Catalysis Letters 8 (1991) 367–374

PROBING INTERMEDIATES IN THE REACTION OF ETHYLENE OVER SUPPORTED Ru; USE AND LIMITATIONS OF MULTIPLE QUANTUM SPIN COUNTING

Son-Jong HWANG [1], T.S. KING [2] and B.C. GERSTEIN [1]

[1] *Department of Chemistry and Ames Laboratory, 229 Spedding Hall, Iowa State University, Ames, IA 50011, U.S.A.*
[2] *Department of Chemical Engineering and Ames Laboratory, 231 Sweeney Hall, Iowa State University, Ames, IA 50011, U.S.A.*

Received 13 December 1990; accepted 4 February 1991

Multiple quantum spin counting is shown to yield an upper limit of $n = 6$ for strongly bound, rigid intermediates C_mH_n in the reaction of ethylene over Ru/SiO_2. The results eliminate the possibility of major components of such intermediates being polymer-like coke precursers. A precurser to 2-butene is one possible intermediate.

Keywords: Ethylene on ruthenium, ^{13}C NMR, multiple quantum spin counting

Supported bimetallic catalysts have been of recent interest both because of their use in petroleum reforming, and as valuable model systems in fundamental investigations of catalytic phenomena [1–4].

Proton NMR of chemisorbed hydrogen has recently been used to probe surface compositions of metals in the supported catalysts R/SiO_2 and $Ru\text{-}M/SiO_2$, [5–8], with M being Cu, Ag, and Au. The reaction of ethylene with supported $Ru\text{-}Cu/SiO_2$ has been studied by Hong et al. [9] and the reaction of ethylene over Ru/SiO_2 [10] and over $Ru\text{-}Cu/SiO_2$ [11] has been studied by high resolution solid state NMR of ^{13}C in our laboratories.

Ethane hydrogenolysis over supported Ru-Cu [12] and over supported Ru-Cu and Ru-Ag [13] has been studied by Smale and King. Fischer-Tropsch reactions over supported Ru-Cu and Ru-Au have been reported by Kelzenberg and King [14].

It has been seen that the use of a variety of nuclear spin dynamics involving single and double resonance techniques in NMR of ^{13}C and ^{1}H can be quite diagnostic in following the reaction of ethylene over supported $Ru\text{-}M/SiO_2$ catalysts. A problem in the use of chemical shifts or ^{13}C to follow these reactions, however, has been that there exist rigidly bound intermediates in the reaction of ethylene over these catalysts that exhibit a very broad NMR spectrum (~ 150 ppm wide) under high resolution conditions of magic angle spinning and strong proton decoupling [9]. The NMR spectrum of these intermediates has maxima at roughly 85 ppm and 20 ppm, which suggest the presence of acetylid and of aliphatic species respectively.

The proton NMR of the system consisting of the rigid species left after mobile components are removed by pumping under either a single pulse excitation or under high resolution conditions [15] is singularly uninteresting. The problem is that a majority ($> 95\%$) of the protons in this system are silanol protons of the support, and it is these that are seen under single pulse or multiple pulse homonuclear decoupling experiments. The proton NMR spectrum observed under a single pulse excitation is almost symmetric with a full width half maximum linewidth of 10 ppm (2,200 Hz) corresponding predominantly to shielding anisotropy of partially motionally averaged silanol protons. The means in which those protons belonging to the C_mH_n fragments are detected above background in the present case are discussed below.

It is the purpose of this work to determine the extent to which the use of multiple quantum coherence [16–25] of dipolar coupled protons in the strongly adsorbed, rigid, C_mH_n intermediates may shed further light on the identities of these species. To this end we have employed the use of a single quantum propagator [26] in multiple quantum spin counting of coupled protons in the residual species left on the surface after the reaction of ethylene over Ru/SiO_2.

