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n-Butane Hydrogenolysis over Silica-Supported Ru–Cu Catalysts

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The hydrogenolysis of *n*-butane was studied over silica-supported ruthenium and a series of ruthenium–copper catalysts of varying copper content. The catalytic activity and the product selectivities were determined in the temperature range of 413–493 K. The turnover frequency based on the amount of ruthenium at the surface did not vary with copper content, indicating that geometric or ensemble effects were absent. Reaction products were formed via terminal, internal, and multiple carbon–carbon bond scission reactions of the parent molecule. Multiple carbon–carbon bond scission reactions of the adsorbed intermediate which increase the selectivity for lower hydrocarbons have been noted even at the lowest temperature studied. With higher reaction temperatures, the rate of the multiple scission reactions dominated the product selectivities. It is proposed that copper deposited on the ruthenium particles changes the product selectivities by two mechanisms. First, copper decreases the number of multiple splitting reactions by enhancing the desorption rate of the hydrogenolysis products. Second, copper increases the propensity of the hydrogenolysis reaction for a single internal scission reaction, favoring the formation of ethane. The first mechanism is suggested to involve weakly bound hydrogen on the surface which is affected by the presence of copper at the surface of the metal particle. The second mechanism is proposed to involve either a minor electronic interaction between ruthenium and copper or the unique ability of copper to interact strongly with hydrogen but only weakly with carbon, or both.

INTRODUCTION

The investigations of model reactions over supported metal catalysts have received much attention because of the potential to improve the understanding of the functionalities involved in catalytic processes (*1–24*). One class of model reactions is the hydrogenolysis of alkanes over supported monometallic and bimetallic catalysts (*10–24*). While the reaction studies of smaller hydrocarbons such as ethane and propane provide information about the kinetics involved in the breaking of carbon–carbon bonds of essentially the same chemical nature, higher hydrocarbons such as *n*-butane allow the study of product selectivities derived from the scission of different bonds. These bonds are located at the end or in the middle of the reactant molecule and are commonly referred to as terminal and internal carbon–carbon bonds, respectively.

The hydrogenolysis reaction of *n*-butane has been studied over a variety of different unsupported or supported metal and bimetallic catalysts. Kempling and Anderson (*12, 13*) used an alumina-supported ruthenium catalyst to study the reaction of *n*-butane. They reported that the breaking of different carbon–carbon bonds of an *n*-butane molecule proceeded at an equal rate and that the selectivity changed only slightly in the temperature range of 353–398 K. Sarkany *et al.* (*25*), studying alkane hydrogenolysis over ruthenium, rhodium, and iridium blacks, reported that a strong dependence on hydrogen partial pressure exists for the product selectivities. They inferred that strong interactions between dehydrogenated species (formed in the course of the hydrogenolysis reaction) and the metal re-

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sulted in a long residence time on the catalyst surface, leading to multiple scission of carbon–carbon bonds in the adsorbed species. They concluded that under the conditions where multiple scission dominated, product desorption was the rate-limiting step of hydrogenolysis.

An investigation of the effect of catalyst structure on the activity and selectivity in alkane hydrogenolysis reactions was conducted by Guczi *et al.* (*16*). They showed that changes in the catalyst structure caused by the support, impregnating compound, alloying, or poisoning with H_2S for platinum and ruthenium catalysts resulted in a characteristic variation in activity and selectivity for hydrogenolysis reactions. The selectivity for methane was generally decreased with increasing dispersion on the metal particles, suggesting that the carbon–carbon bond scission in the middle position of the butane molecule is enhanced as the metal crystallite size is decreased. This was explained by arguing that on large crystallites the butane molecule has a tendency to be strongly attached to the surface at more than two surface metal atoms. This strong interaction would produce highly dehydrogenated species leading to multiple carbon–carbon bond scission reactions and consequently the formation of methane with high selectivity.

The effect of combining an active metal with an inactive one such as copper, silver, or gold to form a catalytic bimetallic particle has been studied for a variety of reactions and catalysts (*6–9, 19–23, 26–28*). It has been shown that when hydrogenolysis, isomerization, and cyclization reactions are occurring simultaneously (e.g., conversion of *n*-hexane to benzene and smaller alkanes) combining metals to form alloys or bimetallic catalysts can alter selectivity patterns. For example, in the cases of Ni–Cu (*26, 27*) and Pt–Au (*26, 28*) systems, the addition of the second, relatively inactive metal decreased the selectivity for the hydrogenolysis reaction. This was attributed to a geometric or ensemble effect, i.e., the reaction needs large ensembles of contiguous active metal atoms to occur. When these large ensembles are partitioned by alloying, the hydrogenolysis activity decreased more than the activity in the less demanding reactions of isomerization and cyclization. It is interesting to note that for Pt–Cu the opposite effect was observed. In this case, the hydrogenolytic activity increased and the activity for isomerization and cyclization decreased with increasing copper content (*7*).

