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Iztok Arčon,[ab*] Alain Tuel,[c] Alojz Kodre,[db] Guy Martin[c] and Arnaud Barbier[c]

[a]Nova Gorica Polytechnic, Vipavska 13, 5000 Nova Gorica, Slovenia, [b]Institute Jozef Stefan, Jamova 39, 1000 Ljubljana, Slovenia, [c]Institut de Recherches sur la catalyse, CNRS, 2 av. A. Einstein, 69626, France, [d]Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, Slovenia,
Email:iztok.arcon@ses-ng.si

The metallic Co catalyst for the Fischer-Tropsch reaction is prepared by reduction of Co salts impregnating microporous silica. The average size of the metallic Co clusters is determined from the average number of neighbours deduced from Co K-edge EXAFS of catalyst samples. A model EXAFS signal constructed from the scattering paths of Co metal *fcc* lattice with lengths up to 5 Å is calibrated on a reference spectrum of Co metal foil. Catalyst spectra are interpreted with the same model expanded with variable neighbour fractions of the four nearest shells. Cluster size is obtained from comparison with the neighbour fractions of consecutive *fcc* magic-number clusters.

Keywords: Co K-edge EXAFS, Co clusters

The catalytic action of metallic cobalt dispersed on microporous silica for the Fischer-Tropsch reaction depends critically on the size of the Co clusters. In the present study, an estimate of the average cluster size in the samples prepared by three different routes is deduced from the numbers of consecutive neighbours obtained in Co K-edge EXAFS analysis.

Co-1 sample was prepared by reaction of silica (silica FK 310, 800 m^2/g) with CoF_3 in diglyme, to yield 1.83 wt % of Co in the catalyst. Samples Co-2 and Co-3 were prepared by mixing silica (A 200 from Degussa, 200 m^2/g) into aqueous solution of cobalt nitrate with target Co concentrations in the catalyst of 17.6 wt % and 3.2 wt %, respectively. With excess ammonia $Co(OH)_2$ was precipitated. Finally, all compounds were reduced under H_2 at 923 K for 2 h.

EXAFS spectra at Co K-edge were measured at the E4 station of HASYLAB at DESY. The station provides a focused beam from an Au-coated mirror and a Si(111) double-crystal monochromator with 1.5 eV resolution at Co K-edge. Harmonics are effectively eliminated by a plane Au coated mirror and by a slight detuning of the monochromator crystals, keeping the intensity at 60% of the rocking curve with the beam stabilization feedback control. Due to low concentration of Co in the samples, the powder was compressed in a liquid absorption cell with kapton windows into a ~1 mm thick homogeneous layer, with Co K-edge jump of about 0.5 and total absorption thickness of 1.5 above the edge. Reference spectra were measured on the empty absorption cell. EXAFS spectrum of Co metal foil served as standard.

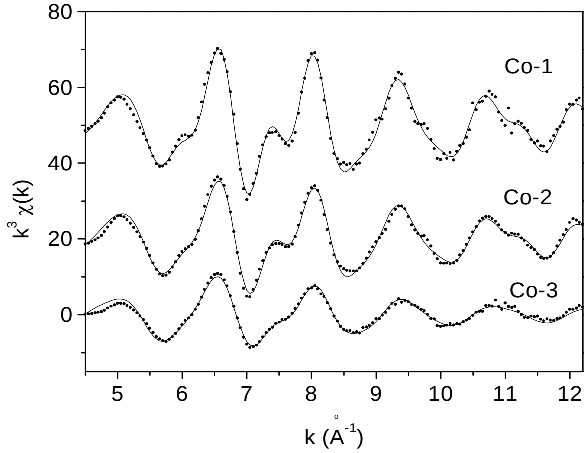

Figure 1
The k^3 weighted Co K-edge EXAFS spectra of catalyst samples: experiment (dots) and best-fit (solid line). The spectra are displaced vertically for clarity.

