

Section 8

ESR EXAMINATION OF CARBON ON AN ALUMINA-SUPPORTED RUTHENIUM CATALYST

8.1 Introduction

The deactivation of Ru-based catalysts during methanation and Fischer-Tropsch synthesis has been attributed to carbon fouling.^{1*} The carbon deposits on the catalyst surfaces that form free radicals can be studied by electron spin resonance (ESR). Also ESR can also provide information on the valence state of the catalytic metal ion. To provide information on the character of the surface carbon species formed in Fischer-Tropsch synthesis we have used ESR.

8.2 Experimental Program

The catalyst contained 1.5 wt% ruthenium on an alumina support.¹ A small amount of catalyst (0.074 g) containing 1.5 wt% Ru on Al_2O_3 was placed in a quartz reactor (0.3 mm ID) and mounted in the ESR cavity. ESR measurements could be made while the catalyst was exposed to various gases (H_2 , CO, and He) and while heating.

The CO was passed through a trap (containing activated Al_2O_3 and copper turnings) and cooled to dry ice temperature to remove iron carbonyl. To remove oxygen the He was passed over reduced copper turnings at 675 K. The hydrogen and oxygen (prepurified grade, Matheson) were used without further treatment.

*References for Section 8 appear on page 8.6.

The ESR apparatus was a Varian E-12 system equipped with a Fieldial, a dual cavity, and a special Dewar assembly to heat the sample in situ to 725 K. Absolute spin density measurements were made by a first-moment analysis of the first derivative ESR curves using a 0.1% pitch sample (Varian) to calibrate spin concentration.

8.3 Experimental Results

After the catalyst was dried in He, the principal feature of the ESR spectrum was a low intensity, broad resonance at a g value of 2.25 and with a line width, $\Delta h = 1200$ Oe. The catalyst was then heated in flowing H_2 at atmospheric pressure at 725 K for a total of 2.5 hr. A broad, asymmetric resonance appeared ($g = 2.46$ and $\Delta h = 1000$ Oe) whose intensity reached a maximum after heating for 10 min (see Figure 8-1a), decreased to one half that intensity after heating for 20 min, and was undetectable after heating for 50 min. The resonance was also undetectable at 300 K after heating in H_2 for 2.5 hr. At the maximum intensity the absolute spin concentration was estimated to be 1.6×10^{19} spin/g catalyst.

The effects of CO on the reduced catalyst were examined at 560 K, which is the temperature used to examine the catalytic properties and deactivation of this catalyst.¹ For a gas mixture of 5 vol% CO in He flowing at $50 \text{ cm}^3/\text{min}$, only a weak narrow resonance appeared ($g = 2.0028$ and $\Delta h = 8.0$ Oe) (Figure 8-1b). The resonance intensity was not further increased by using pure CO.

However, when the catalyst at room temperature was exposed to 5 vol% CO in He, an asymmetric resonance was produced whose intensity increased to constant value after about 5 min. The resonance was anisotropic and appeared to have three components (Figure 8-1b). The strongest line was at a g value of 2.0087 and had a line width of 22 Oe, and the

weaker, unresolved resonances had g values at about 2.0030 and 2.040. This anisotropic ESR spectrum was produced only at room temperature on exposure of the reduced catalyst to CO. The ESR line intensity was about of the same intensity as observed when the catalyst had been heated and then cooled in CO. The maximum intensity of this anisotropic resonance corresponded to 3.9×10^{15} spins/g catalyst.

The anisotropic resonance was unaffected by passing He or H₂ over the catalyst at room temperature. However, when the catalyst was heated in He to about 400 K, the resonance intensity and line width decreased markedly. The remaining resonance had about the same intensity at 400 K and room temperature, and was also similar in intensity to the resonance produced by the initial CO exposure of the catalyst at 560 K.

Subsequent heating of the catalyst in a gas mixture of 5% O₂ in He at 725 K for about 10 min produced a strong anisotropic resonance (at 725 K, g = 2.72 and $\Delta h = 1200$ Oe; at 300 K, g = 3.00 and $\Delta h = 1900$ Oe) whose intensity was about 3×10^{19} spin/g catalyst. This oxygen treatment decreased by one-half the intensity of the narrow resonance ($\Delta h = 8.0$ Oe) remaining after the prior exposure to CO and heating in He.