The changes in product selectivities for the hydrogenolysis of *n*-butane over supported ruthenium and ruthenium–copper catalysts have received little attention (*19, 20*). Bond and Yide (*20*), studying the reversible formation of ruthenium–copper clusters by oxidation and reduction, came to the conclusion that the distribution of products formed from *n*-butane is insensitive to Cu content. Nazimek (*19*) reported that when copper was added to a ruthenium catalyst the selectivity for the reaction products in *n*-butane hydrogenolysis changed significantly. It must be noted that these two investigations were performed at different temperatures, using a differential reactor in one case (*20*) and an integral reactor operating at 80% conversion in the other (*19*).

In this paper we report the results of our study of *n*-butane hydrogenolysis over silica-supported ruthenium and ruthenium–copper catalysts using a laboratory-scale differential microreactor. The effect of copper on the activity and selectivity of this reaction was investigated in an attempt to determine whether the ensemble effect or other synergistic effects are important in the Ru–Cu bimetallic system.

EXPERIMENTAL

Detailed procedure for catalyst preparation has been reported elsewhere (*29*). In short, the catalysts were prepared by incipient wetness impregnation using an amorphous, fumed silica (Cab-O-Sil HS-5) with a surface area of 300 $m^2 g^{-1}$ as the support. Coimpregnation was accomplished from an aqueous solution of $Ru(NO)(NO_3)_3$ and

$Cu(NO_3)_2 \cdot 6H_2O$. The ruthenium loading was kept at 4% by total weight for all catalysts. The copper loading for the bimetallic catalysts was varied between 5 and 45 at.% of total metal. The catalysts were characterized previously using hydrogen chemisorption and nuclear magnetic resonance (NMR) of chemisorbed hydrogen (*29*). The total metal dispersion was approximately 29% for the bimetallic catalysts and 26% for the pure ruthenium catalyst.

n-Butane hydrogenolysis was studied using a continuous flow, tubular microreactor system described elsewhere (*22*). The hydrogen feed was purified using Oxiadsorbent (Alltech) and a molecular sieve trap filled with Davison Molecular Sieve. n-Butane of 99.5% purity (Matheson) was used in the feed without further purification. A typical catalyst bed consisted of 20–80 mg catalyst diluted with 100–200 mesh crystalline silica and had a total volume of 3.0 cm^3. The temperature inside the reactor was monitored via a thermocouple axially inserted in the middle of the catalyst bed. Product analysis was performed by on-line gas chromatography using a Varian 3700 gas chromatogrpah equipped with a thermal conductivity detector and a 6-ft, 80/100 mesh Hayesep Q packed column.

The catalyst was reduced in purified hydrogen with a flow rate of 270 cm^3/min (STP) at 723 K for 2 hr. After the reduction was completed the temperature was lowered over a 2-hr period to the reaction temperature. The feed stream was a mixture consisting of hydrogen (270 cm^3/min) and n-butane (30 cm^3/min) with a molar ratio of 9 : 1. Samples for analysis were taken after 5 min on line except for the deactivation studies, in which numerous samples were analyzed over a period of 10 hr. The reactor was operated at a pressure somewhat about atmospheric pressure and in a temperature range from 413 to 493 K. The conversion was always kept below 10% (in most cases below 5%) to ensure that differential condition was maintained in the reactor.

TABLE 1

Total Metal and Ruthenium Dispersions of Ru and Ru–Cu/SiO_2 Catalysts Measured by Strong Hydrogen Chemisorption and NMR of Protons (*29*)

Cu atomic percent	Total metal[a]	Ru[b]
0.0[c]	0.264	0.264
6.1	0.293	0.258
12.1	0.297	0.233
17.9	0.296	0.070
34.6	0.300	0.024
45.2	0.300	0.018

[a] By volumetric strong hydrogen chemisorption.

[b] By ^1H NMR.

[c] Prepared independently from (*29*).

RESULTS

The reaction rate data are given for the rate of n-butane consumption expressed as moles of n-butane reacted per mole of ruthenium per second and also in terms of the turnover frequency, TOF, with unit of moles of n-butane reacted per mole of surface ruthenium per second. The calculation of turnover frequencies is based on the previously determined ruthenium dispersions for the Ru–Cu bimetallic catalysts reported by Wu *et al.* (*29*) (see Table 1). The same Ru–Cu bimetallic catalysts were used in the present study.

Figure 1a shows the activity of several catalysts as a function of time on line at a reaction temperature of 473 K. All catalysts deactivated noticeably with time, losing about 35–40% of their initial activity within the first 60 min on line. The activities of the Ru–Cu bimetallic catalysts were considerably less than that of the pure Ru catalyst. However, no significant differences in deactivation rates between the pure Ru and the Ru–Cu bimetallic catalysts were observed. In Fig. 1b we show the activity of a silica-supported ruthenium catalyst as a function of time on line at various reaction temperatures. It is noted that deactivation proceeds somewhat faster at the higher temperatures.

