

An ESR Study of Zeolite-Supported Ruthenium Hydrodenitrogenation Catalyst

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(Received December 9, 1985)

A hydrodenitrogenation catalyst based on ruthenium sulphide supported on HY zeolite has been described recently [1]. The ruthenium-containing Y-zeolite (3.33% Ru by weight on NH_4Y) was prepared by ion exchange with hexaammine ruthenium(III) tribromide, air dried (80 °C) and sulphided by heating (350 °C in a stream of $\text{H}_2\text{-H}_2\text{S}$ or $\text{H}_2\text{-CS}_2$) for 3 h. The catalytic activity of the RuY catalyst compared favourably with a commercial catalyst in the overall conversion of quinoline as model nitrogenous base. To investigate the form of the ruthenium in the sulphided RuY catalyst, its ESR spectral properties were studied over a wide range of temperatures, typical of its likely operating conditions.

It has been shown that cation exchange of $\text{Ru}(\text{NH}_3)_6^{3+}$ into the Y-zeolite takes place without decomposition of the hexaammine complex [2]. However, decomposition of the complex takes place on heating in oxygen to 70 K, resulting in the formation of several different ruthenium complexes so the conditions used to prepare the catalyst require careful control if a well defined chemical species is to be formed in the zeolite. Accordingly, the ruthenium containing Y-zeolite, prepared by ion exchange, was air dried at room temperature and sulphided by passing H_2S through the zeolite bed (0.1 g) at room temperature (10 ml/min) for 10 min, during which time the colour of the solid changed from pale yellow to a tan colour. The X-band ESR spectrum of the sulphided material recorded at sample temperatures of -153 °C consisted of a broad resonance centred at $g = 2$. When the temperature of the zeolite was raised to 125 °C with continued passage of hydrogen sulphide, the ESR spectrum shown in Fig. 1 was obtained. This well-defined ESR spectral result ($g_{\parallel} = 1.980$; $g_{\perp} = 2.055$) persisted in samples heated

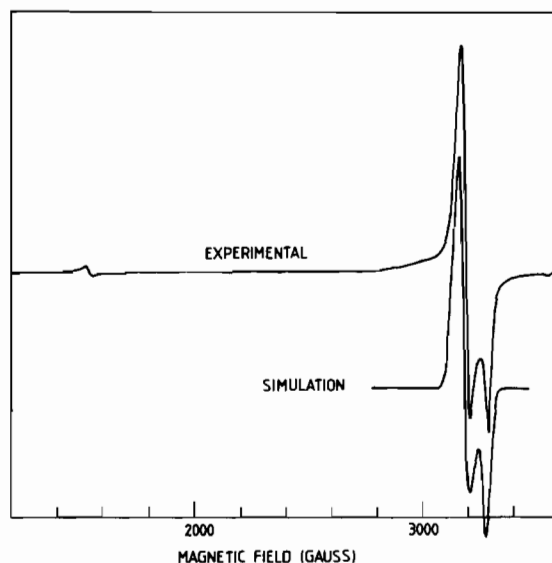


Fig. 1. ESR spectrum at -153 °C due to ruthenium(III) hexaammine exchanged Y-zeolite, air dried (20 °C) and sulphided at 125 °C. Microwave frequency 9.111 GHz.

to 350 °C, thereafter decreasing in intensity when heating of the zeolite was continued to 400 °C. When the initial treatment of the RuY-zeolite with hydrogen sulphide was carried out on a sample which had been air dried at 80 °C, the ESR spectrum shown by Fig. 2 was obtained, which has a central feature similar to that of Fig. 1, flanked by a broader resonance. The same ESR results were obtained with ruthenium exchanged into both Na-Y and $\text{NH}_4\text{-Y(HY)}$ zeolites. The passage of hydrogen (10 ml/min) for 10 min at 350 °C caused the complete disappearance of the ESR signal in both cases.

Expressions for the g -values obtained by computer simulation of the ESR spectrum shown by Fig. 1 have been given by a number of authors [3–5]. In keeping with notation used by Wan and Lunsford [3], we use the form derived by Wertz and Bolton [4] but with the inclusion of an orbital reduction factor [5] k to reflect a degree of covalency. Therefore

$$g_{\parallel} = g_e(\cos^2\omega - \sin^2\omega) - 2k \sin^2\omega \quad (1a)$$

$$g_{\perp} = g_e \cos^2\omega - 2\sqrt{2}k \sin\omega \cos\omega \quad (1b)$$

where

$$\tan 2\omega = \frac{\sqrt{2}\eta}{1 + 0.5\eta} \quad (2)$$

The free electron value g_e is taken to be 2 for purposes of the present analysis. The parameter η is defined by

