CHEMISTRY LETTERS, pp. 1483-1486, 1983.

CATALYSIS OF $HFe_3(CO)_{11}^-$ GRAFTED IN A HYDRATED NaY ZEOLITE IN THE WATER GAS SHIFT REACTION

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The anionic hydride $HFe_3(CO)_{11}^-$ species grafted in the zeolite by ionic interaction with an Al^{3+} ion showed high catalytic activity for the water gas shift reaction, which was comparable to that of iron carbonyl in homogeneous phase. Kinetic and spectroscopic measurements indicated a reaction of $HFe_3(CO)_{11}^-$ with H_2O as a rate determining step.

The relationships among homogeneous catalysis, organometallic chemistry, and heterogeneous catalysis have lately been the subject of interest in surface science. Direct observation of the catalyses of molecular cluster carbonyls supported on the surface of oxides is a possible approach to study the basic phenomena or elementary steps of surface chemistry at a molecular level. We wish here to report on the catalysis of the $HFe_3(CO)_{11}^-$ species grafted in the zeolite by ionic interaction with an Al^{3+} ion.[1a] The water gas shift reaction (WGSR) was selected as a model reaction on the following bases. Recent investigations have shown that the WGSR can be carried out at the temperatures lower than 473 K by using homogeneous catalysts,[2-6] which is consistent with the more favorable thermodynamic equilibrium.[7] The relatively low turnover frequency for $Fe(CO)_5$[4] makes it unlikely to be a practical catalyst even under ideal conditions. However the iron carbonyl-zeolite system is an exemplary model system for the catalysis of immobilized metal carbonyls owing to the established reaction mechanism in solution[2,4] and worth studying from this viewpoint.

The $HFe_3(CO)_{11}^-$/NaY system was prepared by adsorption of $Fe_2(CO)_9$ on a hydrated NaY at 333 K.[1b] The presence of $HFe_3(CO)_{11}^-$ was confirmed by a 540 nm absorption peak in the diffuse reflectance UV-vis spectrum, 2040, 1987, and 1950 cm^{-1} IR absorption bands of linear carbonyls and a 1600 cm^{-1} band of a bridging carbonyl, and an analysis of the gas phase during the adsorption of $Fe_2(CO)_9$. The catalytic run was carried out in a conventional closed recirculation system of 132 cm^3. Unless otherwise stated, a sample containing 7.81×10^{-5} mol of $HFe_3(CO)_{11}^-$ in 1.0 g of the NaY zeolite ($HFe_3(CO)_{11}^-$/NaY=1.33 mol/mol) was used. The pressure of H_2O was maintained at 2.4 kPa during the reaction. The gases were analyzed by gas chromatography using N_2 or He as a carrier gas.

$$3Fe_2(CO)_9 + 2OH^- \rightarrow 2HFe_3(CO)_{11}^- + 3CO + 2CO_2 \qquad (1)$$

The $HFe_3(CO)_{11}^-$/NaY system was active for the WGSR in the range 333-453 K. The results at 373 K are shown in Fig.1. The decrease in CO could not be measured

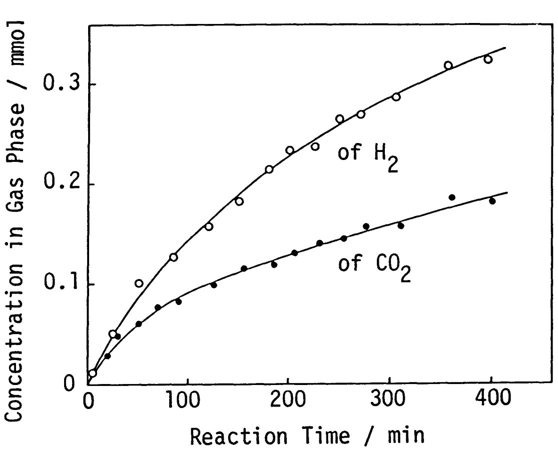

Fig. 1. The WGSR on the $HFe_3(CO)_{11}^-$/NaY catalyst at 373 K. The initial pressure of CO was 14.1 kPa and 7.81×10^{-5} mol of $HFe_3(CO)_{11}^-$ was used as a catalyst.

