# Surface characterisation of an iron oxide catalyst (ethylbenzene → styrene): An XPS study

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**Abstract.** Surface chemistry and structural changes of a potassia promoted, chromia stabilised iron oxide catalyst were examined before and after the non oxidative dehydrogenation of ethylbenzene to styrene using x-ray photoelectron spectroscopy (XPS).

XPS binding energies of the $Fe(2p, 3s, 3p, 3d)$, $K(2p, 3s, 3p)$, $Cr(2p, 3s, 3p)$ and $O(1s)$ levels along with characteristic shifts in the binding energies, spin-orbit splittings and satellite, multiplet splittings help in identifying surface active species such as $Fe_2O_3$, $Fe_3O_4$, $FeOOH$ at the surface of fresh and used catalysts.

## 1. Introduction

In an earlier paper (Sayyed *et al* 1985), we have reported the catalytic performance (conversion and selectivity) results on dehydrogenation of ethylbenzene to styrene over a potassia promoted iron oxide catalyst. The catalyst was characterised by x-ray diffraction, scanning electron microscopy and $Fe^{57}$ Mössbauer spectroscopy (transmission and conversion modes).

Since catalytic reactions basically occur at the surface, the same catalyst has also been studied using a modern surface analytical tool, namely x-ray photoelectron spectroscopy (XPS) to understand the electronic structure of surface active species and the catalytic reaction.

In this paper we report the XPS experimental results and its analysis. The surface active species such as $Fe_2O_3$, $Fe_3O_4$, $FeOOH$ were identified through the characteristic shifts in their binding energies, spin-orbit splittings, satellite and multiplet structures. All these results are evaluated in comparison with the bulk experimental data to speculate on the mechanistic aspects of the catalytic reaction.

## 2. Experimental

X-ray photoelectron spectra of the fresh and used catalysts were recorded at room temperature on a VG scientific ESCA 3 MK II spectrometer. MgK$_\alpha$ (1253·6 eV) radiation was used for excitation. The catalyst sample was mounted on a suitable holder and photoelectron spectra were recorded for the as-received, etched (using argon ion bombardment), fractured and powdered pellets. Binding energies (BE) were determined

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using the C(1s) level as reference (285·0 eV). Photoelectron spectra of standard compounds like KCl, $K_2CrO_4$, $KNO_3$, α-$Fe_2O_3$, $Fe_3O_4$, $FeCr_2O_4$, $Cr_2O_3$ etc. were also recorded for standardisation and identification of the surface species.

## 3.   Results

X-ray photoelectron spectra of Fe(2p, 3s, 3p, 3d), O(1s), K(2p, 3s, 3p) and Cr(2p, 3s, 3p) levels of the fresh and used catalysts were scanned at room temperature. Tables 1 and 2 summarise the BE values of fresh and used catalysts for the respective levels of different constituents.

**Table 1.**   Binding energy values of the Fe(2p, 3s, 3p), K(2p), O(1s) levels in eV from XPS spectra of the fresh catalyst.

| Sample | Fe | | | | | K | | O |
|--------|---------|------|-------------------------------|-------------|-------------|-------------|-------------|------|
|        | $3p_{1/2}$ | $3s$ | $3s$ multiplet structure | $2p_{3/2}$ | $2p_{1/2}$ | $2p_{3/2}$ | $2p_{1/2}$ | $1s$ |
| As-received | 55·6 | 93·2 | 100·1 | 710·5 | 724·6 | 292·7 | 295·6 | 529·5 |
|  |  |  |  |  |  |  |  | 531·7 |
| Etched (I) with argon ions | 55·1 | 93·1 | 99·7 | 710·5 | 723·6 | 292·6 | 296·0 | 529·9 |
|  |  |  |  |  |  |  |  | 531·8 |
| Etched (II) with argon ions | 55·3 | 93·3 | 100·2 | 710·5 | 723·6 | 292·7 | 295·7 | 529·8 |
|  |  |  |  |  |  |  |  | 531·7 |
| Powdered | 55·5 | 93·3 | 99·9 | 710·6 | 723·6 | 292·8 | 295·6 | 529·5 |
|  |  |  |  |  |  |  |  | 531·7 |

**Table 2.**   Binding energy values of the Fe(2p, 3s, 3p), K(2p), Cr(2p), O(1s) and CL(2p) levels in eV from XPS spectra of the used catalysts.

