THE EFFECT OF COPPER ON THE REACTION OF ETHYLENE ON SILICA-SUPPORTED Ru-Cu CATALYSTS AS STUDIED BY ^{13}C NMR

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The adsorption and reaction of ethylene on silica-supported bimetallic Ru-Cu catalysts has been studied by solid state, high-resolution ^{13}C NMR in order to elucidate the effect of copper on the catalytic behavior. Copper itself exhibits no inherent activity for the reaction of ethylene whereas Ru is highly active, producing dimeric products (butenes and butanes) and ethane. The ability to form dimeric products is not changed by the introduction of copper into the metal particles. However, the bimetallic catalysts have significantly less hydrogenation capabilities than the supported monometallic ruthenium catalyst. Since copper is known to populate low-coordination, defect-like lattice positions such as edges and corners, it is postulated that these sites play a crucial role in hydrogenation reactions.

1. Introduction

Binary alloys have been investigated extensively in single-crystal studies and in studies of bimetallic catalysts. Copper and ruthenium are virtually immiscible in the bulk [1], yet bimetallic clusters of these two metals have been used as a model system for numerous reaction studies [2–9]. Several theoretical and experimental studies employing different techniques have provided more information about the surface mixing behavior of Ru-Cu. A recent theoretical investigation suggested that copper will preferentially populate edge and corner, and other defect-like sites, before it begins to cover the low index planes and forms two-dimensional clusters [10]. Experimental evidence for this behavior has been presented by Kim et al. [11] via ultraviolet photoelectron spectroscopy of copper deposited on ruthenium single-crystal surfaces. Furthermore, a recent study of ethane hydrogenolysis over this type of catalyst suggested that the tendency of copper to segregate to structurally distinct sites altered the catalytic behavior [8,12]. This structure sensitive-behavior was explained by proposing that the defect-like sites of the supported ruthenium particles are most active for the desorption of

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hydrogen and the low-index planes are active for the breaking of carbon-carbon bonds. Similar distinct activities between edge and corner, and low-index plane sites have been found by Smith et al. [13], who studied hydrogenation reactions on supported palladium catalysts.

The adsorption and reaction of ethylene on pure ruthenium surfaces has been investigated on single crystals [14–17] employing ultra-high vacuum techniques and on silica-supported ruthenium catalysts via ^{13}C NMR [18]. The NMR experiments led to the identification of several types of chemisorbed species and product molecules experiencing a weak interaction with the catalyst.

This paper reports the results of studies probing the adsorption and reaction of ethylene on silica-supported ruthenium-copper bimetallic catalysts. The objective of this work was to examine the effect of copper as it selectively populated defect-like sites on the surface of the ruthenium particles. The ability to form carbon-carbon bonds did not appear to be altered by the addition of copper to ruthenium, but the hydrogenation reactions were essentially eliminated if enough copper was added to populate defect-like sites.

2. Experimental

Several Ru-Cu/SiO_2 catalysts of varying compositions and a Cu/SiO_2 catalyst were prepared by methods outlined previously [19,20]. The ruthenium loading was kept at 4% by total weight for all ruthenium and ruthenium-copper catalysts. The copper loading for the bimetallic catalysts was varied between 5 and 30 at.% of total metal. The pure copper catalyst had a copper content of 5% by weight. All catalyst samples were supported on Cab-O-Sil HS-5 amorphous, fumed silica (BET surface area of 300 m^2/g). The metal dispersion was approximately 29% for the bimetallic catalysts and about 6% for the pure copper catalyst.

The samples for the NMR experiments were prepared with 80 to 100 mg of catalyst placed in a 5.0-mm Norell XR-55 NMR sample tube. After reduction for 2 hrs at 450°C in 760 Torr hydrogen atmosphere, where the hydrogen was evacuated and replaced every 30 min, the samples were evacuated to a pressure of less than 10^{-5} Torr and then cooled to liquid nitrogen temperature. Ethylene was allowed to adsorb on the catalyst samples at this temperature. The amount of ethylene dosed into each sample was estimated to be approximately 10 molecules of ethylene for each surface metal atom. After adsorption, the sample tubes were sealed using a microtorch. The samples were allowed to warm to room temperature before subsequent analysis.