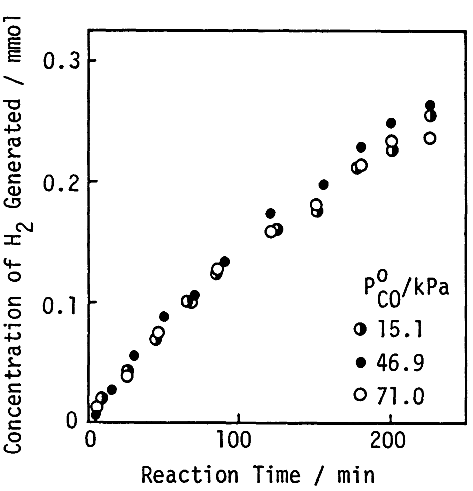

Fig. 2. Dependence of the WGSR on the partial pressure of CO. The reaction was carried out at 373 K over 7.81×10^{-5} mol of $HFe_3(CO)_{11}^-$.

accurately because of the presence of an excess of CO introduced and generation of CO resulting from partial decomposition of the carbonyl. It is clear that the concentration of CO_2 measured was less than that of H_2 at all pressures investigated. The similar phenomenon was observed in each experiment. The dominant cause for this disagreement was confirmed to be adsorption of generated CO_2 onto the zeolite by thermal desorption experiments and IR study of the used catalysts. The rate of hydrogen production, $R(H_2)$, was measured to determine the rate of the WGSR.

When hydrated NaY, NaX, and NaA zeolites were used as the supports for $HFe_3(CO)_{11}^-$, the respective $R(H_2)$ at 373 K were 29.5, 6.0, and 1.4 mol-H_2/mol-complex·day. The hydrated NaY was thus the appropriate carrier for the WGSR. The iron ion-exchanged NaY zeolites, Fe^{2+}NaY and Fe^{3+}NaY, and Fe/NaY obtained through the decomposition of $HFe_3(CO)_{11}^-$/NaY at 473 K in a dynamic vacuum were little active for the WGSR. This indicates that iron is active for the reaction in the form of the iron carbonyl at this temperature range.

With $HFe_3(CO)_{11}^-$/NaY serving as a catalyst, the WGSR was first order with respect to the $HFe_3(CO)_{11}^-$ content on NaY in the range complex/NaY < 4 mol/mol, independent of the initial CO pressure in the range P^0_{CO}=15.1-71.0 kPa (Fig.2), and had a temperature dependence corresponding to an activation energy of 69.5 kJ/mol at temperatures ranging from 333 to 393 K. It has been reported4) that the homogeneous $Fe(CO)_5$ catalyst showed an activity for the WGSR of 2000 mol-H_2/mol-complex·day at 453 K and 4080 kPa (40.3 atm). The $R(H_2)$ obtained at 453 K in the present system was unreliable because of too fast reaction, and hence the turnover frequency at 373 K was converted to the $R(H_2)$ of 1550 mol-H_2/mol-complex·day at 453 K, using the above overall activation energy. This value is comparable to the above. It follows that the present $HFe_3(CO)_{11}^-$/NaY system is a good catalyst for the WGSR, since the homogeneous catalyst was active only under the high pressure and changed to $Fe(CO)_3$ inert for the reaction at low pressure4) while the present system was active even at a pressure lower than 101.3 kPa (1 atm). In addition, the $HFe_3(CO)_{11}^-$/NaY is the most active solid catalyst in the range 333-453 K among the heterogeneous catalysts re-

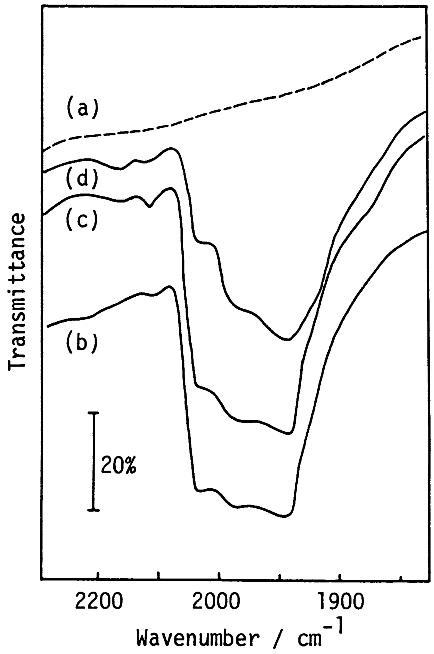

Fig. 3. Infrared spectra (transmission mode) in the linear carbonyl region of the NaY background (a), after the adsorption of $Fe_2(CO)_9$ on the hydrated NaY at 333 K (b), and after the WGSR at 393 K (c) and 433 K (d).