| Sample | Fe | | | | | K | | Cr | O | CL |
|--------|---------|------|-------------------------------|-------------|-------------|-------------|-------------|------|------|------|
|        | $3p_{1/2}$ | $3s$ | $3s$ multiplet structure | $2p_{3/2}$ | $2p_{1/2}$ | $2p_{3/2}$ | $2p_{1/2}$ | $2p$ | $1s$ | $2p$ |
| As-received | 56·3 | 94·5 | 102·7 | 711·6 | 725·1 | 293·4 | 296·2 | | 530·8 | 199·0 |
|  |  |  |  |  |  |  |  |  |  | 200·8 |
| Etched (I) with Ar ions | 54·6 | 92·7 | 98·3 | 709·9 | 723·0 | 294·0 | 296·6 | 576·3 | 529·6 | 199·0 |
|  |  |  | 102·6 |  |  |  |  |  | 531·6 | 201·4 |
| Etched (II) with Ar ions | 54·8 | 92·7 | 98·3 | 709·9 | 723·2 | 294·1 | 296·7 | 576·6 | 529·6 | 199·7 |
|  |  |  | 102·2 |  |  |  |  |  | 531·6 | 201·0 |
| Fractured | 55·1 | 93·0 | 98·8 | 709·9 | 723·2 | 292·8 | 296·5 | 576·9 | 530·1 | nil |
|  |  |  | 102·8 |  |  |  |  |  |  |  |
| Powdered | 55·8 | 93·4 | 99·2 | 710·3 | 724·3 | 292·7 | 295·7 | 576·8 | 530·4 | nil |
|  |  |  | 101·8 |  |  |  |  |  |  |  |

### 3.1 Fresh catalyst

In the high resolution scan of the Fe(2p) region, Fe($2p_{1/2}$) and ($2p_{3/2}$) levels were detected at BE $723.9$ eV and $710.5$ eV respectively. The spin orbit splitting of the $2p$ bands ($\Delta E_{2p} = E2p_{1/2} - E2p_{3/2}$) is $\approx 14.1$ eV. A $2p_{3/2}$ shake-up satellite (ss) is detected at BE $718.5$ eV corresponding to an energy separation $\Delta E_{ss} \approx 8.0$ eV. These binding energies, together with the broad satellite are characteristic of an $Fe^{3+}$ species (Brundle *et al* 1977; Rao *et al* 1979; Kurtz and Henrich 1983).

The Fe(3s) level at BE $93.2$ eV has a multiplet structure at BE $\approx 100.1$ eV. The magnitude of multiplet splitting for $3s$ core level holes for various iron compounds has been observed to be as large as $7.0$ eV, but is smaller for levels having different principal quantum numbers (Carver *et al* 1972). These values are characteristic of high spin ferric species in compounds like $Fe_2O_3$, $FeCl_3$ etc. (Carver *et al* 1972; Rao *et al* 1979). We have used both Fe(2p) shake-up satellites and Fe(3s) multiplet splitting in our identification of the surface iron species (Carlson 1975; Frost *et al* 1974; Okamoto *et al* 1975). The Fe(2p, 3s) peak positions do not show appreciable change in the BE values after repeated etching with argon ions or when the as-received pellets are fractured and powdered.

A broad asymmetric O(1s) band is recorded in the high resolution scan of the fresh catalyst. From the spectrum, O(1s) peak at $529.8$ eV is easily distinguishable from a weak shoulder around $531.7$ eV. These BE are typical of oxide and hydroxyl species (Brundle *et al* 1977) and the latter persists after etching and powdering.

The observed peaks at BE $292.8$ eV and $295.6$ eV are due to the K($2p_{3/2}$) and K($2p_{1/2}$) levels respectively and lie in the range of K(2p) BE values. The potassium species were assigned to $K_2O$, which has been added as a promoter. Cr(2p, 3s, 3p) bands were not clearly observed at the surface of the fresh catalyst.

### 3.2 Used catalyst

For the used catalyst, the as-received, etched and powdered samples give x-ray photoelectron spectra with characteristic differences as discussed below.

The high resolution scan in the Fe(2p) region for the used, as-received, catalyst gave Fe($2p_{3/2}$, $2p_{1/2}$) bands centred at BE $711.6$ eV and $725.1$ eV respectively. The energy separation, $\Delta E_{2p}$ was $\approx 13.5$ eV. Fe(2p) satellite structure was not detected. The BE values are characteristic of high spin $Fe^{3+}$ ions (Brundle *et al* 1977). X-ray photoelectron spectra observed for etched, fractured and powdered samples in the Fe(2p) region were similar. The Fe($2p_{3/2}$, $2p_{1/2}$) levels were centred at lower BE $709.9$ eV and $723.0$ eV respectively with Fe(2p) spin orbit splitting $0.4$ eV less than that of as-received catalyst. This value is known to decrease slightly with lower oxidation state (Rao *et al* 1979). The broad Fe($2p_{3/2}$) band has a shoulder on the lower BE side. The main peak is assigned to the $Fe^{3+}$ state and the shoulder to $Fe^{2+}$ state (Brundle *et al* 1977; Rao *et al* 1979; Asami *et al* 1976). A Fe($2p_{3/2}$) shake-up satellite is also detected at BE $715.8$ eV giving a characteristic $Fe^{2+}$ exchange splitting $\approx 5.9$ eV. The Fe($2p_{1/2}$) peak is also broad and asymmetric indicating the presence of a shoulder at lower BE.

