XPS study of the silica-supported Fe-containing catalysts for deep or partial H_2S oxidation

G.A. Bukhtiyarova[*], V.I. Bukhtiyarov, N.S. Sakaeva, V.V. Kaichev, B.P. Zolotovskii

*Boreskov Institute of Catalysis, Lavrentieva prospekt, 5, Novosibirsk, 630090, Russia*

Abstract

Catalytic properties of silica-supported Fe-containing catalysts in H_2S oxidation have been correlated with their surface composition characterized by XPS. This allows us to show that iron sulfate supported on silica is active in sulfur production with 100% selectivity, whereas the decrease in selectivity to sulfur is accompanied by the appearance of iron disulfide phase in the catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: X-ray photoelectron spectroscopy (XPS); Fe-containing catalysts; H_2S oxidation

1. Introduction

Oxidation of hydrogen sulfide to elemental sulfur:

$$H_2S + 1/2\,O_2 = 1/n\,S_n + H_2O \tag{1}$$
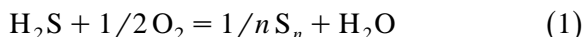
is of practical importance being a widely-used method for purification of technological gases, such as Claus tail gas, natural gas, etc. Along with selective oxidation, the deep oxidation of hydrogen sulfide to sulfur dioxide may occur:

$$H_2S + 3/2\,O_2 = SO_2 + H_2O \tag{2}$$
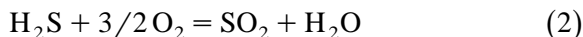
to decrease the overall sulfur yield. On the other hand, Eq. (2) is of significance itself in those cases when SO_2 produced is converted to valuable chemical products or fed back to the Claus plant [1].

In spite of long-standing interest of researchers to both reactions, the structure of active centers governed by partial or deep oxidation of H_2S is still a disputable point. Recently, a great deal of attention is turned to Fe-containing supported systems. Thus, a number of authors [2,3] have suggested that the selectivity decreases due to iron sulfide, which catalyzes Eq. (2), formed as a result of the catalyst modification by reaction medium. On the other hand, the activity of catalysts containing Fe, Cu, Zn, Co, or Ni sulfides in oxidation of hydrogen sulfide to sulfur has been concluded in Ref. [4].

To tackle this problem, we tried to prepare a number of silica-supported iron-containing catalysts for H_2S oxidation using various precursors and to select those which exhibit an essentially different level of selectivity towards sulfur. Then, their surface composition has been characterized using X-ray photoelectron spectroscopy (XPS).

---

[*] Corresponding author.

2. Experimental

Samples were prepared by impregnation of SiO_2 (KSK-1, 0.25–0.5 mm) with an aqueous solution of iron(III) nitrate or with an aqueous solution of iron(II) sulfate. After impregnation, the samples were dried at ambient conditions and then the former sample was calcined at 500°C (denoted as N500) and the latter one — at 550°C (S550).

The concentration of Fe analyzed with a Baird atomic-emission spectrometer using plasma atomic-absorption method was about 10 wt.% in both samples. To achieve this concentration in the case of the S550 sample, multiple impregnation was used.

X-ray photoelectron spectra were measured using a VG ESCALAB HP electron spectrometer with MgKα irradiation ($h\nu = 1253.6$ eV) and were calibrated against Si 2p spectrum with $E_b = 103.5$ eV used as internal reference [5]. Atomic element ratios to silicon were calculated according to the following equation:

$$\frac{n_i}{n_{Si}} = \frac{\dfrac{I_i}{ASF_i}}{\dfrac{I_{Si}}{ASF_{Si}}}$$

where ASF_i and ASF_{Si} are the atomic sensitivity factors taken from Ref. [5], and I_i, I_{Si} are the intensities of XPS lines for the analyzed elements (i) and silicon, respectively.