Ru/SiO_2 was prepared by the impregnation procedure used by Gay [27] on Cab-O-Sil-HS-5 with the exception that $Ru(NO)(NO_3)_3$ was used instead of $RuCl_3$ as previously described [6]. The metal loading was 12%. The catalyst was reduced with H_2 at 723 K for one hour. After doping with ethylene at 20 Torr and allowing to react at room temperature for one hour, residual gas and mobile, weakly adsorbed species were removed by pumping to 2×10^{-6} Torr for one hour. All chemical treatment was performed with the sample in a 5 mm NMR tube, which could then be sealed for subsequent NMR measurements.

NMR experiments were performed on the same home-built spectrometer operating at 220 MHz used for previous studies [5] of hydrogen on supported bimetallics, with the exception that a fast 8-bit digital phase shifter [28] was incorporated in the rf switching section of the spectrometer in order to perform the phase shifting by increments of $2\pi/k$ necessary to detect multiple quantum coherence up to order k.

As previously mentioned, a problem with the use of multiple quantum spin counting to probe residual species left when ethylene reacts with Ru/SiO_2 is that there exist silanol protons in the support which will also contribute to the observed multiple quantum coherence. In order to determine the effect of these, background experiments were performed in which the multiple quantum coherence, under a time development of 300 μsec, was observed; (a) for the support in the absence of metal loading and with no ethylene (fig. 1) and (b) for the metal loaded support with no ethylene (fig. 2). In both cases, the highest order of multiple quantum coherence observed in the absence of ethylene was $k = 2$.

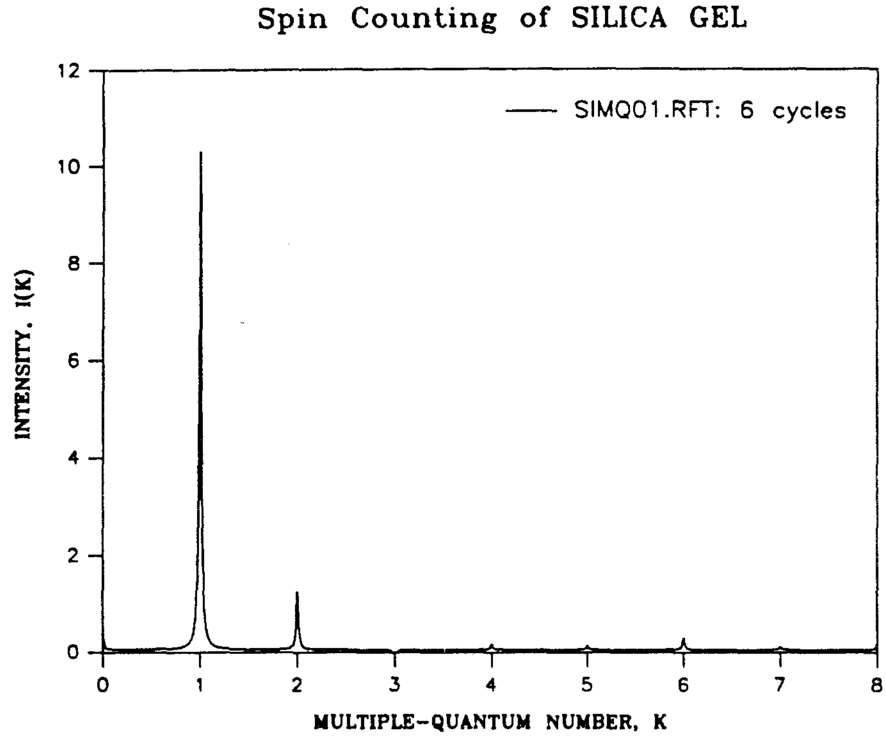

Fig. 1. Multiple-quantum spectrum of coupled protons on silica gel support.