The selectivity with which a product is formed in the hydrogenolysis reaction has

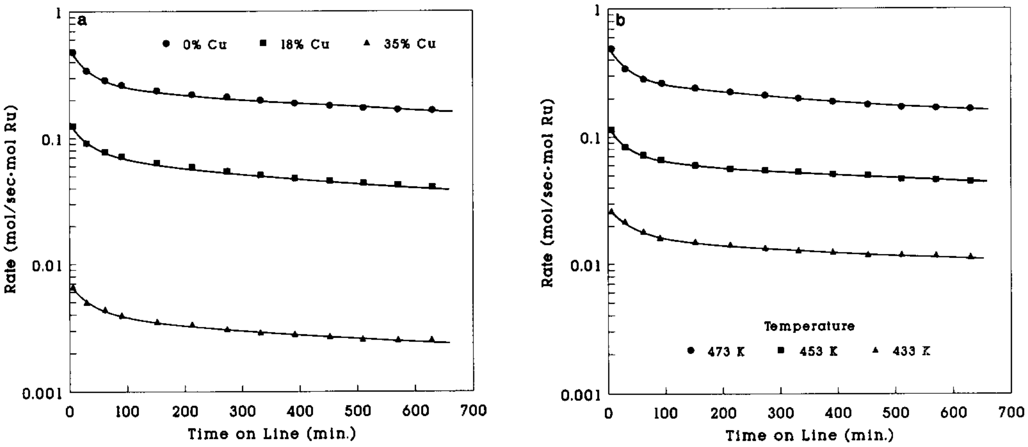

FIG. 1. (a) n-Butane hydrogenolysis activity of a silica-supported Ru catalyst and two Ru–Cu catalysts as a function of time on line at 473 K. (b) n-Butane hydrogenolysis activity of a silica-supported Ru catalyst as a function of time on line at various temperatures.

been calculated in terms of percentage of n-butane reacted. Product selectivities as a function of catalyst deactivation for the pure ruthenium catalyst at a reaction temperature of 473 K are shown in Fig. 2a. The selectivities were virtually independent of the degree of catalyst deactivation, with only minor selectivity changes within the first 100 min on line. This result was qualitatively the same for all the Ru–Cu bimetallic catalysts, as illustrated in Fig. 2b for a bimetallic catalyst with 35 at.% Cu.

Figure 3 shows the activity (rate per total ruthenium) of the catalyst as a function of the copper atomic fraction at several reaction temperatures. We noted a decrease in the catalyst activity with increasing copper content in the composition range of 0–30

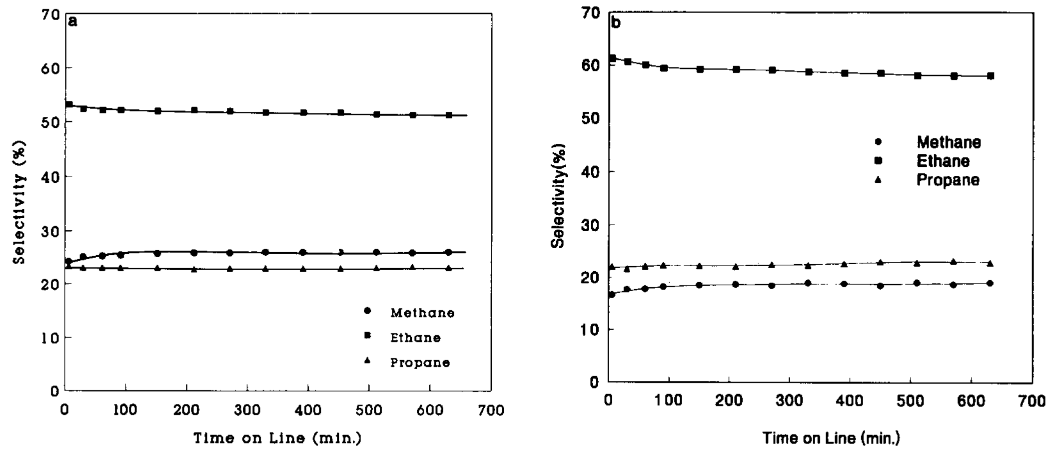

FIG. 2. (a) n-Butane hydrogenolysis product selectivities of a silica-supported Ru catalyst as a function of time on line at 473 K. (b) n-Butane hydrogenolysis product selectivities of a silica-supported Ru–Cu bimetallic catalyst with 35 at.% Cu as a function of time on line at 473 K.

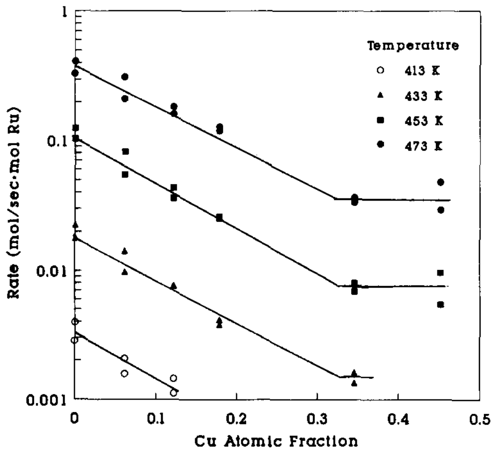

FIG. 3. Rate of n-butane hydrogenolysis per total Ru for silica-supported Ru–Cu catalysts.