Catalytic properties were tested at normal pressure and 250°C in an external recirculation reactor, using catalyst fraction of 0.25–0.5 mm. Additional checking of circulation multiplicity and particle size effect indicated no diffusion limitations under these conditions for the reaction studied. The composition of the inlet gas was: 2 vol. % of H_2S, 0.5–3 vol.% of O_2, 30 vol. % of H_2O, and He to balance. Catalytic properties of the samples were characterized by the steady-state rate of H_2S oxidation, and by selectivity to sulfur at the concentrations in the circulation loop being 1 vol.% H_2S, 0.5 vol.% O_2. Concentrations of O_2, H_2S and SO_2 were measured using a chromatograph with TCD. Before unloading the samples from the reactor after catalytic testing, they were cooled in flowing helium to room temperature.

3. Results and discussion

Catalytic testing of H_2S oxidation on the catalysts reveals unstable catalytic properties of the sample prepared using Fe(III) nitrate aqueous solution (N500): concentration of SO_2 among the reaction products increases constantly in time. After 12 h, when the activity and the selectivity reach the steady-state level, SO_2 is a predominant product of H_2S oxidation (Table 1). In contrast to N500, the sulfate-originated catalyst (S550) provides the stable 100% selectivity of H_2S oxidation to sulfur.

Fig. 1 shows the Fe $2p_{3/2}$ and S 2s core level spectra for the fresh and treated (after achieving steady-state catalytic properties) samples of the N500 catalyst, XPS spectra for the treated sample being measured two times: immediately after catalytic testing and after storage in the atmosphere air. Choice of the S 2s core level

Table 1
Activity and selectivity of N500 and S550 samples in H_2S oxidation (reaction temperature is 250°C)

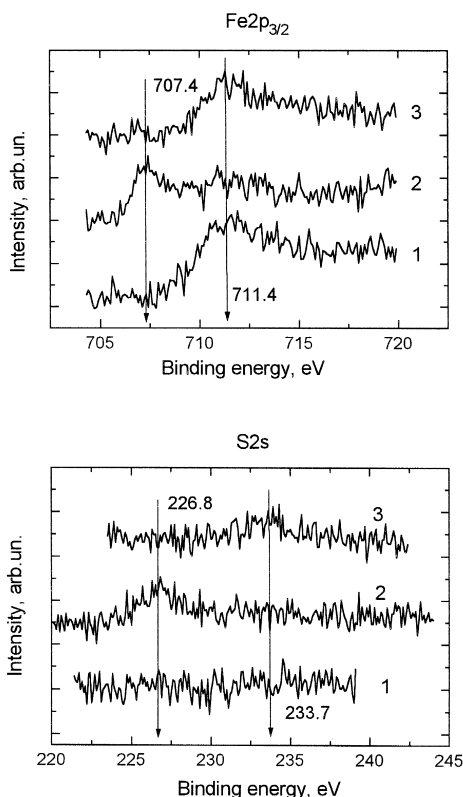| Sample	Pre-treatment conditions	Fe content, mass %	Selectivity of H_2S conversion to S_n	Reaction rate, H_2S molecules g^{-1} s^{-1}
N500	12 h in reaction mixture at 250°C	10.3	11	9.0×10^{18}
S550	8 h in reaction mixture at 250°C	10.1	100	8.3×10^{18}
S550	4 h in reaction mixture at 300°C and			9.4×10^{18}
	2 h in reaction mixture at 250°C	10.1	84	

Fig. 1. Fe $2p_{3/2}$ and S 2s spectra for the fresh (1) and treated (2,3) samples of N500 catalysts. The spectra of the treated sample were recorded immediately after catalytic testing (2) and after storage in the atmosphere air (3) for 2 months.

spectrum for analysis instead of the most intensive sulfur line, S 2p, is explained by the overlapping of the S 2p region ($E_b \sim 160$–169 eV) with one of the levels of the support — Si 2s ($E_b \sim 155$–165 eV). To recalibrate the S 2s binding energy value to the S 2p one, we have measured both spectra for the $FeSO_4/Al_2O_3$ sample and determined the difference $E_b(S\ 2p) - E_b(S\ 2s) = 64.0 \pm 0.2$ eV. This recalibration was necessary to compare our data with the reference ones [5,6].