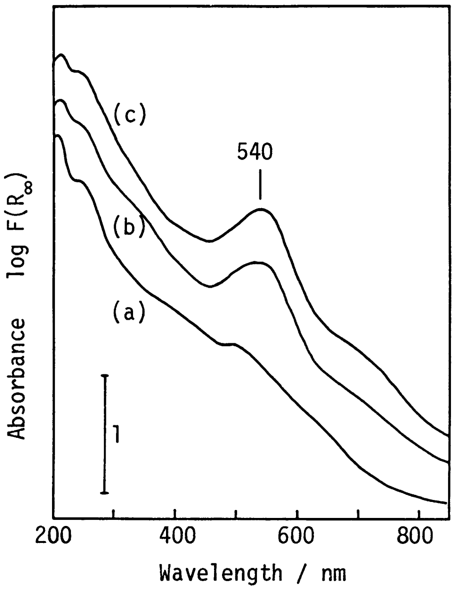

Fig. 4. Diffuse reflectance UV-vis spectra of NaY (a) and $HFe_3(CO)_{11}^-$/NaY after the adsorption of $Fe_2(CO)_9$ at 333 K (b) or after the WGSR at 373 K (c). Spectra were recorded with the zeolites in the form of loose powders contained in a vacuum-tight quartz cell. The DRS are reported as plots of the Kubelka-Munk function, $F(R_\infty)$, vs. wavelength.

ported so far.[7,8]

The results of IR and UV-vis measurements are summarized in Figs.3 and 4. They clearly show that the $HFe_3(CO)_{11}^-$ species was stable in the range 333-433 K and decreased somewhat in amount at 453 K and that no other kind of carbonyl species was present on the zeolite. A plausible mechanism can be put forth which explains the

$$HFe_3(CO)_{11}^- + H_2O \rightarrow H_2Fe_3(CO)_{11} + OH^- \quad (2)$$

$$H_2Fe_3(CO)_{11} \rightarrow H_2 + Fe_3(CO)_{11} \quad (3)$$

$$Fe_3(CO)_{11} + CO \rightarrow Fe_3(CO)_{12} \quad (4)$$

$$Fe_3(CO)_{12} + OH^- \rightarrow HFe_3(CO)_{11}^- + CO_2 \quad (5)$$

observed kinetic and spectroscopic data. Here step 2 is rate determining. This mechanism is different from those[2-6,9] suggested for the WGSR in water phase because of the stability of $HFe_3(CO)_{11}^-$ in the zeolite lattice and the low partial pressure of water due to the WGSR in gas phase.

Although a large number of carbonyl-support system have so far been reported in zeolites,[10] all of these works have been carried out in rigorously dehydrated zeolites, as far as we are aware. The present work is the first example of catalysis of a carbonyl cluster grafted in the hydrated zeolite. The results show a change in the reactivities of carbonyls in homogeneous and heterogeneous phases and shed more light on the chemistry of surface science.

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b) Before the adsorption of iron complex, the NaY (UCC, SK-40) was treated in the following way: NaY was heated slowly under vacuum (1.3×10^{-2} Pa) up to 673 K,

exposed to oxygen (13.3kPa, 1 h), and evacuated (1.3×10^{-2} Pa, 1 h) at the same temperature. The support was then rehydrated by introduction of water vapor (2.4 kPa) at 298 K for 1 h and evacuated at 298 K (1.3×10^{-2} Pa). The hydrated NaY-$Fe_2(CO)_9$ system was warmed at 333 K in order to get a sufficient vapor pressure and then the sample was evacuated at the same temperature for 30 min. The NaY became pink colored and the generation of the anionic hydride species $HFe_3(CO)_{11}^-$ grafted on the aluminum cation by ionic interaction was confirmed as follows. The adsorbed species showed an absorption maximum at 540 nm in the diffuse reflectance UV-vis spectrum which is characteristic of $HFe_3(CO)_{11}^-$.[11] The IR spectrum of the species gave an absorption peak of medium intensity at 2040 cm^{-1}, two broad and intense band at 1987 and 1950 cm^{-1} for the linear carbonyls and a broad band of smaller intensity at 1600 cm^{-1} in the bridging region. The values are in agreement with those for $[NR_4][HFe_3(CO)_{11}]$[12] and $HFe_3(CO)_{11}^-$ supported on alumina.[13] The shift of about 100 cm^{-1} to lower frequency of the ν(CO) band of the bridging carbonyl is due to the interaction between the aluminum cation and the oxygen lone pair of a coordinated CO.[13,14] The small red shifts of the ν(CO) bands corresponding to the linear carbonyls are presumably attributable to the inner electrostatic fields of the zeolites.[15]

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(Received June 24, 1983)