

## Conversion of Cyclohexane on Ni–(Sb, Pb, Cu)/Al<sub>2</sub>O<sub>3</sub> Bimetallic Catalysts

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Alumina-supported Ni catalysts, containing Sb, Pb, or Cu as a second metal (termed here the “bimetal”), were studied in the conversion of cyclohexane. Activity and selectivity strongly depend on the reaction conditions as well as on the composition and the pretreatment of the catalysts. Each of the three second metals caused very similar positive effects, namely suppressed hydrogenolysis, enhanced dehydrogenation, and prolonged lifetime, as far as the conversion at 500°C is concerned, but at 300°C only a negative, poisoning effect was observed. The conditions for a maximum positive “bimetal effect” are restricted to a Ni: second metal ratio of 9:1 and to calcination and reduction temperatures each of 500°C. TPR experiments displayed interactions of Cu and of Sb with Ni. The positive bimetal effect is explained by an ensemble effect due to a suggested dilution of Ni clusters by the second metals. © 1991 Academic Press, Inc.

### INTRODUCTION

An effect of a second metal has often been observed in the combination of a Pt-group metal with a less active or even inactive metal. This combination causes a characteristic shift of selectivity. The destructive C–C bond splitting is suppressed in favour of nondestructive reactions such as dehydrogenation, aromatization, and isomerization. Moreover, the deactivation by coking is retarded. This has caused them to be extensively applied in the oil refining industry through the world and to be interesting subjects of fundamental research (1–4). In our previous studies we observed the effect of the second metal in alumina-supported Pt-catalysts, combined with Sn, Pb, Sb, and Bi (3, 5–7).

We have now extended our studies to supported Ni catalysts. Ni is similar to Pt in respect to its excellent hydrogenation properties. However, Ni is much more active in hydrogenolytic splitting. Hydrocarbons are

completely converted to methane at elevated temperatures. The combination of Ni with a less active or inactive metal should result in the second metal suppressing just the hydrogenolysis and promoting the non-destructive reactions, thus transforming the Ni catalyst into a Pt-similar catalyst. The study of this problem was the aim of the present paper. For convenience, we refer to the effect of the second metal as the “bimetal effect” in this paper. Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were combined with Sb, Pb, or Cu, and their efficiency was tested in cyclohexane conversion in dependence on the conditions of pretreatment and reaction.

### EXPERIMENTAL

The conversion of cyclohexane at different reaction temperatures was carried out in an integral reactor, which is described in detail elsewhere (8, 9). The hydrogen stream (6 liter/h) was saturated with cyclohexane (127 Torr). The catalyst weight was 0.5 g.

The Ni/Al<sub>2</sub>O<sub>3</sub> and the Ni–Sb/, Ni–Pb/, and Ni–Cu/Al<sub>2</sub>O<sub>3</sub> samples containing 15 wt% Ni with atomic ratios Me/Ni from 0.0

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to 1.0, were prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, previously calcined for 2 h at 500°C in air, with an acidic solution of appropriate concentrations of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and SbCl<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, or Cu(NO<sub>3</sub>)<sub>2</sub>, respectively.

The strong influence of calcination temperature on the behaviour of Ni/Al<sub>2</sub>O<sub>3</sub> in cyclohexane dehydrogenation has been reported previously (8). Therefore, the bimetallic samples were first dried at 100–200°C for 2 h and then calcined for 4 h immediately before the catalytic test at predetermined temperatures ranging from 100 to 600°C. The calcination was followed by a reduction in flowing hydrogen for 4 h at 500°C. The TPR investigations of catalysts were carried out in an apparatus described elsewhere (7, 8).

## RESULTS

We studied the bimetal effect as a function of the reaction time and the reaction temperature, of the content and the nature of added metal, and of the calcination and the reduction temperature.