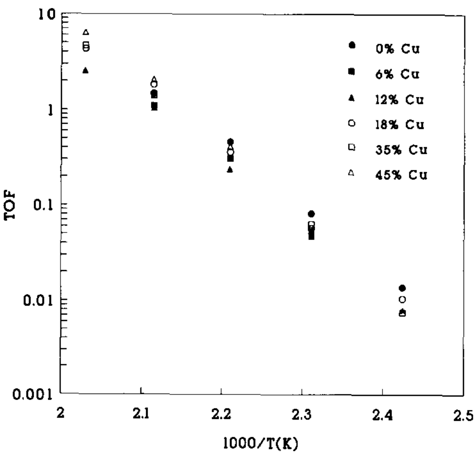

FIG. 5. Arrhenius plots for Ru/SiO_2 and $Ru–Cu/SiO_2$ catalysts.

at.% copper. At the highest copper loadings the reaction rate appeared to be nearly level. The activity expressed as turnover frequency versus the bulk composition of the Ru–Cu bimetallics is plotted in Fig. 4. Note that the turnover frequencies for n-butane hydrogenolysis over supported ruthenium and ruthenium–copper catalysts were essentially independent of the amount of copper. The apparent slight rise in TOF at the higher copper concentrations is not considered significant because of the accumulated experimental errors from both the surface composition measurements and the rate determinations of these relatively inactive catalysts. Figure 5 shows the rate data presented in an Arrhenius plot of turnover frequency versus inverse temperature. The data for the different catalysts are very close together, also indicating that the turnover frequency was essentially independent of the amount of copper. The lines between data points (not drawn) were approximately straight with only a minor curvature at the high-temperature end. The apparent activation energies for the different catalysts within the temperature range of 433–473 K varied between 125–145 kJ/mol with no obvious relationship to the amount of copper.

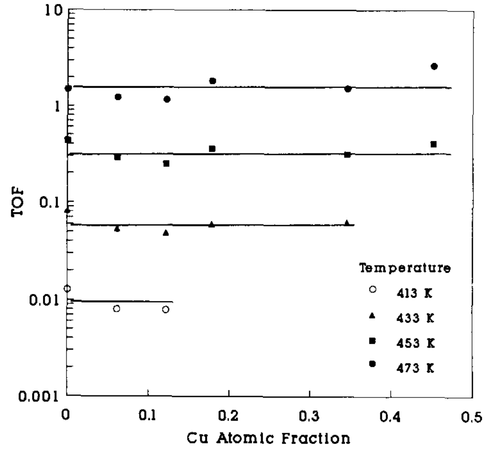

FIG. 4. Rate of n-butane hydrogenolysis per surface Ru as measured by proton NMR.

We conducted a series of experiments at different temperatures and catalyst compositions to investigate the fragmentation pattern for n-butane hydrogenolysis as a function of conversion. The results are represented by the data given in Figs. 6a–6c. These results showed that the product selectivities were almost constant at low conversions (<3%, see Fig. 6a) but exhibited detectable changes as conversion increased, as illustrated in Fig. 6c.

