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Role of Cu in the Hydrogenolysis of Pentane on Cu Alloy Catalysts

H. C. DE JONGSTE AND V. PONEC

Gorlaeus Laboratoria, Rijksuniversiteit Leiden, Post Office Box 9502, 2300 RA Leiden, The Netherlands

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In this article an attempt is made to establish the role of Cu in the activity of Cu alloy catalysts for hydrogenolysis. For this purpose a comparison was made between supported Pt, Ir, Ni, and Pd catalysts and their Cu alloys. In all cases the amount of active metal (10 μmole) per gram of catalyst was the same. It was observed that all highly diluted Cu alloys showed an increased activity for hydrogenolysis. Two explanations for this behavior are suggested, but both involve the "inactive" Cu atoms in the formation of the cracking products.

INTRODUCTION

Hydrogenolysis (hydrocracking) of hydrocarbons is an important industrial process and many fundamental studies have already been devoted to it. Several reviews now available cover exhaustively the work which has been done in this field (*1–3*). In the last 20 years many aspects of the mechanisms of reforming reactions (isomerization, dehydrocyclization, cracking) of hydrocarbons have been elucidated (*1–3*). At the moment it is generally accepted that hydrogenolysis of hydrocarbons on metals is a reaction which proceeds on large ensembles (i.e., several contiguous metal atoms) of active metal atoms (*4–8*). The fact that a hydrocarbon must first be dehydrogenated before the C–C bond can interact with the surface and that after bond fission several species must be bound to the surface by several metal–carbon bonds makes this idea very plausible. However, the main support for this idea came from the studies on hydrogenolysis by alloys. Many authors (*4–8*) observed with different alloy systems a decrease in hydrogenolysis activity if the ensemble size was decreased by alloying an active group VIII metal with an inactive group IB metal. Not only alloy formation, but also surface blocking with carbon or metals insoluble in the group VIII metal has a similar effect, namely, the selectivity with respect to hydrogenolytic cracking decreases. It was therefore puzzling why with Pt–Cu catalysts a decrease in the Pt-ensemble size caused an increase in the selectivity for cracking (*9*). In Ref. (*9*) this behavior was first mentioned and the authors speculated on the possibility of the existence of "mixed ensembles" (i.e., ensembles containing both Pt and Cu atoms), which would be less active than pure Pt ensembles, but nevertheless more active than Cu itself. In order to gain more information on the mentioned phenomenon, hydrogenolysis of pentane has been studied in this paper on several group VIII metals and their alloys with group IB metals. It is obvious that the possible role of "mixed ensembles" or of Cu itself could only be observable at very high dilutions of group VIII metals. Therefore, we have confined this study to the behavior of highly diluted alloys specified below.

EXPERIMENTAL

Catalyst preparation. In Table 1 all the catalysts used are shown. First, catalysts were prepared containing only the active metal, either Pt, Ir, Ni, or Pd. Approximately 10 μmole of the metal (in the form of solutions of the metals in aqua regia) was impregnated per gram of silica (Merck, kieselgel 60, <230 mesh). This resulted

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TABLE 1

Details of the Catalysts

Metal/alloy	Composition (atom%)	Metal loading (wt%)	Active metal (μmole/g cat)
Pt	100	0.2	10.3
Ir	100	0.2	11.2
Ni	100	0.06	10.2
Pd	100	0.1	10.7
Pt–Cu	0.6	9	9.3
Ir–Cu	0.7	9	10.2
Ni–Cu	0.8	9	11.9
Pd–Cu	0.8	9	11.7
Pt–Au	0.7	24	9.0
Ir–Au	0.7	24	8.5
Pt–Ag[a]	—	—	~10

[a] The Pt–Ag catalyst was prepared in such a way (explained in the text) that the exact alloy composition and metal loading were unknown.

(after reduction in H_2) in extremely low metal loadings ranging from 0.06 to 0.2 wt%. For the preparation of the alloys the same procedure was followed. The carrier was coimpregnated with 10 μmole of the active metal plus 1500 μmole of the second component (either Cu or Au, also dissolved in aqua regia).

