JOURNAL OF CATALYSIS **76**, 231–234 (1982)

^{1}H-NMR Study of Hydrogen Species in Reduced Copper–Chromium Oxide Catalysts

Copper–chromium oxides are used as catalysts for the selective hydrogenation of carbon–carbon double bonds in vegetable oils (*1*). The existence in such catalysts of a new crystalline phase, analogous to γ-Cr_2O_3 but having a (Cu/Cr) ratio equal to unity, was already reported (*2*). Used as catalyst, it showed nearly 100% selectivity in the hydrogenation of 1,3- and 1,4-pentadienes to pentenes.

We have now investigated by ^{1}H-NMR, both in the continuous wave mode (CW-NMR) and using a high power Fourier transform instrument (FT-NMR), the nature of hydrogen in the reduced phase of such catalysts. The NMR observations are correlated with the amount of hydrogenated products obtained from isoprene hydrogenation in static conditions, in the absence of gaseous hydrogen.

Copper–chromium oxide (Cu/Cr = 1) was prepared by coprecipitation of copper and chromium hydroxides with ammonia, followed by their thermal decomposition in a nitrogen flow at temperatures up to 370°C (*2*). Chromium hydroxide (needed as reference for quantitative NMR measurements) was prepared similarly and further dehydrated to α-Cr_2O_3 as monitored by thermogravimetry.

For the CW-NMR measurements, the samples (ca. 3 g) were pretreated in a fixed-bed reactor under N_2/H_2, N_2, or N_2/O_2 flow at variable temperatures, enabling the NMR analysis to be made without exposure to air. Reaction tests with isoprene were performed in static conditions in the same reactor. Isoprene was diluted with N_2 and the reaction products were analyzed by gas chromatography.

Wide-line CW-NMR measurements were performed at ambient temperature using a Varian V 4502 spectrometer equipped with a V 4210 A bridge. The proton signals were generally observed at 8 MHz, and, also in some cases, at 16 MHz. Care was taken to avoid instrumental signal broadening (*3*). The chemical shifts were evaluated with reference to aluminium nitrate, $Al(NO_3)_3 \cdot 9H_2O$, to which 5% of water was added. Quantitative intensities and evaluations of the proton concentrations were obtained by double integration of the different lines after deconvolution of the spectra and by using as references chromium hydroxide samples in two states of dehydration. The first reference (R1) was $Cr(OH)_3 \cdot 1H_2O$, as shown by thermogravimetry. Its NMR signal results from the superposition of a narrow lorentzian line and of a wide gaussian line. When the water excess is eliminated by heating R1 for 2 hr at 100°C, a new reference (R2) is obtained which exhibits only one wide gaussian NMR line.

For FT-NMR measurements, sealed samples (300 mg) in the reduced and in the reoxidized states have been examined at room temperature with a CXP 200 Bruker spectrometer operating in the Fourier transform mode. A RF-field $\pi/2$ pulse amplitude of 1 μs and a sweep width of 125 kHz were used to accumulate 1000 FIDs before Fourier transformation.

