Surface Compounds of Iron Studied by Mössbauer Spectroscopy

JAN BLOMQUIST,[a] STEFAN CSILLAG,[a] LEIF C. MOBERG,[a] RAGNAR LARSSON[b] and BERND REBENSTORF[b]

[a] Institute of Physics, University of Stockholm, Vanadisvägen 9, S-113 46 Stockholm, Sweden and [b] Division of Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

Surface compounds of iron on silica gel have been studied by Mössbauer spectroscopy. Two different coordinatively unsaturated surface compounds of iron on silica gel have been established. The iron atoms in one of these compounds are in a ferrous high spin state ($S=2$) and it is believed that the other compound rather yields iron in a ferric high spin state ($S=5/2$). When the iron concentration exceeds about 0.5 % a saturation occurs and the excess iron is not adsorbed on the surface.

The coordinatively unsaturated surface compound of iron on silica gel has been used to catalyse the reduction and decomposition of NO and other reactions, and it has been suggested that such compounds could be used as "model surface sites" of transition metal oxides.[1,2] The details of the reaction mechanisms are influenced by the electronic structure of the active site and the present work is an attempt to study this structure by the aid of Mössbauer spectroscopy. Since the use of nuclear gamma resonance presumes the existence of fairly welldefined sites the present study will reveal whether this requirement is fullfilled. A series of measurements has been performed with different ligands added to the unsatured surface compound $Fe^{n+}(SiO)_n^-$ and with different iron concentrations. The aim has also been to characterize the electronic structure in terms of parameters like the valence state and spin state, if possible.

EXPERIMENTAL

The methods for sample preparations have been described elsewhere.[3] Analysis of Fe^{2+} was performed with O_2-free $KMnO_4$ solution[4] avoiding contact with air during titration. With the known amount[3] of Fe the oxidation number of our samples could be calculated as 2.22 (0.35 % Fe), 2.23 (0.7 % Fe), 2.18 (1.4 % Fe) and 2.12 (2.1 % Fe). The iron (II) chloride used for the impregnation was found to be 100 % Fe^{2+}.

All measurements were performed with a constant acceleration Mössbauer spectrometer. The $^{57}CoPd$ source was kept at 25 °C and the isomer shift data are always referred to iron in a Pd matrix. The absorber material was contained in glass cells with very thin windows. The cells could not be cooled, and hence all measurements were performed at 25 °C. All samples (except one, which contained C_2H_4) were evacuated and filled with N_2.

The velocity scale was calibrated by an isotope-enriched metallic iron foil. The absorption lines were fitted to Lorentzians since the absorbers could be considered as thin, using the standard least squares procedure. In most fittings the precision was about 0.05 mm/s or better. To overcome convergence problems constraints were imposed on the fittings, and with a few exceptions only symmetrical doublets were allowed.

RESULTS

All Mössbauer spectra have been interpreted as sums of superimposed doublets. Each doublet is characterized by the isomer shift (δ), the quadrupole splitting (Δ), the line width (Γ) and the amplitude. The results are given in Table 1, the spectra are shown in Figs. 1 and 2.

The isomer shift is linearly related to the electron density at the nucleus $\rho(0)$:

$$\delta = \alpha \left(\rho(0)_{absorber} - \rho(0)_{source} \right) \tag{1}$$

Table 1. Experimental isomer shifts (δ), quadrupole splittings (Δ) and relative areas of absorption lines of the surface compounds of iron(II) on silica gel with different ligands and iron concentrations. The isomer shifts are given relative to Pd. A and B indicate the two proposed types of surface sites and E represents excess iron. T_{act} is the temperature of pretreatment (activation).

