

Silica grain labelling and EDX spectroscopy; evidence for inter-grain diffusion of $\text{Pt}(\text{NH}_3)_4^{2+}$ species during Pt/SiO_2 catalyst preparation by ionic exchange

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Labelling of silica grains and energy dispersive X-ray spectroscopy (EDX) in a TEM-FEG (field emission gun) were used to demonstrate the migration of $\text{Pt}(\text{NH}_3)_4^{2+}$ species from one grain to another during Pt/SiO_2 catalyst preparation by the ion-exchange procedure.

The reaction of $\text{Ti}(\text{OPr})_4$ with the surface of silica grains can be used to graft Ti species. It is therefore possible to mark out some grains incorporated into a silica grains population in order to trace their behavior during for example, the adsorption processes of metal precursors in aqueous media.

The concept of interfacial coordination chemistry was proposed by Che¹ to describe the interaction of transition metal ions with oxide surfaces. In aqueous solution, the transition metal ions are complexed and interaction occurs frequently *via* ionic exchange. For platinum supported on silica, the silica surface protons are exchanged by $\text{Pt}(\text{NH}_3)_4^{2+}$ ions to form a surface complex $(\text{SiO}^-)_2\text{Pt}(\text{NH}_3)_4^{2+}$.² The decomposition of this complex under oxygen or hydrogen leads to Pt particles.³ Although this method is commonly used, the fixation and dispersion processes of the species are not well-characterized. The aim of this work is to show that the use of Ti labelled silica grains demonstrates that the exchanged species migrate from one silica grain to another when impregnated and non-impregnated silica grains are mixed.

The concentration of Pt in aqueous solution for increasing interaction time with silica⁴ is reported in Table 1. Clearly, the adsorption equilibrium of $\text{Pt}(\text{NH}_3)_4^{2+}$ on the silica surface is reached within < 1 min. For low metal loading (*ca.* 1 wt%), one may thus wonder whether the adsorbed platinum complex is homogeneously distributed all over the silica surface and among the silica particles.

In an initial experiment,⁵ EDX analyses⁶ of 1 wt% Pt/SiO_2 samples (Fig. 1) demonstrate that after 5 min of contact between the solution and silica, some of the silica grains do not support any Pt whilst others exhibit Pt/Si ratios far from the expected value corresponding to 1 wt% (*ca.* 0.003). Conversely, after 24 h, most of the particles exhibit a Pt/Si atomic ratio close to 0.004. This is most certainly due to the fast fixation of $\text{Pt}(\text{NH}_3)_4^{2+}$ ions on some silica grains and subsequent redistribution to the other grains. The migration of $\text{Pt}(\text{NH}_3)_4^{2+}$ can occur either on the silica surface or *via* the liquid phase.

In a second experiment,⁷ Ti-labelled⁸ silica grains were mixed with previously impregnated unlabelled silica. EDX

Table 1 Concentration of $\text{Pt}(\text{NH}_3)_4^{2+}$ in solution for increasing times of interaction with 1 g of silica

Time/min	0	1	10	40
[Pt]/mmol l ⁻¹	0.97	0.13	0.11	0.11
pH of solution	11.8	8.2	7.9	7.9

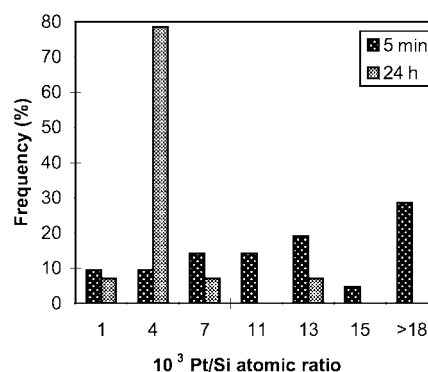


Fig. 1 Pt/Si atomic ratio obtained by EDX on silica grains after 5 min and 24 h of contact during the preparation of the Pt (1 wt%) catalyst.

analysis of the sample clearly shows (Fig. 2) that the migration of species from previously impregnated grains to other grains occurs even at low contact times (5 min) since all Ti-labelled grains that were analyzed contain Pt. After 24 h, the Pt content tends to become homogeneously distributed over all the grains and the average atomic ratio Pt/Si reaches 0.004. Before addition of unlabelled silica, the amount of $\text{Pt}(\text{NH}_3)_4^{2+}$ present in solution (3.3 μmol) is much smaller than the amount of Pt complex adsorbed on silica (48.0 μmol), and thus these results clearly demonstrate that $\text{Pt}(\text{NH}_3)_4^{2+}$ ions can migrate between silica grains, even at low metal loading and thus at very low liquid phase concentration, at the adsorption equilibrium.