### *The Influences of the Atomic Ratio Me/Ni and the Time on Stream*

The conversion of cyclohexane was studied as a function of the time on stream at 500°C. The alumina-supported catalysts used were Ni (15%), Ni-Sb, Ni-Pb, and Ni-Cu with a constant amount of Ni and with the atomic ratio (Me/Ni) of 1/9. Both the calcination and the reduction of the catalysts were carried out at 500°C for 4 h. The results are shown in Fig. 1. The activity of Ni, indicated by the cyclohexane conversion, decreases sharply with increasing time on stream. The bimetallic catalysts are more active, and they display almost no deactivation. The selectivity for benzene increases in the initial period and then remains nearly constant.

However, in the case of Ni/Al<sub>2</sub>O<sub>3</sub>, the selectivity for benzene is lower and decreases slightly with the time on stream. Thus, all the added metals display an improving effect

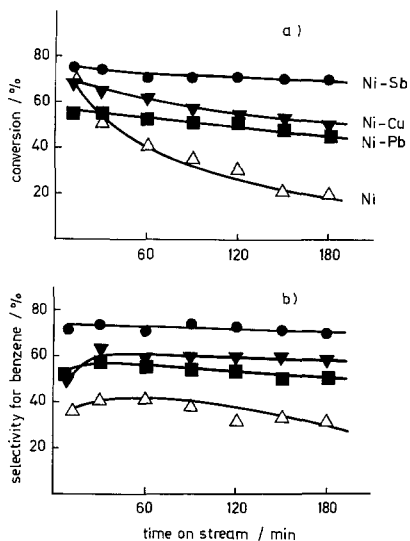


FIG. 1. Dependence of cyclohexane conversion (a) and selectivity for benzene (b) of Ni-Me/Al<sub>2</sub>O<sub>3</sub> (Me/Ni = 1/9) catalysts at 500°C on the time on stream.

on the activity, stability, and selectivity of supported Ni in the cyclohexane dehydrogenation.

Further experiments under the same conditions showed that this improving effect is strongly governed by the atomic ratio Me/Ni. This is presented in Fig. 2, where activities and selectivities after 2 h on stream are plotted against the Me/Ni atomic ratios. It can be seen that small amounts of Sb, Pb, or Cu distinctly promote the activity and selectivity of catalysts. Remarkably, in each case a maximum is reached at the constant ratio of Me/Ni = 1/9. However, higher amounts of Sb or Pb, i.e., higher atomic ratios, cause the opposite effects, decreasing both the activity and selectivity. Only in the case of Cu is this opposite effect not observed.

### *The Influence of the Reaction Temperature*

The conversion of cyclohexane is already strongly varied by different reaction temperatures, using only the monometallic Ni catalyst (15 wt% Ni, calcined and reduced at 500°C). This is to be seen in Fig. 3. Activities

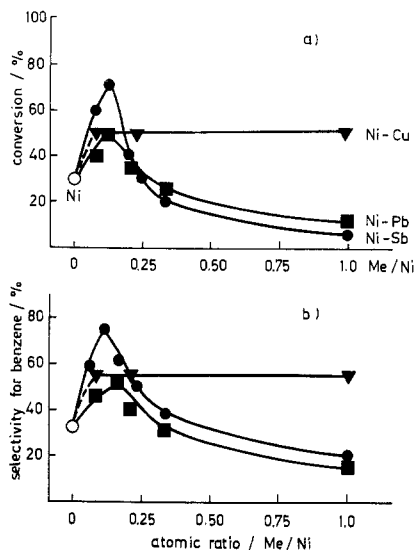


FIG. 2. Cyclohexane conversion (a) and selectivity for benzene (b) of Ni-Cu, Ni-Pb, and Ni-Sb catalysts after 2 h on stream at 500°C as a function of atomic ratios.

and selectivities at reaction temperatures between 300 and 550°C are plotted against the time on stream. The temperature rise between 300 and 400°C causes a normal increase of activity; the selectivity for benzene remains high and constant. However, at temperatures higher than 400°C, the Ni catalyst suffers severe deactivation both with increasing temperature of reaction and with increasing time on stream. The deactivation is accompanied by a typical shift of selectivity from benzene formation toward methane formation.

