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The Characterization of Alkyl Intermediates on Silica-Supported Ruthenium with ^{13}C Nuclear Magnetic Resonance Spectroscopy

I. INTRODUCTION

The combined results of transient-response isotopic tracers (*1*) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (*2*) reveal that four forms of nonoxygenated carbon exist on a silica-supported ruthenium catalyst during CO hydrogenation. These species are identified as carbidic carbon (C_α), two types of alkyl groups (C_{β_1} and C_{β_2}), and unreactive, graphite-like carbon. The alkyl groups differ in their motional properties; the less mobile species were designated C_{β_1}.

We report here the further characterization of C_{β_1} species with high-resolution ^{13}C NMR spectra obtained while spinning a catalyst sample at the magic angle. The isotropic shifts of the resolved NMR peaks are consistent with linear alkyl species; the average length of the chains may be determined from the relative intensities of the peaks.

II. EXPERIMENTAL PROCEDURES

The Ru/SiO_2 sample studied here was characterized initially in a previous study (*2*), in which it was designated sample B (*steady-state*, D_2-prepared Ru/SiO_2). Briefly, 0.34 g of 4.3 wt% Ru on silica was used to catalyze the reaction between ^{13}CO and D_2 for 5 min at 463 K. After which, ^{13}CO was removed from the sample by changing the reactant mixture to ^{12}CO and D_2 for 30 sec, leaving only nonoxygenated ^{13}C on the catalyst. Finally, the catalyst was quenched to room temperature (rm temp) and sealed. The ^{13}C NMR spectrum obtained within days after preparation revealed the catalyst contained 2.9×10^{-5} g-mol of ^{13}C, distributed as ~5% C_α, ~93% C_β, and ~2% unreactive carbon (*2*). The C_β peak, which is the superposition of C_{β_1} and C_{β_2} lineshapes, was well fit by a Lorentzian peak, centered at 14 ± 1 ppm, with a halfwidth of 1.10 kHz. The catalyst was then stored at rm temp for 15 months under an atmosphere of He (200 Torr), ^{12}CO (200 Torr), and D_2 (360 Torr).

The ^{13}C NMR spectra were measured at 50.34 MHz with a Bruker CXP-200 spectrometer, using an inversion–recovery sequence detailed elsewhere (*2*). For all spectra, the repetition time between scans was 3 sec. High-resolution spectra were obtained by spinning 0.12 g of catalyst in a Delrin (polyformaldehyde) rotor at 2625 ± 25 Hz. The background signal due to the Delrin was eliminated by subtracting the spectrum of an empty rotor measured under identical conditions. The ^{13}C chemical shifts are reported on the δ scale, relative to tetramethylsilane (TMS), such that downfield lies to the left.

III. RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of the Ru/SiO_2 catalyst measured 15 months after preparation is shown in Fig. 1. The integrated area of the spectrum, compensated for saturation, indicates the sample contains 2.7×10^{-5} g-mol ^{13}C. Using a model presented previously (*2*), the spectrum is decomposed into C_α (11%), C_β (72%), and unreactive carbon (17%). The C_β peak is fit by a Lorentzian centered at 18.5 ppm with a halfwidth of 1.10 kHz. Thus, although the total amount of ^{13}C on the catalyst remained constant, the nonoxygenated forms of carbon interconverted during storage

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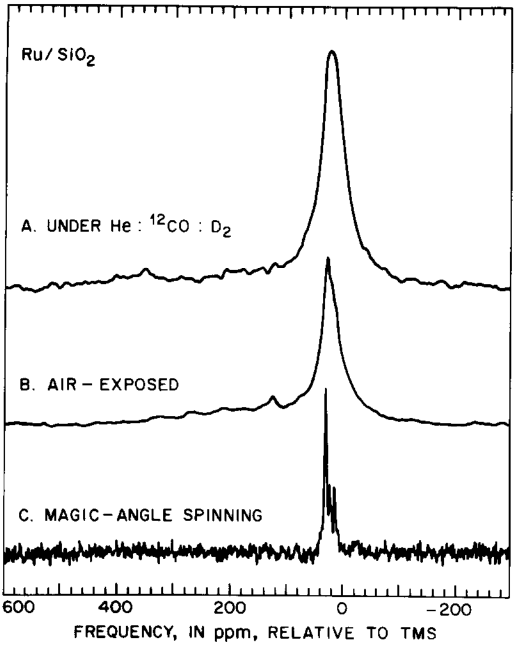

