

Application note

The active sites of catalysts determined by LEIS

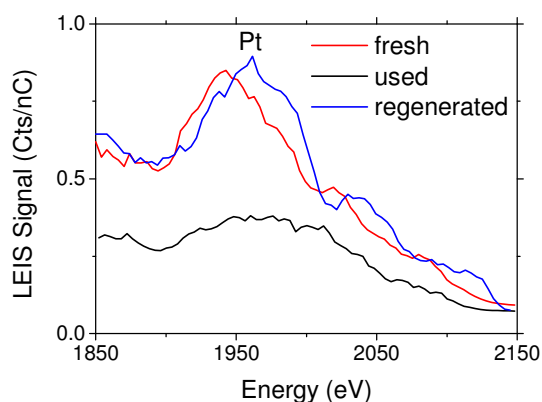
- Location of coke
- Determination of nucleation site
- Location of promoters

Introduction

There is an ongoing need for performance improvement of catalysis because of both economical and environmental reasons. Catalyst deactivation by poisoning is a major bottleneck in the design of catalytic processes. The time scale of deactivation can vary from seconds to years. Understanding of the identity of the poisoning species and the site that it blocks is a first step in trying to regenerate the catalyst. Only LEIS is capable of determining the site that has been poisoned, by selectively probing the atoms in the outer surface. This note explains that LEIS can be a unique tool for research on deactivation and improvement of the performance of catalyst surface.

Location of poisons

In a project with the Eindhoven University of Technology the effect of a cold start on a commercial Three Way Catalyst (Pt/Rh nanoclusters on a highly dispersed mixed oxide support) was investigated [1,2]. The catalytic activity was found to be significantly reduced by the cold start.



The number of Pt in the outer surface has dropped significantly after use in acetylene conversion at cold-start conditions. After regeneration the Pt signal is fully restored, confirming the coke removal.

Analysis of the surface with LEIS showed that the reduction correlated quantitatively with the reduction of the amount of Pt and Rh at the outermost atomic layer. To verify that coke was responsible for this reduction, the catalyst was then treated with atomic oxygen to remove the coke as CO and CO₂. The original surface was restored as shown by the LEIS measurement. The effect of a cold start was thus indeed the result of coke deposition on the Pt/Rh nanoclusters.

High sensitivity LEIS enables the detection of the blocking by coke already in a very early stage. Often the coke formation nucleates at a certain site. In case of an FCC catalyst LEIS showed, for instance, that it was not the active phase nor the support, but the binder of the catalyst that was responsible for the nucleation. Replacing the binder strongly reduced the coke formation.

Location of promoters

High sensitivity LEIS can also be used to detect and quantify the presence of promoters. Analogous to the influence of poisons on the LEIS spectrum, the adsorption of a promoter will cover its adsorption site. This site is then no longer in the outer surface. Comparison of the LEIS analysis with and without the promoter reveals its presence.

Conclusions

The presence of poisons such as coke and sulfur on a catalyst can be detected by many surface analytic techniques. LEIS is unique since it can selectively analyze the composition of the outer atoms of the surface. Therefore only LEIS is capable of identifying the adsorption site, by comparing the LEIS spectra of the fresh (or regenerated) and the deactivated catalyst.

High-sensitivity LEIS has the sensitivity to detect and quantify even the low concentrations of promoters on commercial catalysts.

For more information on LEIS studies on active sites of catalysts:

- [1] Coke deposition on automotive three-way catalysts studied with LEIS, J.M.A. Harmsen, W.P.A. Jansen, J.H.B.J. Hoebink, J.C. Schouten and H.H. Brongersma, Catal. Lett. 74 (2001) 133-137.
- [2] Noble metal segregation and cluster size of Pt/Rh/CeO₂/γ-Al₂O₃ automotive three-way catalysts studied with low – energy ion scattering, W.P.A. Jansen, J.M.A. Harmsen, A.W. Denier van der Gon, J.H.B.J. Hoebink, J.C. Schouten and H.H. Brongersma, J. Catal. **204** (2001) 420-427.

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