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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 α-Fe to amorphous structures and that complex reactions may occur between iron and the promoter oxides to produce compounds such as $FeAl_2O_4$ [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_2O_3, 0.5–1.0% K_2O, 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 cm^2) 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(Kα)-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 $\Delta E/E = 3$. The ion gun was focussed to a spot size of about 1 mm^2 and was continuously rastered over about a 0.5 cm^2 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 ($2p_{3/2}$) and nitrogen (1s) photoemission results obtained before and after reduction in H_2 and 5% NH_3/H_2 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 H_2 or 5% NH_3/H_2 at 470–500 °C for one hour or more, iron was well-reduced ($90\%^+$) to the metallic state with Fe($2p_{3/2}$) = 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 H_2-activation, the nitrogen surface concentration was increased greatly after treatment with 5% NH_3/H_2. It is important to note that this was the only significant difference in fused iron surface composition that was detected when comparing activation by H_2 and NH_3/H_2 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

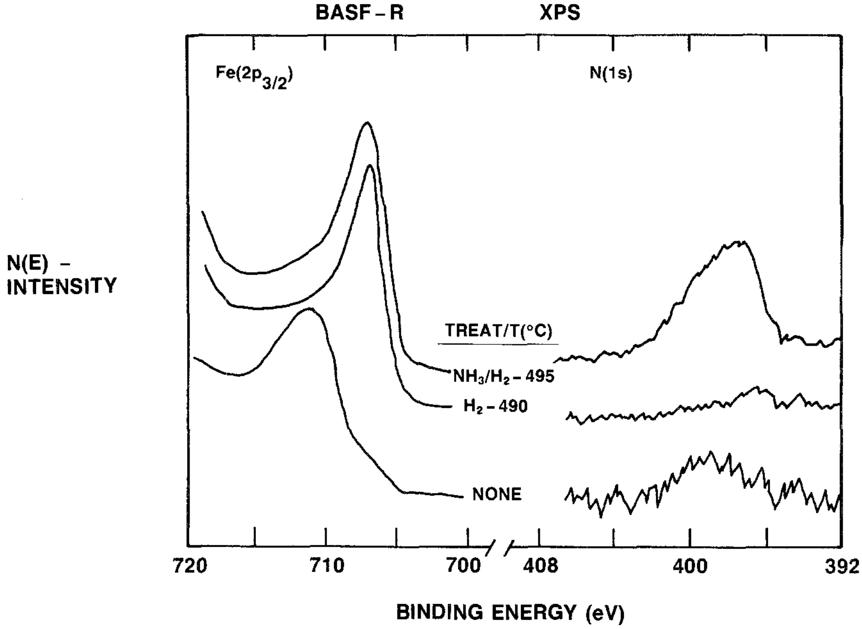

Fig. 1. Iron ($2p_{3/2}$) and nitrogen (1s) Photoemission results for BASF-R fused iron after treatment with H_2 and 5% NH_3/H_2.

most (ca. 95%) of the iron surface is covered by these species. Our results for BASF-R are also consistent with this conclusion.

Low energy helium ion scattering spectra displayed in fig. 2 more clearly emphasize that the concentration of uncovered iron sites present in the well-reduced catalyst is very small indeed. The scattering peak due to potassium and/or calcium dominated the LEIS spectrum under all conditions supporting the view that most of the surface is covered by these particular promoters. For 1/keV initial energy, scattering peaks due to oxygen, sodium/magnesium, silica/

Table 1
XPS atomic ratios and binding energies for fused iron catalysts with variable pretreatment

Catalyst/treat	XPS atomic ratio [a]			Binding energy (eV) [b]		
	(Al/Fe)	(Ca/Fe)	(K/Fe)	Al(2s)	Ca($2p_{3/2}$)	K($2p_{3/2}$)
BASF-R/None	0.85	0.49	0.70	119.4	347.6	292.6
BASF-R/H_2-490°C	2.0	1.2	0.78	119.5	347.5	293.8
BASF-R/NH_3-H_2-495°C	1.7	1.1	0.69	119.4	347.3	293.7
Washed BASF-R/ H_2-500°C	1.3	0.88	0.093	119.3	347.7	293.6
KOH/BASF-R/ H_2-495°C	2.2	0.63	3.7	119.1	347.0	293.8

[a] ± ca. 15%

[b] ± 0.3 eV relative to Fe($2p_{3/2}$) at 706.8 eV for reduced catalysts and 710.8 eV for fresh catalyst

