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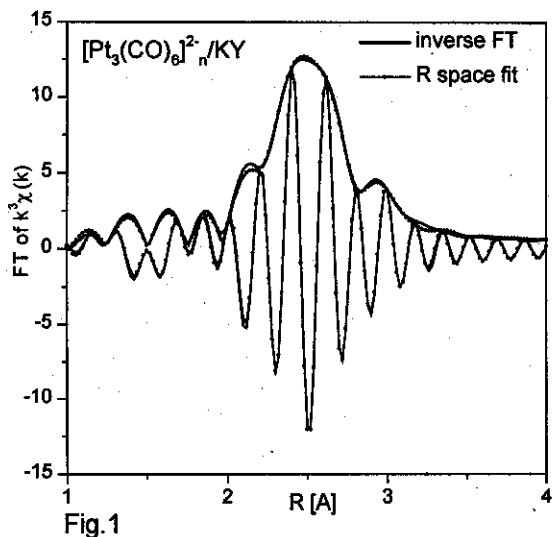
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Report:

Introduction. Well dispersed Pt catalysts are commonly used in a variety of applications including naphtha reforming processes and the removal of CO and NO from exhaust gases. The preparation of a system consisting of small uniform Pt particles is difficult due to the strong tendency of noble metals to sinter. The anionic Pt carbonyl complexes $[\text{Pt}_3(\text{CO})_6]^{2-n}$ synthesized in zeolites [1] seem to be suitable precursors for the preparation of particles smaller than 1 nm. Anionic Pt carbonyl complexes are also of great interest due to their possible application in the field of electronic and optical devices.

The orange $[\text{Pt}_3(\text{CO})_6]^{2-n}$ complexes were synthesized directly in the zeolite cavities by the carbonylation of $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ions exchanged into the zeolite KY. The crystalline $[\text{Pt}_{15}(\text{CO})_{30}][\text{NEt}_4]_2$ complex was synthesized according to literature [2] for comparison purpose because its structure is known from XRD analysis [3]. The aim of this EXAFS study was to confirm the presence of $[\text{Pt}_3(\text{CO})_6]^{2-n}$ complexes entrapped in the zeolite cages and to determine their nuclearity (n in the general formula).

Results. The Pt L_{III} edge EXAFS spectra of $[\text{Pt}_3(\text{CO})_6]^{2-n}/\text{KY}$ and $[\text{Pt}_{15}(\text{CO})_{30}][\text{NEt}_4]_2$ were measured between 4.2 and 298 K, Pt foil and $\text{W}(\text{CO})_6$ were used as reference compounds. The k^3 weighted EXAFS function was Fourier transformed into R - space in the k range from 3.5 to 18 \AA^{-1} . The inverse FT was



	$[\text{Pt}_{15}(\text{CO})_{30}][\text{NEt}_4]_2$			$[\text{Pt}_3(\text{CO})_6]^{2-n}/\text{KY}$		
	R	C.N.	$\sigma^2 \cdot 10^{-3}$	R	C.N.	$\sigma^2 \cdot 10^{-3}$
Pt-Pt (I)	2.69	2.0	0.8	2.66	2.1	0.3
Pt-Pt (II)	3.12	1.6	8.1	3.04	1.3	6.9
Pt-C_{bridge}	2.15	2.1	-2.3	2.05	2.0	2.4
Pt-C_{terminal}	1.99	1.0	-4.6	1.88	1.0	0.4
Pt-O_{terminal}	3.06	0.9	-4.3	3.03	1.0	-3.9

calculated to obtain a filtered EXAFS function and the R range of the inverse FT was taken from 1.1 to 3.3 Å. The inverse FT was fitted in R space.

The best results were obtained from the analysis of the EXAFS spectra measured at very low temperatures. The results of curve fitting analysis of the samples measured at 4.2 K are shown in the table and Fig.1. A very good accordance between our measured EXAFS data and the reported X-ray of the crystalline complex [3] is observed. The distance between two adjacent Pt atoms in the basic triangular unit of the complex (Pt-Pt (I) distance in the table) is reported 2.66 Å according to XRD data [3]. This is in a good agreement with the 2.69 and 2.66 Å distances obtained by EXAFS for the crystalline complex and for the carbonyl anchored in the zeolite, respectively. The Pt – Pt (II) distance between two platinum atoms in neighboring units should give us an answer concerning the total number of triangular units in the whole complex. According to XRD data, this distance varies from 3.08 to 3.10 Å as the number of the units in the complex grows from $n = 3$ to 5. Hence, the distance Pt-Pt (II) 3.12 Å obtained from EXAFS is correct for $[\text{Pt}_{15}(\text{CO})_{30}][\text{NEt}_4]_2$ ($n = 5$), and the distance of 3.04 Å would correspond to small carbonyl complexes $[\text{Pt}_3(\text{CO})_6]^{2-n}$ with $n = 2$ and/or 3. The same size was obtained from UV/VIS and FTIR spectra [1]; probably a mixture of $n = 2$ and $n = 3$ is formed. This conclusion is also supported by the observed coordination number of 1.3 for Pt – Pt (II). Comparing Pt-C and Pt-O distances of the crystalline complex and the complex inside the zeolite cavities, it is obvious from the shorter interatomic distances that the complex entrapped in the supercages of the KY zeolite is slightly contracted.

References

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