Ligand	δ (mm/s)	Δ (mm/s)	Area (%)	Site	T_{act} (°C)	Iron conc. (%)
—	0.42	1.16	5	(B)	300	0.7
	0.83	1.87	95	(A)		
	0.56	0.91	56	B	1000	0.7
—	0.78	2.28	38	A		
	0.97	2.67	5	E		
	0.56	0.92	59	B	1000	1.4
—	0.84	2.10	24	A		
	0.94	2.79	18	E		
	0.60	0.90	39	B	1000	2.1
—	0.84	2.10	30	A		
	0.98	2.80	31	E		
C_2H_4	0.61	0.85	35	B	1000	0.7
	0.86	1.89	57	A		
	1.05	2.66	8	E		
O_2	0.67	0.80	32	B	1000	0.7
	0.51	1.06	8	B		
	0.42	2.91	39	(A)		
	0.82	2.34	11	A		
	0.99	2.78	9	E		
H_2O	0.88	1.97	100	(A)	1000	0.7
$OH(O_2+H_2O)$	0.19	0.80	62	B	1000	0.7
	0.89	2.13	28	A		
	0.97	2.84	10	E		
NO	0.55	0.71	8	B	1000	0.7
	0.28	1.67	60	B		
	0.82	2.26	32	A+E		
NO_2	0.55	0.91	3	B	1000	0.7
	0.26	1.31	73	B		
	0.93	2.49	24	A+E		

and the quadrupole splitting to the electric field gradient at the nucleus $V_{zz}(0)$:

$$\Delta = \tfrac{1}{2}eQV_{zz}(0)(1 + \tfrac{1}{3}\eta^2)^{1/2} \qquad (2)$$

where Q is the quadrupole moment of the nucleus, η is the asymmetry parameter.

The spectra are superpositions of several quadrupole doublets (at most five) which are strongly overlapping. The interpretation is further obscured by the high degree of dilution of iron (not [57]Fe-enriched), and by the absorption of the resonant radiation by the glass windows of the absorber cell. This yields unresolved absorption lines and poor statistics.

The doublets are interpreted as basically due to two different surface sites (two different configurations) and due to excess iron, presumably in the form

of Fe(OH)$_2$, (FeCl$_2$ is excluded since energy dispersive analysis with a scanning electron microscope (JEOL JSM-U3) has shown no traces of chlorine after heat treatment at 900 °C).

The interpretation of one doublet of the spectrum as due to excess iron (i.e. iron which is not present as a surface component on the silica gel) is in accord with the observation that the enhancement of this
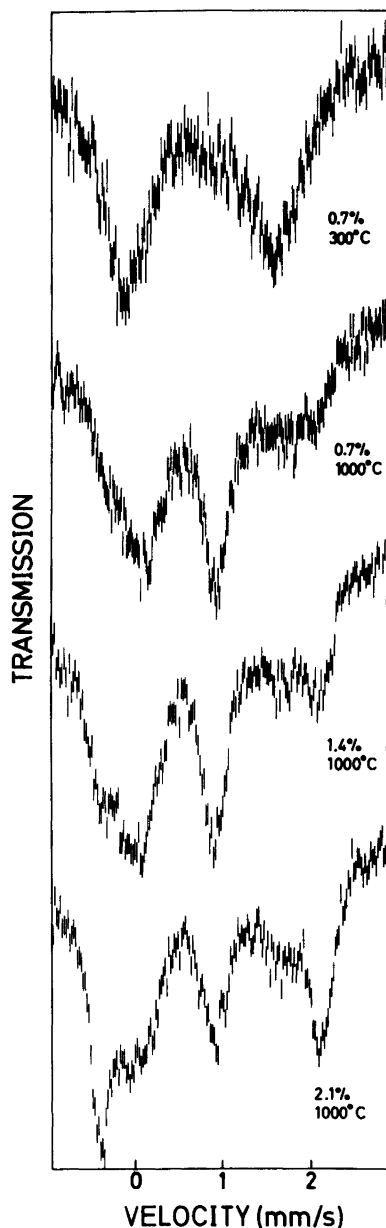

