

NOTES

Cyclopropane Hydrogenolysis Reactions over Ni-Cu/SiO₂ Catalysts

Cyclopropane (CP) hydrogenolysis activities and selectivity to ring opening were studied over a series of well-characterized Ni-Cu/SiO₂ catalysts (1). These reactions have been used before to study ensemble and ligand effects (2-4), but surface composition estimates for supported Ni-Cu catalysts have not been available. Magnetic, adsorptive, and coupled magnetic-adsorptive analyses were used to estimate the average crystallite size and surface composition for each catalyst (1). The magnetic phase composition does not change upon addition of copper to nickel, above a few percents copper, indicating that copper enriches the surface of each crystallite. The "cherry" model (2) is convenient for visualization. However, it is important to account for mass balance limitations in highly dispersed systems, as there is not enough copper to envelop the crystallites (1, 5, 6). This results in more gradual changes in surface composition than observed for bulk Ni-Cu alloys (2, 7), and may account for the conclusion of homogeneity in other work on supported Ni-Cu (8). Details of catalyst preparation and characterization, as well as a discussion of the assumptions used to estimate surface composition, are presented in Ref. (1).

Table 1 lists the sample average surface composition of each catalyst sample with the corresponding nominal composition and average crystallite size. These surface compositions are reproducible between samples to within ± 0.04 . There has been no report of significant crystallite size effects for cyclopropane and hydrogen reactions over nickel in the size range of this work. However, a crystallite size-dependent surface composition, inherent in mass balance-

limited enrichment, creates a crystallite size effect. Due to the distribution of crystallite sizes within samples, any surface composition-dependent property will be an average. In order to limit the impact of this size effect on conclusions, the average crystallite size of each sample was kept close. Also, the breadth of the crystallite size distribution apparently does not depend significantly on copper content (1).

Kinetic work was performed on the unperturbed catalyst samples, after *quasi in situ* characterizations, in the same sample cell/reactor (1). The reactions were run in differential mode for ease of analysis as well as to minimize thermal effects and the impact of flow maldistribution (9). The pressure was slightly above 1 atm, as required for flow, with the CP pressure kept at 0.1 atm. Thus the ratio of H₂ to CP was at least 10. The temperature was 298 K. Standard criteria for no interferences due to temperature and/or concentration gradients are well satisfied (9). After kinetics, the catalyst samples were studied magnetically to verify that redistribution of the metals had not taken place. This does not provide a check against surface rearrangement; however, the distribution of surface atoms is not known anyway.

Areal rates, per square meter of nickel determined by H₂ chemisorption assuming an H:Ni ratio of one (1), for ring opening and fragmentation were determined for each catalyst by measuring conversion to propane and ethane, respectively. Selectivity to ring opening was determined from the ratio of propane to ethane produced, and any error in surface area cancels. Conversions were recorded after they had stabilized, and reproducibility of kinetics results

TABLE 1
Surface Fraction Copper

Nominal Cu ^a (%)	Metal loading ^b (%)	Average crystallite size ^c (nm)	Surface fraction Cu ^d
0.0	22.9	2.1	0.0
2.6	25.1	1.9	0.18
6.0	25.3	1.9	0.35
12.0	27.9	1.9	0.48
21.1	27.1	2.0	0.59
31.1	27.2	1.9	0.73
39.8	21.6	1.5	0.78

^a $\text{Cu}/(\text{Cu} + \text{Ni}) \times 100$.

^b $(\text{Ni} + \text{Cu})/(\text{Ni} + \text{Cu} + \text{SiO}_2) \times 100$.

^c Equivalent hemispherical radius, determined as detailed in Ref. (1).

^d Taken to be the dispersion adjusted specific area ratio estimated as in Ref. (1).

between samples was within 10%. Fragmentation rates for Ni/SiO₂ from Fig. 1 are about 10% higher than those of Sinfelt *et al.* (10), when their rate form is used to adjust operating conditions, while the rate for ring opening is about twice their reported value. The last disparity may reflect lower self-poisoning in this study; nevertheless, the agreement is good.

Fragmentation trends upon dilution by copper compare well with those in the literature, showing a rapid decrease in activity (2, 3). No maximum in ring opening at low copper content was found, which again indicates that self-poisoning was small (11). This is expected with the operating conditions used. The decline in areal rate indicates that large-scale clustering of surface nickel atoms does not exist. However, some clustering at higher copper content is indicated, and is expected for the endothermic Ni-Cu system (12). The decrease in activities may also indicate that copper selectively occupies the more active sites. Certainly copper would tend to occupy the sites of lower coordination. As no information is available in this regard, each original site is assumed to be uniform in activity. The increase in selectivity to ring opening

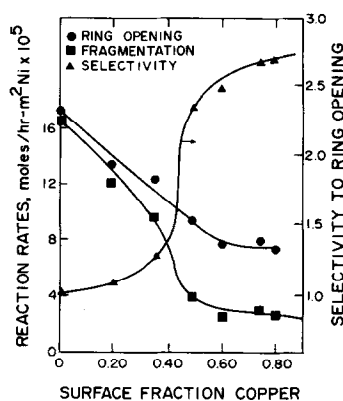


FIG. 1. The areal rates of ring opening and fragmentation, and selectivity to ring opening, against surface copper content.

by a factor of 2.5 is in good agreement with the results of Beelen *et al.* (13) on bulk Ni-Cu catalysts.

Figure 2 shows the activities normalized to total metal area, rather than nickel area, against surface copper fraction. The graph has been scaled to run from 0 to 1. This type of graph is often used for determining required ensemble size (2, 14). Assuming activity is determined by the geometric effects of dilution and random surfaces, then:

$$A(y) = A(0)(1 - y)^N, \quad (1)$$

where A is activity, y is the surface fraction of copper, and N is interpreted as the nickel ensemble size required for a given reaction. Within the accuracy of the data, the curve for $N = 2$ fits the ring opening results, while $N = 3$ fits the results for fragmentation. Accepting the surface composition estimates, clustering apparently occurs in the higher-copper-content catalysts, keeping the activities higher than those of a random surface. A common diadsorbed intermediate is indicated, as suggested by Anderson and Avery (15), with the availability of a third site required for further adsorption and fragmentation.

The ensemble effect explains the activity trends observed in this study, in line with past work on Ni-Cu (2-4). Accounting for mass balance-limited enrichment in the de-

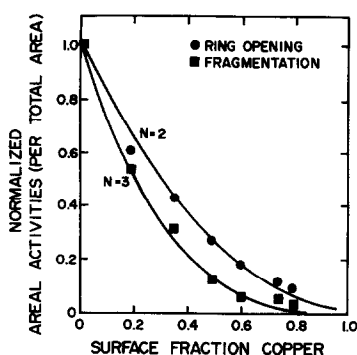


FIG. 2. Normalized areal rates (based on total metal area) for ring opening and fragmentation, for the determination of ensemble size.

termination of surface composition was critical for this interpretation. Considering the size effect on surface composition inherent in mass balance-limited enrichment and an unknown extent of clustering, the fits in Fig. 2 are remarkable. In fact, these results help to justify the assumptions used in calculating surface compositions. The extent of any ligand effect cannot be assessed with the data available, which is usual (3).

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