JOURNAL OF CATALYSIS 62, 401–403 (1980)

# Self-Diffusion of Hydrogen in $H_{1.65}MoO_3$

The hydrogen molybdenum bronze, $H_{1.65}MoO_3$, forms with a composition outside that previously expected for bronzes of tungsten, molybdenum, and other metals. The compound used in the present work was prepared by hydrogen spillover on dry, powdered $MoO_3$, on which was deposited finely dispersed platinum (*1, 2a*). While it appears that $H_{1.65}MoO_3$ may be prepared by wet methods (*2b*) and is identical to the material used in the present research, the only samples investigated in this work were prepared utilizing the dry spillover technique. Vannice *et al.* (*3*) have shown the usefulness of $^1H$ nuclear magnetic resonance in understanding the kinetics of the catalytic reduction, via hydrogen spillover, of a similar chemical system, $H_xWO_3$, by determining the proton mobility. This information suggested that the rate-determining step of the reduction is the penetration of the reducing species below the surface of the $WO_3$ particles. The measurement of proton diffusion within the bulk $H_{1.65}MoO_3$ should therefore aid in determining the rate-determining step for the formation of $H_{1.65}MoO_3$.

The formation of $H_{1.65}MoO_3$ by hydrogen spillover has been described by Cirillo and Fripiat (*1*) as occurring in three steps: first, dissociative chemisorption of molecular hydrogen on the surface of the platinum; second, transfer of the hydrogen species formed to the oxide; and third, reduction of the oxide lattice. Levy and Boudart (*4*) have shown water to be an efficient carrier for the second step. Cirillo and Fripiat noted that even when working with dry hydrogen gas it can be assumed that surface hydration produces a small amount of water which could act as a carrier. However, the absence of water from the sample has been confirmed by $^1H$ NMR using magic angle spinning (*5*).

The measurement of proton diffusion within the bulk at 298 K by nuclear magnetic resonance is facilitated by an effective transverse relaxation time, $T_2^*$, of approximately 3 msec. This relaxation time, which is unusually long for protons in solids, can be explained in terms of motional averaging of static homonuclear dipolar interactions. That such motional averaging takes place is indicated by the comparison of spectra obtained under a single-pulse experiment and under a multiple-pulse homonuclear decoupling experiment (*6*). The results of these two experiments are shown in Figs. 1a and

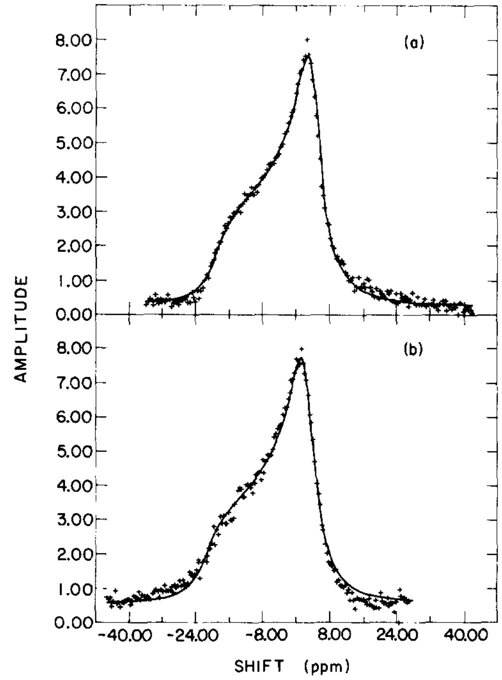

FIG. 1. $^1H$ NMR absorption spectra of $H_{1.65}MoO_3$ under (a) single-pulse excitation and (b) the MREV-8 homonuclear decoupling experiment. Reference is an external water sample.

