The nucleation sites for BaO on g-Al_2O_3 studied by high sensitivity LEIS

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Introduction

The extreme surface sensitivity of Low Energy Ion Scattering (LEIS) enables a non-destructive (static) and quantitative analysis of the outermost atoms of the surface. Using high-sensitivity LEIS low loadings of the active phase on a highly dispersed support can be detected [1]. For oxidic spinels it was found that only the cations that are present in the octahedral sites are at the outer surface, while the cations in the tetrahedral sites reside just below this surface. A 1:1 correlation between LEIS and catalysis was demonstrated for the selective reduction of nitro- to nitrosobenzene [2]. Techniques such as XPS, that probe much deeper, do not show this correlation.

Recently Kwak et al. [5], using ultra-high-field solid-state MAS^{27} Al-NMR, observed the presence of penta-coordinated Al^{3+} ions at the surface of γ-Al_2O_3. The impregnated catalytic phase (BaO) was found to anchor preferentially to these sites. If the penta-coordinated Al^{3+} ions are indeed at the outer surface, these Al ions should be clearly visible with LEIS, especially since the shielding of these ions by oxygen would be lower.

Materials and Methods

The LEIS spectra were obtained with a high-sensitivity high-mass resolution LEIS instrument using a double toroidal energy analyzer and parallel energy detection [3,4].

The BaO/ γ-Al_2O_3 samples with loadings of 0 – 20 wt% were prepared by incipient wetness impregnation, using aqueous Ba $(NO_3)_2$ solutions and a 200 m^2/g (Condea) support. The samples were dried and calcined (500 ^{0}C for 2h). A BaO standard was used as LEIS reference for the Ba. In the preparation chamber of the LEIS equipment the samples were cleaned with atomic oxygen (removal of organic contamination due to transport and storage). The surfaces were analyzed with 3 keV $^4He^+$ ions.

Results and Discussion

The Ba, Al and O-signals have been studied as function of the BaO loading. In fig. 1 a LEIS spectrum is shown for a sample with a 2wt% BaO loading. The masses of O, Al and Ba are so different, that they can easily be separated with $^4He^+$. Thus analysis with heavier noble gas ions is not necessary. The high sensitivity of HS-LEIS makes it possible to cover a wide range of loadings. Information on the precise Ba concentration in the outer surface and the adsorption site are presented. For a series of BaO loadings, the results by high-sensitivity LEIS are compared and contrasted with the earlier NMR results.

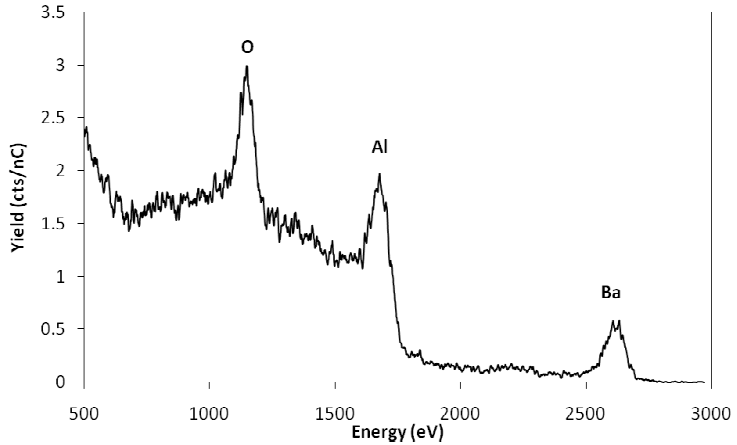

Figure 1. 3 keV $^4He^+$ LEIS spectrum for γ-Al_2O_3 with a 2 wt% loading of BaO.

Significance

γ-Alumina-supported alkali and alkaline earth oxide-based NO_x storage/reduction operating under "lean" conditions. Detailed understanding of the γ-alumina – BaO interaction is important for the design of improved catalysts. High-sensitivity LEIS can selectively and quantitatively analyze the outer surface, thus precisely the atoms where the interaction takes place.

References

1. H.R.J. ter Veen, T. Kim, I.E. Wachs, H.H. Brongersma, *Catal. Today* xxx, xxx (2008) in press.
2. J.-P. Jacobs, A. Maltha, J.G.H. Reintjes, J. Drimal, H.H. Brongersma, *J. Catal*. 147, 294 (1994).
3. H.H. Brongersma, M. Draxler, M. de Ridder and P. Bauer, *Surf. Sci. Repts* 62, 63 (2007).
4. www.iontof.com
5. J.H. Kwak, J.Z. Hu, D.H. Kim, J. Szanyi, C.H.F. Peden, *J. Catal.* 251, 189 (2007).