Conversion of Cyclohexane and n-Heptane on Pt–Pb/Al$_2$O$_3$ and Pt–Sn/Al$_2$O$_3$ Bimetallic Catalysts

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Using Pt–Pb and Pt–Sn catalysts supported on η-Al$_2$O$_3$ the dehydrogenation of cyclohexane, the dehydrocyclization of n-heptane, the coke deposition during the conversion of n-heptane, and the chemisorption of hydrogen were studied. Additions of Pb or Sn have similar effects. On the bimetallic catalysts the dehydrogenation of cyclohexane is decreased at low temperature, and increased at high temperature; the dehydrocyclization of n-heptane can be increased or decreased in dependence on the hydrogen pressure and the reaction temperature. The efficiency of the bimetallic catalysts is determined by the reaction conditions. Under mild conditions the reactions are inhibited, whilst under severe, deactivating, and destructive conditions the aromatization can be increased, whereas the hydrogenolysis is decreased. A modification of the Pt sites by the second metal and by the coke is discussed.

INTRODUCTION

Platinum on alumina is a well-known catalyst for conversions of hydrocarbons, whereas lead or tin catalysts are inactive or even poisonous. Nevertheless, Pt–Sn and Pt–Pb catalysts have recently been found to give surprising catalytic effects and their technological application in the reforming process is proposed in a number of patents (*1*). Few theoretical investigations have been published so far. Supported Pt–Sn catalysts enhance the aromatization of paraffins (*2–4*). Poisoned acidic sites (*5*) or inhibited hydrogenolysis (*6*) is reported to decrease the cracking. With Pt–Pb catalysts higher yields of aromatics can be obtained in the reforming process (*7*). Addition of tin to Pd or Ni catalysts causes in some reactions a poisoning, in others a promotion (*8*).

The aim of the present work was to investigate the influence of bimetallic catalysts in different reactions, to investigate the dependences on the amount of the second metal and on the reaction conditions, and finally to contribute to solving the problem that additions of lead or tin obviously can slow down or enhance reaction rates.

EXPERIMENTAL

The catalysts were prepared by impregnation of η-Al$_2$O$_3$ with an acidic solution containing the calculated amounts of H$_2$PtCl$_6$, and SnCl$_2$ or PbNO$_3$. They were dried at 393 K and calcined at 773 K. Before any examination they had to be calcined again at 773 K, in order to obtain a high dispersion of platinum (*9*). Finally, they were reduced in a hydrogen flow for 1 h at 773 K. The Pt content was 0.5 wt% except in the experiments with n-heptane at normal pressure, where it was 0.35 wt%. H$_2$ chemisorption on the catalysts was measured at 273 K by means of a pulse technique using a katharometer as detector. The pulse volume amounted to 0.233 ml; usually the samples (weight 2 g) took up two to four pulses. Before pulsing, the samples were calcined and reduced *in situ*, and then finally treated for 1 h in flowing argon at 773 K in order to desorb the hydrogen. The catalytic measure-

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ments were performed in flow reactors. A flow of 2.26 liters H$_2$/h was saturated with 60-Torr cyclohexane. The amount of catalyst (0.3–0.8 mm diameter) was 0.1 g, diluted with 0.3 g α-Al$_2$O$_3$. The reaction conditions in the *n*-heptane conversions were (i) normal pressure : 3 g catalyst, 1 LHSV, hydrogen/hydrocarbon ration = 4.6 by saturating a flow of hydrogen with *n*-heptane at 323 K, and the addition of *n*-heptane was started at 773 K; (ii) at a pressure of 0.8 MPa : 1.4 g catalyst, 24 LHSV, hydrogen/hydrocarbon ratio = 6.6 by addition of *n*-heptane through a capillary with a starting temperature of 723 K. Gas chromatographic analysis of the gaseous products was made in the re-actions at normal pressure, and of the liq-uid products in the reaction at elevated pressure. Thermogravimetric experiments were performed with an electronic micro-balance. The amount of catalyst was 10 mg. The increase of weight was deter-mined in a flow of an *n*-heptane/hydrogen mixture (1 : 21) with a flow rate of 1 liter/h.