This is, to our knowledge, the first time that Ti labelled silica grains and EDX analysis have been used for the study of the migration of adsorbed species from one grain to another.

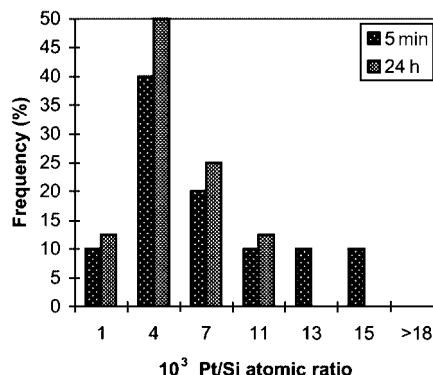


Fig. 2 Pt/Si atomic ratio obtained by EDX on Ti-labelled silica grains after 5 min and 24 h of contact between unlabelled and Ti-labelled silica.

Notes and references

- 1 M. Che, *Proc. 10th Int. Congr. Catal.*, 19–24 July 1992, Budapest, Hungary, ed. L. Guzzi, F. Solymosi and P. Tetenyi, Elsevier Science Publishers, Amsterdam, 1993, p. 31.
- 2 A. H. Benesis, R. M. Curtis and H. P. Studer, *J. Catal.*, 1968, **10**, 328.
- 3 W. Zou and R. D. Gonzalez, *J. Catal.*, 1992, **133**, 202.
- 4 Aérosil Degussa silica grains (SiO_2 , $200 \text{ m}^2 \text{ g}^{-1}$, 10–20 nm) were used as the support. These were freshly treated under flowing dry air at $520 \text{ }^\circ\text{C}$ for 5 h (heating rate $2 \text{ }^\circ\text{C min}^{-1}$) before use. Platinum tetraamine hydroxide [$\text{Pt}(\text{NH}_3)_4(\text{OH})_2$], prepared from $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (Aldrich) by ionic exchange¹ was used as the platinum precursor. 1 g of silica was introduced into a magnetically stirred flask with 30 ml of deionized H_2O and 51.3 mmol of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ at $20 \text{ }^\circ\text{C}$. The amount of Pt introduced corresponds to an expected loading value of 1 wt% of dry silica. The adsorption rate of $\text{Pt}(\text{NH}_3)_4^{2+}$ ions onto the silica surface was measured by elemental (Pt) analysis of samples of the solution taken at regular time intervals. Elemental analysis was performed with a ICP Jovin Yvo apparatus.
- 5 1 g of silica was impregnated in a solution of $51.3 \text{ } \mu\text{mol}$ of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ in 30 ml of deionized H_2O at $20 \text{ }^\circ\text{C}$. Samples taken after 5 min and 24 h of contact were analyzed.
- 6 EDX analysis of solid samples: EDX experiments were performed with a Pentafet-Link ISIS (Oxford Instruments) spectrometer in a JEOL JEM 2010-F TEM (200 kV) equipped with a high resolution pole piece. The samples were dried in an oven at $80 \text{ }^\circ\text{C}$ before EDX measurement. The probe size was adjusted to the grain size of *ca.* 10 nm. Only isolated grains were analyzed in order to avoid simultaneous analysis of two different grains.
- 7 0.5 g of silica was impregnated in a solution of $51.3 \text{ } \mu\text{mol}$ of $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ in 30 ml of deionized H_2O at $20 \text{ }^\circ\text{C}$ for 1 h. Then 0.5 g of Ti-labelled silica was mixed with 0.5 g of unlabelled impregnated silica and samples corresponding to 5 min and 24 h of contact between the two silica populations were analyzed.
- 8 Ti labelled silica grains: 1 g of silica was treated at $500 \text{ }^\circ\text{C}$ under vacuum during 24 h, then $\text{Ti}(\text{OPr})_4$ in hexane solution was introduced at room temperature under flowing argon and the suspension stirred for 4 h at room temperature. Next, the solid was extracted by filtration under argon, dried under vacuum for 24 h and then treated at $500 \text{ }^\circ\text{C}$ under flowing $\text{O}_2\text{-N}_2$ (20:80) for 2 h. The Ti loading, measured by elemental analysis, was 0.4 wt%. EDX measurements indicated that the silica grains were labelled with Ti. It was also established that the loading of 1 g of Ti labelled silica does not vary when it is impregnated with 30 ml of deionized H_2O and NH_4OH (pH 10) at $20 \text{ }^\circ\text{C}$, stirred for 24 h and then washed four times with deionized water. The Ti loading of the sample is low with only 3% of the silica surface being covered by TiO_2 . Two samples of Pt/ SiO_2 prepared in the same manner, using unlabelled and Ti labelled silica exhibit the same Pt loading (1 wt%) and the same metallic particle size distribution. We thus concluded that Ti labelling did not influence the results.