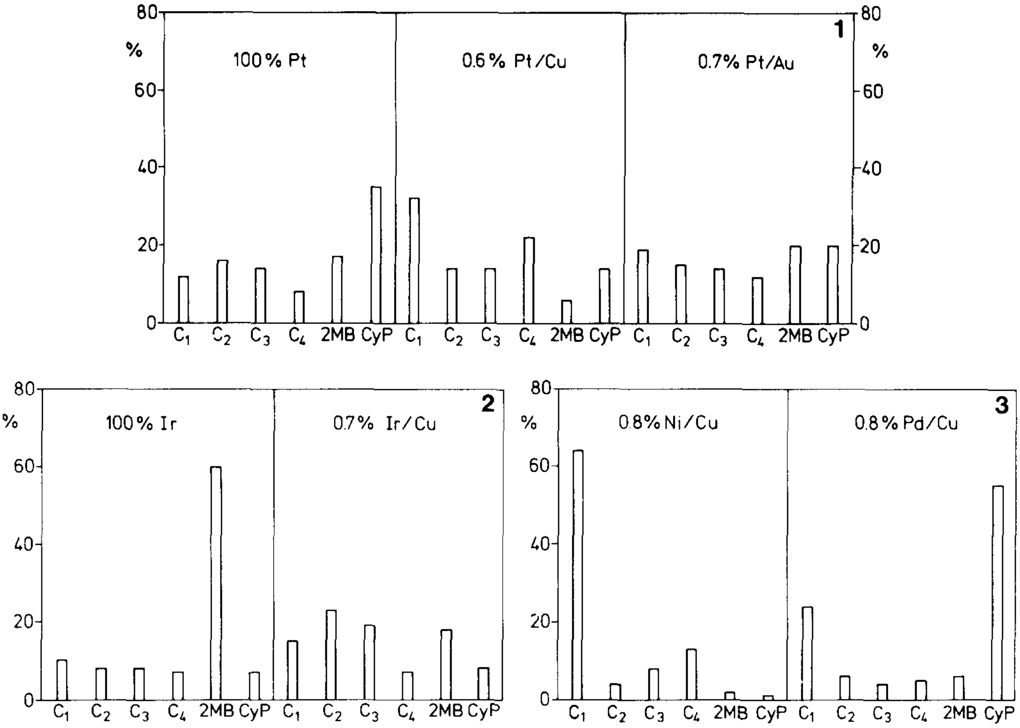
The Pt–Ag catalyst was prepared in a different way. A reduced Pt catalyst (0.2% on SiO_2) was suspended in an aqueous solution of $AgNO_3$. For 2 hr H_2 was bubbled through this suspension. During this procedure Ag was deposited by catalytic reduction on the surface of the Pt crystallites (*10*). Hereafter the catalyst was filtered off, dried, and sintered in a H_2 flow for 15 hr at 450°C. Since diffusion of Ag into the bulk is very slow, it can be expected that the Pt concentration in the surface of these alloys is low and the alloys thus behave like the other extremely diluted alloy catalysts used.

The final step of the preparation of all alloys was a reduction at 450°C for at least 15 hr at 1 atm H_2 pressure. For these highly diluted alloys there is unfortunately no direct means to check alloy formation. However, in the case of Pt–Cu alloys a detailed study had been performed in a previous investigation (*9*) with X-ray diffraction on Pt–Cu alloys at higher Pt contents. It appeared that for all compositions alloy formation was easily achieved under similar conditions as described in this paper. The presence of pure unalloyed Pt seems to be improbable because of the large excess of Cu which is rather mobile on a silica carrier. On the other hand, unalloyed Cu is inactive under the conditions applied and its presence is not disturbing. In the case of the other alloys the same considerations apply. Changes in selectivity (Pt–Cu, Pt–Au) or appearance of activity of Cu (Ni, Pd alloys) are indications that the alloys were formed, these indications being stronger for Cu than for Au alloys.

Reactions of pentane were studied in the flow apparatus described in Refs. (*6, 11*). The hydrogen–hydrocarbon ratio was 12 and the total pressure, 1 atm. Analysis and calculations of conversion α, selectivity S, and fission parameter M_f are also described in Refs. (*6, 11*). The catalysts used appeared to be very stable and their activity and selectivity varied reversibly with temperature; in the course of the experiments no deactivation took place.

RESULTS

The most relevant results are shown in Figs. 1–3 in the form of product distributions. It should be noted that under the conditions specified above no measurable conversions could be obtained for the Ni and Pd catalyst (<0.05% total conversion). Obviously the metal loading was too low. However, the corresponding Ni–Cu and Pd–Cu catalysts showed readily measurable activities. Quite surprisingly, the addition of the "inactive" Cu caused an *increase* in the overall activity. To exclude trivial errors in the comparison of the activities the following experiment was performed. The inactive Ni catalyst prepared and tested as described was taken out of the reactor and impregnated with the required amount of copper nitrate, then placed back in the reactor and reduced *in situ* again. The Ni–Cu catalyst prepared in this way showed the same activity and selectivity as the one prepared by coimpregnation fol-



FIGS. 1-3. Product distributions for the reactions of pentane. For reaction temperatures, see Table 2.

lowed by reduction. Evidently Cu plays a role in making the catalyst active (or more active).

The selectivities of the various tested catalysts are shown in Table 2 together with the reaction temperatures at which the product distributions were recorded (see Figs. 1-3).