8.4 Discussion

Hydrogen reduction can be expected to reduce the RuCl₃ originally introduced on the Al₂O₃ support¹ to the metal state. RuCl₃ does not exhibit an ESR signal² even though the orbital configuration, 4d⁵, would allow 1, 3, or 5 unpaired electrons. The appearance of the broad signal (g = 2.46) on hydrogen reduction, may be the result of RuCl₃ decomposition and formation of another ruthenium complex, perhaps an oxide, by reaction with water bound to the RuCl₃ or the Al₂O₃. If the resulting ruthenium complex had a sufficiently asymmetric crystalline electric field about the Ru ion, an ESR signal could be observable. When we calculate the absolute spin concentration for the maximum line

intensity, we obtain a value of 2.4 spins/Ru atom, which is within the expected range for a $4d^5$ ion. The observed g value at 2.46 is close to the g_{\perp} reported for some Ru^{+3} complexes;³ however, we did not observe a line corresponding to $g_{\parallel} \approx 1.7$, perhaps because of the broadness of this weak line in the spectrum. The disappearance of the 2.46-line upon extended H_2 reduction undoubtedly resulted from reduction of the ruthenium to the metallic state, which is not expected to exhibit an ESR signal.

Treatment of the reduced catalyst at room temperature with CO resulted in an anisotropic spectrum, probably a result of some form of CO sorbed on ruthenium metal. The sorption bond must be weak, since this spectrum disappeared when the catalyst was heated in He at 400 K and was not restored when the catalyst was cooled. The surface concentration of this species, calculated from the absolute spin analysis, is 6×10^{-4} spins/surface Ru atom (assuming the surface area is $205 \text{ m}^2/\text{g Ru}^1$ and the surface sites density is 10^{15} cm^{-2}). The narrow anisotropic spectrum resulting from CO-treatment at room temperature shows three components possibly due to a sorbed species having axial symmetry. Such a species might be a CO^- molecule chemisorbed by net donation of electrons from the ruthenium to the CO.

The weak narrow line ($g = 2.0028$) remaining after the CO-treated catalyst was heated at 560 K (Figure 8-2b) represents a species that is only partially reactive with oxygen. The fraction of the line that was decreased by the O_2 -treatment may be due to an amorphous surface carbon species that was oxidized by O_2 . Heating in oxygen also produced a broad resonance ($g = 2.72$ to 3.00), probably some form of oxidized ruthenium ions in the catalyst bulk. The spin density calculation yields a value of 4.8 electrons/Ru atom, which probably indicates the presence of Ru^{+4} .

These ESR spectra are not in agreement with those reported by Kobayashi and Shirasaki⁴ on the CO-treatment of silica- and graphite-supported ruthenium for which the observed anisotropic spectrum (g values of 2.35, 2.19, and 1.99) is attributed to ruthenium carbonyl. The experimental conditions of Kobayashi and Shirasaki's study differed from ours in several respects: they used different supports, they did not reduce the catalysts in hydrogen, and they did not purify the CO gas so iron carbonyl contamination may have been a factor. The spectra that they attributed to ruthenium carbonyl therefore are more likely to be due to iron carbonyl contamination. In our experiments, exposing the reduced catalyst to CO produced a broad intense spectrum only when the CO gas was not purified.

8.5 Summary

Hydrogen reduction of the catalyst resulted in a strong resonance, probably due to a solid-state Ru⁺³ complex with an asymmetric crystalline electric field. Upon continued reduction this resonance disappeared as the ruthenium was reduced to a lower valence state, probably to the metal.

Carbon monoxide treatment resulted in three kinds of sorbed species: a weakly sorbed CO species associated with the anisotropic spectrum that was produced by CO-treatment at room temperature and that decreased in intensity when the CO-treated catalyst was heated in He; a more tightly sorbed carbon species, perhaps amorphous carbon, as evidenced by the decrease in the intensity of a narrow symmetrical line when the CO-treated catalyst was heated in O₂; and another carbon species, which was essentially unreactive with O₂ and may be graphitic carbon, indicated by the narrow symmetrical resonance remaining after the O₂-treatment.

As a guide to further work, we speculate that the graphitic species may be the cause of carbon fouling of the catalyst.

