In Situ NMR Observation of a π-Allylic Intermediate on Zinc Oxide Catalyst

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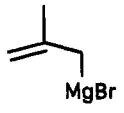
Amorphous metal oxides with basic or amphoteric surfaces are active catalysts for a variety of important reactions including olefin isomerization, hydrogenation, and functional group elimination.[1,2] For example, 1-butene is converted to 2-butene on zinc oxide with a very high cis to trans ratio, and this remarkable selectivity was the first implication of an organometallic-like surface π-allylic intermediate. The recent in situ NMR[3] observation that the weakly acidic probe molecule nitromethane chemisorbed on basic MgO as the anion[4] prompted us to consider whether even more weakly acidic compounds such as olefins, terminal alkynes, and nitriles would yield chemisorbed species on metal oxides that could be regarded as either formal carbanions or organometallic surface species. We were especially interested in the NMR characterization of species proposed as intermediates in heterogenous catalysis.

Carbanion-like organometallic compounds[5,6] can be formed from a variety of metals, and their structures and reactivities in solution are of great synthetic and theoretical interest. A number of different bonding modes are possible depending on the metal, solvent, and state of aggregation.[5–8] These include the η^1 (σ-allyl) structures typified by the Grignard reagent **1**, the σ,π complex represented by solid (2-methylallyl)$_2$Zn (**2**),[6] and the η^3 (π-allyl) structure found for allyl potassium[5] and solid (2-methylallyl)ZnCl (**3**).[6] Although X-ray structures have been determined in exceptional cases, NMR has been the most important probe of the structures and dynamics of these compounds; thus, NMR studies of analogous surface species benefit from the rich literature on stoichiometric compounds.



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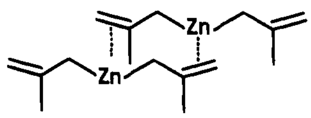

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Various preliminary in situ NMR studies suggest the emergence of a rich metal oxide catalyst surface organometallic chemistry. The 2-methylpropene/ZnO system was selected for the first report for three reasons: The readily observed C_1,C_3 label exchange is an example of olefin isomerization. ^{13}C NMR data were available for solid **3**,[6] a reasonable model compound for the chemisorbed intermediate. Finally, the mechanism of label exchange for propene on ZnO, including a π-allylic intermediate, has precedence in the pioneering infrared studies of Dent and Kokes.[9,10] The zinc oxide sample was the Kadox 15 type, which has previously been used in other catalytic and infrared studies; it has a reported surface area of 8.40 m^2 g^{-1}, and it was activated by a previously reported method.[11,12]

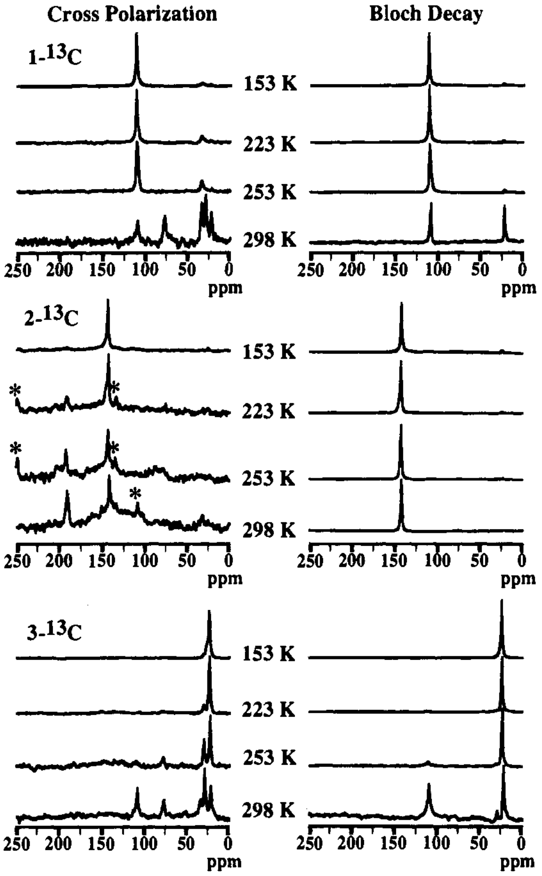

Figure 1. In situ 50.1 MHz ^{13}C MAS solid state NMR spectra of 2-methylpropene undergoing degenerate olefin isomerization on zinc oxide catalyst. The three series of spectra are from parallel experiments in which ca. 1 monolayer each of the 1-^{13}C, 2-^{13}C, and 3-^{13}C isotopomers (CDN Isotopes) reacted. Spectra acquired at higher temperatures (not shown) confirmed that C_1,C_3 exchange proceeded to a statistical distribution of label, while the C_2 label remained isolated even at 523 K. The Bloch decay spectra (90° pulse, 8 s pulse delay, 400 scans) are quantitative, whereas the cross polarization spectra (4 ms contact time, 1 s pulse delay, 400 scans) overemphasized the intensities of the chemisorbed species by up to a factor of 4 and greatly attenuated the signals from mobile, physisorbed olefin. Asteriks denote spinning sidebands in the 2-^{13}C experiment.