FIG. 1. Chemisorption of hydrogen on bimetallic Pt catalysts, containing Pb (O) or Sn (□).

RESULTS

1. Chemisorption of Hydrogen

The adsorption of hydrogen on Pt in bimetallic catalysts is shown in Fig. 1. The adsorbed amount of hydrogen is calculated as H/Pt ratio, because Pb and Sn do not adsorb hydrogen. The adsorption on Pt decreases with increasing amount of the second metal. Tin inhibits the adsorption more strongly than lead.

The value of 1.2 H/Pt on the pure Pt is very high. Usually one Pt atom adsorbs not more than one H atom. Only in very dis-persed systems could higher adsorptions be observed. They are discussed as spillover (10) or as higher coordination of Pt in very small clusters.

The decrease of adsorbed hydrogen on Pt is probably due to a chemical modification of the Pt by the second metal. Electronic interactions between Pt and Sn could be found by Mössbauer spectroscopy (3) and
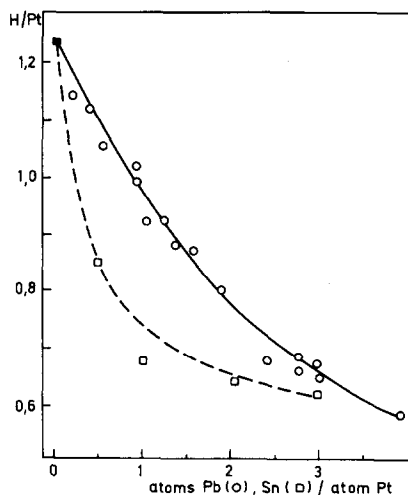
between Pt and Pb by ir spectroscopy (11). This would be in line with a decreased hydrogen adsorption on Pt–Sn alloys, which is discussed as a ligand effect (12). An ensemble effect, as discussed for alloys (13), cannot be excluded but the differences in chemisorption between added tin and lead can hardly be explained in this way. A further possibility of a decreased adsorp-tion could be a considerable increase of the particle size of the Pt. But X-ray experi-ments on Pt–Sn (3) and Pt–Pb catalysts (14) evidenced that the particle size re-mained under 2.5 nm in the mono- and bimetallic catalysts.

The adsorption data and the spectro-scopic measurements indicate the existence of bimetallic clusters in these dispersed systems. Pt and the second metal must be fixed in adjacent positions, whereas 99% of the surface of the alumina remains free. The formation of the bimetallic clusters is only little influenced by whether during the impregnation complexes with Pt can be formed, as in the case of Sn, or if not, as in the case of Pb. This follows from the cata-lytic results, described below.

2. Conversion of Cyclohexane

The dehydrogenation of cyclohexane has

been studied both at low and at high temperatures. In the low-temperature experiments activities have been determined in the temperature range between 530 and 620 K. Reaction rates per gram of Pt have been calculated, using a zero-order rate equation and correcting the yield of benzene by the equilibrium concentration of cyclohexane. The activities of various catalysts at 588 K, taken from Arrhenius plots, are shown in Fig. 2. The Pt content in all catalysts was 0.5 wt%. With increasing amount of added Pb the dehydrogenation slows down. The only product is benzene. All bimetallic catalysts are less active than the pure-Pt catalyst. The activation energy increases from 58 kJ/mole on the pure-Pt catalyst to about 100 kJ/mole on catalysts containing 2–3 atoms Pb per atom Pt. In some additional experiments a similar poisoning by Pt–Sn catalysts has been found.