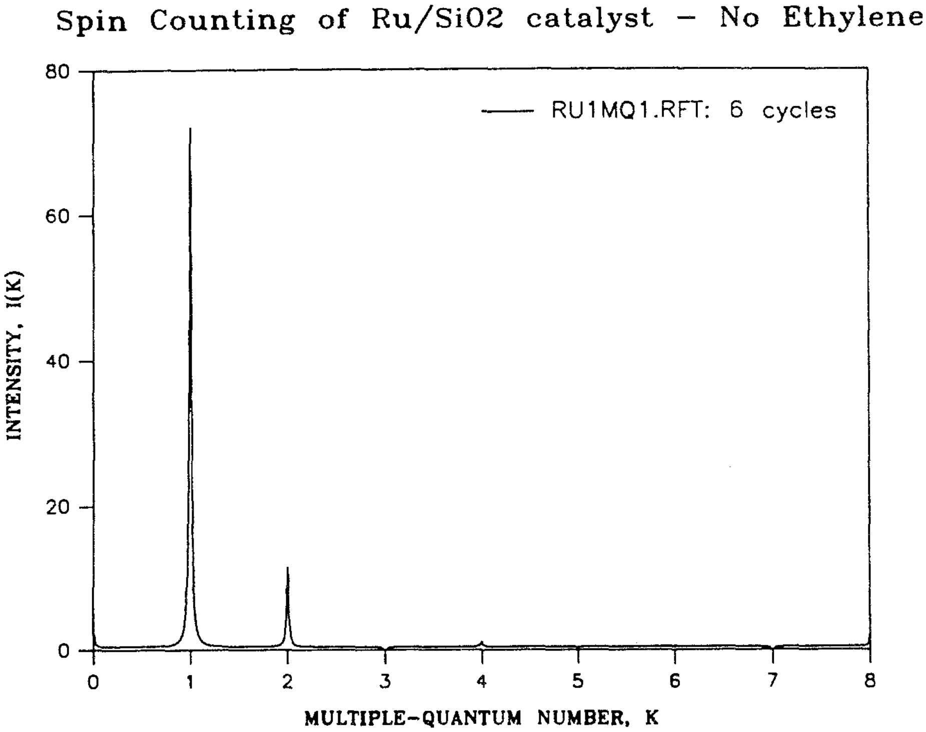

Fig. 2. Multiple-quantum spectrum of coupled protons on metal loaded silica gel support.