A series of ^{13}C NMR experiments on a home-built spectrometer operating at 100.06 MHz and 25.16 MHz for ^{1}H and ^{13}C, respectively, was performed. NMR of ^{13}C using cross-polarization (CP) and magic-angle-spinning (MAS) allowed observation of chemisorbed species and product molecules [18]. The product molecules exhibit "liquid-like" motion and consist of either physically adsorbed species or gasphase molecules experiencing restricted motion in the silica pores. Gas phase species outside the pores can also be observed if present in large enough quantities for NMR detection. The spectra shown below were acquired by using strong proton decoupling. All samples were analyzed at various times between 1 day and 1 mo after preparation. A detailed description of the sample preparation method and experimental conditions of the NMR technique has been given previously [18,19].

3. Results and discussion

Figure 1 shows an NMR spectrum obtained earlier in our laboratory in an investigation of single-labeled (99% ^{13}C) ethylene adsorbed on Ru/SiO$_2$ catalysts [18]. The results of the CP/MAS experiments of ethylene dosed onto the bimetallic Cu/SiO$_2$ and Ru-Cu/SiO$_2$ catalysts are represented by the NMR spectra in figs. 2 and 3, respectively.

In the spectrum shown in fig. 1, two types of resonance lines could clearly be distinguished: a group of narrow, Lorentzian peaks and a pair of broad features located between 160 ppm and −50 ppm. The delta scale is used; negative numbers are upfield of the reference TMS. The narrow peaks representing weakly interacting species are located at 126 ± 1 ppm (a), 26 ± 1 ppm (b), 18 ± 1 ppm

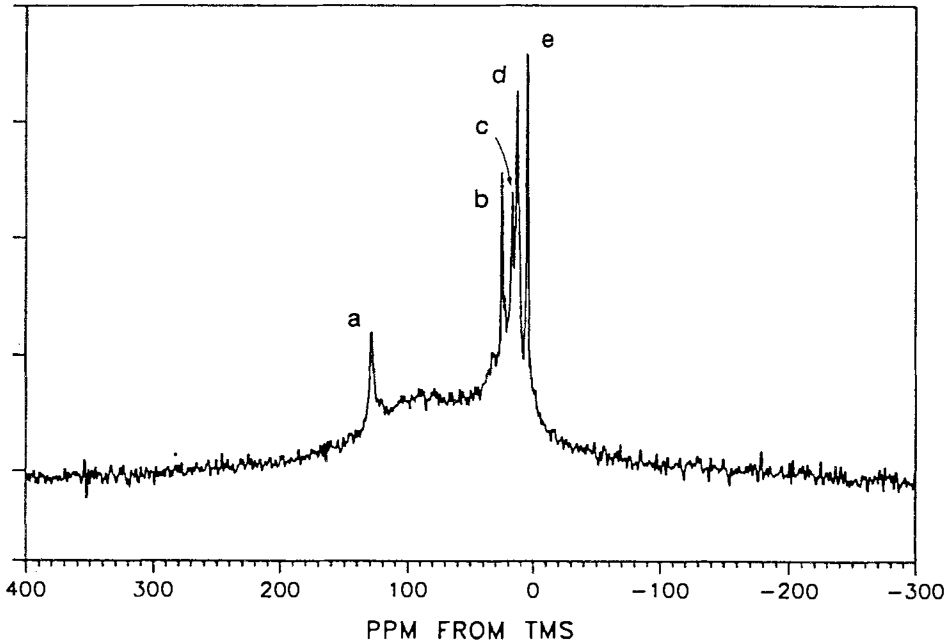

Fig. 1. ^{13}C CP/MAS spectrum of species adsorbed on silica-supported ruthenium as a result of decomposition of ethylene at room temperature for 7 days. The catalyst is 12% by weight ruthenium.