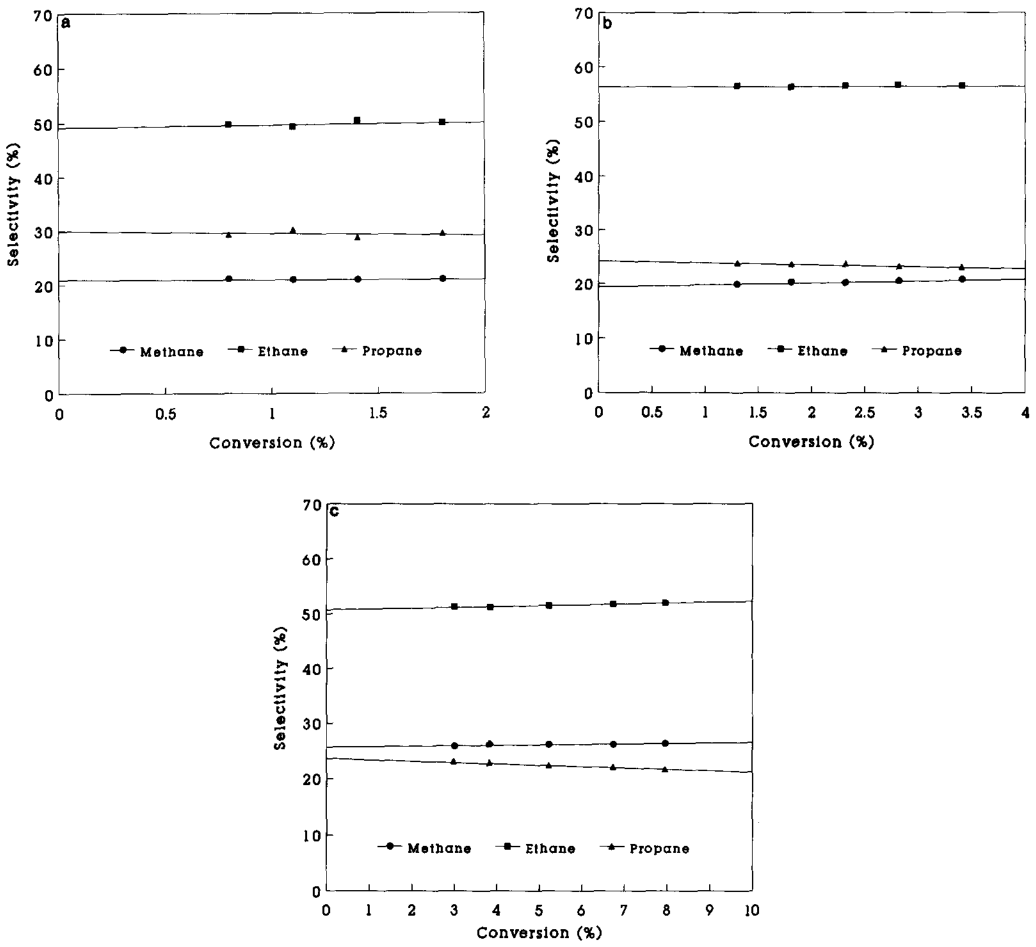

FIG. 6. (a) *n*-Butane hydrogenolysis product selectivities for a silica-supported Ru catalyst as a function of conversion at 443 K. (b) *n*-Butane hydrogenolysis product selectivities for a Ru–Cu catalyst with 18 at.% Cu as a function of conversion at 473 K. (c) *n*-Butane hydrogenolysis product selectivities for a silica-supported Ru catalyst as a function of conversion at 473 K.

The effect of temperature on the fragmentation pattern of *n*-butane hydrogenolysis over supported ruthenium catalysts is shown in Fig. 7. There was an appreciable change in the relative amounts of propane and methane produced. A plot of product selectivity at 453 K versus copper atomic fraction is shown in Fig. 8. The data presented in Figs. 7 and 8 were obtained at low conversions ($\leq 5\%$). Varying the amount of the constituent metals of the catalytic particles changed the product selectivities only modestly. With increasing copper content, the selectivity toward methane was decreased, while the selectivity for ethane formation was increased. However, the selectivity toward propane decreased only slightly.

DISCUSSION

Ru–Cu Crystallites

For the interpretation of the reaction data it is useful to have a model of the bimetallic crystallites in the catalyst. Such an model has been developed previously for face-centered cubic crystals using Monte-Carlo sim-

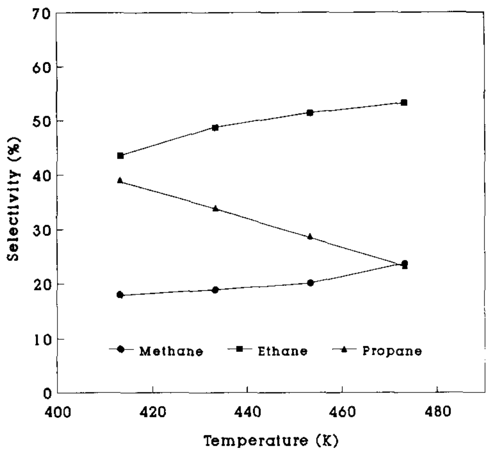

FIG. 7. n-Butane hydrogenolysis product selectivities for a silica-supported Ru catalyst as a function of reaction temperature.

ulations (*9, 22, 30*). The application of the results of this simulation to real catalyst systems has certain limitations which are imposed by the technique. A rigorous discussion about these limitations and its consequences for application to real catalysts has been published elsewhere (*9, 23*). For the purpose of this study, we think simulations serve to give a qualitative picture of the metal crystallites in the catalysts. Results of the Monte-Carlo simulations for the ruthenium–copper system with varying amount of copper have been reported elsewhere (*9, 22*). The simulations suggest that at low copper content copper tends to populate edge, corner, and other defect-like sites at the surface of bimetallic crystallites.

Experimental evidence for this behavior has been presented by Kim *et al.* (*31*) studying copper deposited on ruthenium single-crystal surfaces via ultraviolet photoelectron spectroscopy. If the amount of copper content is further increased the model predicts that copper begins to cover the basal planes and forms two-dimensional islands without breaking up ensembles of ruthenium atoms. This result is consistent with observations of several researchers investigating the deposition of copper on ruthenium single crystals (*32–37*). An important result of the Monte-Carlo simulations and the single-crystal studies is that copper does not atomically mix with ruthenium on the low index planes. Therefore, bimetallic catalysts of these metals should not show geometric effects even if the active site for the reaction is an ensemble of metal atoms.

The preferential deposition of copper on defect-like Ru surface sites could alter the selectivity of certain reactions. A recent ^{13}C NMR investigation in our laboratory (*38, 39*) probing the adsorption and reaction of ethylene over silica-supported ruthenium–copper catalysts found very different product distributions on the catalyst surface depending on the amount of copper deposited on the ruthenium particles. It was observed that with an increasing amount of copper the formation of ethane was greatly reduced but the formation of dimeric products such as butenes and butane was almost unaffected. However, the relative amounts of butenes as compared to a pure ruthenium catalyst increased with the deposition of copper on the ruthenium and in some cases butadiene could be observed on the surface of the bimetallic catalysts. These observations of varied hydrogenation rates for eth-

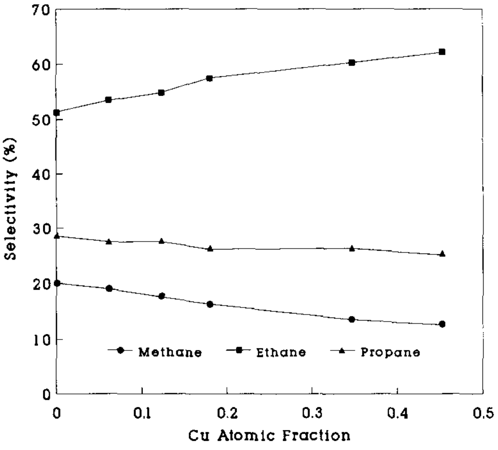

FIG. 8. n-Butane hydrogenolysis product selectivities for silica-supported Ru and Ru–Cu catalysts at 453 K.

ylene and butenes indicated an important role of edge, corner, and other defect-like surface Ru sites.