TABLE 2

Selectivities for Hydrogenolysis (cr), Isomerization (iso), and Dehydrocyclization (cycl) of Pentane for the Various Catalysts

Metal/alloy	S_{cr}	S_{iso}	S_{cycl}	T (°C)
Pt	0.31	0.23	0.46	361
Pt-Cu	0.68	0.09	0.23	362
Pt-Au	0.42	0.29	0.29	367
Pt-Ag	0.30	0.27	0.43	400
Ir	0.18	0.73	0.09	364
Ir-Cu	0.57	0.32	0.11	363
Ir-Au[a]	—	—	—	367
Ni[a]	—	—	—	363
Ni-Cu	0.88	0.09	0.04	367
Pd[a]	—	—	—	391
Pd-Cu	0.20	0.05	0.74	395

[a] No measurable conversions obtained (<0.05% total conversion).

In Figs. 4 and 5 the hydrogenolysis activity per gram of catalyst is compared for the various catalysts. It can be seen that in every case the addition of Cu to either Pt, Ir, Ni, or Pd causes an *in*crease in the activity, in some cases even more than by a factor of 10. Other alloy components like Au or Ag always lead to a *de*crease in cracking activity. Obviously Cu with addition of small amounts of several group VIII metals favors hydrogenolytic cracking. The cracking pattern of the Cu alloys can be characterized by the fission parameter M_f (see Ref. (*6*) for definition). When this parameter is <1, several C–C bonds are broken during one sojourn in the adsorbed state (multiple splitting); with $M_f \sim 1$ there is a consecutive process taking place of terminal C_1-group splitting; and when $M_f \ll 1$ a molecule is preferentially split in its middle. As can be seen from Table 3 different Cu catalysts reveal different cracking

TABLE 3

Fission Parameter M_f

Alloy	M_f
Pt–Cu	2.9
Ir–Cu	9.5
Ni–Cu	0.7
Pd–Cu	1.3

patterns. This means that the individuality of the transition metal atoms is possibly preserved also in the alloys.

DISCUSSION

Two main points have to be explained:

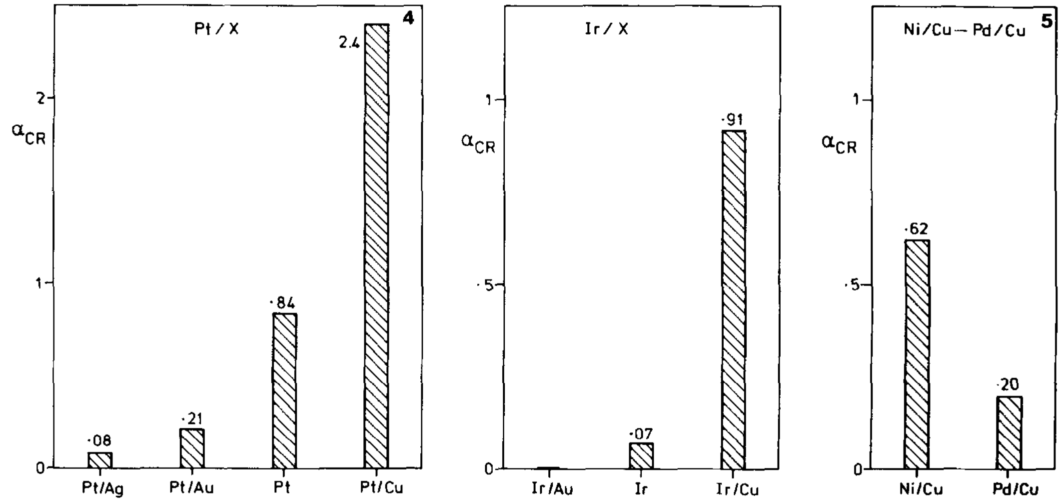
(1) why does Cu increase the contribution of the hydrogenolysis reaction to the overall conversion, and

(2) why was this behavior not recognized in earlier studies with Cu alloys?

Let us start with the second point. As already mentioned in the Introduction, in general the dilution of an active group VIII metal in an inactive or much less active group IB metal decreases the selectivity for cracking. Evidence for this is abundant (Ni–Cu) (*1, 11, 16*), Ir–Cu (*13*), Rh–Cu (*14*), Ru–Cu (*17*), Os–Cu (*17*), Ni–Ag (*16*), Pd–Au (*12*), Pt–Au (*6*), Ir–Au (*5, 13*). As can be seen, also for some Cu alloys a decrease was observed in the hydrogenolysis activity. However, the investigations with metals very active in cracking (Ni, Ir, Rh) were never performed under sufficient dilution of the transition metal. Yet it is evident that only with very strong dilution can the intrinsic activity of Cu be observed. Only with a metal which itself is not very active in cracking, like Pt, is the activity of Cu visible also at higher concentrations of the transition metal (*9*). Actually, there are some indications in the literature for the role of Cu, but they have not received the attention they require. For example, in the paper by Ponec and Sachtler (*11*), on Ni–Cu alloys, an increase was observed in the hydrogenolysis selectivity when Ni was strongly diluted in Cu. However, at that time the authors did not trust the results for the most diluted Ni alloy and it was not recognized that this could be a quite general picture.

