tascon GmbH
Analytical Services & Consulting

The Active Sites of Catalysts Determined by LEIS

TAS-AN-L4E

There is an ongoing need for performance improvement in catalysis for both economic and environmental reasons. Catalyst deactivation by poisoning is a major bottleneck in the operation of catalytic processes. The time scale of deactivation can vary from seconds to years. The understanding of the identity of any poisoning species and the sites that it blocks is a first step in trying to regenerate the catalyst. Here, Low Energy Ion Scattering (LEIS) can deliver a valuable analytical contribution. Only LEIS is capable of determining the site that has been poisoned, by selectively probing the atoms in the outer 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.

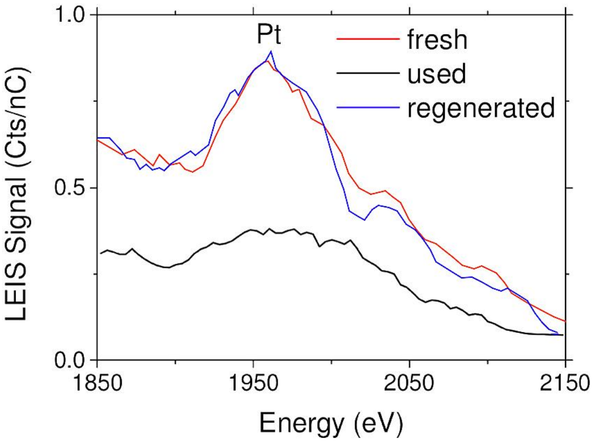

Figure 1: The number of Pt atoms in the outer surface has dropped significantly after use in acetylene conversion at cold-start conditions; after regeneration the Pt signal is fully restored, confirming the coke removal

LEIS was used to quantify the elemental composition at the respective surfaces. The experiments showed (Fig. 1) that the reduction in activity 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 reactive oxygen atoms to remove the coke as CO and CO_2. The original surface could be restored as shown by the LEIS measurement. The negative effect of a cold start was thus indeed identified as coke deposition on the Pt/Rh nanoclusters.

Further analysis options:

Determination of nucleation site

High sensitivity LEIS enables the detection of the blocking by coke even at a very early stage. Often the coke formation nucleates at a certain site. In the 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. (Data not shown here)

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 available in the outer surface and can no longer be seen with LEIS. Comparison of the LEIS analysis with and without the promoter can reveal its location.

Conclusions

The presence of poisons such as coke and sulphur on a catalyst can be detected by many surface analytical techniques. However, LEIS is unique since it can selectively analyse 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.

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

References

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

1. J.M.A. Harmsen, W.P.A. Jansen, J.H.B.J. Hoebink, J.C. Schouten and H.H. Brongersma, Coke Deposition on Automotive Three-Way Catalysts Studied with LEIS, Catalysis Letters 74, 133 – 137 (2001).

2. 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, Noble Metal Segregation and Cluster Size of Pt/Rh/CeO_2/γ-Al_2O_3 Automotive Three-Way Catalysts Studied with Low-Energy Ion Scattering, Journal of Catalysis 204, 420 – 427 (2001).