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Chemical states of localized Fe atoms in ethylene matrices using in-beam Mössbauer spectroscopy

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Abstract The reaction products of isolated single iron atoms in a low concentration matrix of ethylene were studied using in-beam Mössbauer spectroscopy with a short-lived ^{57}Mn ($T_{1/2} = 1.45$ m) beam. The in-beam Mössbauer spectrum of ^{57}Fe arising from ^{57}Mn in a matrix of ethylene and argon measured at 16 K was analyzed with four components. Density functional theory calculations were carried out to confirm the assignments. It was suggested that the reaction produced monoiron species of $Fe(C_2H_4)$ with a spin state of $S = 2$.

Keywords In-beam Mössbauer spectroscopy · ^{57}Mn · ^{57}Fe · Ion implantation · Isolated atoms · Matrix-isolation technique · Ethylene matrix

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1 Introduction

In-beam Mössbauer spectroscopy using a short-lived ^{57}Mn ($T_{1/2}$ = 1.45 m) implantation in gas matrices at low temperatures is one of the simplest systems for investigating chemical reaction products between single Fe atoms and matrix molecules [1–4]. This method provides useful information on chemical states and coordination environments around isolated ^{57}Fe atoms decayed from ^{57}Mn in the matrices. We previously studied the electronic states of Fe atoms in the novel products in several gas matrices of argon, xenon, oxygen, and methane using ^{57}Mn implantation methods. In an Ar matrix, monovalent $^{57}Fe^{+}$ with an excited state atomic configuration of $3d^7$ was observed at low temperatures. The production mechanism of Fe^{+} ($3d^7$) in the excited state could be explained in terms of a charge transfer process between charged particles and the surrounding Ar atoms [1, 2]. In a solid Xe matrix, four components, Fe^{+} ($3d^7$), Fe^{+} ($3d^64s^1$), Fe^{0} ($3d^64s^2$), and Fe^{0} ($3d^74s^1$), were obtained [3]. Combination with free electrons in the solid Xe stabilized the neutral ^{57}Mn atom, and β-decay of ^{57}Mn produced Fe^{+} in various electronic states. The free electrons also reduced Fe^{+} to produce Fe^{0}. The β-decay of ^{57}Mn does not disturb the surrounding cubic symmetry of the *fcc* Xe solid, and thus no doublet peaks were observed. We also reported the reaction products of ^{57}Fe atoms with O_2 at low temperatures. The obtained spectra could be analyzed by four components, which are assigned to be novel Fe species of FeO, $Fe(O_2)$, $(O_2)FeO_2$, and $Fe(O_2)_2$ [4]. In these investigations, the assignments were carried out with the aid of density functional theory calculations, because the novel species produced by such reactions are unstable and the conventional references for spectral data are not available.

Reaction mechanisms of Fe ions with hydrocarbons have attracted much attention for a long time from the viewpoint of catalytic chemistry. There are many experimental studies and theoretical calculations on the reaction mechanisms and products between iron ions and hydrocarbons [5–7]. Recently, we measured in-beam Mössbauer spectra of ^{57}Fe after ^{57}Mn implantation into a pure CH_4 matrix and mixture matrices of CH_4 and Ar at 18 K [1]. The spectrum obtained in the pure CH_4 matrix was analyzed with two components of a doublet and a singlet. Each component was assigned to individual constitutional isomers of $Fe(CH_4)_2^{+}$ as derived from the DFT calculations and the Mössbauer parameters. The doublet component originated from a Fe^{+} ion connected to edges of two tetrahedrons of CH_4, while the singlet was caused by a Fe^{+} attached to the faces of two tetrahedrons of CH_4. $Fe(CH_4)_2^{+}$ species are formed, in which Fe^{+} ions are located at the interstitial octahedral or tetrahedral positions in the CH_4 matrix, and have more than two CH_4 molecules in the nearest neighborhood of Fe^{+}.

The interactions and chemical reactions between matrix-isolated Fe atoms and ethylene have been investigated using Mössbauer and infrared spectroscopies [8–10]. These studies have been performed using resistively evaporated or laser-evaporated Fe atoms. No reaction products of highly energetic Fe atoms with ethylene have been reported yet. In this study, the in-beam Mössbauer spectrum of ^{57}Mn implantation into a mixed gas matrix of C_2H_4 and Ar was measured. ^{57}Mn implantation Mössbauer study differs from ^{57}Co emission and/or ^{57}Fe absorption Mössbauer spectroscopy in that ^{57}Mn as the Mössbauer mother probe is a highly charged particle, decaying to ^{57}Fe in several charge states. This technique was selected to characterize the exotic chemical products after the reaction of Fe^{n+} ions with C_2H_4 molecules.

