Anomalous Small-angle X-ray Scattering Studies of Ni/Fe Catalysts on Al_2O_3 Alumina Support for Clean Hydrogen Production

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Introduction

We develop Al_2O_3 supported catalysts for the reductive conversion of methane and higher-order hydrocarbons to obtain clean, sulfur-free hydrogen [1]. The decomposition products are hydrogen and carbon. Carbon is deposited in solid form, often as carbon nanotubes, on the catalyst support. Costly noble metals used as catalyst active material typically show superior performance. However, to make hydrogen fuel a successful and economical alternative to traditional fossil fuel, peripheral costs such as catalysts and processes have to be minimized. We have shown that binary, Fe-based catalysts may be a promising and economical alternative to noble metal catalysts [1]. To optimize the catalyst performance and study the pathogenesis of catalyst constituents, a thorough characterization during the whole stage of catalyst processing and hydrocarbon production is necessary. Since this catalyst contains the Al_2O_3 matrix, pores, binary catalyst particles, and solid carbon precipitates, we attempt to use anomalous small-angle x-ray scattering (ASAXS) for contrast variation of the scattering of the catalyst metals. This technique has been successfully applied to catalyst research for a number of years now [2, 3].

Methods and Materials

Supported catalysts were prepared by adding an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ to a slurry of γ-alumina (Al_2O_3, 150 m^2/g surface area), then precipitating metal oxyhydroxide on alumina by raising the pH of the slurry with the ammonia solution. After the slurry was washed several times, it was dewatered, and the resulting paste was extruded and vacuum-dried to form pellets. Stoichiometric ratios were chosen so that a catalyst with 50% Ni and 50% Fe and a total metal content of 10 wt% was obtained. The catalyst was reduced for 2 hours with H_2 at 700°C. It was then employed as a catalyst for methane conversion. Three samples (as-prepared, reduced, and after-catalysis) were subjected to SAXS at BESSRC-CAT beamline 12-ID at the APS. The samples were crunched and mortared and finely dispersed on clear adhesive tape for the SAXS experiments. Scattering curves at photon energies between 8100 and 8395 eV for the Fe contrast and between 6900 and 7963 eV for the Ni contrast were recorded for scattering vectors between 0.001 1/Å and 0.25 Å. For reference purposes, a blank Al_2O_3 catalyst was prepared, but it had no metal contents.

Results

Figure 1 shows the scattering curve of the Al_2O_3 sample and the according Porod fit. Subtraction of the Porod fit from the data curve yields a data curve with two pronounced Guinier ranges at 0.006 1/Å and 0.3 1/Å, with radii of gyration of 300 Å and 70 Å. This is a bimodal size distribution of the pores in the Al_2O_3 catalyst substrate.

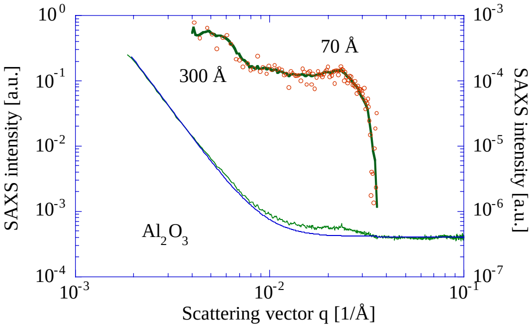

FIG. 1. SAXS curve of Al_2O_3 reference (green lower curve), Porod fit (blue, drawn line), and data curve after Porod subtraction (open circles). The line through open circles is the smoothed curve.

Figure 2 shows the ASAXS scattering curves of the "A" series as prepared (oxidized), after reduction with H_2 (reduced), and after employment as a catalyst (time-on-stream or TOS). These curves are actually the weighted difference of scattering curves obtained at x-ray energies before and behind the nickel K-shell absorption edge (contrast variation), with weighting ratios obtained from tabulated values for the atomic form factors f′ and f′′ for nickel, as exercised in Refs. 2-5.

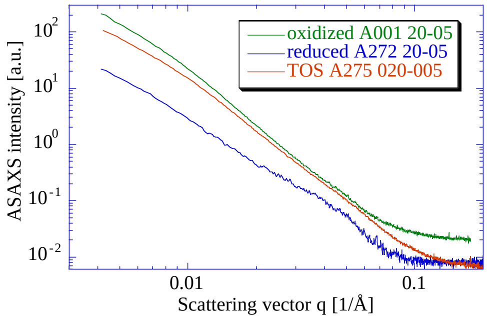

FIG. 2. ASAXS curves of the 50%Fe/50%Ni catalyst during different processing stages.

The contrast variation reveals the presence of a significant structural feature at around q = 0.05 1/Å. These are the metal particles precipitated in the porous alumina matrix during catalyst processing. Guinier analysis shows that the original metal clusters have a radius of gyration R_g of 52 Å. Reduction with hydrogen causes slight shrinking of the clusters toward 45 Å. After catalytic activity (reduction of methane, hydrogen generation, and carbon nanotube formation), R_g is 38 Å. Figure 3 shows the ASAXS curve of the catalyst after time on stream (TOS, solid line below). The dotted curve is the Porod fit and served to highlight the deviations from Porod scattering and to facilitate the Guinier fit. The data curve with open symbols is the ASAXS curve after Porod subtraction, and the solid line is the corresponding Guinier fit.

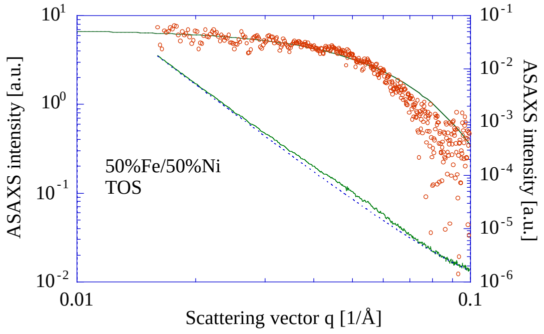

FIG. 3. ASAXS curves of the 50%Fe/50%Ni catalyst after TOS (green curve), Porod fit (blue dotted curve), subtracted curve (open symbols), and Guinier fit (solid line).

Discussion

The metal nanoparticle size seems to be rather large compared to that of the other published systems. However, we aimed for a higher catalyst loading (10% versus 2%) for the initial ASAXS experiments; consequently, larger particles are expected. Our x-ray absorption and Moessbauer spectroscopy results on similar systems show that the "as-prepared" Fe-based catalysts are prone to oxidation. Typically, a subsequent reduction of the catalyst is required in order to achieve satisfactory conversion performance. The reduction of oxidized metal species normally causes a shrinking of the sample, because metal phases tend to exist in dense phases. This effect of shrinkage after reduction (52 to 45 Å) is observed here. The continued shrinking during or after TOS (45 to 38 Å) is not resolved yet. One possible scenario is that part of the metal atoms leave the cluster during catalytic activity in order to build up the carbon nanotubes. It is an established fact that Fe clusters serve as "atomic brick layers," and we have made corresponding electron microscopy observations. The analysis of the other samples (B, C) as well as contrast variation of the Fe absorption edge is ongoing and will be reported on later.

Acknowledgments

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