

## Intrinsic Effect of Cu on the Selectivity shown by Supported Pt/Cu Alloy Catalysts in the Hydrogenolysis of n-Hexane

Adrianus J. den Hartog, Paul J. M. Rek, and Vladimir Ponec\*

Gorlaeus Laboratories, Leiden University P.O. box 9502, 2300 RA Leiden, The Netherlands

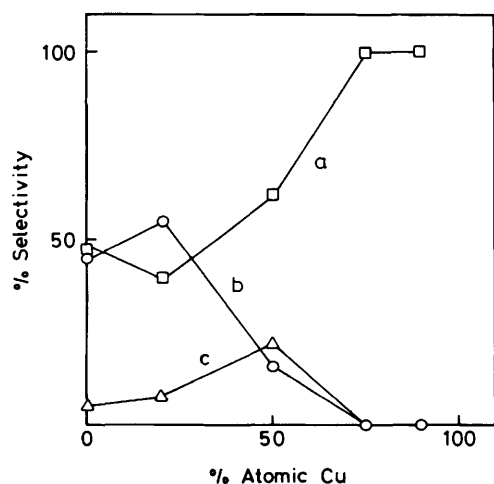
The effects of Pt/Cu/SiO<sub>2</sub> catalysts on n-hexane/H<sub>2</sub> reactions were studied; a pulsed flow system was used in order to determine possible effects of carbonaceous deposits and it was found that the increase in the hydrogenolysis selectivity was not carbon induced.

In hydrocarbon reactions, alloy catalysts play an important role in the determination of the factors that govern selectivity patterns.<sup>1</sup>

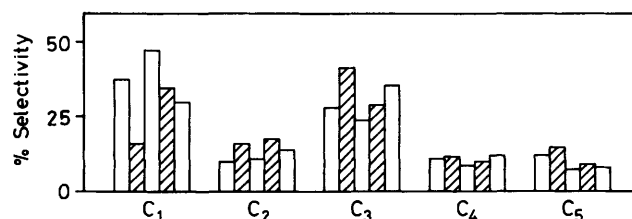
It has been shown that combining or alloying an active group VIII metal with an inactive group Ib metal often results in a decrease in the selectivity of hydrogenolysis. This has been demonstrated for systems like Ni/Cu<sup>1,2</sup> and Pt/Au.<sup>1,3</sup> This decrease in the hydrogenolysis selectivity was explained

by assuming that hydrogenolysis is a demanding reaction, *i.e.* the reaction needs large ensembles of contiguous active metal atoms to occur.<sup>1,4</sup> When these large ensembles are removed by alloying, hydrogenolytic activity decreases more than the activity in the less demanding isomerization and cyclization reactions.

However, with Pt/Cu,<sup>5</sup> and more recently with Ir/Cu,<sup>6</sup> it has been demonstrated that the opposite trend is found. Addition of Cu to Pt or Ir results in an increase in the hydrogenolytic selectivity. It has been suggested that this effect is related to the operation of so called mixed ensembles. In these mixed ensembles, both the Pt (or Ir) and the Cu should play an active role in hydrogenolysis of the hydrocarbon. However the authors,<sup>5,6</sup> could not exclude that the increase in hydrogenolysis was due in part to the effect of Cu on the deposition of carbonaceous layers. Deposition of carbonaceous species is known to suppress demanding reactions,<sup>7</sup> and since addition



**Figure 1.** Group selectivities for a series of Pt/Cu catalysts vs. the % of Cu atoms in the alloys. Reaction temp. = 625 K. (a) Hydrogenolysis (□); (b) isomerization (○); (c) dehydrocyclization (△).



**Figure 2.** Fission pattern for the Pt and Pt/Cu alloy catalysts. Selectivities normalized to 100. Reaction temp. = 625 K. First bar: 100% Pt; second bar: Pt/Cu = 4:1; third bar: Pt/Cu = 1:1; fourth bar: Pt/Cu = 1:3; fifth bar: Pt/Cu = 1:8.

of Cu, Au, or Ag results in a decrease in the deposition of carbonaceous layers,<sup>8</sup> hydrogenolysis could be promoted by this effect.

In order to check the latter effect, Pt/Cu catalysts were studied in the reaction of n-hexane using a pulsed flow apparatus.<sup>9</sup> Small pulses of n-hexane/H<sub>2</sub> (50 µl) were fed over the catalyst. Products were frozen in liquid N<sub>2</sub> prior to the g.c. analysis and injected into the g.c. after all products had been collected (some of the products, especially the hydrogenolytic products desorb slowly from the catalyst surface). A continuous flow of H<sub>2</sub> was led over the catalyst (pressure = 2.7 atm.). The Pt/Cu/SiO<sub>2</sub> catalysts were prepared using a classical impregnation method.<sup>5</sup> The definition of the various selectivities is described elsewhere.<sup>5</sup> During the first pulses an irreversible adsorption of the n-hexane takes place. At the end of this period the ratio of the number of carbon atoms retained to the total number of surface atoms is <0.05. In all cases studied the selectivity stays constant from the very first pulse.

The results obtained with a series of Pt/Cu catalysts are presented in Figure 1. It is obvious that addition of Cu to the Pt/SiO<sub>2</sub> results in an increase in the hydrogenolysis selectivity, also in a pulse regime. As already mentioned, the selectivity does not change when more pulses are led over the same catalysts, and the total activity changes only marginally. Similar to the results from the continuous flow experiments, the activity decreases strongly when Cu is added.

Addition of Cu to supported metal catalysts results in changes in the cracking patterns. Addition of Cu to Ni (Ni being a typical terminal and multiple cracking catalyst) results in an increase in the internal splitting<sup>2</sup> whereas adding Cu to Ir (a metal showing a high propensity to internal cracking) results in an increase in the terminal cracking modes.<sup>6</sup> In the continuous flow experiments it was found that the effect of Cu

on Pt is similar to that on Ir, although the change is much smaller. This intermediate behaviour of Pt is also reflected in the propensity of Pt towards intermediate internal cracking. Contrary to the results found in the continuous flow apparatus, the pulsed flow experiments show little or no shift in the cracking pattern, as is shown in Figure 2.

The conclusion is that the increase in selectivity to hydrogenolysis when Cu is added to the Pt catalysts is not carbon induced but is an intrinsic property of this system. This corroborates with the idea that Pt and Cu (or Ir and Cu) form mixed ensembles in which both the metal components are somehow active. The exact role of Cu in these mixed ensemble remains unknown.

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