Activities

Catalyst deactivation in alkane hydrogenolysis is believed to be due to the formation of carbonaceous overlayers which eliminate part of the metal surface from reaction (*40*). The results for catalyst deactivation represented by the data shown in Figs. 1a and 1b indicate that deactivation proceeds slightly faster at higher temperatures on the pure ruthenium catalyst. Significant differences in the deactivation behavior among pure ruthenium catalysts and the various bimetallic ruthenium–copper catalysts are not obvious (Fig. 1a). This result is in contrast to the findings by Bond and Yide (*20*), who reported the same qualitative deactivation behavior with respect to temperature but found bimetallic ruthenium–copper catalysts deactivated more rapidly than the pure ruthenium catalyst. It has also been reported (*41*) that inactive metals such as Cu, Ag, or Au introduced into active metals decrease the deposition of carbonaceous overlayers. However, the findings for the deactivation in *n*-butane hydrogenolysis in this study suggest that no significant differences exist between ruthenium and ruthenium–copper catalysts at the temperatures studied. This result is consistent with observations made earlier in an independent study of the reaction and decomposition of ethylene on supported ruthenium and ruthenium–copper catalysts (*38, 39*), where the product distribution on both types of catalysts was distinctly different, although no apparent differences were observed in the amount and nature of the strongly adsorbed, highly dehydrogenated species. It is not clear whether the deposition of carbonaceous overlayers is preferential or indiscriminate on different Ru sites. However, since we observed constant selectivities during deactivation for both Ru and Ru–Cu catalysts, we can only infer that deposition of carbonaceous overlayers does not alter significantly the relative concentration of reaction intermediates on all Ru sites at the conditions of this study.

Alkane hydrogenolysis reactions are commonly considered to be demanding reactions, i.e., requiring large ensembles of contiguous metal atoms to form an active site (*17, 20, 21, 26*). However, as discussed earlier, copper and ruthenium are not expected to atomically mix on the low index planes of the metal crystallites. Consequently, catalysts of these metals should not show geometric effects even if a larger ensemble of ruthenium atoms is required to form the active site for the hydrogenolysis reaction. Smale and King (*22, 23*), studying ethane hydrogenolysis over supported ruthenium and ruthenium–copper catalysts, found that after the edge, corner, and other defect-like sites of the metal particles are populated by copper no change in the TOF could be observed upon further increasing the amount of copper in the particles. In other words, no geometric effects were noted. The activity changes in the lower copper concentration range (0–18 at.% Cu) were attributed to differences in the hydrogen adsorption/desorption capabilities of copper and ruthenium.

If we consider the results for the activity of the *n*-butane hydrogenolysis in terms of the turnover frequency (Fig. 3) we note that the activity does not change significantly with varying amounts of copper deposited on the ruthenium particles. This result is in qualitative agreement with the findings by Smale and King (*22, 23*) for ethane hydrogenolysis. However, ethane hydrogenolysis exhibits a characteristic variation in the activity over the copper composition range of approximately 0–18 at.%. We discussed earlier that within this composition range copper populates the edge, corner, and other defect-like sites of the ruthenium particles. Smale and King proposed that copper blocks ruthenium lattice positions on which dissociatively adsorbed hydrogen recombines and desorbs. Through this blocking mechanism the effective hydrogen concentration on the metal particles would inhibit the hydrogenolysis reaction, which has a strong negative order of reaction with respect to hydrogen by reducing the rate at which weakly bound hydrogen could be shuttled to and from the adsorbed hydrocarbon fragment. Similar changes in the hydrogenolytic activity in the lower copper composition range were not observed for *n*-butane hydrogenolysis in this study. This can be explained by a much less negative order of reaction for hydrogen in *n*-butane hydrogenolysis. In fact, under certain reaction conditions slightly negative (−0.2 to 0) to strongly positive (0.55 to 0.8) hydrogen orders of reaction have been reported (*1, 19, 42*). We conclude therefore that *n*-butane hydrogenolysis over supported ruthenium and ruthenium–copper catalysts is not strongly influenced by the relative population of edge, corner and other defect-like sites, i.e., a structure-sensitive effect is also not observed. This result is in contrast to the ethane hydrogenolysis results we reported earlier (*22*), in which we observed a structure-sensitive effect in the Ru–Cu system. The lack of structure sensitivity for the *n*-butane hydrogenolysis may be a result of a decreased difference in bonding strength between the adsorbed reaction intermediates and various Ru sites on carbonaceous-overlayer sites due to the presence of electron-donating methyl and ethyl groups in the adsorbed species.