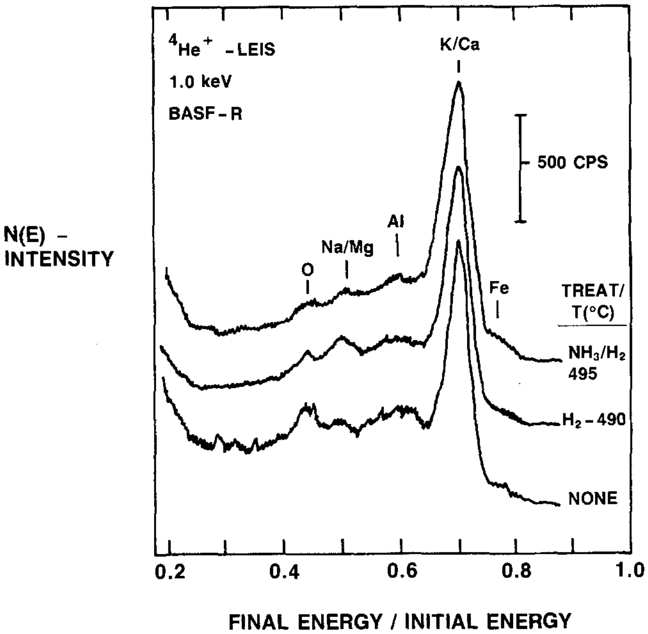

Fig. 2. Energy distributions for 1.0 keV He^+ scattering from BASF-R fused iron after treatment with H_2 and 5% NH_3/H_2.

aluminum, and iron were barely detectable. Apart from a reduced intensity for scattering from oxygen sites, no significant differences in the LEIS energy distributions were detected after catalyst reduction in either H_2 or 5% NH_3/H_2.

Correcting the raw LEIS peak heights for detection sensitivity using scattering cross-sections tabulated for the Moliere approximation to the Thomas-Fermi screening function in a Coulomb potential [13], the fraction of surface represented by exposed iron sites can be roughly estimated to be no more than 3–5%. It is notable that this estimate compares favorably with the small iron site density inferred from CO-chemisorption measurements. Specifically, CO-uptake at 25 ° C following H_2-activation at 480 ° C yielded a site density of 13 μmole/gr. With a surface area of 15 m^2/g, this uptake corresponds to only about 2.6% of the total catalyst surface area.

LEIS results obtained for a range of initial He^+ energies are displayed in fig. 3. We have previously discussed the dependence of first and second layer scattering on initial energy [14], and the changes in the energy distributions for fused iron with energy well underscore this dependence. Specifically, for low initial energies where only top-layer scattering is detectable, the LEIS results are dominated by K and/or Ga. However, at higher energies near 2 keV where second layer scattering contributes to the spectrum [14], scattering features due to iron and aluminum become easily recognizable. These changes are not associated with sputtering; rather, they suggest that both iron and oxidized aluminum are largely

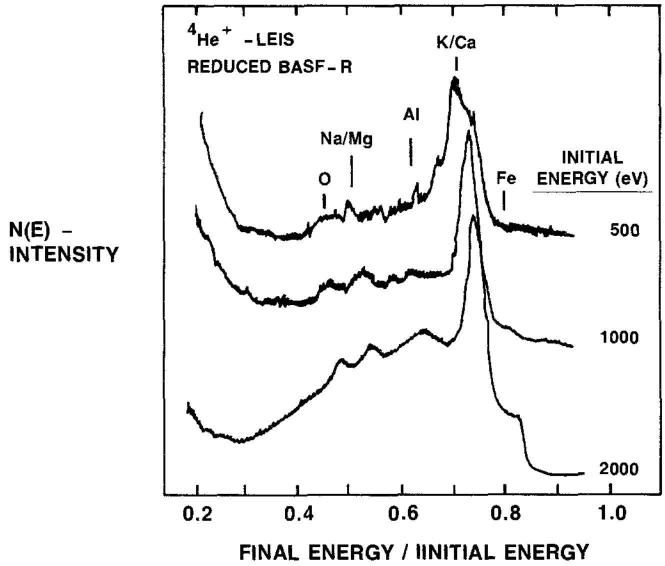

Fig. 3. Energy distributions for 0.5–2.0 keV He^+ scattering from H_2-reduced BASF fused iron.

covered by a potassium and/or calcium oxide overlayer. The shift of the scattering peaks with increasing energy is not well understood. It is likely associated with localized surface charging, reionization of helium neutrals along the outgoing trajectory [15], or a combination of these processes. At higher energies, the peak positions closely approach those expected for classical binary scattering.