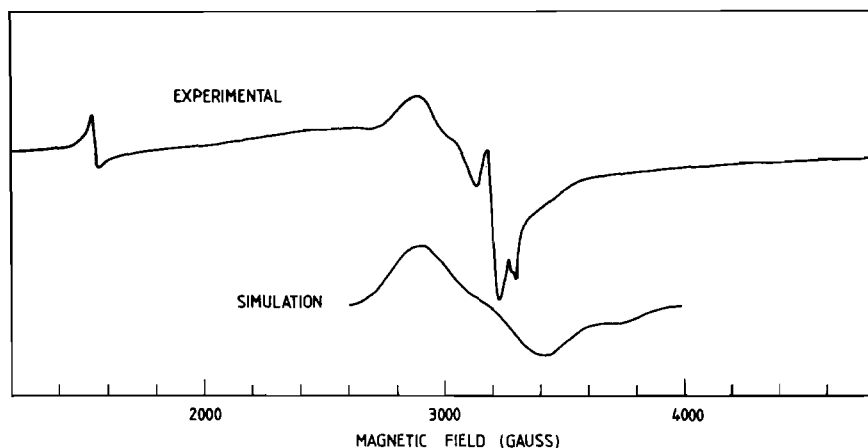


Fig. 2. ESR spectrum at -153°C due to the ruthenium(III) hexaammine exchanged Y-zeolite air dried (80°C) and sulphided at 125°C . Microwave frequency 9.111 GHz. The lower curve shows the computer simulation of the broader features using the parameters $g_{\parallel} = 2.055$, $g_{\perp} = 1.970$; ruthenium(III)–ruthenium(III) distance = 4.10 Å.

$$\eta = \lambda/\delta \quad (3)$$

where λ is the spin orbit parameter related to the one-electron parameter ζ [6] by

$$\lambda = -\zeta/2S \quad (4)$$

and δ is the splitting between the d_{xy} and the d_{xz} , d_{yz} degenerate pair of levels. In this case $2S = 1$ for a hole in a 't_{2g}' shell. Taking account of this, the value for δ quoted by Wan *et al.* [3] should be five times larger, though in view of the fact that they have not allowed for any orbital reduction in the value of λ used, the correction factor is probably nearer 3. (A recent paper by Daul and Goursot [7] also correctly uses $\lambda = -\zeta$ for ruthenium(III)).

If the orbital reduction factor $k = 1$, then $\eta = \lambda/\delta \sim -0.25$ [5]. Taking $\lambda \sim -800 \text{ cm}^{-1}$, then $\delta \sim 3200 \text{ cm}^{-1}$. On the other hand, use of $k = 0.7$ in the equation leads to $\eta \sim -1$ and $\delta \sim 800 \text{ cm}^{-1}$, a much more reasonable value.

A possible explanation for all or part of the broad ESR spectral features shown in Fig. 2 is that they are due to a magnetic dipolar interaction between a pair of neighbouring Ru(III) ions. The simulation shown in Fig. 2 is a computed spectrum due to dimeric or dinuclear species based on the computer program, GNDIMER [8] with a Ru(III)–Ru(III) spacing of about 4.1 Å. This does not account for all the extra features of Fig. 2 but provides a basis for a plausible explanation of the observed data. A spectral component is observed at $g = 4$ attributable to the $\Delta M_s = \pm 2$ transition in the triplet state formed by the magnetic dipolar interactions in the Ru(III) pair. Up to this point we have taken a simple view of an axial dimeric or dinuclear configuration.

It is concluded that a sulphido–ruthenium(III) species is formed at comparatively low temperatures (above 125°C) showing tetragonal distortion at single

ion exchange sites on the zeolite which at higher temperatures (400°C) show a degree of aggregation within the supercages and undergo reduction by hydrogen regardless of the presence or not of H_2S over the catalyst. Hence, under catalytic conditions (with a high H_2S partial pressure) the denitrogenation catalyst appears to consist of a sulphido species of ruthenium in a low oxidation state, possibly ruthenium(II), in aggregated form within the zeolite structure. If the ruthenium(III) hexaammine exchanged zeolite is subjected to quite mild heat treatment, sulphiding leads to the formation of dimeric or dinuclear ruthenium(III) sulphido species, which again is reduced by hydrogen at elevated temperatures. The observation of a sharp ESR spectrum due to monomeric zeolite bound sulphido–ruthenium(III) allows the point at which temperature dependent aggregation of single site zeolite bound sulphido species to be observed and its disappearance in a hydrogen atmosphere suggests that ruthenium in a lower oxidation state forms the active catalyst.

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