To discuss the first point, let us summarize all the possible effects which might be responsible for the observed behavior in the activity and selectivity of the alloys tested in this paper.

(1) A trivial explanation for the observed increase in the hydrogenolysis activity of metals such as Pt, Pd, or Ir shown in Figs. 4 and 5 would be a redispersion or a better



FIGS. 4, 5. Activity in hydrogenolysis (α_{cr}) for Pt, Ir, Ni, and Pd alloys.

reduction of these components caused by addition of Cu. This effect cannot be very strong and can hardly explain the large increase (more than ten times) in the activity as sometimes observed. Further, why should this effect be unique for Cu and why should Au not show it? Moreover, it is expected that the redispersed (i.e., better dispersed) group VIII metal would not favor hydrogenolysis but rather a reaction like dehydrocyclization.

(2) Due to the addition of the Cu salt, a part of the group VIII metal remains unreduced and forms (acidic) centers for cracking. This is unlikely, because a rather inert carrier (SiO_2) has been used which is known not to stabilize transition metal ions. Activity would then be dependent on the preparation method. However, for the Pt–Cu and Ni–Cu catalysts several methods were applied and results did not show any systematic dependence on the conditions of preparation.

(3) The selectivity and activity of the catalysts are determined not only by their surface composition but also by the amount of carbon deposited on the surface. A possible explanation would then be that Cu suppresses the carbon deposition to such an extent that the surface of the Cu alloy is finally more active in cracking than the surface of the pure group VIII metals. However, this is again not very likely because of the difference between the Cu and Au alloys. One would expect that Au eliminates carbon deposition even better than Cu and yet Au suppresses hydrogenolytic cracking.

(4) Cu (but not Au) promotes a "one-site" cracking mechanism via "metal carbenium ions." This mechanism would be analogous to the one-site isomerization mechanism which has been suggested by McKervey *et al.* (*15*) and which helped to rationalize some phenomena observed with Pt–Au alloys (*6*). To explain why Cu but not Au promotes cracking, we have to assume some electronic structure effects (both Cu and Au dilute the transition metal), different for Cu and Au. The "metal carbenium ion" mechanism would be promoted by withdrawal of electrons from the transition metal atom. One would expect that both Cu and Au change the structure of the transition metal atoms only marginally and if they do, they shift their electrons toward the transition metal rather than in the opposite way. This shift would even be greater for Cu than for Au. However, according to this, a suppression rather than a promotion of this mechanism by Cu would be predicted and therefore we are inclined to reject this explanation.

(5) Another possible explanation is that what is observed is actually the activity of Cu, Cu itself being much less active because of a too low hydrogen coverage. However, H atoms can be supplied by the active centers (transition metal atoms) and in this way the reaction is kept running on a much higher level than on pure Cu. However, this does not explain why all Cu alloys have different cracking patterns (Table 3) and selectivities (Table 2) because the supply of H atoms would be more or less the same for the different group VIII metals.

(6) This brings us to the last possibility. It is suggested that the group VIII metal atoms with the Cu atoms form the active site for hydrogenolysis. There are two ways in which this can take place:

(i) the hydrocarbon intermediate is partially bound to a group VIII metal atom and to a Cu atom and on this "mixed ensemble" is converted to cracking products;
(ii) the hydrocarbon is dehydrogenated on the group VIII metal to a greater or less extent and this dehydrogenated species can then undergo hydrogenolysis also on the Cu atoms surrounding the active center, the whole process of dehydrogenation and cracking being completed in one adsorption on the surface.

It is not our intention to pretend that the problem of highly diluted alloys has been completely solved by this paper. However, we believe that the main effect reported, i.e., the fact that an apparently inactive alloy component such as Cu is "forced" to become active when small amounts of group VIII metals are present as "active centers" is sufficiently interesting to be reported. Moreover, it is obvious from this paper that in future work on alloys attention must be paid also to the regions of the highest dilutions.

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Note added in proof. One more possibility should be considered here. The group VIII ions are protected against reduction by their position in the SiO_2 structure and only after addition of Cu^{++} ions which replace them, the group VIII ions become reducible. This is not very likely for the inert carrier used but a mere possibility of such mechanism weakens our arguments based solely on "activity."

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