The behaviour of the bimetallic catalysts as a function of the temperature of reaction is seen in Fig. 4. Typical Ni, Ni-Sb, Ni-Pb, and Ni-Cu samples were selected, containing a constant amount of 15 wt% Ni and the added second metal in the ratio Me: Ni = 1:9. The alumina-supported catalysts were pretreated in air and in hydrogen, each procedure lasting 4 h at 500°C. The values for conversion and selectivity after 2 h on stream were chosen in order to include deactivation effects.

It can be seen that the second metals exert

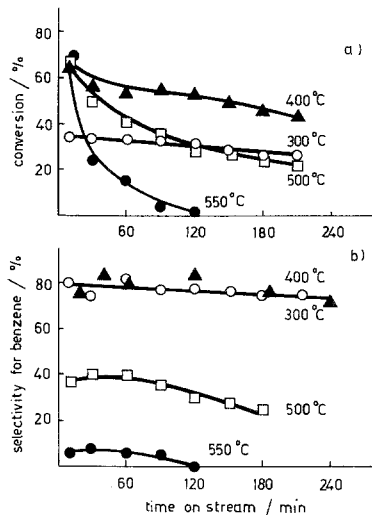


FIG. 3. Cyclohexane conversion (a) and selectivity for benzene (b) of Ni/Al<sub>2</sub>O<sub>3</sub> (15 wt% Ni) at reaction temperatures between 300 and 550°C as a function of the time on stream.

quite opposite effects in dependence on the reaction temperature. At 300°C, activities and selectivities are lower than those of the monometallic Ni sample. This is called a

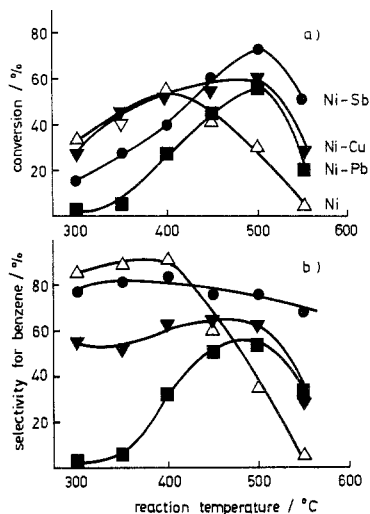


FIG. 4. Cyclohexane conversion (a) and selectivity for benzene (b) of Ni-Me/Al<sub>2</sub>O<sub>3</sub> catalysts (Me/Ni = 1/9) after 2 h on stream as a function of the reaction temperature.

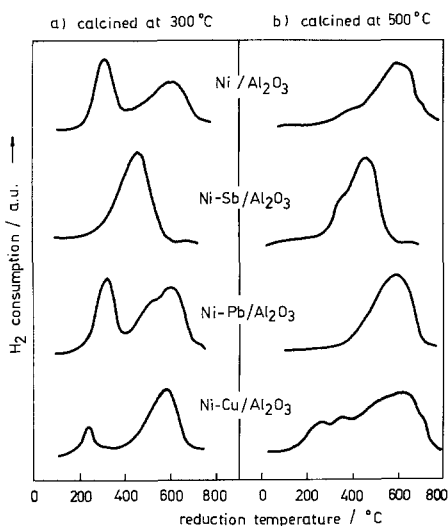


FIG. 5. The TPR-profiles of Ni(15)/Al<sub>2</sub>O<sub>3</sub> and Ni-Me/Al<sub>2</sub>O<sub>3</sub> (Me/Ni =  $\frac{1}{3}$ ), catalysts, calcined at 300°C (a) and 500°C (b), respectively.

“negative bimetal effect.” However, at 500°C the corresponding values are higher than those of the Ni sample. This is called a “positive bimetal effect” (10).

