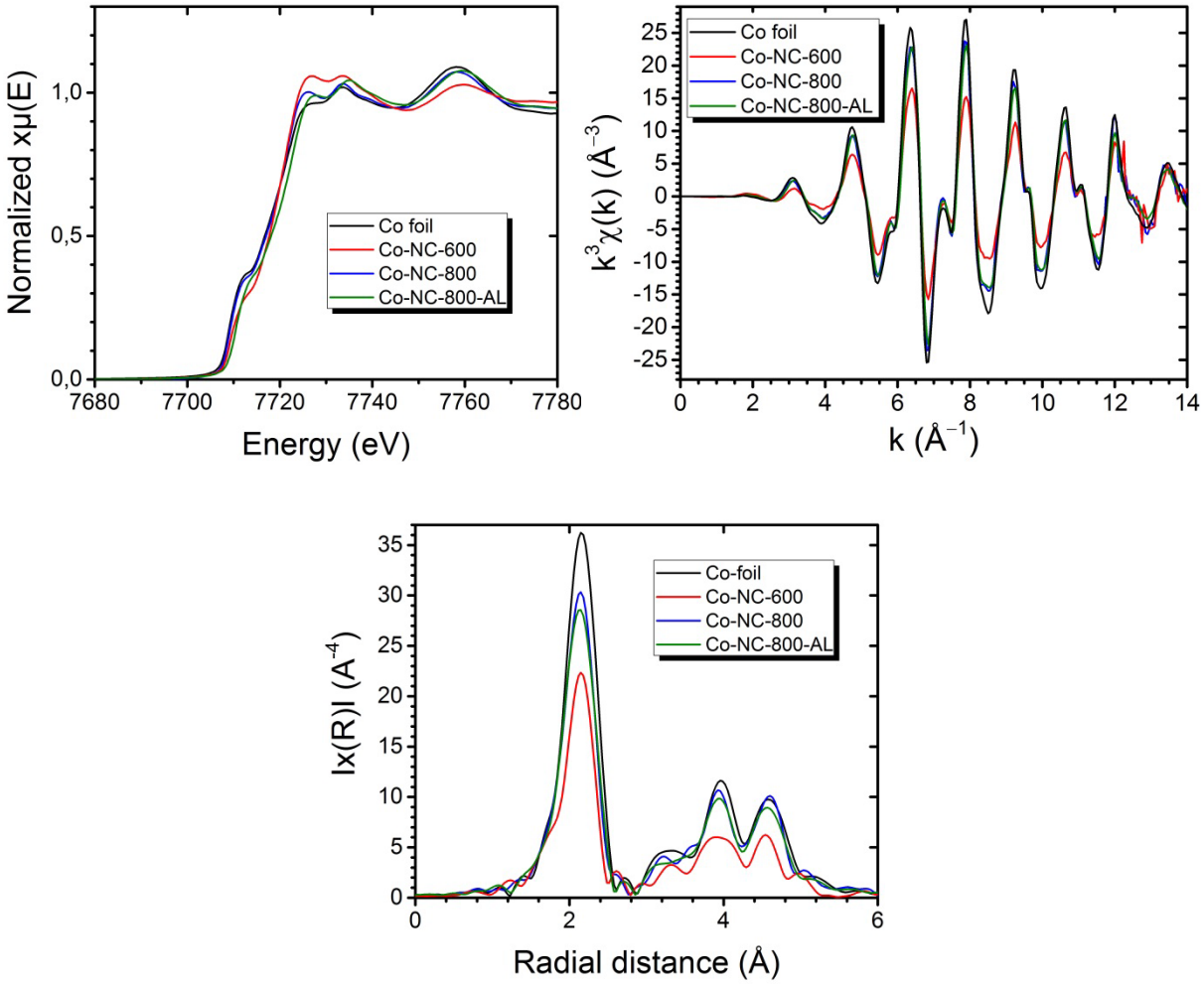

Figure 1: A) Co K-edge XANES, B) k-space EXAFS and C) R-space EXAFS spectra for cobalt foil reference (black) and Co@NC catalysts prepared by pyrolysis of ZIF-67 at 600°C (red) and 800°C before (blue) and after (green) acid leaching.