0021-9517/80/040401-03$02.00/0

b, respectively. Figure 1a shows the $^1H$ NMR absorption spectrum under a single-pulse excitation, which is the Fourier transform of the free induction decay (FID). Both the lineshape and the magnitude of the anisotropy are characteristic of anisotropic magnetic shielding. Figure 1b shows the $^1H$ NMR absorption spectrum under the MREV-8 multiple-pulse sequence (*6*). This sequence has been shown to remove static homonuclear dipolar broadening to first order. When the frequency scaling under the MREV-8 sequence is taken into account, no difference is observed between the spectra obtained from the two experiments at 298 K. The observed spectral linewidth is associated with shielding anisotropy, which is not removed by the particular motion responsible for averaging the homonuclear dipolar broadening.

The diffusion coefficient was measured by the pulsed field gradient technique of Stejskal and Tanner (*7*). These authors have shown that when $G_A \gg G_0$, where $G_A$ is the applied field gradient and $G_0$ is the steady background gradient due to the susceptibility of the sample, the attenuation of the spin echoes in the presence of two gradient pulses ($G_A$) of duration $\delta$ separated by a time $\Delta$ is given by

$$\frac{A(G)}{A(0)} = \exp\left\{-\gamma^2 D\delta^2 G_A{}^2\left(\Delta - \frac{1}{3}\delta\right)\right\}. \quad (1)$$

Here, $A$(G) is the echo amplitude in the presence of the applied gradient, A(O) is the echo amplitude without the applied gradient, $\gamma$ is the gyromagnetic ratio, and $D$ is the translational self-diffusion coefficient. The background gradient of $H_{1.65}MoO_3$ was estimated to be $G_0 \sim 15$ gauss/cm by the comparison (8) of a single spin echo amplitude to the echo amplitude under the Carr-Purcell sequence. Using an applied field gradient of $G_A \sim 300$ G/cm to meet the condition of $G_A \gg G_0$, a proton diffusion coefficient of $D = (7.9 \pm 1.6) \times 10^{-6}$ cm$^2$/sec was obtained for $H_{1.65}MoO_3$ by varying $\delta$. The results are shown in Fig. 2. The standard used for this diffusion experiment was $H_2O$. In order to determine the effect upon the measured value of the diffusion coefficient by eddy currents induced by the applied gradient within the sample, the experiment was repeated applying a constant gradient $G_A$ for a constant time $\delta$, such that any induced background gradient would be constant. The diffusion coefficient was obtained by varying only $\Delta$, the time between gradients. Within experimental error, the same value of $D$ was obtained.

A diffusion coefficient on the order of $4 \times 10^{-7}$ cm$^2$/sec has been calculated with the correlation time of proton motion obtained from a measurement of the temperature dependence of the longitudinal relaxation times (*5*). Since the value obtained from the $T_1$ measurements was calculated with the assumption of isotropic motion, the difference between the two values may give an indication of the degree of anisotropy in the proton motion within the bronze. It should also be noted that a high temperature (~300 K) plateau in the effective transverse relaxation times, $T_2^*$ has been observed (*1*) and may also be a reflection of anisotropic diffusion. However, the measured value for $H_{1.65}MoO_3$ is comparable to the proton diffusion coefficient for $H_xWO_3$ of $D = 7 \times 10^{-6}$ cm$^2$/sec calculated from longitudinal relaxation times (*3*).

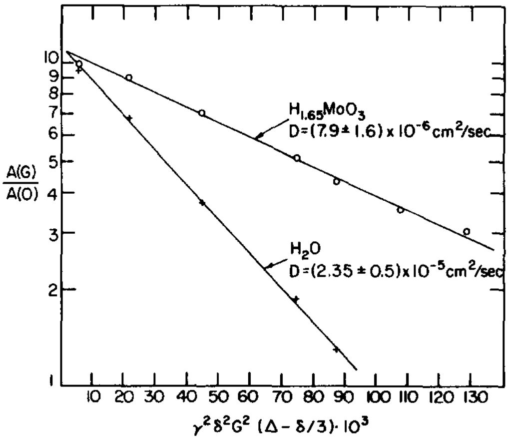

FIG. 2. $^1H$ translational self-diffusion coefficient for $H_{1.65}MoO_3$ at 298 K.