FIG. 1. ^{13}C NMR spectra of a Ru/SiO_2 catalyst quenched after 5 min of CO hydrogenation, then (A) after stored at rm temp for 15 months, (B) after exposure to air, and (C) while spinning at the magic angle at 2625 Hz. Spectra A and B represent the accumulation of ca. 30,000 scans each. Spectrum C is the difference between the spectrum of the catalyst in a Delrin rotor (90,000 scans) and the empty Delrin rotor (90,000 scans).

at rm temp. The C_β species decreased, the amount of C_α doubled, and the unreactive carbon increased from 2% to 17%. The conversion of C_β to C_α has been described previously; at 463 K the conversion occurs in a few seconds (*1*).

Spectrum B in Fig. 1 is the ^{13}C NMR spectrum of the catalyst after exposure to air at rm temp.[1] The amount of ^{13}C on the catalyst has decreased to 1.2×10^{-5} g-mol, principally due to the complete disappearance of the C_α peak and a decrease in the C_β peak. The distribution of nonoxygenated carbon after exposure to air is 60% C_β and 40% unreactive carbon. In addition, the C_β peak has narrowed and shifted downfield; the peak is centered at 22 ± 1 ppm and has a Lorentzian halfwidth of 0.81 kHz. We attribute the change in the C_β peak to the loss of the C_{β_2} species upon exposure to air based on the following observation. It was shown that the C_β peak of samples prepared with H_2 consists of the superposition of two peaks: the C_{β_1} component which is a factor of four broader than in the D_2-prepared samples, and the C_{β_2} component which showed little change (*2*). When a H_2-prepared sample was exposed to air, only the broadened component of the C_β peak remains, suggesting the loss of the C_{β_2} species (*3*).

The C_β lineshape narrows and is resolved into a collection of peaks when the air-exposed catalyst sample is spun at the magic angle, as shown in spectrum C of Fig. 1. The integrated area of spectrum C is 0.7×10^{-5} g-mol of ^{13}C and its overall center of mass is 22.7 ppm. Figure 2 shows a least-squares fit of the magic-angle-spinning spectrum to the sum of five Lorentzian functions. The parameters are given in Table 1. Although the unreactive carbon persists on the catalyst after air exposure, spinning does not yield a sharp peak at its isotropic shift, 89 ppm. This is expected since the spectrum of ^{13}C-enriched graphitic carbon would not be appreciably narrowed for rotation speeds less than 5 kHz.

We note that the ^{13}C NMR spectra indicate that the alkyl species did not react with oxygen, although the surface of the Ru particles are probably saturated with oxygen, which has displaced the adsorbed CO. For example, Fig. 1C contains no peaks in the range of alcohols and alkoxides (65–75 ppm). Furthermore, we believe that the alkyl species remain attached to the Ru surface after the adsorption of oxygen. That is, as will be discussed, the alkyl species appear to be only four to five carbon units long. If the adsorption of oxygen displaced the alkyls, then these volatile species would

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[1] Initial exposure to air was unintentional and probably occurred during a brief transfer of the catalyst under an argon atmosphere. We estimate the dry box contained approximately 10 ppm O_2, which would result in a slow oxidation of the Ru surface such that the Ru particles did not warm substantially.

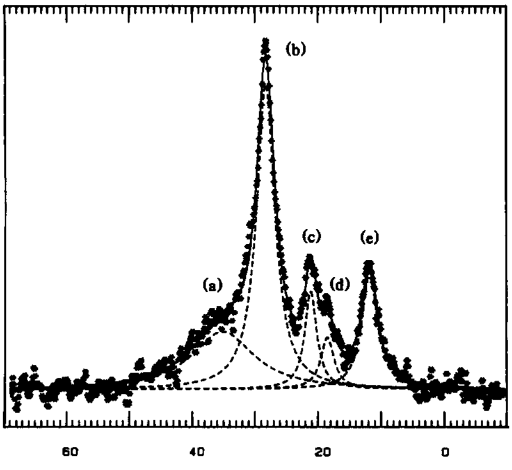

FIG. 2. A least-squares fit of a superposition of five Lorentzian peaks to the ^{13}C NMR spectrum obtained during magic-angle spinning. the results of the fit are summarized in Table 1.

have desorbed and would not be present in the ^{13}C NMR spectra, contrary to Fig. 2.