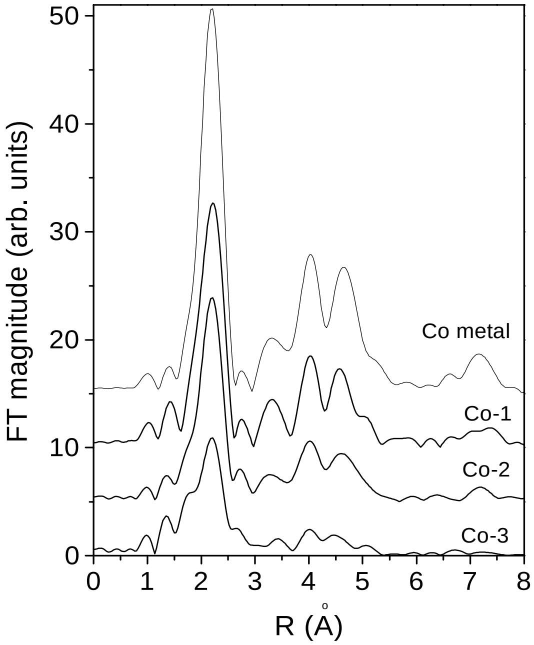

Figure 2
The k^3 weighted Fourier transform magnitude of Co K-edge EXAFS spectra of Co metal foil and catalysts calculated in the k range of Fig. 1. The spectra are displaced vertically for clarity.

The EXAFS spectra were analysed by the UWXAFS code (Stern *et al.*, 1995, Rehr *et al.*, 1992) in the k-range 5 – 12 Å^{-1}, using k^3 weight and a Hanning window. The k^3 weighted Co K-edge EXAFS spectra of catalyst samples Co-1, Co-2 and Co-3 are shown on Fig. 1. Fourier transforms of the EXAFS spectra (Fig. 2) show typical local structure of metallic Co in *fcc* crystal lattice in all samples. Comparison with the spectrum measured on Co metal foil reveals, however, that the average number of Co neighbours in the consecutive coordination shells in the samples is lower than in the Co foil, decreasing from the sample Co-1 to Co-3, indicating that clusters with *fcc* structure of Co metal are formed. The size of the clusters can be deduced from the observed reduction of the average number of neighbours (Kakar *et al.*, 1997; Borowski, 1997; Frenkel, 1999). For the Co-3 sample, an estimate of the size can be given also by the cutoff in the FT spectrum. The absence of a prominent peak observed at 7.5 Å in FT spectrum of bulk Co provides an upper limit for the diameter.

A quantitative analysis is based on FEFF model of *fcc* crystal structure of Co metal with the lattice constant a = 3.61 Å, comprising all single and multiple scattering paths up to 5.9 Å. The model is calibrated by the Co foil spectrum, yielding an excellent fit for the region from 1.5 Å to 5.0 Å with just four variable parameters: the lattice expansion ($\Delta r/r$), the amplitude reduction factor (S_0^2), the Debye temperature (TD) in modeling the Debye-Waller factors of all paths (Stern *et al.*, 1995), except the first, for which a separate factor (σ_1^2) is introduced. The shell coordination numbers and unperturbed radii are fixed at their *fcc* values.

In modeling the clusters, the fixed values of S_0^2 (=0.86(3)) is retained, while TD, σ_1^2 and $\Delta r/r$ are varied, and the *fcc* shell coordination numbers in the model are multiplied with variable average neighbour fractions (n_i) with the results in Table I. The quality of the fit is demonstrated in Figs. 1 and 3. For Co-3 sample an additional shell of 0.8(3) oxygen atoms at R= 1.97(3) Å with σ^2 = 0.004(1) Å^2 has to be introduced for a fit of equivalent quality.

The average neighbour fractions (n_i) of the first four shells in the Co-1, Co-2, and Co-3 samples are compared with values from model *fcc* magic-number clusters. These clusters are obtained by filling consecutive crystallographic shells, i.e. shells of sites with all permutations of the same crystallographic indices with regard to the central atom. The model neighbour fractions are obtained by summing the number of i-th neighbours over all atoms of the cluster and dividing by the corresponding number in the bulk. (Table 2). The best agreement (bold rows) is obtained with clusters containing 135, 55 and 19 atoms (diameters of 13.5, 10.2, and 7.2 Å) for Co-1, Co-2, and Co-3, respectively. The agreement in all four shells for the two smaller clusters is remarkable. It is possible that the larger deviations for Co-1 clusters indicate deformation from the globular shape.

The oxygen neighbours observed in Co-3 sample presumably originate from the contact layer with the substrate. Their contribution is appreciable only for the smallest clusters where most of the Co atoms in the cluster are on its surface.

An increase of the Debye-Waller factors (and a corresponding decrease of Debye temperature) from the bulk Co value is observed in all three cluster samples. The effect is more pronounced for smaller clusters and can be ascribed to the increase in the static disorder in the clusters [Kakar *et al.*, 1997; D'Acapito *et al.*, 1997].

We observe a reduction of interatomic distances only for the smallest cluster size (Co-3 sample), consistent with similar observations for Cu clusters [Montano *et al.*, 1986; D'Acapito *et al.*, 1997). Larger clusters of Co-1 and Co-2 samples show no significant contraction of the interatomic distances from their bulk Co values.

