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NOTES

Laser-Raman Spectroscopy of the Alumina-Supported Rhenium Oxide Metathesis Catalyst

The metathesis of alkenes has attracted considerable attention because of its interest from a practical and theoretical point of view (*1, 2*). A typical example of this reaction is the conversion of propene into an equimolar mixture of 2-butene and ethene. A number of catalysts have been reported to be active in the metathesis reaction (*3*). Most attention has been given to silica- and alumina-supported tungsten, molybdenum, and rhenium oxide. The interest in the tungsten and molybdenum catalysts is not surprising considering the fact that they are also used in hydrodesulfurization and oxidation. Special attention has been given to rhenium oxide catalysts which are active even at room temperature and at low pressure. As the structure of this catalyst is not fully understood, we have investigated this system to elucidate the nature of the interaction between promoter and support.

Recent publications show that laser-Raman spectroscopy is a valuable tool in catalytic research. Brown *et al.* (*4*) and Medema *et al.* (*5*) have successfully applied laser-Raman spectroscopy in the identification of species present on molybdenum catalysts. Tungsten oxide supported on silica was studied by de Vries and Pott (*6*) and by our group (*7*). In the case of silica-supported tungsten oxide we showed the presence of at least two tungsten species:

(1) crystalline tungsten trioxide with main Raman lines at 809 and 715 cm^{-1};

(2) a not-yet-identified species with a broad band around 970 cm^{-1}.

This second species was tentatively identified as a polymeric compound consisting of distorted tungsten octahedra. It is remarkable that a similar band was observed in the spectrum of a 15-wt.% tungsten-oxide-on-alumina catalyst (*7*). Also Medema *et al.* (*5*) observed a broad band at 950 cm^{-1} in the case of alumina-supported molybdenum oxide. So the laser-Raman spectra of both metathesis catalysts show a broad band around 960 cm^{-1}.

We were interested in whether a similar band could be observed in the spectra of rhenium oxide on alumina. Olsthoorn and Boelhouwer (*8*) have investigated this system by in situ infrared spectroscopy. From the absence of characteristic alumina hydroxyl groups they concluded that at a high rhenium content (20 to 26 wt.% Re_2O_7) the carrier is completely covered with a monolayer. The new hydroxyl groups were attributed to rhenium-bonded hydroxyl groups.

We measured the laser-Raman spectra of NH_4ReO_4, ReO_4^- in aqueous solution and of a number of rhenium-oxide-on alumina catalysts. The catalysts were prepared by wet impregnation of γ-alumina with aqueous solutions of ammonium perrhenate, drying at 390 K for 16 hr and subsequent calcination in oxygen for 4 hr at 830 K. A detailed description of the system is given by Kapteijn *et al.* (*12*). The spectra were recorded on a Ramanor

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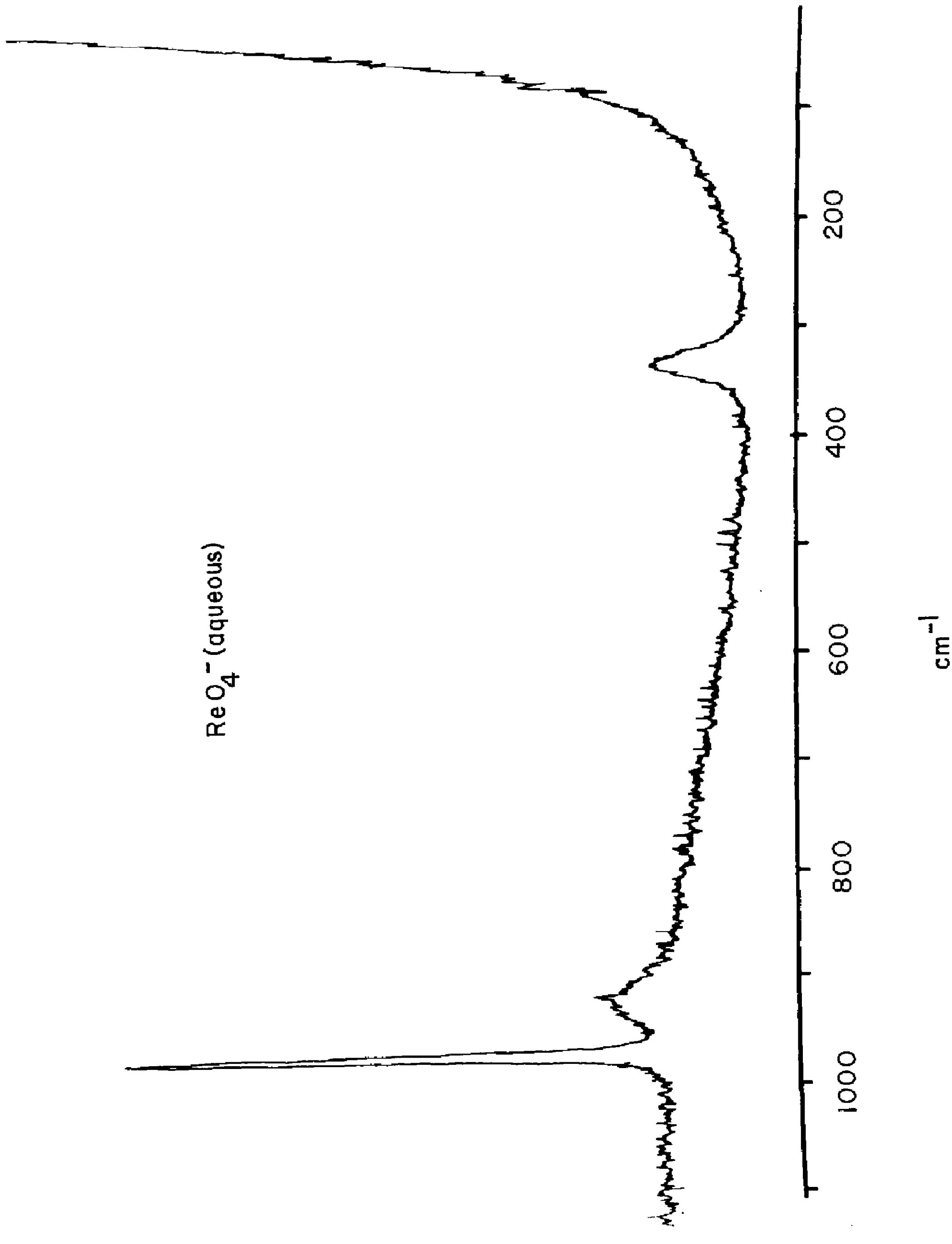

