



	Experiment title: In-situ EXAFS study of Cs influence on properties of Pt supported onto Cs/beta-zeolite catalysts	Experiment number: CH-1394
Beamline: BM29	Date of experiment: from: 05-févr-03 to: 08-févr-03	Date of report: <i>Received at ESRF:</i>
Shifts: 9	Local contact(s): Simone DE PANFILIS	
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Report:

We made use of the 9 shifts assigned to this project to study, by EXAFS spectroscopy, the influence of the basicity of beta zeolite on the state of supported platinum which is used as catalyst in different reactions of interest in the fields of petrochemistry and production of fine chemicals.

X-ray absorption spectra (XANES and EXAFS) were collected at the BM29 beamline, equipped with a Si(311) double crystal monochromator. All spectra were recorded at variable temperature up to 500°C inside the user's environmental chamber in transmission mode at the Cs K-edge over the range 35.6-37.1 keV, with an average sampling step of 1 eV and an integration time of 2 s for each point. Incident and transmitted photon fluxes have been detected with ionisation chambers filled with Kr. Each spectrum has been acquired three times. The samples were loaded into the BN sample-holders of the in-situ cell and measured during treatments. Sample homogeneity was checked by reading the transmitted photo-current while scanning the sample area along the x-y axes.

Selected Cs-beta, Pt/Cs-beta and Cs_x-Pt/Cs-beta have been measured, and the experiments have been carried out on the just prepared hydrated samples and at the end of the following in-situ treatments : 1) thermal activation by calcination in flowing air or O₂ at different temperatures up to 500°C; 2) *in-situ* reduction in flowing H₂ in temperature ramp up to 500°C.

Extracted $\chi(k)$ data have been averaged before the EXAFS data analysis and error bars have been evaluated from the experimental standard deviations. Experimental $\chi(k)$ data were extracted from absorption data by a conventional procedure. The k^3 -weighted $\chi(k)$ data were Fourier transformed over a Kaiser window, with $\tau=2.5$, in the k range of 3-15 Å⁻¹. Main contributions to the Fourier transform modulus were

filtered in order to obtain metal nearest-neighbour shells. The so obtained filtered contributions were analysed using the programs developed by Michalowicz. Phase shift and amplitude functions of scattering atoms have been extracted from the experimental spectra of the model compound samples (Cs oxide, Cs hydroxide, Cs carbonate).

The aim of the XAS measurements at the Cs edge was to identify the local surrounding of the Cs-counteranions and/or Cs-oxide inside Cs-beta zeolite, and explain how they modify the zeolite basicity (type of interactions taking place between the Cs species and the zeolitic framework and/or close Pt species). Moreover, together with the results obtained on the same samples at the Pt edge, they allowed to understand the role of Cs in the stabilisation of Pt.

In fact, zeolites functionalised with basic and metal phases, such as Pt/Cs₂O/BEA, are promising materials for heterogeneous catalysis application employed in chemical processes for the valorisation of natural resources. In this composite systems, the interaction between the basic phase and metal particles play a key role in determining the functional behaviour. For these reason, the target of this work was to prepare a nanocomposite material, based on BEA zeolite matrix, in which the basic phase and the Pt particles in interaction with each other are hosted in the zeolite pores. BEA zeolite has a large three-dimensional pore channels with opening pore size of 7.3x6.0 Å. In a Cs-BEA sample, prepared as reference by ion exchange, the basicity is related to the framework oxygen atoms, rendered more electron rich by the presence of counteranionic Cs⁺ species. By a subsequent exchange with [Pt(NH₃)₄]Cl₂, catalyst with 1% of Pt were prepared. The basicity of this sample was further increased using impregnation with CsOH, that allows the formation of Cs₂O particles-like in the catalysts. The presence of different basic phases, related to the presence of Cs⁺ as counteranion or as oxidic particles, was confirmed by IR spectroscopy of adsorbed CO₂ and by the Cs edge EXAFS results. The different basicity of the host matrix significantly affect the form of Pt present in the catalysts after the calcination. In the catalyst prepared by Cs⁺ and then Pt²⁺ exchange, isolated Pt²⁺ centers are the dominant species. On the contrary, for the catalysts prepared by impregnation, Pt^{δ+} and Pt⁰ sites (due to auto-reduction process) at the surface of Pt_xO and Pt particles, respectively, are observed. The fraction of larger metal particles observed as the Pt/Cs ratio increases strongly suggests an intimate contact between Pt and Cs₂O particles. All the data seem to suggest that during the impregnation, Cs⁺ can replace some Pt²⁺ counteranions, which move to the liquid phase in the zeolite cavities to be finally deposited on the framework and/or on the Cs₂O particles while the subsequent calcination produces some PtO particles, that are stabilised on Cs₂O species. After reduction treatment, all oxidic Pt species were converted into metallic Pt ones. TEM analysis performed on these reduced samples cut in microtome slices indicate that Pt is homogeneously located inside the zeolitic framework and that the average diameter of the metal particles decreases regularly from 1.8 to 1.2 nm, as the caesium amount increases. The observed decrease in size should result from the different form of metal precursor and the additional presence of Cs₂O particles in the zeolite pores. For the catalysts where isolated Pt²⁺ species are present as counteranions, the reduction produced highly mobile Pt atoms, which can freely migrate through the zeolites pores and merge in Pt particles. Conversely, for catalysts containing Pt_xO and Cs₂O particles, the reduction of Pt_xO could occur *in situ*, i.e. in contact with the co-encapsulated Cs₂O particles: the smaller size of Pt particles is caused both by the reduced mobility of Pt^{δ+} species in the cavities obstructed by the Cs₂O particles and by their stabilisation on the basic phase. The decrease in size is accompanied by significant changes of Pt electronic surface states, as monitored by IR spectra of adsorbed CO^[1].

The additional results obtained at the Cs edge helped in clarifying the role of the isolated Cs⁺ or Cs₂O like particles in the stabilization and in the catalytic activity of Pt catalysts and produced a work that will shortly be submitted to the Journal of Catalysis.

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[1]: C. Bisio, C. Caldeira, V. Dal Santo, G. Martra, P. Massiani, R. Psaro, M.F. Ribeiro, J.M. Silva, L. Stievano, *Inorg. Chem. Acta* 349, 227 (2003).