Different hydrogen species. The freshly

0021-9517/82/070231-04$02.00/0

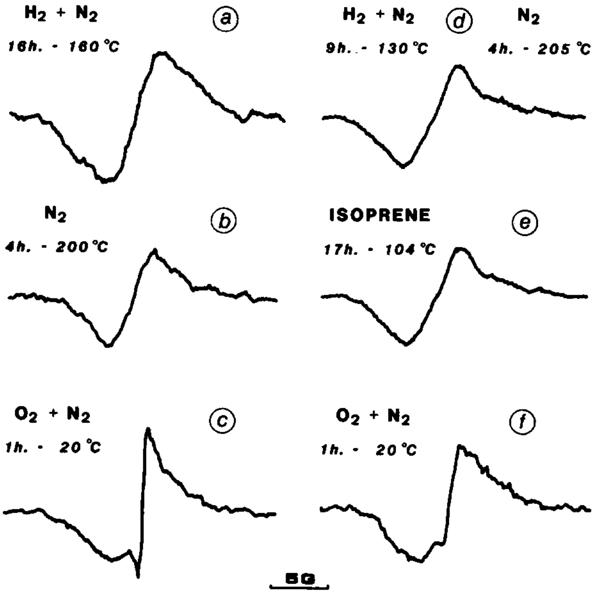

FIG. 1. Wide line CW ^{1}H NMR spectra observed at 20°C in a reduced copper–chromium oxide (Cu/Cr = 1) (8 MHz). Wide line intensities: (a) $n_{OH^-}/Cr^{3+} = 1.0 \pm 0.1$; (b, c, d, e, f) $n_{OH^-}/Cr^{3+} = 0.8 \pm 0.1$. Narrow line intensities: (c) $n_{\text{"H"}}/Cr^{3+} = 0.12 \pm 0.02$; (f) $n_{\text{"H"}}/Cr^{3+} = 0.04 \pm 0.02$.

prepared catalyst, heated in N_2 at 120°C, did not show any CW-NMR signal. After treatment in a mixture of nitrogen–hydrogen free from water vapor (<1 ppm) for 16 hr at 160°C, a wide line appears (Fig. 1a), corresponding to hydroxyl ions (*4*). These hydroxyls originate from the partial reduction of copper. After complete elimination of hydrogen from the gas phase and further dehydration (Fig. 1b), oxygen is added at 20°C to the carrier gas (nitrogen) and an additional narrow line appears without modification of the wide one (Fig. 1c). The narrow and wide lines in catalyst samples correspond to those observed for the references R1 and R2. The choice of two references was found necessary, because the quantitative NMR response differs in most cases when a wide and a narrow line are simultaneously recorded (*5*). Comparison of R1 and R2 showed that in our NMR conditions, the response factor was 2.27 for the wide line compared to the narrow component. In those conditions, the new narrow line (Fig. 1c) corresponds to 0.12 ± 0.02 "H" for one chromium atom whereas the wide one corresponds to 0.8 ± 0.1 OH^- ion per chromium. Bearing in mind the conditions in which this line appears and also its narrow width, it seems reasonable to assign it to weakly bonded water (physisorbed) stemming from the reaction of oxygen with a species "H" already present in the solid. This water is readily eliminated by increasing the temperature to 100°C under nitrogen flow. A first analysis shows that the wide line is displaced toward weaker fields (−1 G at 16 MHz), whereas the narrow line is very slightly shifted.

In the first case, a linear correlation holds between the NMR frequency, the shift, and the linewidth. This phenomenon is similar to that observed for CrOOH (*6*). It involves both isotropic contact interaction with Cr^{3+} and dipolar interactions, which confirms that OH^- and Cr^{3+} ions are close to each other.

After desorption of the "physisorbed" water, oxygen has no effect on the NMR spectrum, indicating that the "H" species is totally consumed during the first exposure to oxygen. The phenomenon is entirely reversible. A new treatment with hydrogen restores, after reoxidation, the narrow line, with the same intensity and behavior. Such a phenomenon is not observed for pure chromium oxide or for mechanical mixtures of copper and chromium oxides.

No NMR signal of the "H" species being observed by wide-line CW-NMR (the wide line observed after reduction (Fig. 1b) is unchanged after reoxidation (Fig. 1c), we have attempted to obtain evidence for this "H" species by FT-NMR. It is observed that, both in the reduced and the reoxidized catalysts, the OH^- signals become too wide to be detected (Figs. 2a and b), even with important offset variations (± 100 kHz). It can be calculated, from the proportionality between the linewidth and the magnetic field, that resonance broader than 500 kHz may be expected at 200 MHz for the OH^- signal. Hence, this result is not surprising.