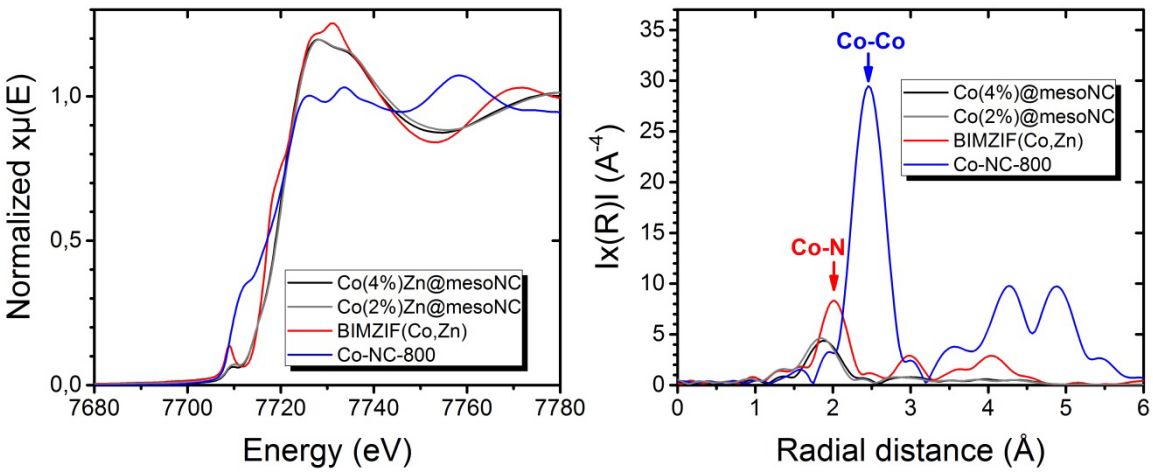

Figure 2: A) Co K-edge XANES and B) R-space EXAFS spectra for BIMZIF(Co,Zn) framework (red), Co@NC catalyst prepared by pyrolysis of ZIF-67 at 800°C (blue) and Co,Zn@mesoNC catalysts with 2% (grey) and 4% (black) cobalt content, prepared by pyrolysis of BIMZIF(Co,Zn) at 900°C.

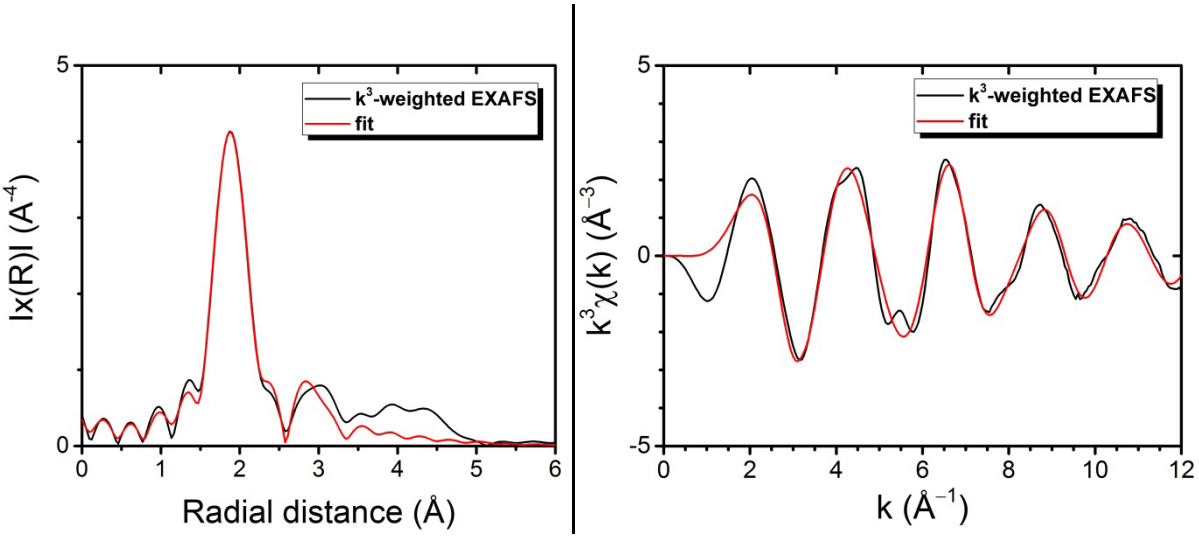

Figure 3: Fitting of EXAFS spectra for Co(4%)Zn@mesoNC-4h catalyst using the model of CoN_4 complex with additional axial O species.

Table 1: Parameters of EXAFS fitting for Co(4%)Zn@mesoNC-4h catalyst

Sample	Shell Number	Scatterer	Coordination number N/-	Distance R/Å	Debye-Waller factor $\Delta\sigma^2$ / Å^2
Co(4%)Zn@mesoNC-4h	1	N	4.06 ± 0.95	1.92 ± 0.02	0.006 ± 0.003
	2	C	8.1 ± 1.9	2.89 ± 0.04	0.015 ± 0.006
	3	N-C	16.2 ± 3.8	3.07 ± 0.06	0.021± 0.009
		O	1.1 ± 0.4	2.07 ± 0.05	0.006 ± 0.003