#### The Characterization of Ni-Bimetal Catalyst by TPR

The effect of the second metal is usually considered to be caused by mutual interactions between the added and matrix metals on the support. In our investigations, TPR is used to study these interactions. Some selected results obtained by TPR study of alumina-supported Ni (15%) and Ni-Sb, Ni-Pb, Ni-Cu (Me/Ni =  $\frac{1}{3}$ ) calcined at 300 or 500°C for 4 h are presented in Fig. 5.

In the case of Ni/Al<sub>2</sub>O<sub>3</sub> two peaks could be observed. These peaks are known from previous experiments (8). The low-temperature peak has been assigned to NiO which had not reacted with the alumina, and will be called “nonrelated” NiO. The high-temperature peak indicated a NiO strongly interacting with the alumina, called “related NiO.” Increasing calcination temperatures promotes the latter type of NiO (8, 11–14).

The TPR profiles of the Ni-Sb and Ni-Cu

samples are already influenced by a calcination temperature of 300°C. Both these second metals shift the low-temperature peak, indicating nonrelated NiO, toward higher temperatures. Obviously nonrelated NiO is very sensitive to the oxides of Sb and Cu. The result of interaction is the higher temperature of reduction. The TPR profile of the Ni-Cu sample shows a small new peak at a temperature of 230°C, lower than the peak temperature of the nonrelated NiO. Further experiments with samples containing much more Cu indicated that this peak is due to metallic Cu.

After calcination at 500°C the monometallic Ni sample displays only the peak of the related NiO. The addition of Sb or Cu, respectively, shifts or broadens this peak toward lower temperatures. This indicates that the oxides of Sb and Cu interact with related NiO, too, perhaps by competing with the interaction of the NiO with the alumina. The result is to be seen in the lowered reduction temperature. Altogether the TPR profiles reveal distinct hints that Ni atoms are in close neighbourhood with

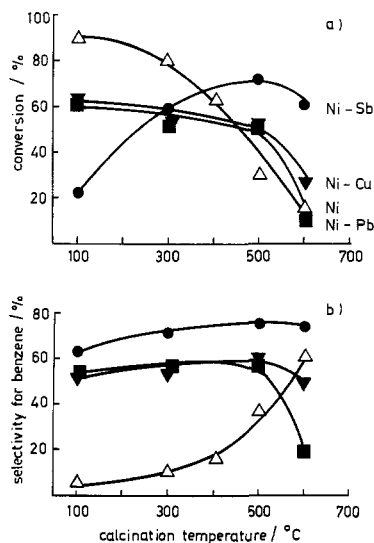


FIG. 6. Cyclohexane conversion (a) and selectivity for benzene (b) of Ni-Me/Al<sub>2</sub>O<sub>3</sub> (Me/Ni =  $\frac{1}{3}$ ) catalysts at 500°C after 2 h on stream in dependence on the calcination temperature.

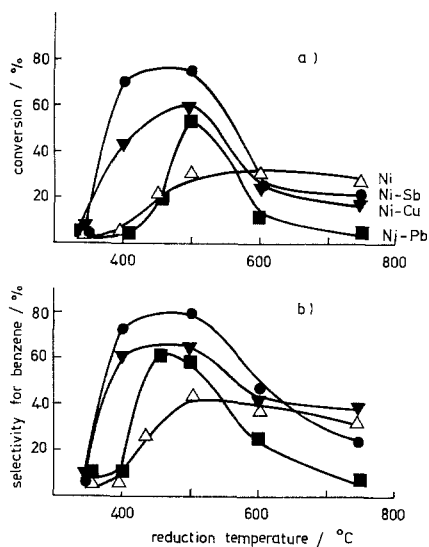


FIG. 7. Cyclohexane conversion (a) and selectivity for benzene (b) of Ni-Me/Al<sub>2</sub>O<sub>3</sub> (Me/Ni =  $\frac{1}{9}$ ) catalysts at 500°C after 2 h on stream in dependence on the reduction temperature.