Figure 1 reports low-temperature in situ ^{13}C MAS solid state NMR studies of each of the 1-^{13}C, 2-^{13}C, and 3-^{13}C isotopomers of 2-methylpropene on ZnO. Figure 1 shows that a slow exchange of the ^{13}C labels between the C_1 and C_3 positions occurred near room temperature and that the 2-^{13}C position was unaffected by this exchange. Formation of the π-allylic intermediate was signaled by the development of cross polarization[13] signals at 78 and 29 ppm (C_1 and C_3) and 192 ppm (C_2)

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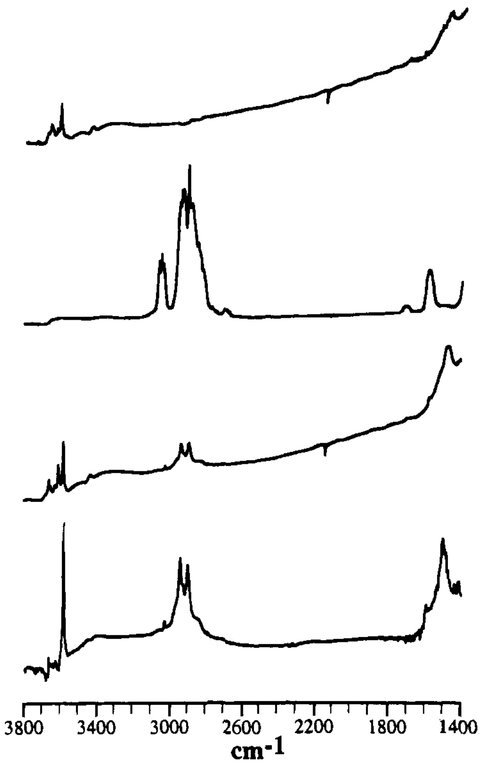
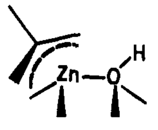


Figure 2. In situ FT infrared study of 2-methylpropene on ZnO catalyst. All spectra were obtained in diffuse reflectance mode at 298 K in a Spectra-Tech catalytic reaction chamber. Spectra shown are (a) that of activated ZnO, (b) that of the catalyst plus an excess of gas phase 2-methylpropene, (c) that after flushing the cell with N_2 at 298 K to remove gas phase and most physisorbed olefin, and (d) the difference spectrum emphasizing signals for chemisorbed species. The key spectral lines include the surface hydroxyl at 3595 cm^{-1} and the characteristic asymmetrical υ(CCC) absorption at 1535 cm^{-1}.

coincident with the onset of olefin isomerization. The 192 and 29 ppm signals survived interrupted decoupling[14] while the 78 ppm did not. Careful comparison of spectra including factors affecting signal intensity allowed the concentration of the intermediate to be estimated at 0.01 monolayer. Additional small signals are consistent with a small amount of dimer formation.[15] The temperature was again reduced to 153 K, and additional spectra (not shown) showed no evidence of dynamical behavior. We conclude that the chemisorbed species is indeed a symmetrical η^3 structure and not η^1 in fast exchange at room temperature.

The 192 ppm ^{13}C shift for C_2 of the intermediate compares favorably with the 207 ppm value for **3** in the solid state.[6] The methyl shift of the intermediate is identical to that for **3**, but the C_1,C_3 shift (78 ppm) is downfield of the typical values measured or calculated for allyllithium compounds[16] or for compound **3**[6] (55 ppm). This difference presumably reflects a characteristic of the structure or electronic properties of the active site that is not well modeled by substituting $ZnCl^+$ for the active site and the remainder of the surface region. Results similar to those presented here have been obtained in preliminary studies of 2-methylpropene on MgO with the exception that the shifts of the intermediate were slightly different. The narrow resonances imply a unique or at least narrow range of structures for the intermediate. The low concentration of the intermediate argues against the active site being a nondefected, low-index plane such as a ZnO pair on the nonpolar $(10\bar{1}0)$ surface,[17] which is known to be an important component of the powdered ZnO surface.[18] Our infrared study of 2-methylpropene on ZnO (Figure 2) supports our NMR assignments and is consistent with earlier IR studies of propene on ZnO[9,10] as well as vibrational spectroscopy of other π-allylic systems.[11] The difference spectrum (Figure 2d) obtained by subtraction of the spectrum of activated ZnO (Figure 2a) from that following adsorption of 2-methylpropene then evacuation (Figure 2c) highlights features due to chemisorption. The sharpness of the O–H stretch at 3595 cm^{-1} indicates that these sites, which are formed by deprotonation of the olefin, are isolated. The C–H stretches at 2972, 2945, and 2920 cm^{-1} are in excellent agreement with the previous work of Dent and Kokes.[10] Finally, the peak at 1535 cm^{-1} is assigned to the asymmetrical υ(CCC) stretch of the π-allylic species.

Our view of the intermediate is that 2-methylpropene is dissociated onto a highly defected ZnO pair (**4**), and the



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coordination of this structure to the rest of the surface is unique but ill characterized. The general features of the investigation reported here were also observed in preliminary NMR studies of propene on metal oxide catalysts.

This study has laid the groundwork for NMR studies of other carbanion-like surface species formed in previously uncharacterized reactions on metal oxides. We also envision the use of 1D and 2D experiments to probe slow exchange between the allylic intermediate and physisorbed olefin. This would constitute a direct measurement of the active site turnover frequency and, in combination with a quantitative measurement of the active site density (from NMR signal intensities), should make it possible to reconcile microscopic and macroscopic measurements of the reaction rate in the same experiment.

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