BEAMTIME REPORT

The silica-supported Fe[N(SiMe$_3$)$_2$] dimer: structure, formation of ultra-dispersed Fe hydrides and their reaction with methane: CH-5585

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Our beamtime was dedicated to the structural and reactivity study of iron(II) bis(trimethylsilyl)amide and iron(II) tris(*tert*-butoxy)siloxide grafted on the surface of partially dehydroxylated silica ($SiO_{2\text{-}700}$ and $SiO_{2\text{-}1080}$). The beamline staff provided us with a very good support. For our experiments, XAS at Fe *K*-edge with fluorescent mode of detection was utilized. After initial testing, we approached XANES and EXAFS measurement of the standard samples, i.e. iron(0) foil, iron nitride, iron(II) oxide, iron(III) oxide, iron silicide, …), including molecular compounds (iron siloxides). In the next step, reactor for in-situ measurements was tested (temperature calibration, proper sealing) and in-situ experiments were carried out. However, due to a failure of a heating system in the later stage, in-situ experiments were substituted by measurements of ex-situ samples, isolated from the lab-based reactor under suitable conditions. Such experiments provided us with information on the speciation of iron. Lastly, EXAFS spectra were recorded on the samples treated at 1080 °C to analyse the influence of the high temperature on the nuclearity of the iron centers.

Figure 1 plots fitted EXAFS spectra of the samples iron(II) siloxide grafted on partially dehydroxylated silica (**A**) and a corresponding thermolyzed species (**B**), and Table 1 shows the fitting parameters. The fit of the first spectrum yields three scattering paths, specifically Fe-O, Fe-Fe and Fe-Si with coordination numbers of 1.9, 0.5 and 1.3, and bond lengths of 1.64, 2.96 and 3.35 Å, respectively. The first shell exhibits a significant shoulder, the fitting of which could not be resolved. It might represent either interaction with the TBOS ligand, or with a surface siloxane bridge.

In case of **(1/SiO$_{2\text{-}1080}$)$_{\text{-}1020}$**, the fit suggests the presence Fe-O, Fe-Fe and Fe-Si scattering paths with coordination numbers 1.8, 0.5 and 2.5, similarly to **1/SiO$_{2\text{-}1080}$**. The respective bond lengths are 1.96, 2.96 and 3.35 Å. Noteworthy, the shoulder to the first shell

significantly decreases after thermolysis. These results suggest a low-coordination of iron and a formation of a certain population of iron sites with higher nuclearity (dimers). The absence of higher shells rules out any form of more significant clustering, and confirms the retention of very highly dispersed, essentially, isolated iron centers. In conclusion, the presented results suggest unusual stability of iron(II) single sites on the surface of silica toward thermolysis conditions at temperature over 1000 °C. Even under such conditions, the iron sites remain highly dispersed.

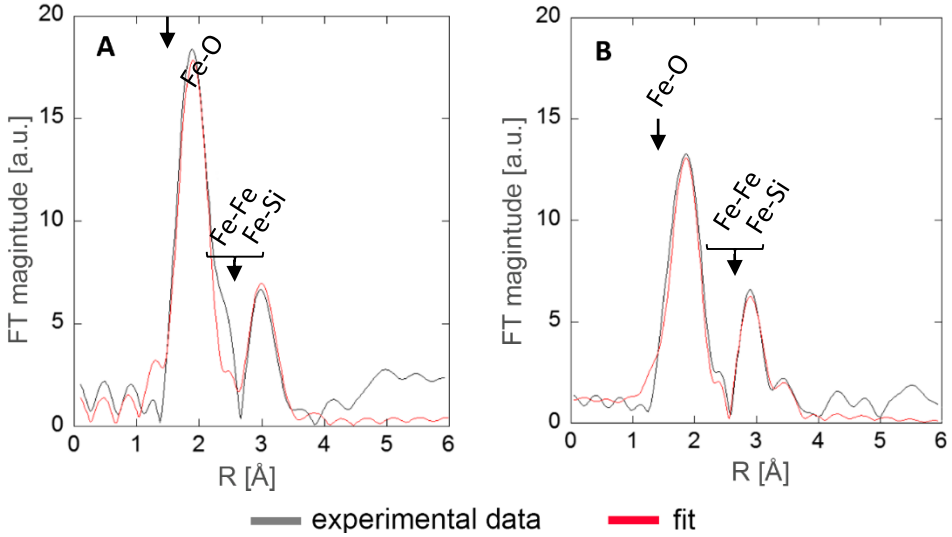

Figure 14. k^3-weighted Fourier transform EXAFS spectra of iron(II) siloxide grafted on partially dehydroxylated silica (**A**) and thermolyzed material at 1020 °C (**B**) together with the corresponding fit.

Table 4. Parameters of EXAFS fits of **A** and **B**.

1/SiO$_{2\text{-}1080}$*				**(1/SiO$_{2\text{-}1080}$)-1020*1**			
element	CN	R [Å]	DW [2 σ^2]	element	CN	R [Å]	DW [2 σ^2]
O	1.9	1.96	0.010	O	1.8	1.96	0.015
Fe	0.5	2.96	0.006	Fe	0.5	2.98	0.009
Si	1.3	3.35	0.035	Si	1.3	3.38	0.018

* k_{min} = 2.5, k_{max} = 10, *R%* = 40.5, χ^2 = 10.5·10^{-6}, *AFAC* = 0.9; *1 k_{min} = 2.5, k_{max} = 10.8, *R%* = 35.6, χ^2 = 6.9·10^{-6}, *AFAC* = 0.9