It is seen from Fig. 1 that the fresh sample is characterized by a wide Fe $2p_{3/2}$ line with $E_b = 711.3 \pm 0.2$ eV and the absence of S 2s signal. The comparison of Fe $2p_{3/2}$ binding energy with the reference data [5] allows us to assign the Fe $2p_{3/2}$ line to Fe(III) ion. Taking

also into account the calcination temperature and full absence of N1s signal, we suggest the formation of Fe_2O_3.

The treatment of the fresh N500 sample in reaction conditions for 12 h gives rise to Fe $2p_{3/2}$ signal at 707.4 eV and S 2s signal at 226.8 eV, whereas the Fe $2p_{3/2}$ line with $E_b = 711.4$ disappeared. Using the difference in S 2s and S 2p binding energies (see above) we have calculated the $E_b(S\ 2p)$ value which is equal to 162.8 eV. The comparison of this value with the table data for SO_4^{2-} (169.1 $\pm$ 0.3 eV), SO_3^{2-} (166.8 $\pm$ 0.2 eV), S_n (164.0 eV), S_2^{2-} (162.9 eV), S^{2-} (161.9 eV) allows us to assign the observed S 2s line to sulfide ions, most probably to S_2^{2-}. The Fe $2p_{3/2}$ binding energy of 707.4 eV can be also assigned to iron disulfide. Indeed, only metallic iron exhibits similar low value of binding energy [5], while much higher E_b values are characteristic of iron ions, for example Fe $2p_{3/2}$ spectrum for iron sulfide, FeS, is characterized by the line at 710.1 eV [5]. The conclusion about the formation of FeS_2 is confirmed additionally by the quantitative XPS data. Fe/Si atomic ratio, determined from XPS intensities of the corresponding lines, is equal to 0.45, which is close to the stoichiometric ratio for FeS_2–0.5.

It should be noted, however, that FeS_2 produced as a result of the reaction mixture treatment is unstable. This conclusion is based on the analysis of the XPS spectra for the air-stored sample: Fe $2p_{3/2}$ signal is shifted to 711.4 eV and S 2s signal — to 233.7 eV. The calculation of $E_b(S\ 2p)$ by means of the procedure described above gives the value of 169.7 eV characteristic of sulfate ions [5]. The shift of the Fe $2p_{3/2}$ spectrum by 4.1 eV to higher binding energies is also in accordance with the formation of iron sulfate. Unfortunately, other methods, but not XPS, are necessary to study in more detail the nature of the sulfate formed. The same variations in the spectra are observed if the treated sample is unloaded from the catalytic reactor without cooling to room temperature.

XPS spectra of the same core levels for the S550 catalyst recorded before and after its treatments under the reaction conditions at different temperatures (250°C and 300°C) are compared in Fig. 2. Positions of both spectra for the fresh sample reflect its sulfate origin: both E_b(Fe $2p_{3/2}$) = 711.3 eV and E_b(S 2p) = E_b(S 2s) − 64.0 = 233.2 − 64.0 = 169.2 eV are in rather good agreement with the data for $FeSO_4 \cdot 7H_2O$ measured by Wagner et al. [6]. Thus, as opposed to the N500 fresh sample, the calcination of the impregnated S550 sample at 550°C does not decompose the phase of the precursor. This fact suggests that the silica-supported iron sulfate is more stable than the iron nitrate phase. Another difference of the fresh S550 sample from N500 is a higher Fe/Si atomic ratio calculated from XPS intensities in the former case:

0.11 against to 0.04, respectively. Taking into account the equal bulk concentration (see Table 1) of Fe measured by chemical analysis for both samples, the variation in the surface iron concentration (XPS data) can be attributed to the differences in the mean sizes of iron-containing supported particles. The higher are the particle sizes, the more effective is the self-screening of Fe $2p_{3/2}$ photoelectrons, and, as a consequence, the lower is the value of Fe/Si atomic ratio determined from XPS data. Then, the fresh S550 sample contains the active phase particles which are smaller in size than those of the N500.