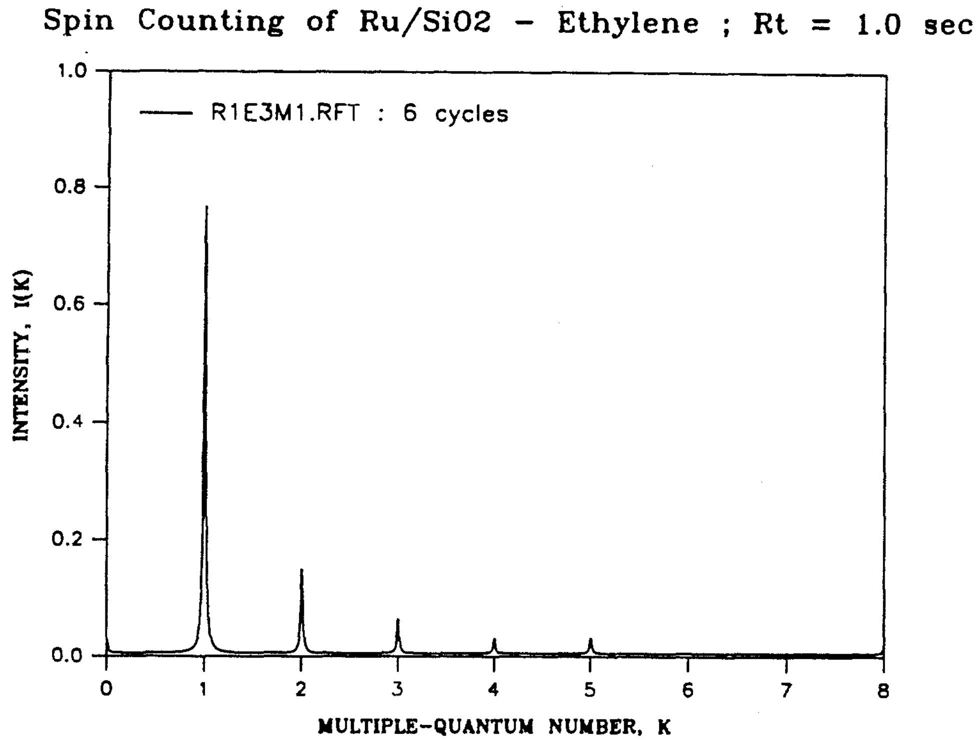

Fig. 3. Multiple-quantum spectrum of coupled protons in the strongly bound C_mH_n residue after the Ru loaded support was dosed with ethylene, reacted at room temperature for one hour, pumped at 2×10^{-6} Torr for one hour, and sealed.

The small negative intensity at $k = 3$, and any small intensities above this k are artifacts associated with noise in the initial data. Under the selection rules operational in this experiment [25], $n_{\text{max}} = k_{\text{max}} + 1$, a maximum of three dipolar coupled protons are observed in the absence of ethylene doping. An important feature of these results, in accord with the linewidth of ~ 2 kHz characterizing these species, is that homonuclear dipolar interactions among the silanol protons are sufficiently weak that the growth of multiple quantum coherence due to these species is slow compared to that due to rigidly bound C_mH_n fragments. Thus, (vide infra), the intensity of multiple quantum coherence due to the C_mH_n fragments of interest dominates the multiple quantum spectrum at $k > 2$, and is a major part of the intensity observed for $k \leqslant 2$, for a time development of 300 μsec.

After doping with ethylene, under a time development of 300 μsec, the maximum order of MQ coh observed was 5 (fig. 3), after which the the multiple quantum intensity dropped sharply to zero. Contrasting these results are those obtained for solid hexamethyl benzene and adamantane given in fig. 4. Under a 300 μsec time development, multiple quantum coherence is still seen strongly at $k = 8$ (we did not count further for purposes of the present work).