Sb or Cu atoms, respectively, and that during the reduction bimetallic clusters are formed.

In contrast to Sb and Cu, the addition of Pb obviously does not influence the reduction of NiO. The corresponding TPR profiles after calcination at 300 and 500°C are very similar to those of the monometallic Ni sample. There is no hint of reduction of Pb. Therefore formation of metallic Ni-Pb clusters can be excluded.

#### *The Influences of the Pretreatment Conditions*

The conversion and selectivity for benzene after 2 h on stream at 500°C were studied as a function of the temperature of their calcination. The catalysts used were alumina-supported Ni (15%) and Ni-Me (Me = Sb, Pb, Cu; with Me/Ni =  $\frac{1}{9}$ ). The reduction of these samples was carried out at 500°C in a H<sub>2</sub>-flow for 4 h. The results of activity and selectivity are shown in Fig. 6. Increasing calcination temperature decreases the activity with the exception of Ni-Sb. The selectivities of Ni-Sb and Ni-Cu are high and

are almost unaffected by the calcination temperature. Ni is rather nonselective after a low calcination temperature, and very selective after a high one, while Ni-Pb displays just the opposite trend.

The effect of the reduction temperature on activity and selectivity was studied on the same samples precalcined at 500°C for 4 h. The time of reduction was 4 h, too. The observed activities and selectivities after 2 h on stream are shown in Fig. 7. Activities and selectivities are increased with increasing reduction temperatures in the range between 300 and 500°C and the bimetallic samples surpass the monometallic one. Further increasing reduction temperatures are detrimental. Activities and selectivities decline. Remarkably this decline is stronger with the bimetallic than with the monometallic samples and finally, after reduction at 750°C, pure Ni is the best catalyst.

## DISCUSSION

### *Deactivation of Ni*

The results reveal that the second metal can modify the Ni as a promoter or as an inhibitor, depending on the temperature of the reaction. However, these temperatures modify Ni itself, too. At 300°C cyclohexane is dehydrogenated to benzene in a stable and rather selective reaction. At 550°C Ni is rapidly deactivated and the main product then is methane. Obviously at high temperatures coke is produced and this modifies the Ni surface. We suggest the following mechanism. Pure Ni sites are responsible for the dehydrogenation. At high temperatures one part is blocked by coke and this slows down the conversion. Another part is modified by coke and these coked Ni sites are responsible for the hydrogenolytic C-C bond rupture resulting in the formation of methane and of further coke.

### *Positive Bimetal Effect*

The second metal can display a positive bimetal effect in comparison to the monometallic Ni sample, as seen in Figs. 1 and 2.

This means the stability is increased and the selectivity is shifted toward benzene formation. This effect is restricted to high temperatures (500°C) and to advanced time on stream. These are conditions of a severe deactivation. Basically, the bimetal effect is to be seen as a retarded deactivation. As outlined above, pure Ni itself is deactivated by coke and the selectivity is shifted from dehydrogenation toward hydrogenolysis. Bimetals inhibit or delay this deactivating process. This means they inhibit the hydrogenolytic C-C bond splitting.

The reason for the inhibited hydrogenolysis is explained by a suggested formation of mixed clusters, containing the active Ni and the second metal or metallic species as an inactive component. According to the ensemble effect (1-3) this dilution of the active Ni causes a shift of selectivities from a demanding reaction, the hydrogenolytic splitting, toward a facile reaction, the dehydrogenation of cyclohexane. The suppression of methane formation was observed in the experiments.