The high-temperature conversion has been studied at 773 K, a typical temperature for the reforming process. The Pt catalysts quickly suffer a severe deactivation at this temperature. Therefore activity/time dependences have been determined at a constant temperature. Such a curve is
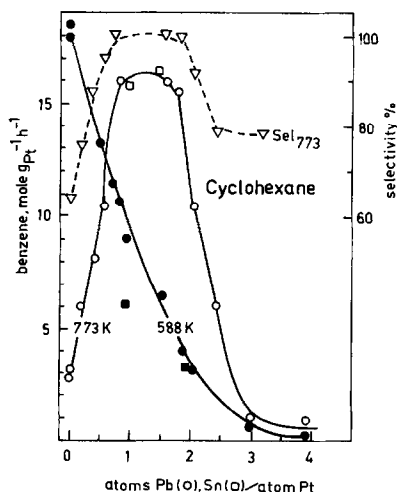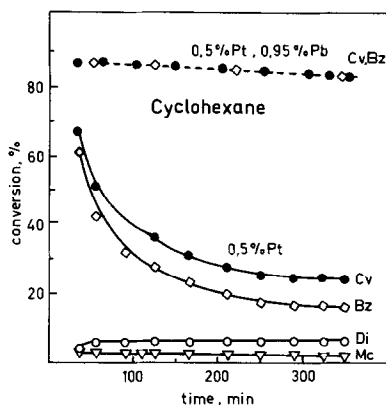

FIG. 3. Activity/time curves of the conversion of cyclohexane at 773 K on a bimetallic catalyst (0.5 wt% Pt; 0.95 wt% Pb; broken line) and on a Pt catalyst (0.5 wt% Pt; solid lines). Cv = conversion; Bz = benzene; Di = dienes; Mc = methylcyclopentane.

shown in Fig. 3. The total conversion decreases very quickly at the beginning but levels out after about 5 h at a rather low value. The selectivity for benzene formation is initially very high, but decreases with reaction time, whereas the production of dienes increases. The reaction is accompanied by a decreasing formation of C_1-C_5 cracking products, 1.22% after 70 min and 0.27% after 370 min (15).

Bimetallic catalysts behave quite differently. A typical diagram of a Pt–Pb catalyst is shown in Fig. 3. The activity remains nearly constant. The selectivity for the benzene formation remains 100%. In this respect the bimetallic catalysts at 773 K behave like a pure-Pt catalyst at temperatures of about 570 K. However, there is a pronounced difference in the total activity. As can be seen in Fig. 2, the activity of the pure-Pt catalyst at 773 K is considerably lower than at 588 K. At the high temperature the Pt catalyst has become severely deactivated by carbonaceous deposits, whereas the bimetallic catalyst is stable and selective. However, the benzene formation does not exceed the value already obtained at 588 K on the pure-Pt catalyst. The influence of the amount of added lead or tin on the activity and selectivity of the dehy-

FIG. 2. Dehydrogenation of cyclohexane at 588 and 773 K and selectivity for benzene formation at 773 K (Sel$_{773}$) on bimetallic Pt catalysts, containing Pb (O) or Sn (□).

drogenation after a reaction time of 6 h can be seen in Fig. 2. The benzene formation reaches a broad maximum with catalysts containing one to two atoms of lead per atom of platinum. Only these catalysts are stable and selective. The others with a bigger or lower content of lead behave similarly to the pure-Pt catalyst in that they are unselective and suffer deactivation. Tin-containing catalysts give the same effects as the lead-containing catalysts.

3. Dehydrocyclization of n-Heptane

(a) *Reaction at normal pressure.* The conversion of n-heptane at a pressure of 0.1 MPa is clearly influenced by the second metal. This can be seen from the activity/time curves of a pure-Pt catalyst and a Pt–Pb catalyst in Fig. 4. The bimetal effect can be characterized by the following points: (i) The conversion decreases less rapidly. The deactivation is retarded. (ii) The content of toluene in the product is considerably higher. The total aromatization is increased by a higher selectivity and a higher conversion. (iii) The cracking is

inhibited. On the pure-Pt catalyst many cracking products from C_1 to C_6 are formed and only small amounts of C_7 olefins and isomerization products. On the bimetallic catalyst the total amount of all by-products is distinctly lower.

The influence of the amount of added lead and tin is shown in Fig. 5. The activities are taken after a reaction time of 4 h. The pure-Pt catalyst is rather unselective in the aromatization. With increasing content of lead the conversion and especially the selectivity for toluene increase. The curves pass through a maximum. Very large amounts of lead diminish the conversion and the toluene production.