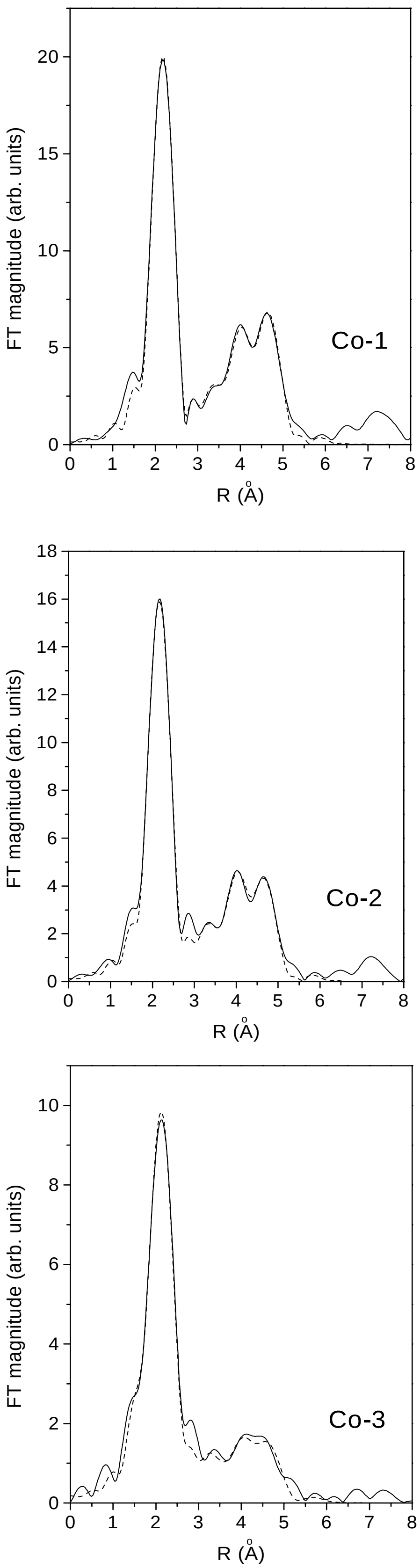

Figure 3
Comparison of the k^3 weighted FT magnitude of EXAFS spectra measured on catalyst samples Co-1, Co-2 and Co-3 (solid line) with the FEFF model (dashed line).

Table 1

Average neighbour fractions (n_i) of Co neighbours in the first four coordination shells in the Co samples. Best fit values for the lattice expansion ($\Delta r/r$), the Debye-Waller factor of the first coordination shell σ_1^2 and the Debye temperature (TD) governing the widths of further shells are added. Uncertainties of the last digit are given in parentheses.

Sample	n_1	n_2	n_3	n_4	$\Delta r/r$	σ_1^2 [Å ^{2}]	T_D [K]
Co-1	0.72(4)	0.63(6)	0.65(4)	0.64(4)	0.053(4)	0.0074(5)	340(20)
Co-2	0.66(5)	0.53(9)	0.42(6)	0.38(8)	0.048(4)	0.0085(6)	350(20)
Co-3*	0.52(4)	0.37(8)	0.21(5)	0.15(5)	0.037(4)	0.010(1)	300(90)
Co metal	1	1	1	1	0.047(4)	0.0068(2)	364(10)

In conclusion, we have shown that different routes of preparation of the metallic cobalt dispersed on microporous silica lead to formation of *fcc* Co clusters of different average sizes. Assuming a spherical shape of the clusters, the samples Co-1, Co-2 and Co-3 contain clusters with average diameters of 13.5 Å, 10.2 Å, and 7.2 Å, respectively.

Table 2

Model: average neighbour fraction (n_i) of consecutive neighbours in *fcc* magic-number clusters.

N at/cl	Cluster dia.(Å)	n_1	n_2	n_3	n_4
13	5.11	0.462	0.308	0.154	0.077
19	**7.22**	**0.526**	**0.316**	**0.211**	**0.158**
43	8.84	0.6045	0.512	0.372	0.302
55	**10.21**	**0.655**	**0.546**	**0.400**	**0.346**
135	**13.51**	**0.741**	**0.667**	**0.548**	**0.482**
201	16.14	0.786	0.657	0.607	0.572
344	19.76	0.818	0.737	0.678	0.637
380*	20	0.809	0.732	0.674	0.625
1300*	30	0.870	0.820	0.781	0.747
3000*	40	0.904	0.865	0.835	0.809

**Analytical estimate of $N_{at/cl}$ and n for a given cluster diameter (Borowski, 1997).*

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