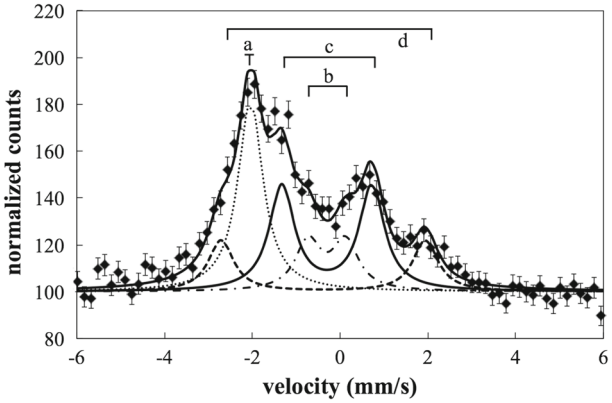

Fig. 1 In-beam Mössbauer spectrum of ^{57}Fe obtained upon ^{57}Mn implantation in a gas matrix of C_2H_4:Ar = 3:7 measured at 16 K. The isomer shift is given relative to α-Fe metal at room temperature. The sign convention used is that for an emission source experiment

2 Experimental

The experiment was carried out at the Heavy-Ion Medical Accelerator in Chiba (HIMAC) at the National Institute of Radiological Science (NIRS). The premixed gases of C_2H_4 and Ar (C_2H_4:Ar = 3:7) with high purities (C_2H_4 99.9%; Ar 99.9999%) were introduced to the plate using a gas-flow controller for 36 h through a single nozzle at 2 sccm. The gas mixtures were condensed on a brass plate cooled down to 16 K by a pulsed-tube-type helium refrigerator. The size of the plate was 40 mm (width) $\times$ 50 mm (height). The thickness of the solid gas-matrix after the aggregation was estimated to be more than 2 mm.

A secondary beam of ^{57}Mn was produced by the nuclear projectile fragmentation reaction between a primary ^{58}Fe beam (E = 500 MeV/nucleon) and the production target of ^{9}Be. The ^{57}Mn particles were electromagnetically separated and optimized by an in-flight RI beam separator. After passing through the separator, the purity of ^{57}Mn was approximately 90% of the secondary beam. The typical intensity and energy of the ^{57}Mn beam before passing through the energy degraders and a collimator (ϕ 20 mm) in front of the gas matrix sample were about 1.2×10^6 particles per pulse and 256 MeV/nucleon, respectively. As energy degraders, a 4-mm-thick Pb plate, a 4-mm-thick Al plate, and two wedge-shaped acrylic plates were used to stop all of the ^{57}Mn nuclei at an adequate depth in the sample.

A parallel-plate avalanche counter (PPAC), i.e., a gas-filled resonance detector, was employed for obtaining the Mössbauer spectrum. The PPAC detects internal conversion electrons emitted after Mössbauer resonance absorption. The parallel plates in the PPAC were a cathode of ^{57}Fe-enriched stainless-steel foil and a graphite anode. Electronic avalanches occur by gas ionization in the gap between these plates. Octafluoropropane (C_3F_8) was used as the counter gas. The PPAC was mounted on a Mössbauer transducer (Wissel, MVT-1000). Velocity calibration of the Mössbauer spectra was performed using a ^{57}Co/Fe source at room temperature. A plastic scintillator (BC-400, Bicron) was placed in front of the PPAC and used for the $\beta - \gamma$ anti-coincidence measurement to reduce the background caused by β-rays emitted from ^{57}Mn [11].

Table 1 Mössbauer parameters for $Fe/C_2H_4/Ar$ system

Species	Experimental (mm/s)		Calculation[a] (mm/s)	
	δ[b]	ΔE_Q	δ	ΔE_Q
Fe^+ ($3d^7$)	−2.04(2)	–	–	–
Fe^+ ($3d^64s^1$)	−0.30(6)	0.85(1)	–	–
$Fe(C_2H_4)$ ($S = 2$)	−0.33(6)	2.05(7)	0.41	2.37
$Fe(C_2H_4)$ ($S = 3/2$)	−0.40(5)	4.66(9)	1.02	4.36
$Fe(C_2H_4)_2$[c]	−0.54(1)	2.46(1)	–	–

[a]The ORCA 3.0.0 program with B3LYP/VTZP/CP(PPP) basis set was employed [12]

[b]The sign of the isomer shift is opposite to the conventional absorption geometry. The isomer shift is relative to α-Fe at room temperature

[c]Ref. [10]