Selectivities

For *n*-butane hydrogenolysis three types of scission reactions for the adsorbed C_4 species (*40*) are possible: (1) terminal splitting forming methane and propane; (2) internal splitting forming only ethane; and (3) multiple splitting forming only methane or both methane and ethane. The selectivities in *n*-butane hydrogenolysis reactions are determined by the cracking pattern of the parent *n*-butane molecule with the above analysis and possibly also by the extent of cracking with sequential scission of the C_3 and C_2 surface species as well as readsorption/desportion of lower alkane molecules, as suggested in the Kempling–Anderson mechanism (*13*). Therefore it must be established whether subsequent sequential reactions of intermediate products are significant in this study. The results presented in Figs. 6a–6c indicate that the product selectivities were virtually unchanged with conversion (at low conversions, <3%), suggesting that sequential reactions due to readsorption are insignificant under these conditions and the measured selectivities are the initial selectivities from the splitting of the parent *n*-butane molecule. At relatively higher conversions (3–10%) (Fig. 6c) we observed modest increases in the selectivities toward methane and ethane with increasing conversion. However, the changes in the product selectivities at conversions up to 10% are much less than the variations caused by changing the temperature and by the introduction of copper into the metal crystallites. *n*-Butane is more active for the hydrogenolysis reaction than either propane or ethane, and hence it is not surprising that we observe little readsorption and reaction of the partially cracked product molecules. There is also the potential for the adsorbed surface reaction products (e.g., a C_3 species) to undergo a subsequent carbon–carbon bond cleavage (*13*) in a "rake-like" mechanism. However, this mechanistic view is at odds with the understanding that the rate-limiting step in alkane hydrogenolysis is the carbon–carbon bond cleavage reaction (*43–46*). The adsorbed product species hydrogenate rapidly to form the gas-phase alkane product. Given the absence of sequential reactions, the nonmechanistic analysis employed by van Broekhoven and Ponec (*40*) describing the three general types of bond splitting reactions noted above seems reasonable.

An important result of the deactivation studies that were discussed earlier is the effect of catalyst deactivation on the selectivity of the hydrogenolysis reaction (see Figs. 2a and 2b). We noted only minor changes in the selectivity of the reaction within the first 60 min on line. This result is especially important when considering that the catalyst loses about 35–40% of its initial activity within this time frame. Therefore, it is concluded that the selectivity of the *n*-butane hydrogenolysis reaction over ruthenium and ruthenium–copper catalysts is independent of catalyst deactivation.

In the absence of sequential reactions of intermediate hydrogenolysis products, changes in the product selectivities with reaction temperature, or catalyst composition must result from changes in the intrinsic rate for the primary formation of the products propane, ethane, and methane. Work by Huang and Ekerdt (*47*), using a reactive scavenging technique to test for the presence of alkyl species in the reaction of *n*-butane and *n*-butene over a supported ruthenium catalyst, indicated that *n*-butane adsorbs on the ruthenium surface as *n*-butyl and *sec*-butyl species. These species are possible intermediates in the reaction to form the hydrogenolysis products. Their result suggests that it is possible that the formation of propane and ethane proceeds independently from one another through different reaction intermediates.

To investigate the extent to which the above-mentioned three reactions contribute we need to consider relative changes in the product selectivities and also if certain stoichiometric selectivity ratios are met. For example, in the absence of multiple scission reactions the selectivity ratio of methane to propane (percent of converted butane that forms methane to the percent that forms propane) must be 1/3 according to the terminal scission reaction. (Note that this analysis assumes that sequential hydrogenolysis of intermediate products does not occur as discussed above.) If we investigate the data presented in Fig. 7 according to this criterion we find that at any temperature the ratio noted above exceeds 1/3 and increases exponentially with increasing temperature. We conclude that within the temperature range reported in this study a significant number of multiple scission reactions occurs in the conversion of *n*-butane over supported ruthenium catalysts. Investigation of the bimetallic ruthenium–copper catalysts at the various temperatures led to the same result (see Fig. 2b).

Changes in the product selectivities with increasing amount of copper (shown in Fig. 8) are moderate. There was a decrease in the selectivity toward the formation of propane and an increase toward the formation of ethane as more copper was added to the ruthenium catalyst. This observation suggests a relative increase in internal splitting reactions. The same observation with respect to terminal or internal splitting of carbon–carbon bonds in alkanes was reported by Ponec and Sachtler (*27*) for copper–nickel catalysts.