(b) *Reaction at a pressure of 0.8 MPa.* The reaction at the higher pressure will be characterized by the sum of the dehydrocyclization products toluene and benzene. The dependence of the aromatization on the second metal is shown in Fig. 6. At the higher temperature of 803 K an increase by bimetallic catalysts can be observed, similar to the maximum of activity found in the conversion at normal pressure (Fig. 5). However, at 773 K no improvement by bimetallic catalysts could be achieved, and
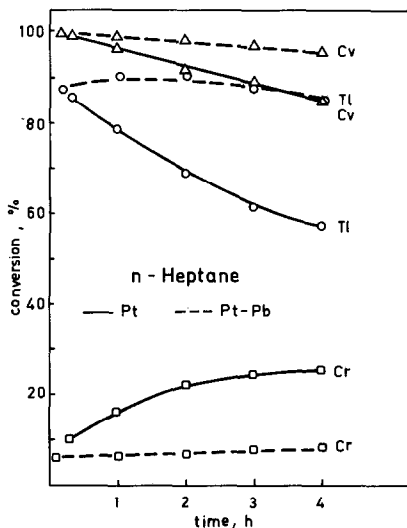
FIG. 4. Activity/time curves of the conversion of n-heptane at 0.1 MPa and 773 K on a bimetallic catalyst (0.35 wt% Pt; 0.37 wt% Pb; broken lines) and on a Pt catalyst (0.35 wt% Pt; solid lines). Cv = conversion; Tl = toluene; Cr = cracking products.
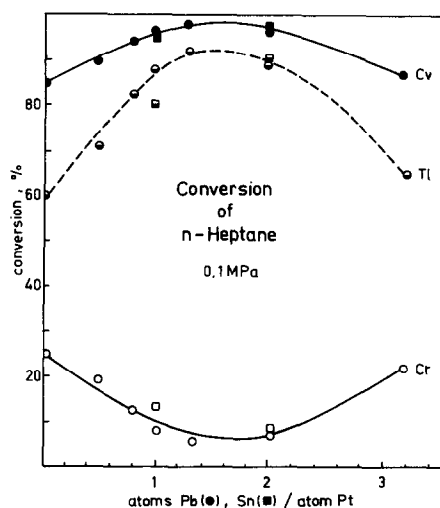
FIG. 5. Conversion of n-heptane at 0.1 MPa and 773 K on bimetallic Pt catalysts, containing Pb (O) or Sn (□). Cv = conversion; Tl = toluene; Cr = cracking products.
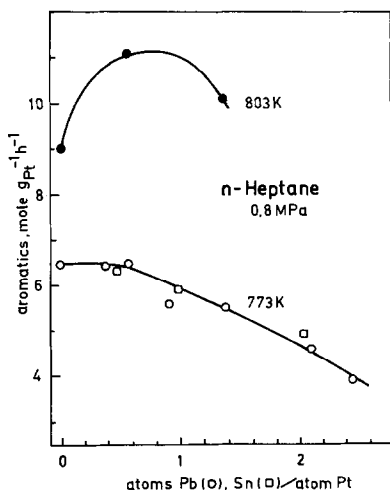
FIG. 6. Formation of aromatics from n-heptane at 0.8 MPa on bimetallic catalysts, (●) Pt–Pb at 803 K after 4 h; (○) Pt–Pb and (□) Pt–Sn at 773 K after 5 h on stream.

larger amounts of the second metal distinctly poisoned the reaction. Further characteristic data of the catalysts are summarized in Table 1. There exists a typical shift in the activity/time curves with increasing content of lead. The pure-Pt catalyst is very active in the beginning, but the activity decreases. Bimetallic catalysts are less active, but rather constant; i.e., they proved to be very stable.