Fig. 1. Mössbauer spectra of iron-containing silica gel with different iron concentrations and pretreatment temperatures.
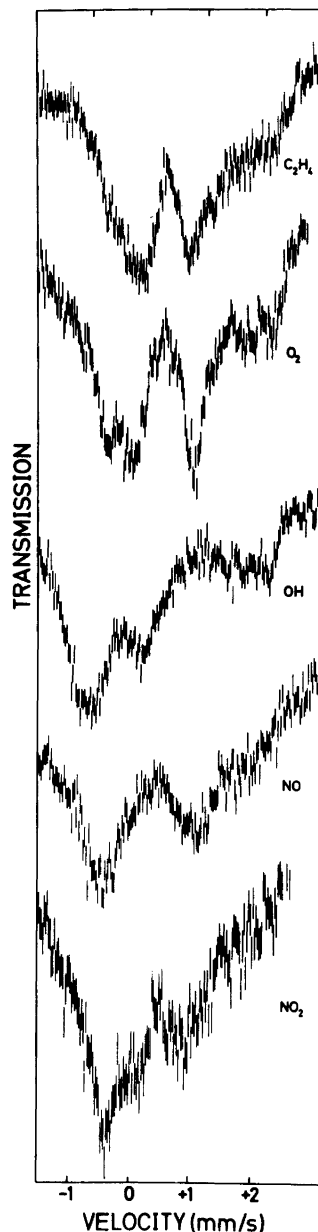
Fig. 2. Mössbauer spectra of iron-containing silica gel (0.7 % iron, pretreatment: 1000 °C) and with C$_2$H$_4$, O$_2$, OH, NO, and NO$_2$ adsorbed.
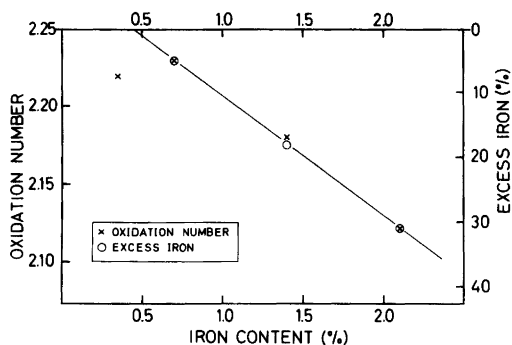
Fig. 3. Oxidation number of iron (left ordinate scale) and excess iron, *i.e.* per cent of the total absorption area, (right ordinate scale) *versus* iron concentration. The oxidation number 2.22 (0.35 % Fe) is outside the linear range.
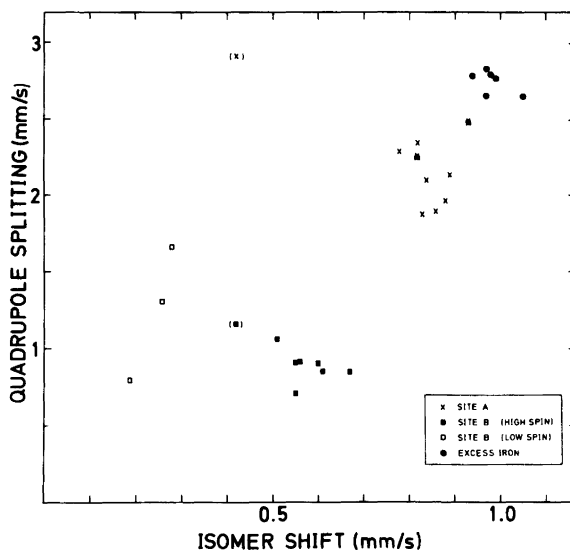
signal follows the increase of iron content (from 0.7 % to 2.1 %). In fact, the intensity of this signal is a linear function of the iron concentration. From Fig. 3 it follows, that a saturation of the active sites occurs at an iron concentration of about 0.5 %. The parameters of this signal (approximately $\delta = 1.0$, $\Delta = 2.7$) correspond well with typical data of ferrous high spin states, and the explanation in terms of

excess Fe^{2+} is also supported by the trend of the oxidation numbers as listed in the section Experimental (*cf.* also Fig. 3).

The remaining doublets should probably be related to two different surface sites. The doublets due to different sites with different ligands are represented by points in a diagram (Fig. 4) with the quadrupole spitting Δ *versus* the isomer shift δ. The data are apparently separated into four different sets including the set representing excess iron (for similar Mössbauer data, *cf.* Ref. (5)).

The set of points with isomer shift in the range 0.8 – 0.9 mm/s is without any doubt representing iron in a ferrous high spin state (Fe^{2+}, $S = 2$). These quadrupole doublets are associated with a coordinatively unsaturated surface site which will be referred to as site A. We consider a spatial configuration of the type *trans* ($\geqslant Si - O - Fe - O - Si \leqslant$) is a reasonable assumption.[6]

The set of points with isomer shift in the range 0.5 – 0.6 mm/s cannot unambigously be associated with a particular charge state, but in view of the small quadrupole splitting (0.7 – 0.9 mm/s) we attribute this set to a ferric high spin state (Fe^{3+}, $S = 5/2$). This is further supported by the values of the oxidation numbers, which have been found to be considerably greater than 2 (see Experimental).

