FUSED IRON SURFACE COMPOSITION AS MEASURED BY LOW ENERGY ION SCATTERING

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Low energy He\(^+\)-scattering was used to simply demonstrate that the surface of a typical fused iron ammonia synthesis catalyst is largely covered by promoter oxides of calcium and/or potassium. Complementary photoemission results indicate that atomic nitrogen is deposited in the near surface region during catalyst activation in NH\(_3\)/H\(_2\)-mixtures.

The surface properties of promoted fused iron catalysts have been extensively investigated from the viewpoint of ammonia synthesis. Studies using N\(_2\) [1] and CO [2] chemisorption, X-ray photoemission [3], and Auger spectroscopy [4,5], for example, consistently indicated that the concentration of exposed iron sites represents only a few percent (e.g. 2–20\%) of the total catalyst surface area (ca. 20 m\(^2\)/g). Photoemission and Auger results clearly revealed that promoter oxides of aluminum, calcium, and potassium all segregate in the catalyst near surface region upon reduction [3–5]. X-ray diffraction and Mössbauer results also indicated that the reduced iron phase can vary from crystalline \(\alpha\)-Fe to amorphous structures and that complex reactions may occur between iron and the promoter oxides to produce compounds such as FeAl\(_2\)O\(_4\) [6,7]. Recent model catalytic studies using aluminum and potassium doped iron surfaces showed that complex, mixed metal oxides form in this case as well [8]. In this communication we report studies of a typical, triply promoted fused iron ammonia synthesis catalyst using X-ray photoemission (XPS) and low energy helium ion scattering (He\(^+\)-LEIS). The LEIS results simply and clearly demonstrate that the active surface of well reduced fusion iron is mostly covered by promoter oxides of calcium and/or potassium. On the one hand, these studies simply confirm earlier Auger spectroscopy results reported by Silverman and Boudart [4] and Ertl et al. [5]. On the other hand, these results strongly complement earlier studies which indicated that He\(^+\)-LEIS is an invaluable research tool for surface composition studies using practical heterogeneous catalysts [9]. Photoemission results also suggest that surface nitride formation accompanies catalyst activation in NH\(_3\)/H\(_2\) mixtures.

The fused iron catalyst investigated in this work was a commercially available BASF-R material which nominally contains 2–3\% Al\(_2\)O\(_3\), 0.5–1.0\% K\(_2\)O, and
0.5–1.5% CaO along with minor concentrations of Na, Mg, and Si-oxides. Catalyst activation and surface analysis studies were carried out in an apparatus equipped with a UHV-stage for XPS and LEIS studies and a microreactor stage where in situ pretreatment could be carried out at atmospheric pressure and 25–550°C [10]. Small samples (100–150 mg) of 100/150 mesh catalyst in the form of thin (1 mm × 1 cm²) wafers gently pressed into an OFHC copper holder were transferred between the stages with the aid of magnetic manipulators that were mounted on a differentially pumped buffer chamber maintained below 10⁻⁸ Torr. Photoemission spectra were collected 10–20° off normal from the macroscopic surface of the pressed wafer samples using Al(Ka)-excitation with a Leybold-Heraeus hemispherical energy analyzer operated at 50 or 100 eV pass energy. Helium ion scattering spectra were obtained at a scattering angle of 120° with the analyzer operating in the retarding ratio mode with ΔE/E = 3. The ion gun was focussed to a spot size of about 1 mm² and was continuously rastered over about a 0.5 cm² region. The beam current was 30–100 nA, and spectra were averaged over 10–20 scans collected over a 5–8 minute period. Consecutive scans revealed no changes except at long (ca. 30 min.) times when preferential sputtering of Ca and/or K became detectable. Data acquisition and manipulation were carried out using an HP 1000 computer equipped with the LH-DS5 software package.

Iron (2P₃/₂) and nitrogen (1s) photoemission results obtained before and after reduction in H₂ and 5% NH₃/H₂ at about 500°C are displayed in fig. 1. While the BASF-R catalyst was obtained from the manufacturer in a prereduced form, the surface region was largely converted to oxides as judged by XPS. Upon reduction in H₂ or 5% NH₃/H₂ at 470–500°C for one hour or more, iron was well-reduced (90%+) to the metallic state with Fe(2P₃/₂) = 706.8 eV. As indicated in fig. 1, the initially fresh catalyst exhibited small concentrations of surface nitrogen. While this nitrogen was largely eliminated after H₂-activation, the nitrogen surface concentration was increased greatly after treatment with 5% NH₃/H₂. It is important to note that this was the only significant difference in fused iron surface composition that was detected when comparing activation by H₂ and NH₃/H₂ treatment.

Photoemission studies also revealed a variety of promoters in the near surface region of BASF-R including oxide-like forms of Na, Mg, Si, Al, K, and Ca. In agreement with earlier work [3], all promoters appeared to persist as oxides following catalyst reduction as indicated by their binding energies and the oxygen concentration of the near surface region [11]. Table 1 summarizes binding energies and XPS atomic ratios [12] for the major promoters as a function of catalyst pretreatment. Even though the nominal bulk loading of each promoter is only about 1 wt.% or less, the surface concentrations were clearly much higher as indicated by the magnitude of the XPS atomic ratios. Previous XPS [3] and Auger [4,5] studies using reduced Haldor-Topsoe KM-I and BASF catalysts suggested that the promoter oxides are all segregated in the near surface region and that