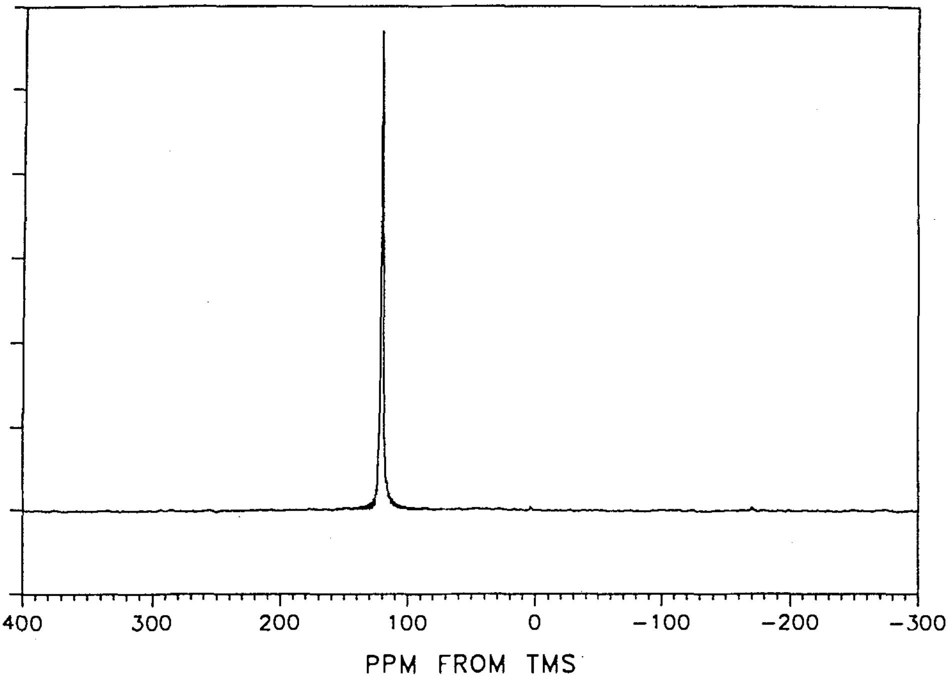

Fig. 2. ^{13}C CP/MAS spectrum of ethylene adsorbed on silica-supported copper.

(c), 14 ± 1 ppm (d), and 6 ± 1 ppm (e). These weakly adsorbed species were identified on the basis of chemical shifts, relative intensities of the NMR lines and J-splittings as (a) a superposition of CH carbons of trans- and cis-2-butene, (b) a CH_2 carbon of butene, (c) a CH_3 group of trans-2-butene, (d) methyl groups in butane and cis-2-butene, and (e) CH_3 groups of ethane [18]. The broad ^{13}C resonances, underlying the sharp signals, represent species chemically bound to the metal. It was suggested [18] that the resonances at ~ 85 ppm represent chemisorbed acetylide, $-C\equiv CH$, the formation of which is also well documented on Ru(001) [14–16] and Ru(1,1,10) [17]. The resonances at 0 to 40 ppm were assigned to various surface attached alkyl groups (e.g., ethyl).

Figure 2 shows the spectrum of ethylene adsorbed on a Cu/SiO_2 catalyst. One resonance was observed at ~ 122 ppm, indicating only highly mobile, molecular ethylene on the catalyst surface. The assignment was made by comparison with a spectrum of ethylene adsorbed on pure silica and by examination of J-splittings. The peak revealed a triplet 1 : 2 : 1 splitting with a J constant of 150 Hz when a spectrum was taken with the proton decoupler off. Another spectrum taken using a Bruker MSL-300 spectrometer (not shown) with slow MAS at 0.5 kHz to remove the broadening due to the anisotropy of the magnetic susceptibility, revealed that in addition to the strong resonance at ~ 122 ppm, a weak resonance was observed with a shift matching the one observed for a sample of gaseous ethylene (121 ppm). This result demonstrates that copper has virtually no activity at room temperature for the reaction of ethylene.