3 Results and discussion

The in-beam Mössbauer spectrum of ^{57}Mn implantation into the mixed gasmatrix of C_2H_4 and Ar was measured at 16 K. The spectrum was fitted with four components: a singlet (a) and three doublets of (b), (c), and (d), as shown in Fig. 1. The singlet (a) with the isomer shift $\delta = -2.04(2)$ mm/s was assigned to the excited state of Fe^+ ($3d^74s^0$) surrounded by Ar atoms, and the doublet (b) at $\delta = -0.30(6)$ mm/s with the quadrupole splitting $\Delta E_Q = 0.85(1)$ mm/s was assigned to Fe^+ ($3d^64s^1$) in the ground state, as determined in our previous studies on the atomic configurations of ^{57}Fe in Ar and Xe matrices [1, 2]. The other two components of (c) and (d), shown as a solid line and a dashed line in Fig. 1, were attributed to the reaction products of isolated single ^{57}Fe atoms with C_2H_4.

DFT calculations were carried out to assign the molecular structure of the reaction products. The ORCA 3.0.0 program developed by Neese with the B3LYP/VTZP/CP(PPP) basis set was employed to interpret the values of the isomer shift and the quadrupole splitting [12]. Mössbauer parameters obtained from experimental and calculation results are listed in Table 1. Component (c) was assigned to $Fe(C_2H_4)$ with a neutral valence state of Fe^0 and a spin state of S = 2, that was the most stable electronic structure, from the values of the isomer shift and the quadrupole splitting. The optimized structure of $Fe(C_2H_4)$ is shown in Fig. 2.

Component (d) showed a large ΔE_Q value of 4.66(9) mm/s. $Fe(C_2H_4)_2$ reported previously in the $Fe/C_2H_4/Ar$ system of the matrix-isolation investigations using Fe atoms produced by resistively heating or laser-ablation methods had the Mössbauer parameters $\delta = 0.50$–0.54 mm/s and $\Delta E_Q = 2.20$–2.46 mm/s [8, 10]. The value of ΔE_Q of component (d) in the present study was significantly different from that of $Fe(C_2H_4)_2$, suggesting that component (d) might not be $Fe(C_2H_4)_2$. The derived parameters were also not in agreement with the calculation values of $Fe(C_2H_4)$ with monovalent Fe^+ of a spin state of S = 3/2. If this analysis is accurate, it can be said that component (d) is in distinct chemical states, with one of them being $Fe_x(C_2H_4)_y$, in the C_2H_4/Ar matrix. It is difficult at present to assign the other reaction product. The chemical state of component (d) is currently under consideration. For detailed discussions on the novel Fe species in the C_2H_4 matrix, the in-beam Mössbauer spectrum of a pure C_2H_4 matrix will be needed.

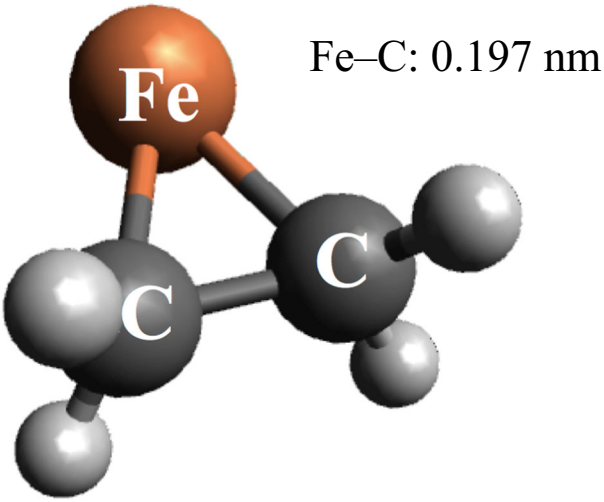

Fig. 2 Optimized geometry of $Fe(C_2H_4)$ with a neutral valence state of Fe^0 and a spin state of $S = 2$

4 Conclusion

The reaction products of isolated ^{57}Fe atoms arising from ^{57}Mn with the mixed gas-matrix of C_2H_4 and Ar (C_2H_4:Ar = 3:7) were investigated using in-beam Mössbauer spectroscopy. The reaction products were assigned by the Mössbauer parameters and density functional theory calculations. It was found that $Fe(C_2H_4)$ with a neutral valence state of Fe^0 and a spin state of $S = 2$ was produced in the C_2H_4/Ar matrix at 16 K. The other component was attributed to the products of isolated single ^{57}Fe atoms with C_2H_4, but could not be definitively identified without measuring the in-beam Mössbauer spectrum of pure C_2H_4 at low temperatures.

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