If one assumes that the 1,2-adsorbed and the 2,3-adsorbed C_4 species are the two major reaction intermediates, as proposed by Bond *et al.* (*48*) for pure ruthenium catalysts, the observed shift from terminal to internal splitting suggests that the Ru–Cu bimetallic surfaces favors the adsorption of the 2,3-intermediate over the 1,2-intermediate as compared with the pure ruthenium surfaces. There are two possible explanations for this phenomenon. First, the surface ruthenium sites may be perturbed electronically by neighboring copper atoms, causing a relative electron deficiency compared with pure ruthenium sites. This minor electronic perturbation between ruthenium and copper has been noted in a previous study by Wu *et al.* (*29*) using NMR of chemisorbed hydrogen, and also in two Cu/Ru(001) single-crystal studies (*37, 49*) using UPS. Since two methyl groups provide a more effective electron donation than a single ethyl group to the two carbon atoms bound to the ruthenium site, the 2,3-adsorbed species is expected to be relatively more abundant at the Ru–Cu bimetallic surfaces. The second explanation is that the presence of copper sites on Ru–Cu surfaces favors the formation of the 2,3-adsorbed species over the 1,2-adsorbed species. Copper atoms deposited on Ru surfaces are capable of chemisorbing hydrogen, as shown by the same proton NMR study (*29*). Copper is known to interact only weakly with carbon, however. Therefore, vacant surface copper atoms are likely to extract hydrogen from either the CH_3– or the –CH_2– group of a butane molecule during the formation of the intermediates on adjacent ruthenium sites. Since the C–H bond in the –CH_2– group is relatively weaker than the one in the CH_3– group, the formation of 2,3-adsorbed C_4 intermediate is favored. However, it is possible that both factors could play a role in the changes of product selectivities.

A second effect of the increase in copper content is noted by comparing the change in the selectivity for methane (Fig. 8) to the change one would expect as a result of the decrease in propane selectivity. The decrease in methane selectivity from approximately 20 to 12.5% for a 0 and a 45 at.% copper catalyst, respectively, far exceeds the expected stoichiometric decrease relative to propane. We can conclude from this observation that in addition to the shift from the terminal to the internal splitting reaction, the introduction of copper into the catalytic particles effectively inhibits multiple scission. The mechanism through which this inhibition of multiple scission reactions proceeds is most likely associated with the abundance of hydrogen adsorbed on the metal surface, especially weakly bound, highly reactive atomic hydrogen. We have already discussed that copper preferentially populates ruthenium lattice positions (edge, corner, and other defect-like sites) which facilitate recombination and desorption of hydrogen and argued that through this mechanism the effective concentration of hydrogen on the basal planes of the ruthenium is increased at steady-state reaction conditions by simply inhibiting its desorption (*23*). Therefore, it is proposed that with increasing hydrogen concentration on the catalyst surface adsorbed fragments which result from the fragmentation of the parent molecule are scavenged from the metal surface through hydrogenation to alkanes. In fact, the same inhibition of multiple scission reactions through an increase in hydrogen concentration on metal surfaces has been found by Coq *et al.* (*50*). They studied the conversion of various alkanes over alumina-supported ruthenium catalysts of varying dispersion. An important result of their study was that when the hydrogen partial pressure was increased, a decrease in the multiple scission reaction was observed. Furthermore, Coq *et al.* found that the apparent hydrogen order of reaction was strongly correlated with the amount of multiple scission reactions dropping from relatively high values (−0.5 to 0) when deep hydrogenolysis prevailed to strongly negative values (−2 to −1) when multiple scission reactions were decreased by increasing hydrogen pressure. They concluded that with more multiple scission, there is a less negative effect of hydrogen on the activity of the hydrogenolysis reaction. With decreasing multiple scissions only the negative effect of competition for site coverage between hydrogen and alkanes was retained. Their result fully explains the apparent disagreement in the literature with respect to apparent hydrogen orders of reaction for *n*-butane hydrogenolysis (*12, 14, 15, 19*).

We did not determine the apparent order of reaction with respect to hydrogen for the catalysts used in this study because the rapid loss of catalytic activity with lower hydrogen partial pressures makes this determination imprecise. However, the fact that we did not observe the same variation in *n*-butane hydrogenolysis activity at low copper coverages as reported for ethane (*22, 23*) and the result that multiple scission reactions were present suggests that the hydrogen order of reaction for *n*-butane hydrogenolysis in this study was approaching zero. We would expect that the hydorgen order of reaction decreases as the amount of copper on the ruthenium particles is increased, since we observed a significant reduction in the number of multiple scission reactions.

CONCLUSION

The investigation of the activity of *n*-butane hydrogenolysis over well-defined, chlorine-free, silica-supported ruthenium and ruthenium–copper catalysts revealed no geometric effect for this particular reaction.

The product selectivities were characterized by terminal, internal, and multiple splitting reactions occurring simultaneously on the catalyst surface. While the deactivation of the catalyst during reaction appeared to have no effect on the product selectivities, reaction temperature and the addition of copper into the catalytic system changed the product selectivities significantly. As temperature increased the number of multiple scission reactions increased greatly, shifting the product distribution toward ethane and methane. It is proposed that the deposition of copper onto the ruthenium particles increases the product selectivity for ethane by two different mechanisms. First, copper reduces the number of multiple scission reactions on the catalyst surface thereby increasing the yield of ethane and propane. This mechanism is possibly due to a site blocking effect by copper, inhibiting the desorption of hydrogen from the ruthenium surface which in turn promotes the desorption of product molecules without undergoing further carbon–carbon bond splitting. Second, copper increases the propensity of the catalyst for the internal splitting reaction producing ethane only. This mechanism is likely to involve either a minor electronic interaction between ruthenium and copper or the unique ability of copper to interact strongly with hydrogen but only weakly with carbon, or both, such that the formation of the 2,3-adsorbed C_4 intermediate is favored.

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