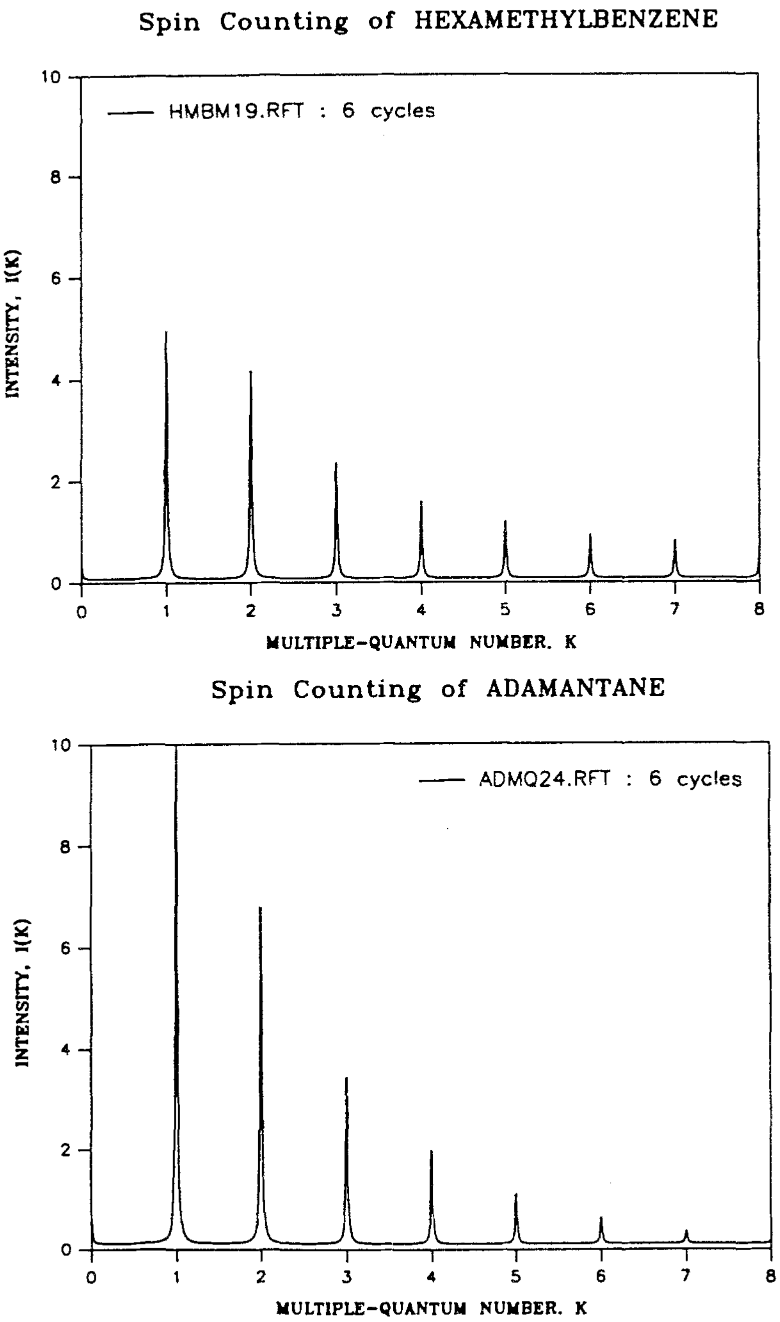

Fig. 4. Multiple-quantum spectrum of coupled protons in hexamethyl benzene (top) and adamantane (bottom) under conditions of time development identical to those used in the experiments represented by figs. 1–3.

In summary, the isotropic chemical shifts of neither ^{13}C nor ^{1}H are completely diagnostic fingerprints of the strongly bound intermediates formed when ethylene reacts over Ru/SiO_2 at room temperature. The maximum number of protons bound in a C_mH_n fragment is investigated as a further means of identifying these species. The maximum order of multiple quantum coherence observed for these species supplies this information. Under a time development which allows $k_{max} > 8$ to be seen in relatively weakly coupled, but infinite systems such as hexamethyl benzene and adamantane, and which only detects $k_{max} = 2$ for silanol protons in the support, $k_{max} = 5$ is found for the strongly bound species remaining after ethylene has reacted with the Ru/SiO_2 catalyst and the weakly bound products removed by pumping. This result means that there exist a maximum of six coupled protons in the species being observed which are bound to the supported metal particles. The present work says nothing about the possible presence of acetylide, with ^{13}C NMR observed in the region of 85 ppm downfield of TMS, as reported in ref. [10], or about the presence of species with less than six coupled protons, such as the fragment $-CH_2CH_3$. However, the result does indicate that an extended polymer such as might be a coke precurser is not present in concentrations comparable to those of the major strongly adsorbed species present.

Possible strongly bound C_mH_n fragments not inconsistent with a value $n_{max} = 6$ might be: (a) neighboring pairs of methyl groups, or (b) neighboring pairs of fragments containing $x + y$ protons, where $x + y = 6$. A simple explanation in accord with the fact that cis- and trans-2-butene are among the observed products, and not in disagreement with previous observations [29–33] is that there is a four-carbon metallocyclic intermediate such as $Ru-CH_2-CH{=}CH-CH_2-Ru$ contributing to the maximum order of observed coherence.

Acknowledgements

The Ames Laboratory is operated by Iowa State University for the US Department of Energy under contract number W-7405-Eng. 82. This work was supported by the Assistant Secretary for Energy Research, Office of Energy Sciences, WPAS-KC-03-02-01.

The authors thank Dr. Marek Pruski for his help and advice in operation of the instrumentation used in acquisition of multiple quantum coherence signals.

References

[1] J.H. Sinfelt, *Bimetallic Catalysts-Discoveries, Concepts, and Applications* (Wiley, New York, 1983).