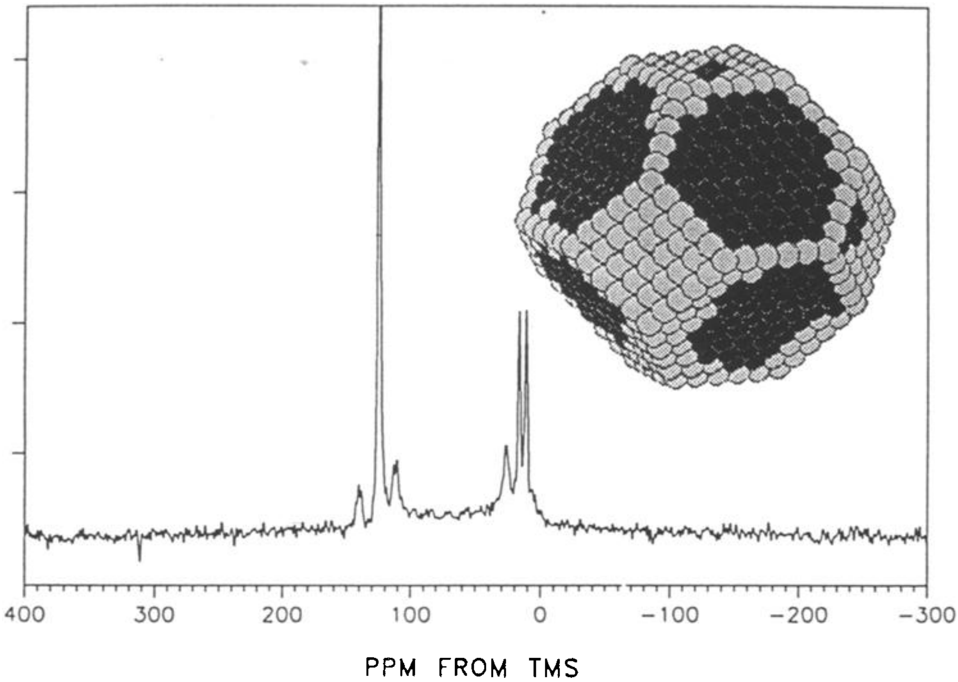

Fig. 3. ^{13}C CP/MAS spectra of species adsorbed on a silica-supported ruthenium-copper bimetallic catalyst as a result of ethylene adsorption and reaction at room temperature for 7 days. The catalyst is 4% by weight ruthenium and copper constitutes 15% (atomic) of the metal. In the schematic representation of a bimetallic particle, the dark atoms are ruthenium.

The NMR spectrum in fig. 3 shows the products of the adsorption and subsequent reaction of ethylene on a bimetallic catalyst with 15 at.% copper. A schematic diagram of the way a bimetallic particle may look is also shown [8,10]. At this copper atomic fraction, essentially all defect-like sites of the metal crystallites are populated by copper atoms [8,10]. A relatively larger amount of butenes was adsorbed on the surface of this catalyst compared to that observed on the pure ruthenium catalyst (fig. 1). Furthermore, no ethane was formed and only very little butane was present in the sample. Another sample with 30 at.% copper showed essentially the same features in the NMR spectrum of ^{13}C. However, a catalyst with a copper atomic fraction of 0.05 (defect-like sites of the metal particles at this composition are only partially populated by copper atoms) showed butenes, butane, and some ethane similar to the result found for the pure ruthenium catalyst (fig. 1). We conclude from these results that the effect of populating the defect-like sites of the ruthenium crystallites with copper atoms is a significant reduction in the hydrogenation capability of the catalyst. In addition, the presence of butenes on the catalyst surface indicates that the formation of dimeric products is not influenced by the population of defect-like sites by copper, suggesting that this formation occurs directly on the basal planes of the ruthenium particles.

For the first time, evidence for the formation of butadiene on supported ruthenium catalysts is given (fig. 3). Two sets of double peaks (114 ppm ± 1 and 139 ± 1 ppm) straddling the peak associated with butenes (126 ppm) are an indication that butadiene is weakly adsorbed in both its cis- and trans-conformation. Similar adsorption behavior for butadiene was also reported by Busca [21] who studied butadiene adsorbed on silica using IR spectroscopy. As is evident from NMR spectra taken without MAS and proton decoupling (not shown), the butadiene is less mobile than ethylene and butenes. The fact that butadiene could only be observed on the bimetallic catalysts and not on the pure ruthenium catalysts suggests that butadiene is a primary product of ethylene adsorbed on the ruthenium surface in the reaction to form other dimeric products like butenes and butane. The hydrogenation of butadiene to butenes and then butane is considerably less facile on the bimetallic catalyst which again suggests that the defect-like sites play a crucial role in this process.

The reason for the reduction in hydrogenation ability as the edge and corner sites are populated by copper is not readily obvious. One possible explanation is that as copper populates edge and corner lattice positions deeply-dehydrogenated species such as acetylide are not produced, and consequently, little hydrogen is available for hydrogenation reactions. We exclude this possibility for two reasons. First, the amount of the strongly adsorbed species per surface ruthenium atom and the chemical nature of these species are not significantly affected by the addition of copper to the catalyst. The spectrum in fig. 3 apparently shows relatively less strongly adsorbed species compared to fig. 1 only because about ten times the amount of ethylene was used in the bimetallic sample. For example, if the intensity of fig. 3 were expanded it would be obvious that the broad resonances associated with the acetylide and other adsorbed species are very similar to those in fig. 1. Second, when gaseous hydrogen is admitted to a ruthenium bimetallic catalyst sample (co-adsorbed) the butadiene is still observed and very little ethane compared to a similarly treated pure ruthenium catalyst is produced.

4. Conclusion

It is shown that the introduction of copper into the metal crystallites of a supported ruthenium catalyst reduces the hydrogenation activity but does not eliminate the ability of the catalyst to form dimeric products. Copper itself proves to be inactive for the reaction of ethylene. After adsorption of ethylene on the metal particles, dimeric products are formed on the basal planes of the bimetallic catalysts. Butadiene is a primary product in this reaction. The hydrogenation of the dimeric products and ethylene is facilitated by edge, corner, or other defect-like sites that are selectively blocked by copper.

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