

# Electron Spin Resonance Spectra Observed in the Course of Grafting Iron Carbonyls on Sodium-Y Zeolites

MASAKAZU IWAMOTO\*, SHIN-ICHIRO NAKAMURA, HIDETO KUSANO, and SHUICHI KAGAWA

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

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**Abstract.** The adsorption and/or decomposition pathway of  $\text{Fe}_2(\text{CO})_9$  or  $\text{Fe}_3(\text{CO})_{12}$  on hydrated or dehydrated NaY zeolites has been studied by an ESR technique. The adsorption resulted in the formation of three paramagnetic species with  $g_{\text{iso}} = 2.0450$ ; 2.0378, and 2.0016, which were attributable to  $\text{Fe}_3(\text{CO})_{11}^-$ ,  $\text{Fe}_2(\text{CO})_8^-$ , and  $\text{Fe}(\text{CO})_4^-$  anion radicals, respectively. These radicals have been suggested as intermediates in the formation of  $\text{HFe}_3(\text{CO})_{11}^-$  on the hydrated NaY zeolite and  $\text{Fe}_3(\text{CO})_{12}$  on the dehydrated NaY zeolite.

**Key words:** Iron Carbonyls,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Fe}(\text{CO})_4^-$ ,  $\text{Fe}_2(\text{CO})_8^-$ ,  $\text{Fe}_3(\text{CO})_{11}^-$ , ESR, Y-type Zeolite.

## 1. Introduction

A large number of metal carbonyl-supported systems have been reported on oxides and zeolites [1]. The relationships among homogeneous catalysis, organometallic chemistry, and heterogeneous catalysis have been studied in order to synthesize effective new catalysts. The decomposition pathways have also been studied. However, previous reports have dealt with infrared and temperature-programmed decomposition techniques, and only rarely by an ESR technique [2]. We wish to communicate our studies of the ESR spectra of iron carbonyl intermediates produced on NaY zeolites. The previous manuscript in this series [3] described IR and UV-VIS spectroscopic studies and gas-phase analyses of the adsorption and decomposition of  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Fe}_3(\text{CO})_{12}$  on hydrated and dehydrated NaY zeolites. An anionic hydride  $\text{HFe}_3(\text{CO})_{11}^-$  was formed on the hydrated NaY, while weakly adsorbed  $\text{Fe}_2(\text{CO})_9$  or  $\text{Fe}_3(\text{CO})_{12}$  complexes were detected on the dehydrated NaY. We show here that several different intermediate radicals are produced by depositing iron carbonyls in hydrated/dehydrated NaY *in vacuo*. Characterization of these paramagnetic species has also been undertaken, with the objective of learning more about the decomposition pathway and the inclusion phenomena.

## 2. Experimental

Before the adsorption of the iron complex, NaY (UCC, SK-40) was treated in the following way to prepare the hydrated NaY (H-NaY). NaY was heated slowly under vacuum ( $1.3 \times 10^{-2}$  Pa) up to 673 K, exposed to oxygen (13.3 kPa, 1 h) and evacuated ( $1.3 \times 10^{-2}$  Pa, 1 h) at the same temperature. The zeolite was then rehydrated by introduction

\* Author for correspondence.

of water vapor (2.4 kPa) at 298 K for 1 h and evacuated at 298 K ( $1.3 \times 10^{-2}$  Pa). NaY without the rehydration treatment in the above procedure is referred to as the dehydrated NaY (D-NaY). The NaY zeolites were mixed with carbonyl complexes (2 mol-complex/mol-zeolite) under a nitrogen atmosphere and then mounted in a fused quartz tube for ESR analysis. The ESR spectra were measured at 298 K or 123 K on a JEOL JES-FE1XG spectrometer after the sample was evacuated at 298 K for the desired period. Spin concentrations were determined by numerical double integration of the first derivative traces, with comparison to a standard single crystal of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Simulated powder spectra were calculated using a modified version of SIM 13 [4].

### 3. Results and Discussion

Evacuation of the  $\text{Fe}_2(\text{CO})_9/\text{H-NaY}$  and  $\text{Fe}_2(\text{CO})_9/\text{D-NaY}$  systems at 298 K for 180 min and 30 min, respectively, resulted in the appearance of ESR spectra depicted in Figure 1(a) and (b). These paramagnetic species were not detected before the evacuation treatment. Figure 1(a) displays the existence of three paramagnetic species. Each is characterized by a single ESR absorption and a unique  $g$  factor: **1**, 2.0450; **2**, 2.0378; **3**, 2.0016. The three paramagnetic species were observed in different relative concentrations when the length of time of evacuation was varied or  $\text{Fe}_3(\text{CO})_{12}$  was adsorbed on the zeolites. All radicals were very oxygen-sensitive.