In an effort to distinguish between oxides of K and Ca as the majority species present at the fused iron surface, limited studies were also carried out using catalysts with variable potassium concentration. A catalyst with reduced K-content (ca. 0.05%) was prepared by washing the as-received BASF catalyst with dilute NH_4OH, whereas a catalyst with excess potassium was prepared by adding KOH via incipient wetness to give a K-loading near 2 wt.%. XPS atomic ratios measured after H_2-activation are included in table 1. In agreement with earlier work [3], these results indicate that washing selectively removed potassium from the near surface region with little effect on the other promoters. By contrast, KOH addition greatly increased the potassium surface concentration. These changes are also reflected in the LEIS energy distributions compared in fig. 4. The well-reduced, washed catalyst with low K-content produced scattering peaks due to O, Na/Mg, Si/Al, and Fe which were much more clearly resolved as compared to the standard BASF catalyst. These changes, along with the ease of potassium removal, clearly indicate that much of the surface (iron sites in particular) is indeed covered by oxidized potassium. The persistence of a strong scattering peak due to oxidized calcium suggests that this species is also well dispersed in the outermost layers of the catalyst near surface region. The catalyst

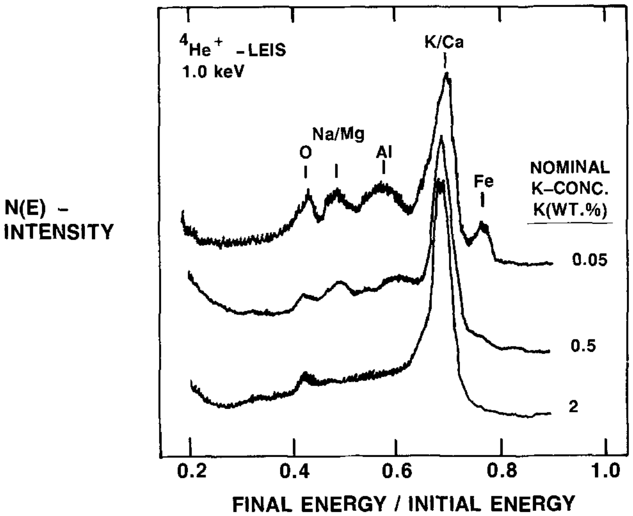

Fig. 4. Energy distributions for 1.0 keV He^+ scattering from H_2-reduced fused iron catalysts with variable potassium content.

containing excess potassium produced a strong peak due to surface K (and/or Ca) with little or no indication for other scattering features. This should not be considered too surprising since the K-loading in this catalyst corresponds to about 3-monolayer equivalents of potassium oxide.

The N(1s) XPS spectrum obtained following NH_3/H_2-treatment contains two or more components with N(1s) binding energies centered near 397.0 and 398.5 eV [11]. The major component with the lower core-level ionization potential clearly appears to be associated with atomic nitrogen strongly bound in the iron near surface region. This conclusion is based on the close similarity of our XPS results with those reported by Ertl [16], Grunze [17], and others [18] for surface and subsurface atomic nitrogen on iron foils and single crystal surfaces. By analogy to the previous work [16–18], the higher binding energy component is believed to represent a combination of one or more surface species including NH, NH_2, and/or chemisorbed NH_3. The atomic nitrogen surface concentration estimated from deconvoluted spectra corresponds to a (N/Fe) atomic ratio of about 0.1. While this ratio is too small to associate with well defined nitrides such as Fe_4N or Fe_2N, it also appears too large to be accounted for by a simple chemisorbed layer, especially in view of the small iron site density and the fact that surface nitrogen was not detectable by LEIS. Accordingly, it appears that much of the atomic nitrogen produced during NH_3/H_2 treatment is dissolved into subsurface sites producing nonstoichiometric surface nitride layers. Direct precedent for this behavior was previously reported by Ertl and coworkers [16] in connection with N_2 and NH_3 chemisorption on Fe(110) and Fe(110) surfaces. Non-stoichiometric iron nitride phases with (N/Fe) = 0.1 have also been reported by Butt et al. [19] in connection with Fischer-Tropsch synthesis over nitrided Fe/SiO_2 catalysts. Formation of this nitride-like phase might explain, or at least contribute, to the improved ammonia synthesis activity which has been frequently reported for iron catalysts activated by NH_3/H_2 treatment [20].

In summary, the LEIS results reported here clearly demonstrate that the surface of a typical triply promoted fused iron ammonia synthesis catalyst is mostly covered by oxidized forms of calcium and/or potassium. This conclusion is in full accord with previous work using both classical adsorption [1,2] and modern surface science [3–8] techniques. Our studies also indicate that atomic nitrogen is deposited in the near surface region upon catalyst activation in 5% NH_3/H_2. The role, if any, of promoter oxides in promoting surface nitride formation represents an important area for further research.

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