Rigorous assignment of the peaks in Fig. 2 can be established only after further study of additional samples prepared with different methanation conditions, to allow correlation of peak intensities over a range of species distributions. However, the isotropic shifts, intensities and linewidths of the peaks suggest a preliminary interpretation, as follows. The peak at 35 ppm is considerably broader than the other peaks. This difference is due to either inhomogeneous broadening caused by a distribution of isotropic shifts, or residual nuclear dipolar coupling because the molecular reorientation of this carbon is more restricted than others. We interpret this peak as the carbon bonded to ruthenium. It follows that the broadening is due, in part, to a distribution of adsorption sites on supported ruthenium, which has also been attributed to the inhomogeneous broadening of the ^{13}C NMR spectrum of carbides formed on the catalyst (*2*). Unfortunately, the limited ^{13}C NMR data on ruthenium alkyls does not provide an adequate basis for judging the validity of this assignment; the isotropic shifts of the α-carbon of η^1-alkyl ligands of ruthenium complexes range from 40 ppm to -10 ppm (*4–6*).

We assume that the alkyl species on the catalyst are almost exclusively (>95%) linear chains. This is the predicted result of chain growth by successive insertion of methylene groups at the base of the chain. With this assumption, the remaining peaks can be assigned by analogies with normal paraffins. For linear alkanes longer than six carbons, the methyl group is at 14 ppm, the β-methylene is at about 23 ppm and interior methylenes are at 30 to 32 ppm (*7*, *8*). Analogous peaks are observed in Fig. 2, but are uniformly shifted upfield by 2 ppm. We interpret the peak at 12 pm as terminal methyls, the peak at 21 ppm as β-methylenes, and the peak at 28 ppm as interior methylene groups.

The catalyst is also expected to contain

TABLE 1

^{13}C NMR Spectral Assignments

Peak[a]	Center of of mass[b]	Relative area	Halfwidth (Hz)	Assignment
(a)	35.1 ± 0.8	0.28 ± 0.06	300	$Ru—C^*H_2—CH_2—$
(b)	28.3 ± 0.2	0.43 ± 0.03	90	$Ru—CH_2—(C^*H_2)_n—CH_2—CH_3$
(c)	21.1 ± 0.1	0.09 ± 0.01	60	$Ru—CH_2—(CH_2)_n—C^*H_2—CH_3$
(d)	18.4 ± 0.1	0.05 ± 0.01	65	$Ru—CH_2—C^*H_2—CH_3$(?)
(e)	11.7 ± 0.1	0.14 ± 0.01	75	$—CH_2—C^*H_3$

[a] See Fig. 2.
[b] In ppm, relative to TMS.

shorter alkyl species such as Ru—CH_3, Ru—CH_2—CH_3, and Ru—CH_2—CH_2—CH_3. We tentatively assign the β-methylene and methyl carbons of the propyl ligand to the peaks at 18 ppm and 12 ppm, respectively. This assignment provides that the total number of β-methylenes (the peaks at 21 ppm and 18 ppm) equal the total number of methyl groups (peak at 12 ppm). The terminal methyl of a Ru—CH_2—CH_3 species is most likely shifted downfield; we propose that this methyl is a component of the peak at 28 ppm. The Ru—CH_3 species is probably also shifted downfield; it may either coincide with the peak at 28 ppm or lie under the broad peak at 35 ppm.

Finally, we note that we attempted to preserve the integrity of the inherently air-sensitive species on the catalyst (C_α and $C_{\beta 2}$) by opening the reactor in a dry box under an argon atmosphere (less than 10 ppm O_2). A delrin rotor was loaded and capped in a dry box and was installed in the N_2-purged probe with minimum exposure to air. However, this procedure was ineffective; the ^{13}C NMR spectrum was indistinguishable from the spectrum measured after the catalyst was exposed to air for 36 hr. Further characterization of the $C_{\beta 2}$ species will require airtight rotors, such as the design reported recently (*9*).

IV. ACKNOWLEDGMENTS

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T. M. DUNCAN
J. A. REIMER*
P. WINSLOW*,†,[2]
A. T. BELL*,†

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

**Department of Chemical Engineering*
and †Materials and Molecular
Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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[2] Present address: Chevron Research, Richmond, Calif. 94802.