It must be mentioned that the beneficial effect of the second metal strongly depends on the content of the second metal, being optimal at the ratio Me : Ni = 1 : 9. Samples with higher ratios Me : Ni suffer decreasing activity and decreasing selectivity for benzene. The decreasing activity could be due to a blocking effect of the additional amounts of the second metal. The selectivity shift is more difficult to explain. It may be that deposited coke on residual pure Ni or on bimetallic Ni shifts the selectivity toward CH<sub>4</sub>, as observed with pure Ni.

#### *Composition of Clusters*

The proposed model essentially relies on the existence of mixed Ni clusters. This thesis is supported by the TPR results, which indicated, as mentioned above, the strong influences of Sb and Cu on the reduction properties of Ni. However, the same was not observed in the case of Pb (Fig. 4). Previous results (15) confirm that under the conditions employed Pb is not reduced in this

system, in contrast to the Ni-Sb and Ni-Cu systems with at least partial reduction of the second metals.

On the other hand, all three bimetallic systems display the same promoting effect in the catalytic dehydrogenation. We assume that the reason for the similar behaviour of these Ni-bimetal systems is the formation of diluted Ni clusters. There is, however, a specialty in the composition of these clusters. The diluting species obviously exists in one case in a metallic state, and in the other case in an oxidic state. Both of them should cause an ensemble effect. The precondition, a dilution of an active metal cluster by an inactive species, is fulfilled in both cases. The existence of this type of ensemble, a mixture of an active metal with an inactive metal oxide or metal sulphide, was also proposed in several other studies on Ni-bimetal and Pt-bimetal catalysts (8, 10, 16-20) and even SMSI effects are explained in a similar manner by the decoration model (17, 21).

A further hint on the formation of a specific cluster is to be seen in the atomic ratio of the inactive to the active species. Remarkably, the maximum of the bimetal effect is reached in all three systems at the constant atomic ratio Me/Ni = 0.1. Only Cu behaves exceptionally insofar as this maximum, once reached, remains maintained even with considerably higher Cu/Ni ratios than 0.1 (Fig. 2). This is in accordance with the well known cherry effect in Ni-Cu alloys (22, 23). These alloys tend to segregate into a Ni core and Ni-Cu shell. The latter maintains a constant composition in spite of a large variation of the overall composition. This constant composition of a surface layer fits well with the observed catalytic effect of Cu.

In general the bimetal effect in the present Ni/Al<sub>2</sub>O<sub>3</sub> system reveals a striking similarity to the Pt/Al<sub>2</sub>O<sub>3</sub> system, studied previously (3, 5-7, 10). In all systems dehydrogenation is improved at the expense of hydrogenolysis and the stability is increased. Especially interesting is the composition of

TABLE 1

Atomic Ratios of Bimetallic Systems Causing a Maximum of the Promoting Effect

Matrix metal Mm	Second metal Bm	Ratio Bm/Mm	References
Pt	Sn	1.5-2.0	(3, 5)
Pt	Pb	1.5-2.0	(3, 5, 7)
Pt	Bi	1.0	(7)
Pt	Sb	1.0	(7, 10)
Ni	Sb	0.1	Present paper
Ni	Pb	0.1	Present paper
Ni	Cu	0.1	Present paper

those bimetal systems displaying the maximum of the bimetal effect. This is shown in Table 1.

The data reveal the following: (i) The optimum composition of the clusters is determined by the matrix metal, being distinctly different between Pt and Ni; (ii) the composition of the clusters is nearly constant within each matrix system; and (iii) the bimetal effect is independent of the nature of the bimetal, as proved with Sn, Pb, Sb, Bi, and Cu. Altogether one can conclude that this positive bimetal effect seems to be a rather general phenomenon in bimetallic systems and that the ensemble theory provides a theoretical interpretation.

Already in 1960 the typical shift of selectivity of Ni by addition of ZnO, CdO, TiO<sub>2</sub>, or ThO<sub>2</sub> in the conversion of cyclohexane was reported by Langenbeck *et al.* (24). However, their interpretation, an electronic modification of the Ni, should be seen now as a result of the theoretical concepts dominating at that time.