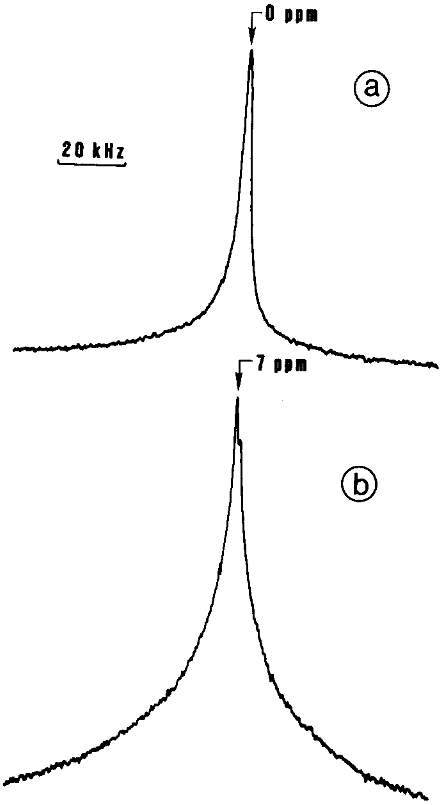

FIG. 2. FT ^{1}H NMR spectra at 200 MHz and 125 kHz spectrum width. NS = 1000; PW = 1 μs. (a) Reduced sample; (b) reoxidized sample.

The small, rather sharp line (4000 Hz), that is observed on the reduced solid (Fig. 2a), has no significant shift. It is also apparent on the reoxidized sample. It corresponds to small amounts of very weakly bonded water, not detectable at first with the less sensitive CW-NMR.

On the reoxidized sample, the previously CW-NMR observed narrow line is restored (10,000 Hz) and it is very slightly shifted (Fig. 2b), but it shows an additional anisotropy effect.

No other signal appears for the reduced sample, clearly demonstrating that the "H" species must be localized with restricted mobility close to the paramagnetic centers (Cr^{3+}).

Reactivity of "H" species. After reduction, a catalyst sample left 17 hr in the presence of gaseous isoprene, in the absence of gaseous hydrogen, gives selective hydrogenation products (95% monoenes and 5% isopentane). This isoprene transformation leaves the NMR wide line unchanged (Figs. 1d and e), while a consecutive oxygen treatment at 20°C reveals only a small residual CW-NMR narrow line (Fig. 1f). Several quantitative measurements proved that the sum of the hydrogen species consumed by isoprene hydrogenation and the oxidized ones, as evaluated by NMR is kept constant (7).

Such quantitative calculations show unambiguously that the "H" species selectively hydrogenate dienes to monoolefins and that they can play an important role in the hydrogenation mechanism.

This study demonstrates the existence of a hydrogen species, other than those found in OH^- ions, in the reduced copper–chromium oxide system. This species does not exist in pure chromium oxide; hence, copper is necessary for its formation. As this H-species cannot be directly observed, even by solid-state high-power FT-NMR, it must be localized, with a restricted mobility, near paramagnetic centers.

REFERENCES

1. Koritala, S., and Dutton, H. J., *J. Amer. Oil Chem. Soc.* **43,** 556 (1966).
2. Wrobel, G., Walter, P., and Beaufils, J. P., *C.R. Acad. Sci. Sér. C* **283,** 335 (1976).
3. Kroon, D. J., *Philips Res. Rep.* **15,** (1960).
4. Pearson, R. M., *J. Catal.* **23,** 388 (1971).
5. D'Huysser, A., Luchetti, A., Wrobel, G., and Bonnelle, J. P., *J. Microsc. Spectrosc. Electron.* **2,** 609 (1977).
6. Ibers, J. A., Holm, C. H., and Adams, C. R., *Phys. Rev.* **121,** 1620 (1961).
7. Aissi, C. F., Daage, M., Wrobel, G., Guelton, M., and Bonnelle, J. P., to be published.

C. F. AISSI*
M. DAAGE*
M. GUELTON*
J. P. BONNELLE*,[1]
J. B. NAGY†
E. G. DEROUANE†

**Laboratoire de Catalyse Hétérogène et Homogène*
E.R.A. C.N.R.S. n° 458
Université de Lille I
59655 Villeneuve D'Ascq Cedex, France
†Laboratoire de Catalyse
Facultés Universitaires de Namur
61 rue de Bruxelles
B-5000 Namur, Belgium

Received January 2, 1980; revised February 23, 1982

---

[1] To whom all correspondence should be addressed.