The treatment of the fresh S550 sample in reaction conditions seems to result in the enlargement of the iron-containing particles due to sintering. This suggestion is based on a triple decrease in the Fe/Si atomic ratio for the treated sample which achieves the level of the corresponding N500 sample (0.04). At the same time, the positions of the Fe $2p_{3/2}$ and S 2s spectra do not change in the reaction course (Fig. 2, curves 2) determining again the stability of the sulfate phase. Only the elevation of the temperature of the reaction mixture treatment causes the appearance of Fe $2p_{3/2}$ line at 707.5 eV and S 2s line at 226.7 eV due to formation of the iron disulfide phase (Fig. 2, curves 3). The formation of FeS_2 is accompanied by the appearance of SO_2 among the reaction products. As a consequence, the selectivity of H_2S oxidation to sulfur decreases, as seen from the data of Table 1.

Thus, XPS characterization of the catalysts with essentially different levels of selectivity towards sulfur shows that iron sulfate provides the activity of the iron-containing catalyst to selective oxidation of hydrogen sulfide to sulfur, whilst the appearance of SO_2 among the products of H_2S oxidation is accompanied by the formation of the iron disulfide phase on the catalyst surface. FeS_2 formed at the reaction conditions is unstable. This is an important point when Fe-containing catalysts for hydrogen sulfide oxidation are ex situ characterized by physical methods.
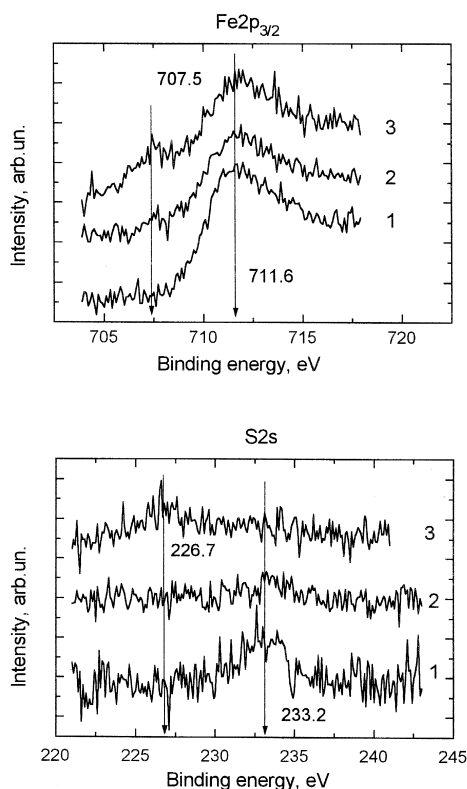

Fig. 2. Fe $2p_{3/2}$ and S 2s spectra for the fresh (1) and treated (2,3) samples of S550 catalysts. The catalyst were treated at different temperatures: 250°C (2) and 300°C (3) (see Table 1).

References

[1] Keeping abreast of the regulations, Sulphur 231 (1994) 33.

[2] P.H. Berben, A. Scholten, M.K. Titulaer, N. Brahma, W.J.J. Van der Wal, J.W. Geus, Stud. Surf. Sci. Catal. 34 (1987) 303.

[3] A. Pieplu, A. Janin, O. Saur, in: Proceed. 1st World Congr. on Environ. Catal. for Better World and Life, Pisa,1995, p. 303.

[4] O.N. Kovalenko, N.N. Kundo, V.M. Novopashina, D.P. Ivanov, in: Proceed. Intern. Symp. Molecular Aspects of Catalysis by Sulfides, St-Petersburg,1998, p. 113.

[5] Practical Surface Analysis, 2nd edn., D. Briggs, M.P. Seah (Eds.), Auger X-ray Photoelectron Spectrosc. Vol. 1 Wiley, 1990.

[6] C.D. Wagner, L.H. Gale, R.H. Raymond, Anal. Chem. 51 (1979) 466.