Sermon and Bond (*2*) have calculated the

TABLE 1

Diffusion Coefficients

| System | Diffusion Coefficient |
|---|---|
| | Hydrogen spillover, $D/(10^{-16}\ \mathrm{cm^2/sec})$ |
| $Pt/WO_3$ | 1.7[a] |
| $Pt/MoO_3$ | 1670.0[a] |
| | $^1H$ self-diffusion, $D/(10^{-6}\ \mathrm{cm^2/sec})$ |
| $H_xWO_3$ | 7[b] |
| $H_{1.65}MoO_3$ | 7.9[c] |

[a] Reference (*2*).
[b] Reference (*3*).
[c] This work.

maximum rates of diffusion coefficients for the hydrogen spillover process in $Pt/WO_3$ and $Pt/MoO_3$. These results are shown in Table 1. It should be noted that the maximum diffusion coefficient for $Pt/MoO_3$ is approximately 1000 times larger than that obtained for $Pt/WO_3$. These data show that the $^1H$ self-diffusion within the bulk is $10^7$ and $10^{10}$ times greater than that calculated for the overall spillover process in $Pt/MoO_3$ and $Pt/WO_3$, respectively. This clearly eliminates diffusion in the bulk of the bronze from being the rate-limiting step. Vannice *et al.* (*3*) presented strong evidence to suggest that the rate-determining step in the reduction is the penetration of the reducing species below the surface of the $WO_3$ particles. In a study of the kinetics and mechanism of spillover, Levi and Boudart (*4*) confirmed that the release of the proton from the carrier with interfacial crossing is rate determining in the presence of sufficient carrier. However, they noted a dependence of the rate on the amount of absorbed carrier below monolayer coverage. In the present study, it is impossible to unambiguously determine the rate-determining step since the rate of reaction may be limited by the amount of surface hydration. Still, in the presence of sufficient carrier (or possibly for the case of intimate contact between the Pt and $MoO_3$ particles), the rate-determining step in such a process in the formation of $H_{1.65}MoO_3$ is the penetration of spilled over hydrogen through the surface of $MoO_3$.

## ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Contract W-7405-Eng-82, Division of Basic Energy Sciences, Budget Code AK-01-03-02-1. The authors thank Dr. A. Cirillo, Department of Chemistry, University of Wisconsin, Milwaukee, for preparation of the sample.

## REFERENCES

1. Cirillo, A., and Fripiat, J. J., *J. Phys. Paris* **39**, 247 (1978).
2. (a) Sermon, P. A., and Bond, G. C., *Faraday Trans.* **72**, 730 (1976). (b) Birtill, J. J., and Dickens, P. G., *Mater. Res. Bull.* **13**, 311 (1978).
3. Vannice, M. A., Boudart, M., and Fripiat, J. J., *J. Catal.* **17**, 359 (1970).
4. Levy, R. B., and Boudart, M. J., *J. Catal.* **32**, 304 (1974).
5. (a) Cirillo, A., Ryan, L. M., Gerstein, B. C., and Fripiat, J. J., in preparation. (b) Cirillo, A., Ph.D. dissertation, University of Wisconsin, Milwaukee, 1979.
6. (a) Mansfield, P., *J. Phys. C* **4**, 1444 (1971). (b) Rhim, W.-K., Elleman, D. D., and Vaughan, R. W., *J. Chem. Phys.* **59**, 3740 (1973). (c) Rhim, W.-K., Elleman, D. D., Schreiber, L. B., and Vaughan, R. W., *J. Chem. Phys.* **60**, 4595 (1974).
7. Stejskal, E. O., and Tanner, J. E., *J. Chem. Phys.* **42**, 288 (1965).
8. Abragam, A., "The Principles of Nuclear Magnetism." Oxford Univ. Press (Clarendon), London, 1961.

R. E. TAYLOR
M. M. SILVA CRAWFORD
B. C. GERSTEIN

*Ames Laboratory, U.S. Department of Energy, and Department of Chemistry, Iowa State University Ames, Iowa 50011*

*Received April 26, 1979; revised December 12, 1979*