FIG. 1. Raman spectrum of ReO_4^- in aqueous solution. Scan speed 100 cm^{-1}/min. Slit width 10 cm^{-1}.

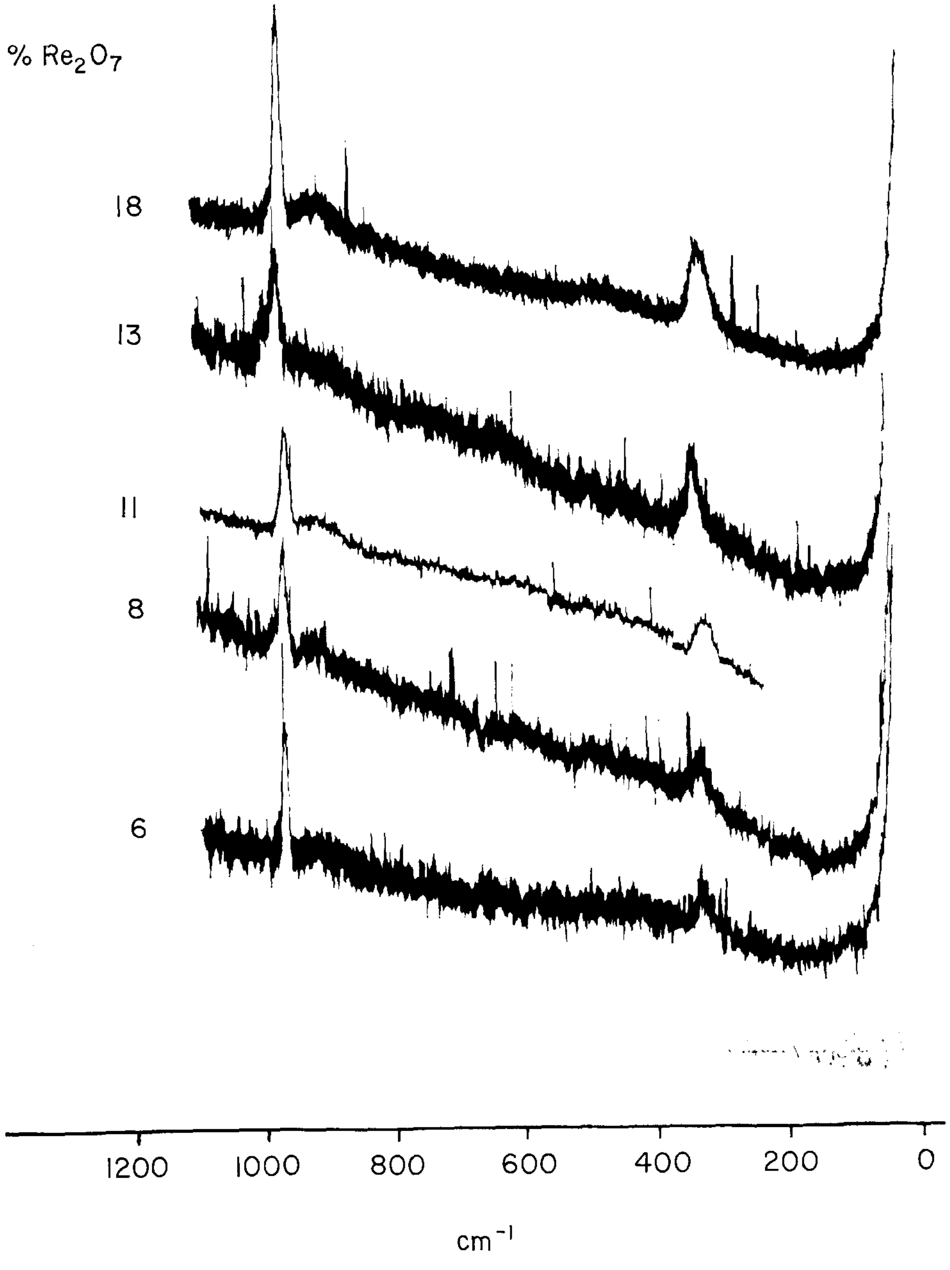

Fig. 2. Raman spectra of alumina-supported Rhenium oxide catalysts. Scan speed 100cm^{-1}/min. Slit width 10 cm^{-1}.

HG2S and a Coderg PHO spectrometer. The samples were measured in capillary tubes. The output power of the laser (Coherent Radiation CR8 argon ion laser) was 700–1000 mW (514.5 nm line). To check a possible decomposition of the samples, duplicate runs were made with rotating samples on a Jeol JRS-1 spectrometer.

Excellent agreement with published results for NH_4ReO_4 (*9, 10*) and ReO_4^- in aqueous solution (*11*) was obtained. The major Raman lines were found at 965 (ν_s ReO), 911 and 890 (ν_{as} ReO), and 339 and 332 (δ OReO) cm^{-1} for the solid perrhenate and 970 (ν_s ReO), 916 (ν_{as} ReO), and 332 (δ OReO) cm^{-1} for ReO_4^- in solution (Fig. 1). Figure 2 shows the spectra of the catalysts. In spite of the low signal/noise ratio a number of bands can be observed. The main lines are located at 968 and 328 cm^{-1}, whereas in most samples a weak broad band is observed at 910 cm^{-1}. Recording the spectra at 20 cm^{-1}/min instead of 100 cm^{-1}/min did not result in a significantly better signal. Because the same frequencies are observed for the catalysts as for ReO_4^- in compounds with a tetrahedral coordination we conclude that on the catalyst surface rhenium is present as ReO_4^- tetrahedra. The broadening of the band at 916 cm^{-1} points to a dynamic distortion of the tetrahedron just as has been observed for ReO_4^- in aqueous solution. This distortion, which can be caused by interaction with the carrier and surface hydroxyl groups, is obviously not static because in that case shifts of Raman frequencies are expected. The fact that alumina-supported rhenium oxide is easily reduced compared to, e.g., tungsten oxide on alumina (*8*) confirms the smaller interaction between carrier and promoter.