When ESR spectra were recorded at 123 K, the Figure 1(a) spectrum drastically changed to yield Figure 1(c), which is similar to Figure 1(b), while the Figure 1(b) spectrum changed little. A computer simulation of the Figure 1(c) spectrum using the parameters given in Table I is shown in Figure 1(d). Figure 1(e) depicts the respective ESR spectra of the paramagnetic species **1**, **2**, and **3**. The values of  $g_{\text{iso}}$  calculated from the respective  $g$  tensors were in good agreement with those measured in Figure 1(a), as shown in Table I. In addition, all of the spectra observed in the present study could be interpreted as a combination of the three paramagnetic species with the parameters summarized in Table I. These indicate the validity of the spectrum analysis. The similarity of Figure 1(c) to Figure 1(b) shows that the paramagnetic species formed in H-NaY at 298 K were essentially the same as those in D-NaY. The isotropy of signals in Figure 1(a) is due to free rotation or tumbling of the paramagnetic molecules in water adsorbed in the zeolite structure. The anisotropy in Figures 1(c) and (b) results from retarding free rotation or tumbling because of the frozen sample or strong adsorption of the radicals onto zeolite lattice.

Krusic *et al.* [5] and El Murr and Chaloyard [6] have studied ESR spectra of iron carbonyl radical anions in THF solution and  $\text{CH}_2\text{Cl}_2$  solution; the former group reported unambiguous assignment of the spectra by using  $^{57}\text{Fe}$  (nuclear spin of 1/2) and  $^{13}\text{C}$ . The  $g_{\text{iso}}$  values observed here for the species **1**, **2**, and **3** are respectively close to the values of 2.0497 ( $\text{Fe}_3(\text{CO})_{11}^-$ ), 2.0385 ( $\text{Fe}_2(\text{CO})_8^-$ ), and 2.0016 ( $\text{Fe}_3(\text{CO})_{12}^-$ ) obtained by Krusic *et al.* Since the spectra of species **1** and **2** at 123 K were axially symmetric, it is reasonable that the signals **1** and **2** are attributable to  $\text{Fe}_3(\text{CO})_{11}^-$  and  $\text{Fe}_2(\text{CO})_8^-$  anion radicals. However, it is doubtful that **3** can be assigned to  $\text{Fe}_3(\text{CO})_{12}^-$ . Generally metal cluster complexes containing three or more metal atoms do not exhibit three dimensional anisotropy in an ESR spectrum because of circulation of electrons. We suggest that **3** is the  $\text{Fe}(\text{CO})_4^-$  radical with a distorted tetrahedral structure. Despite considerable effort by several workers, it has so far not been possible to observe the ESR spectrum of the simplest member of the family, the 17-electron  $\text{Fe}(\text{CO})_4^-$  radical anion. This is probably because it is a short-lived reaction intermediate. However, the closely related ( $\pi$ -olefin) $\text{Fe}(\text{CO})_3^-$  radical anions have been detected [5]. These radicals give

