E.s.c.a. (electron spectroscopy for chemical analysis) Analysis) study of monomodal metal phases in a faujasite X matrix

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A series of faujasite supported catalysts with monomodal dispersed phases of nickel, palladium, and platinum, exhibiting narrow particle size distributions, are chracterized by X.p.s. (X-ray photoelectron spectroscopy).

Keywords: Faujasite X; monomodal metal phase; occluded X.p.s. signal attenuation

Metal-loaded zeolites are widely used in petrochemical processes[1] and are broadly investigated with respect to heterogenized homogeneous catalysis[2], photo-catalysis[3], and selective Fischer-Tropsch catalysis[4]. The zeolite matrix has proved to be especially suited for the production of monomodal metal dispersions[4–8], which have been identified mainly by transmission electron spectroscopy. The conclusion has been drawn from the electron micrographs that monodispersed metal phases can be located exclusively inside the zeolite matrix. It is desirable to check such an assumption by a surface-sensitive method like photoelectron spectroscopy.

The samples were put into a gold basket and placed in a commercial (Leybold-Heraeus) UHV chamber. The zeolite was dehydrated carefully by increasing the temperature at an approximate rate of 5°C min^{-1} to 435°C. The excitation energy (1486.6 eV) of an AlKα source was used. The angle of incidence of the photons was 60°, and the electrons were collected by a hemispherical analyser normal to the surface of the basket. The spectra were recorded using a Nicolet signal averager for data collection.

The zeolite lattices of the samples were characterized by the Al(2s) line (binding energy: 123 eV), the Si(2s) line (binding energy: 157 eV), the O(1s) line (binding energy: 531 eV), and the Na(1s) lines (binding energies: 1073, 1077 eV), which are in fair agreement with values reported previously[9,10]. The line intensity ratio Si(2s)/Al(2s) $\approx$ 1 was found for all samples.

The binding energies of the electron levels, which have been selected to characterize the metal phases of the zeolites, are given in *Table 1*. For samples PtNa-X(1/c), PtNa-X(8/c), PdNa-X(8/p) and NiCa-X5(8p), the metal phases are considered, from electron micrograph evidence, to lie exclusively within the bulk of the zeolite crystals. With the exception of Pt($4f_{7/2}$) and Pt($4f_{5/2}$) for PtNa-X(1/c) and PtNa-X(8/c), no X.p.s. signals were detected for these four samples. The escape depth of photoelectrons is energy dependent and can be estimated[11]. The escape depths of Pt($4d_{5/2}$), Pt($4d_{3/2}$), Pd($3d_{5/2}$), Pd($3d_{3/2}$), Pd($3p_{3/2}$), Pd($3p_{1/2}$), Ni($2p_{3/2}$) and Ni($2p_{1/2}$) are all of the order of 10–20 Å. The escape depths of Pt($4f_{7/2}$) and Pt($4f_{5/2}$) are of the order 20–30 Å, These results suggest that the metal phases lie within the zeolite crystal bulk.

It is possible to deposit the metal phase at the surface of the zeolite, and this has been done for PtNa-X(8/c/O) (see definitions in *Table 1*). Both the Pt(4f) and Pt(4d) lines were observed for this sample. The Pd(3p) and Pd(3d) X.p.s. lines were observed for sample PdNa-X(8/g); and the Ni(2p) signals were observed for sample NiCa-X(8/g). These samples had been prepared by crushing and grinding PdNa-X(8/p) and NiCa-X(8/p), respectively. This preparation was performed to destroy the host lattice and to expose the metal phase assumed to be within. The Ni(2p) lines observed

Table 1 Binding energies (eV) from X.p.s. signals of zeolite supported metal phases

Samples			Analysed levels				
Abbreviation[1]	Composition	Ref.	2p	3p	3d	4d	4f[2]
PtNa-X(1/c)	$Pt_{18}Na_{50}$-X	6	–	–	–	n[3]	75, 78
PtNa-X(8/c)	$Pt_{18}Na_{50}$-X	6	–	–	–	n	75, 78
PtNa-X(8/c/O)	$Pt_{18}Na_{50}$-X	6	–	–	–	320	75, 78
PdNa-X(8/p)	$Pd_{18}Na_{50}$-X	8	–	n	n	–	–
PdNa-X(8/g)	$Pd_{18}Na_{50}$-X	8	–	568	348	–	–
NiCa-X5(8/p)	$Ni_{10}Ca_{10}Na_{46}$-X	7	vw[4]	–	–	–	–
NiCa-X5(8/g)	$Ni_{10}Ca_{10}Na_{46}$-X	7	857, 862 867, 878 885				

[1] Legends to the signs in parenthesis: The numbers denote the mean diameters of the metal particles in nm; c = powder of the zeolite crystals (≈ 25 μm); p = pelletized powder (≈ 0.2 mm); g = ground samples; O = metal phase largely located outside the zeolite matrix
[2] The Al(2p) line contributes only little because of the high platinum loading
[3] n: no signal
[4] vw: very weak unresolved line

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for NiCa-X(8/g) were indicative for the formation of a nickel oxides[12,13].

The O(1s) line of the metal-bound oxygen (binding energy: 533 eV) was found for all the samples. Any oxide film present on the samples having metal phases at the surface has not prevented the escape of photoelectrons from the metal phase. Therefore, the attenuation of the X.p.s. signal from the metal phase of samples PtNa-X(1/c), PtNa-X(8/c), PdNa-X(8/p) and NiCa-X5(8/p) can be attributed mainly to the zeolite crystal bulk.

On the basis of the assumption that no platinum will have migrated to the external surface of the zeolite crystals, but will be occluded and randomly distributed in the zeolite matrix, a signal intensity ratio Pt(4f)/Si(2s) ≈ 6 can be expected from the platinum loading. The experimental ratio of 9, which is found for the samples PtNa-X(1/c) and PtNa-X(8/c), support such an assumption. For the sample PtNa-X(8/c/O), however, a ratio of 50 is found, thus confirming the conclusion drawn from electron micrographs that a partial enrichment of the platinum at the external surface of the zeolite particles occurs if platinum exchanged faujasites are treated with hydrogen. These results agree with deductions obtained from the e.s.c.a. study of platinum loaded Y faujasites[14].

An attempt was made to adsorb CO on the samples, all of which received prior H_2 and CO reduction treatments at temperatures $\leqslant 650$ K. It has been previously observed[15] that chemisorbed oxygen can be removed from platinum metals by this treatment, but incorporated oxygen is removed, if at all, only at higher temperatures with a substantially reduced activity. In this study, reduction was not achieved for any of the samples, as monitored by X.p.s. and u.p.s. (HeII radiation, 40.8 eV), except for a partial reduction of NiCa-X5(8/g). For this sample, an additional O(1s) line (binding energy: 538 eV) was initially present, which decreased in intensity due to the heat treatment and further decreased (but not completely) by the reduction treatment. Before any reduction treatment, the C(1s) lines (binding energy: 285 eV), attributed to hydrocarbon residues within the chamber, were found for all samples. An additional C(1s) line (binding energy: 289 eV), attributed to adsorbed carbon monoxide, was found for PtNa-X(8/c/O) (weak line) and for NiCa-X5(8g) (strong line), but not for PdNa-X(8/g). Even in the case of NiCa-X5(8/g), the amount of reduction achieved was so small that only a small change in the u.p.s. spectra was found, the features of which were not resolved. More effective reduction methods are required to complete the CO adsorption study.

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