[2] P. Biloen, J.N. Heller, H. Verbeek, F.M. Dautzenberg and W.M.H. Satchler, J. Catal. 63 (1980) 112.
[3] P.G. Menon and G.F. Fremont, J. Mol. Catal. 25 (1984) 59.
[4] K. Christmann and G.J. Ertl, J. Mol. Catal. 25 (1984) 31.
[5] T.S. King, Xi Wu and B.C. Gerstein, J. Am. Chem. Soc. 108 (1986) 6056.
[6] X. Wu, B.C. Gerstein and T.S. King, J. Catalysis 118 (1989) 238.
[7] X. Wu, B.C. Gerstein and T.S. King, J. Catalysis 121 (1990) 271.
[8] X. Wu, B.C. Gerstein and T.S. King, J. Catalysis 123 (1990) 43.
[9] A.J. Hong, B.J. McHugh, L. Bonneviot, D.E. Resasco, R.S. Weber and G.L. Haller, *Proc. 9th Int. Conf. Catalysis*, eds. M.J. Philips and M. Ternan, Vol. 3 (Chemical Instit. Canada, 1988) p. 1189.
[10] M. Pruski, J.C. Kelzenberg, B.C. Gerstein and T.S. King, J. Am. Chem. Soc. 112 (1990) 4232.
[11] M. Pruski, J.C. Kelzenberg, M. Sprock, B.C. Gerstein and T.S. King, Colloids and Surfaces 45 (1990) 39.
[12] M.W. Smale and T.S. King, J. Catal. 119 (1989) 441.
[13] M.W. Smale and T.S. King, J. Catal. 120 (1990) 335.
[14] J.C. Kelzenberg and T.S. King, J. Catal. 126 (1990).
[15] B.C. Gerstein, R.G. Pembleton, R.C. Wilson and L.M. Ryan, J. Chem. Phys. 66 (1977) 361.
[16] H. Tanaka, T. Terao and T. Hashi, J. Phys. Soc. Japan 39 (1975) 835.
[17] H. Tanaka and T. Hashi, J. Phys. Soc. Japan 39 (1975) 1139.
[18] W.P. Aue, E. Bertholdi and R.R. Ernst, J. Chem. Phys. 64 (1976) 2229.
[19] G. Bodenhausen, Prog. NMR Spectroscopy 14 (1983) 137.
[20] D. Weitekamp, Adv. Magn. Res. 11 (1983) 111.
[21] G. Drobny, Ann. Rev. Phys. Chem. 26 (1985) 451.
[22] Y.S. Yen and A. Pines, J. Chem. Phys. 78 (1983) 3579.
[23] J. Baum, M. Munowitz, A.N. Garroway and A. Pines, J. Chem. Phys. 83 (1983) 2015.
[24] M. Munowitz and A. Pines, Adv. Chem. Phys. 1986 (1986) 1.
[25] P-K Wang, C.P. Slichter and J. Sinfelt, Phys. Rev. Lett. 53 (1984) 82.
[26] Suggested to us by M. Goldman, and essentially identical to one used by D.N. Shykind, J. Baum, S.-B. Liu and A. Pines, J. Magn. Res. 76 (1988) 149.
[27] I.D. Gay, J. Catal. 80 (1983) 231.
[28] B.C. Gerstein, Jin-Woo Han, Son-Jong Hwang, Pan Hong-Jun and H. Skank, Rev. Sci. Instr. 61 (1990) 2349.
[29] R.A. Grubbs, A Miyashita, M. Liu and P.J. Burk, J. Am. Chem. Soc. 100 (1978) 2418.
[30] R.H. Grubbs and A. Miyashita, J. Am. Chem. Soc. 100 (1978) 1300.
[31] S.J. McClain, C.D. Wood and R.R. Schrock, J. Am. Chem. Soc. 99 (1977) 3519.
[32] J.R. Engstrom, D.W. Goodman and W.H. Weinberg, J. Am. Chem. Soc. 110 (1988) 8305.
[33] P. Basu and J.T. Yates, J. Phys. Chem. 93 (1989) 2028.