A further influence of bimetallic catalysts can be seen in the benzene formation. The ratio (benzene + toluene)/toluene decreases with increasing content of lead (Table 1). The splitting from C_7 to C_6 is inhibited. The reaction is probably a

TABLE 1

Conversion of n-Heptane 0.8 MPa, 773 K, 24 LHSV

Catalyst (wt%)		Aromatics (benzene + toluene) (mole · g_{Pt}^{-1} · h^{-1})		$\left(\dfrac{\text{Dealkylation}}{\dfrac{\text{benzene} + \text{toluent}}{\text{toluene}}}\right)$
Pt	Pb	After 2 h	After 6 h	After 1 h
0.50	—	7.0	6.2	1.17
0.50	0.10	6.9	5.9	1.07
0.50	0.73	6.0	5.5	1.01
0.50	1.10	4.8	4.6	1.00
0.50	1.28	4.0	4.0	1.00

demethylation of the toluene. The results indicate an antihydrogenolytic effect of the bimetallic catalysts.

4. Deposition of Coke

During the conversion of n-heptane the formation of carbonaceous deposits was monitored by thermogravimetric equipment. In a flow of an n-heptane/hydrogen mixture the increasing weight of the catalyst was determined at the reaction temperature of 803 K. The results for several Pt–Pb and Pt–Sn catalysts are shown in Fig. 7. The observed increase of weight indicates that carbonaceous products are deposited, most of them being formed at the beginning of the reaction. A moderate influence of the bimetals on coke formation can be seen. In comparison with the Pt catalyst the amount of C-deposits on the Pt–Sn catalysts is equal or even larger, but on the Pt–Pb catalysts it is slightly lower.

DISCUSSION

The catalytic activities of Pt–Pb and of Pt–Sn catalysts proved to be similar. The Pt clusters must be modified by both the metals in nearly the same manner. Therefore the catalytic effects will be treated together as a bimetal effect, caused by the combination of an active metal with an inactive one.

This effect is similar in the conversion of cyclohexane and of n-heptane. With n-hexane the same trends could be observed (16). The same behaviour in the dehydrogenation and in the dehydrocyclization indicates that the metallic and not the acidic sites are modified by the second metal. This is in contradiction with the conclusions of Bacaud et al. (5).

The main result is that there exist both a positive bimetal effect with increasing activities and selectivities of aromatization and a negative bimetal effect with decreasing activities and selectivities. The contradictory behaviour of these bimetallic catalysts obviously depends on the reaction conditions. A simple rule can be found for
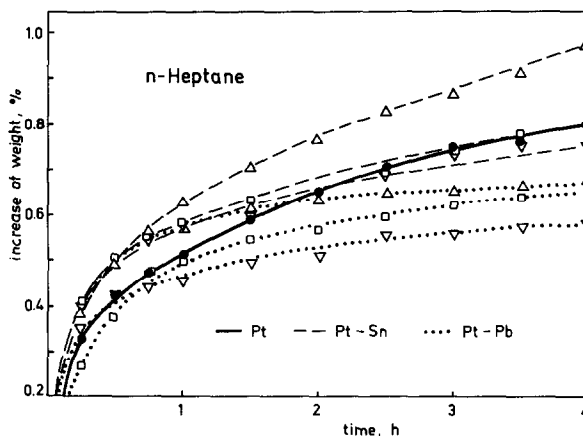
FIG. 7. Increase of weight for mono- and bimetallic catalysts during the conversion of n-heptane at 803 K. Metals in wt% ●———●, 0.50 Pt; ∇–––∇, 0.15 Sn, 0.50 Pt; □–––□, 0.30 Sn, 0.50 Pt; △–––△, 0.60 Sn, 0.50 Pt; △ · · · △, 0.30 Pb, 0.50 Pt; □ · · · □, 0.48 Pb, 0.50 Pt; ∇ · · · ∇, 0.75 Pb, 0.50 Pt.

this dependence. A negative bimetal effect is connected with mild reaction conditions, and a positive one with severe reaction conditions. Under mild conditions the main reaction proceeds selectively without self-poisoning deactivation. These conditions are represented by lower reaction temperatures and/or by higher hydrogen pressures. Under severe conditions the main reaction is accompanied by destructive side reactions and the catalyst is deactivated by carbonaceous deposits. Such conditions are high temperature and/or low hydrogen pressure. The observed strong variations in activity can be described on the basis of this rule.