We compared the information obtained on this catalyst ESR and TPSR (Section 7). TPSR indicated the existence of two carbon species that reacted with H_2 to form CH_4 ; one at room temperature and the other at elevated temperatures (about 500 K).⁵ To be detected by TPSR these species had to be present at a surface coverage of at least 0.1 monolayer. By ESR we did not observe any reaction between H_2 and the radicals at room temperature. The radical concentration observed by ESR corresponds to about 10^{-3} monolayers on Ru, much lower than the surface concentration observed by TPSR. However, the detectably free-radical concentration of chars and carbon is usually less than 1 radical per 1000 carbon atoms.⁶ Hence, the total concentration of carbon indicated by our ESR data may have approached the monolayer level.

8.6 References

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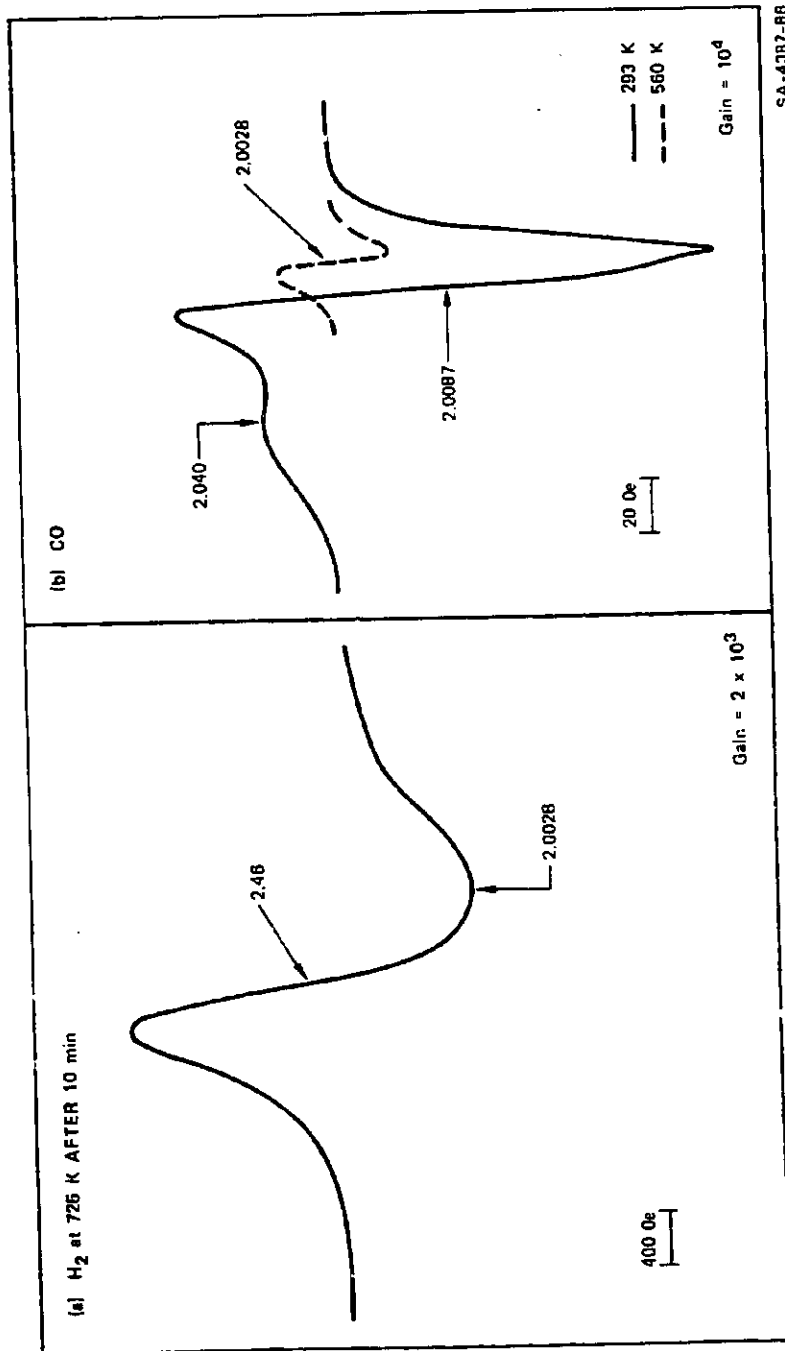


FIGURE 8-1 EFFECT OF H_2 AND CO ON ESR OF 1.5% Ru/ Al_2O_3 CATALYST