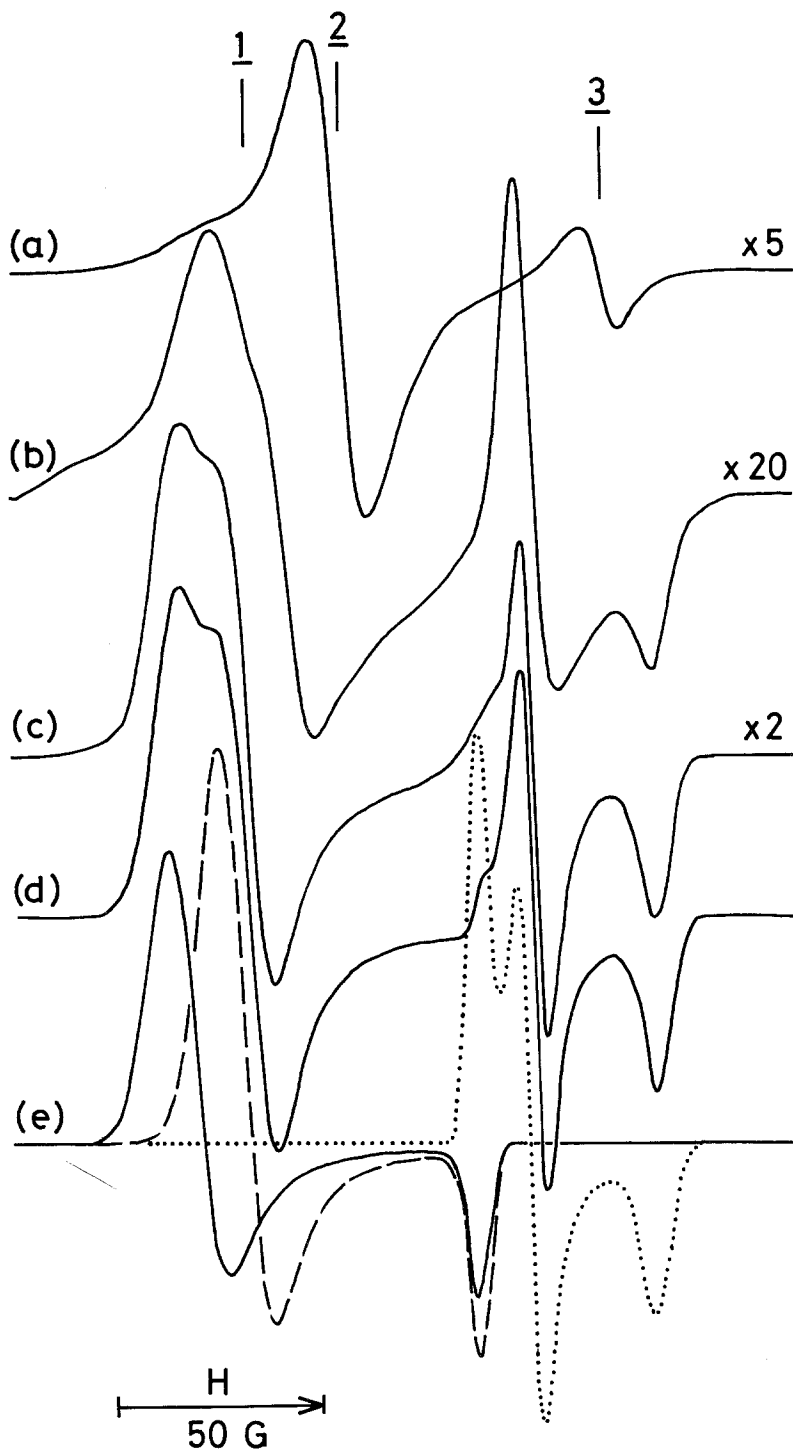


Fig. 1. ESR spectra of intermediate radicals observed during adsorption of the iron carbonyl  $\text{Fe}_2(\text{CO})_9$  on NaY zeolites. The position of each curve in this figure does not show the absolute spectrum; namely, the field of resonance of (c) was quite different from that of (a) and (b) because of the differences of the measurement temperatures and cavities used. (a) Recorded at 298 K after evacuation of the  $\text{Fe}_2(\text{CO})_9/\text{H-NaY}$  system at 298 K for 180 min. (b) Recorded at 298 K after evacuation of  $\text{Fe}_2(\text{CO})_9/\text{D-NaY}$  at 298 K for 30 min. (c) Recorded at 123 K on the same sample as that giving curve (a). (d) Computer simulation of curve (c), using parameters given in Table I. The relative concentrations of 1, 2, and 3 are assumed to be 1.36, 1.55, and 1.00, respectively. (e) Simulated spectra of species 1 (full line), 2 (broken line), and 3 (dotted line). Curve (d) is the trace of the overlap of the three individual spectra.

$g_{\text{iso}}$  parameters in the range 2.03–2.06 depending on the ligands. Furthermore, the powder spectra of these species in frozen samples reveal three different principal values of the  $g$  tensor. These findings are consistent with the above assignment of **3** to the  $\text{Fe}(\text{CO})_4^-$  species. The zeolite matrix would offer a medium for stabilizing the radical anion.

To clarify the characteristics of NaY zeolites as adsorbents, the behavior of  $\text{Fe}_2(\text{CO})_9$  on silica and  $\gamma$ -alumina has been examined. The mixture of  $\text{Fe}_2(\text{CO})_9$  with  $\text{SiO}_2$  or  $\gamma\text{-Al}_2\text{O}_3$  was evacuated in a similar way to the experiments described above. We could not detect any ESR signal attributable to iron carbonyl radicals, except that an ESR signal of  $\text{Fe}^{3+}$  appeared at  $g = 4.9$  on  $\gamma\text{-Al}_2\text{O}_3$  and became larger with increasing evacuation time. With evacuation at 298 K the color of the  $\gamma\text{-Al}_2\text{O}_3$  changed slowly to pink, which is the characteristic color of  $\text{HFe}_3(\text{CO})_{11}^-$  as reported by Basset *et al.* [7], while the  $\text{SiO}_2$  did not show any change. These results show the relatively high reactivity of  $\gamma\text{-Al}_2\text{O}_3$  toward the iron carbonyl complex and the low reactivity of  $\text{SiO}_2$ , in conformity with the previous report [7].