The Fe(3s) band (BE $94.5$ eV) at the surface of as-received used catalyst has a multiplet structure with splitting $\approx 8.2$ eV, characteristic of high spin $Fe^{3+}$ ions. The high intensity of the multiplet structure compared to the main 3s band may be due to an additional contribution from some impurity (perhaps Si) present in the reactor. The magnitude of this multiplet splitting is $1.3$ eV higher than that reported for pure high

spin iron compounds. For the etched, fractured and powdered catalysts, the Fe(3s) band centred around 92·7 eV is broad and asymmetric indicating a superposition of two peaks with close BE values. In addition to the Fe(3s) multiplet structure at BE 102·6 eV characteristic of $Fe^{3+}$ species, another multiplet structure is observed at BE 98·3 eV. This may be assigned to the $Fe^{2+}$ species (Rao *et al* 1979; Carver *et al* 1972). These BE and multiplet splitting values are characteristic of high spin $Fe^{2+}/Fe^{3+}$ species.

A broad asymmetric band at $\approx$ 200 eV detected at the surface of as-received and etched catalysts could be resolved into two peaks at BE 199·3 eV and 200·8 eV respectively. These values are close to the $Cl(2p_{3/2}, 2p_{1/2})$ BE values and may be assigned to chlorine present as an impurity at the surface. They vanish on fracturing and powdering of the used catalyst and are not observed after subsequent catalytic reactions.

The band at 530·8 eV at the surface of the as-received catalyst corresponding to the O(1s) band is assigned to an oxide species (Brundle *et al* 1977). After etching the sample, a broad asymmetric O(1s) band was observed which could be resolved into two peaks at BE 529·6 eV and 531·6 eV. These bands can be assigned to usual oxide and surface defect oxide or hydroxyl species. On fracturing and powdering the catalyst, the O(1s) band (BE 530·1 eV) regains its own symmetry and may be assigned to the predominant oxide species.

The $K(2p_{3/2})$ and $K(2p_{1/2})$ levels for as-received and etched catalysts were at BE about 0·8 to 1 eV higher than that of the fresh catalyst. For the fractured and powdered catalyst surface, these BE values equalled those of the fresh catalyst.

Both sets of binding energies lie within the range of $K(2p)$ BE values and may be assigned to KCl or $K_2O$. $Cr(2p_{3/2})$ bands at the surface of etched, fractured and powdered catalysts were centred at BE 576·7 eV whereas $Cr(3p, 3s, 2p_{1/2})$ levels were very weak. The BE agree with those reported in literature for $Cr^{3+}$ species and may be assigned to $Cr_2O_3$ (Rao *et al* 1979).

## 4. Discussion

The high spin ferric species at the surface of the fresh catalyst is assigned to $Fe_2O_3$ taking into consideration the close agreement of the $Fe(2p, 3s)$ binding energies, spin-orbit and multiplet splittings and conversion electron Mössbauer spectroscopic (CEMS) results reported earlier (Sayyed *et al* 1985). The surface composition is nearly identical with that of the bulk catalyst.

For the used catalyst, CEMS spectra have indicated the presence of $\alpha$-$Fe_2O_3$, $Fe_3O_4$ and $\alpha$-FeOOH. The $Fe^{2+}/Fe^{3+}$ high spin species, identified from XPS data at the surface of etched, fractured and powdered catalyst are attributed to the two oxidation states of iron in $Fe_3O_4$ (Rao *et al* 1979). Since the octahedrally coordinated $Fe^{3+}$ species is not easily distinguishable from the tetrahedrally coordinated $Fe^{3+}$ species (Brundle *et al* 1977), the observed asymmetry in spectra is due to the superposition of the peaks of $Fe_2O_3$ and FeOOH as well. The formation of the FeOOH phase is due to steam. The chemical reaction can be expressed as

$$Fe_2O_3 \underset{H_2O}{\overset{H_2}{\rightleftharpoons}} Fe_3O_4$$
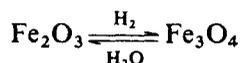
This reduction seems to be necessary as the starting point for the catalytic reaction

occurring at the surface. As a function of time, the equilibrium between $Fe_2O_3$ and $Fe_3O_4$ is established from the surface into the bulk. This thermodynamic balance is responsible for the high selectivity and conversion. Any disturbance of this equilibrium results in a drop in catalytic performance parameters.

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## References

Asami K, Hoshimoto K and Shimodaira S 1976 *Corros. Sci.* **16** 35
Brundle C R, Chuang T J and Wandelt K 1977 *Surf. Sci.* **68** 459
Carlson T A 1975 in *Photoelectron and auger spectroscopy* (New York: Plenum Press)
Carver J C, Schweitzer G K and Carlson T A 1972 *J. Chem. Phys.* **57** 973
Frost D C, McDowell C A and Woolsey I S 1974 *Mol. Phys.* **27** 1473
Kurtz R L and Henrich V E 1983 *Surf. Sci.* **129** 345
Okamoto Y, Nakano H, Imanaka T and Teranishi S 1975 *Bull. Chem. Soc. Jpn.* **48** 1163
Rao C N R, Sharma D D, Vasudevan S and Hegde M S 1979 *Proc. R. Soc. London* **A367** 239
Sayyed B A, Gupta M P, Date S K, Kamble K R, Sonsale A Y and Chatterjee A K 1985 *Proc. Indian Acad. Sci.* (*Chem. Sci.*) **95**