Fig. 4. Quadrupole splitting *versus* isomer shift. The different symbols are representing different sets as indicated in the diagram. Symbols in parenthesis are considered uncertain due to difficulties in the data fitting (see discussion).

This gives evidence for the interpretation in terms of another surface site, which we believe should be related to the spatial configuration

$$\underset{\geq}{\text{Si}} - \text{O} - \text{Fe} - \text{O} - \underset{\leq}{\text{Si}}, \text{ site B.}$$
$$|$$
$$\text{O}$$
$$|$$
$$\text{Si}$$
$$/|\backslash$$
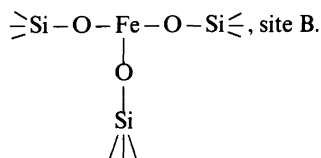
Also this surface site is affected when different kinds of molecules are adsorbed, most likely as ligands at the vacant coordination sites. This explanation makes probable the conversion of a certain amount of Fe^{2+} to Fe^{3+}, always occurring during the preparation of the sample.

The third set of points representing the NO, NO_2 and OH ligands (the latter from O_2 and H_2O) should also be associated with iron in a ferric state, where the iron atom is bound to NO^-, NO_2^- and OH^-. From the relative intensities of the components, we conclude that these points originate from site B, although in this case the smaller isomer shift and somewhat larger quadrupole splitting (at least for NO and NO_2) rather suggest a low spin state.

COMMENTS

The results indicate the existence of basically two different unsaturated surface sites, both high spin but ferrous in one case (site A) and ferric in the other (site B).

In the ferric high spin state the contribution to the quadrupole splitting from the valence electrons of the iron atom should be small, although substantial terms may arise also in this case due to covalency. If not so, the ligand contribution is likely to be dominating. Then, by regarding the ligands as point charges an approximate value of $V_{zz}(0)$ is easily obtained. The small value ($\Delta \cong 1$ mm/s) calculated for the configuration of type B is in accord with the interpretation of the ferric high spin doublet ($\delta = 0.5 - 0.6$, $\Delta = 0.8 - 0.9$ mm/s) as due to a site of this type, while the configuration corresponding to site A yields a larger value.

The ferric high spin state of iron at site B is converted to ferric low spin when NO, NO_2 or OH ($O_2 + H_2O$) is adsorbed which is consistent with the smaller isomer shift and larger quadrupole splitting found in these cases. The association with

site B follows from the behaviour of the relative intensities. For a more exhaustive analysis of these data a comparison with independent experimental information or theoretical molecular orbital calculations is desirable, but very few such data of polynitrosyl complexes are available.[7] When structural data are lacking, we can only say that the five-coordinate complexes have their highest symmetry as C_{2v}.

At low iron concentrations the stoichiometric ratio for adsorbed NO and NO_2 (NO or NO_2: Fe) is 1.5:1. At least half of the iron atoms have two such ligands adsorbed,[3] and if two or none are adsorbed at each iron site 75 % of the iron atoms will be coordinated to two NO or NO_2 ligands. Accordingly the best computer fits to the experimental spectra are in these cases obtained by adding one component corresponding to the unsaturated compound with no added ligands binding to the iron.

Also with oxygen adsorbed the best fits are computed with the assumption that each site (A and B) will give rise to two different doublets, which certainly is in accordance with the fact that only about 20 % of the iron atoms will adsorb oxygen.[3] The fitted data indicate less than 50 %, but it must be remembered, that the fitting in this case is very difficult (five different doublets) and the significance of the results should not be overestimated.

With low pretreatment temperature (300 °C) mainly a site of the type $Si - O - Fe(H_2O)_2 - Cl$ is assumed.[6] The data of this site are similar to the findings for site A.

With pretreatment at 1000 °C and with H_2O added at 100 °C/(1 Torr) only one doublet with data compatible with site A is observed, rather unexpectedly.

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