The low signal/noise ratio for the catalyst samples is caused by fluorescence. In case of a 3-wt.% rhenium oxide catalyst it was even impossible to record a reasonable spectrum because of the fluorescence. Furthermore, the absence of a correlation between peak intensity and rhenium loading is probably caused by a slight variation of the experimental conditions which could hardly be avoided.

It is interesting to compare our results with the conclusions of Medema *et al.* (*5*) and Giordano *et al.* (*13*) with respect to molybdenum on alumina. At low promoter contents this system contains only tetrahedral molybdenum species. At higher molybdenum contents (above 10 wt.%) other compounds were found, viz., octahedrally-coordinated molybdenum species, aluminum molybdate and free molybdenum trioxide. However, neither from X-ray diffraction measurements nor from laser-Raman spectroscopy is there an indication that other rhenium species, e.g., octahedrally coordinated rhenium or Al/Re/O compounds, are formed. This difference with the molybdenum catalysts can partly be explained by the fact that rhenium has a much higher atomic number than molybdenum and, therefore, at the same weight percentage the surface density for rhenium is lower (10 wt.% molybdenum oxide on alumina can be compared with 17 wt.% rhenium oxide).

Summarizing, we conclude that laser-Raman spectroscopy confirms the presence of a single rhenium species on the alumina surface. This species consists of tetrahedral ReO_4^- ions which are dynamically distorted by, for example, the carrier or surface hydroxyl groups.

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