Table I. ESR parameters of the signals observed during adsorption of iron carbonyls on NaY zeolites

Species	$g_{zz}(g_{\parallel})$ ( $\Delta H$ ) <sup>a</sup>	$g_{xx}(g_{\perp})$ ( $\Delta H$ ) <sup>a</sup>	$g_{yy}$ ( $\Delta H$ ) <sup>a</sup>	$g_{\text{iso}}$		Assignment	ESR parameters in solutions <sup>c</sup>
				Calcd.	Measured <sup>b</sup>		
<b>1</b>	2.0142	2.0595	–	2.0444	2.0450	$\text{Fe}_3(\text{CO})_{11}^-$	$g_{\text{iso}} = 2.0497^5$ $g_{\text{iso}} = 2.050^6$
	5.0	12.5	–				
<b>2</b>	2.0140	2.0518	–	2.0392	2.0378	$\text{Fe}_2(\text{CO})_8^-$	$g_{\text{iso}} = 2.0385^5$
	5.0	11.8	–				
<b>3</b>	1.9875	2.0060	2.0140	2.0025	2.0016	$\text{Fe}(\text{CO})_4^-$	$(\text{Olefin})\text{Fe}(\text{CO})_3^-$ $g_{\text{iso}} = 2.03\text{--}2.06^5$
	7.0	4.7	4.7				

<sup>a</sup>  $\Delta H$  indicates a Gaussian line width in gauss.

<sup>b</sup> The values observed in Figure 1(a).

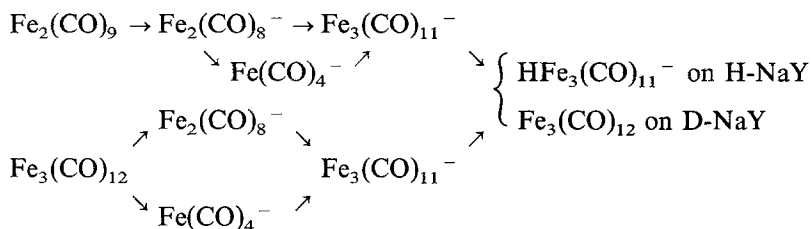
<sup>c</sup> In  $\text{THF}^5$  or  $\text{CH}_2\text{Cl}_2^6$  solution.

Dependencies of the whole spin concentration and the relative intensities of the three species on the evacuation time have been examined. With the progress of the reaction of  $\text{Fe}_2(\text{CO})_9$  with H-NaY, species **2** is seen first and then species **1** and **3** appear. The maximum total spin concentration of **1**, **2**, and **3** was observed after 180 min-evacuation of the system. It was approximately  $1.9 \times 10^{22}$  spin/mol- $\text{Fe}_2(\text{CO})_9$  or 3.2% of the iron complex used. When  $\text{Fe}_3(\text{CO})_{12}$  was employed as an adsorbate on H-NaY, species **2** and **3** appeared at the same time and subsequently **1** was formed. The rates of formation of radicals were slow and even after 300 min evacuation the intensities of the signals did not reach the maximum. This is presumably due to the molecular size of  $\text{Fe}_3(\text{CO})_{12}$  [9], being close to the diameter of the zeolite window [10]. The entire concentration at 300 min was only  $0.5 \times 10^{22}$  spin/mol- $\text{Fe}_3(\text{CO})_{12}$ .

In considering the decomposition pathway it is worth noting that the final compound found in the supercharge of H-NaY is different from that of D-NaY, though the same kinds of intermediate radicals are observed on both zeolites, as was mentioned previously. The final stable complex on H-NaY at 298–333 K was the  $\text{HFe}_3(\text{CO})_{11}^-$  hydride anion which has been characterized by its 540 nm UV–VIS absorption [11]. On the other hand, the detection of 355, 450, 612 nm bands on the  $\text{Fe}_2(\text{CO})_9/\text{D-NaY}$  system indicate that  $\text{Fe}_3(\text{CO})_{12}$  [12] is

produced in D-NaY. When  $\text{Fe}_3(\text{CO})_{12}$  was adsorbed, the same results were obtained, the slow rate notwithstanding.

In conclusion, plausible decomposition pathways can be put forth which explain all the above data:



The  $\text{Fe}_3(\text{CO})_{12}$  is decomposed to afford a dinuclear and a mononuclear complex, and these intermediates form a trinuclear complex in the supercage of the zeolites. Further study of the iron carbonyl-NaY systems is needed to confirm the suggested decomposition pathway. The results may however lead to an improved understanding of the behavior of carbonyl complexes in zeolite structures.

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