Positive bimetal effects were also observed with supported Ni catalysts combined with Sn or Pd (25, 26), and with supported Pt catalysts combined with Sb or Te (27).

#### Negative Bimetal Effect

At the reaction temperature of 300°C the second metals are less active and less selec-

tive than the monometallic Ni sample. This is the negative bimetal effect. The disappearance of the positive bimetal effect is connected with the low reaction temperature. At this temperature no deactivation of the Ni occurs. Therefore the precondition of the positive bimetal effect, a coked Ni surface, is not fulfilled and consequently the bimetal cannot retard a deactivation. The poisoning effects of the second metals at low reaction temperatures display distinct specific differences. Sb and Cu are less poisoning, but Pb nearly completely slows down the activity and selectivity. As shown in the TPR experiments, PbO remains unreduced during the hydrogen treatment in contrast to Cu and Sb. It may be that Pb<sup>n+</sup> can cause a special long-range interaction by a "through-the-space" electrostatic interaction, as observed with adsorbed CO (28).

#### Pretreatment

The temperature of calcination modifies the mono- and bimetallic samples, too. The activities of Ni, Ni-Cu, and Ni-Pb decrease with increasing temperature. This should display a normal sintering. The increasing activity of Ni-Sb may be due to a spreading effect. The selectivity of Ni increases considerably with increasing calcination temperature. This is in accordance with the explanation of previous results (8). Calcination at low temperatures forms NiO which does not interact with the support alumina. This nonrelated NiO is highly active in hydrogenolytic splitting in its reduced form. This species is represented by the first peak in the TPR curve (Fig. 5). High-temperature calcination leads to an NiO which strongly interacts with alumina. This species is represented by the second peak in the TPR curve. The reduction forms related Ni, which suppresses hydrogenolytic splitting and is selective in hydrogenation and dehydrogenation. This was ascribed to a suggested [Ni-NiO] mixed cluster. The present results completely confirm this model.

Contrary to Ni, all the bimetallic samples already display a high selectivity after the

very low calcination temperature of 100°C. This indicates that this mild treatment was a sufficient condition for an interaction of Ni with the second metal but not for the interaction with alumina. Higher calcination temperatures have almost no influence on the selectivity of Ni-Cu and Ni-Sb. Remarkably these high selectivities are reached by monometallic Ni only after calcination at 600°C. This is a hint that now the proposed [Ni-Me] clusters and the [Ni-NiO] cluster are comparable. Only the Ni-Pb sample, calcined at 600°C, is an exception, the selectivity being very low. It could be that the suggested [Ni-Pb<sup>n+</sup>] cluster becomes thermally unstable at this temperature.

#### CONCLUSION

Addition of Sb, Pb, or Cu to Ni/Al<sub>2</sub>O<sub>3</sub> can cause dramatic variations of the properties of the Ni catalyst. The hydrogenolytic splitting can be suppressed in favour of a selective dehydrogenation connected with an improved stability. The occurrence of this positive bimetal effect is restricted to special conditions, which are:

- (i) high temperatures of reaction, where hydrogenolytic C-C splitting takes place (at lower temperatures the bimetallics cause a poisoning, a negative bimetal effect);
- (ii) small range of added second metals, the optimum ratio of Me/Ni being 0.1;
- (iii) the temperatures of calcination and of reduction should be about 500°C.

The mechanism of the positive bimetal effect is explained by a cluster model, suggesting cluster formation of Ni with the second metals in the zero-valent as well as in an oxidized state. These clusters should modify selectivity and stability according to an ensemble effect.

The observed close similarity of the bimetal effect in the systems Ni-(Sb, Pb, Cu)/Al<sub>2</sub>O<sub>3</sub> and Pt-(Sn, Pb, Sb, Bi)/Al<sub>2</sub>O<sub>3</sub> suggests the conclusion that cluster formation

and bimetal effect is a more general principle in bimetallic systems.

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