The dehydrogenation of cyclohexane at about 600 K proceeds under mild conditions, and benzene is the only product. Addition of Pb or Sn strongly inhibits the activity. This is the negative bimetal effect (Fig. 2).

At about 770 K the conditions are severe. The Pt catalyst suffers strong self-poisoning and becomes unselective (Fig. 3). Its activity is even lower than at 588 K. Now some bimetal catalysts are much more active, selective, and stable (Figs. 2, 3). They demonstrate a positive bimetal effect.

The conversion of n-heptane has also been studied under different conditions. It

is a well-known experience from the reforming process that the deactivation of the catalyst is inhibited by high hydrogen pressures. Therefore the reaction conditions of 0.8 MPa and 773 K are relatively mild. Indeed, no increase of the aromatization by bimetallic catalysts was observed (Fig. 6). If at the same pressure the temperature is increased, then especially cracking and deactivation increase, and the conditions become more severe. At 803 K bimetallic catalysts give a positive bimetal effect (Fig. 6). Another possibility of increased severity is to lower the pressure. At 0.1 MPa the increased aromatization on bimetallic catalysts has been demonstrated (Fig. 5).

To sum up, all the experiments are in accordance with the conclusion that the bimetal effect drastically changes with the transition from severe to mild conditions. This gives the possibility of varying activity and selectivity of bimetallic catalysts in a desired way. This is interesting not only from a theoretical but also from a practical point of view. Dehydrogenation and dehydrocyclization under severe conditions are the most important reactions of the reforming process. It is just under these conditions that the bimetallic catalysts become advantageous.

The reason for the variable activity of

bimetallic sites can be explained by a model of twofold modified Pt clusters; under mild conditions they are modified by the second metal only, whilst under severe conditions they are modified by poisoning carbonaceous residues and this modification is influenced by the second metal.

Under mild conditions one observes only a decreased activity on bimetallic catalysts, as can be seen in the dehydrogenation of cyclohexane at 588 K (Fig. 2). From spectroscopic measurements an electronic interaction between Pt and Pb (11) or Sn (3) has been concluded. Therefore Pt sites should be chemically modified according to a ligand effect (17). This could be the reason for the decreased activity of the bimetallic clusters. This is in accordance with the observed increased activation energy on bimetallic catalysts. Under severe conditions the Pt clusters are modified by the second metal and by poisoning carbon deposits. Under these conditions the bimetallic clusters exhibit new and interesting properties. In comparison with the effects of Pt catalysts, the hydrogenolytic splitting of C–C bonds is inhibited, the aromatization is increased, and the deactivation of the catalyst is retarded.

The inhibition of the hydrogenolysis is demonstrated by the decreased amount of cracking products in both reactions (Figs. 3, 4) and the ratio of benzene and toluene in the products (Table 1).

The inhibition can be explained according to an ensemble effect. It is known that the hydrogenolysis requires bigger ensembles than the dehydrocylization or the dehydrogenation (18). The dilution of an active metal, for instance, a group VIII metal, with an inactive one, for instance, a group Ib metal, causes the strongest blocking in the biggest ensembles. Therefore the selectivity shifts from the hydrogenolysis towards the other reactions. This model can be applied in the present case, too. The active Pt ensembles are blocked by inactive Pb or Sn. The hydrogenolysis decreases and the aromatization increases. Moreover,

small amounts of the second metal are relatively more effective in the blocking of the ensembles than large amounts. In catalysts with large amounts of the second metal the observed poisoning of the Pt by an electronic modification could become the dominant influence, resulting in an inactive and unselective catalyst. In this way the maxima of aromatization with bimetallic catalysts, observed in both reactions, can be explained.

Up to now it has not been clear whether the supported clusters are alloys or not, and it is more a matter of convenience that the term metallic cluster is used. There exist certain hints that at least Sn is not in the zerovalent state in the clusters (19). However, for the above discussion it should be of no influence whether the Pt ensembles are blocked by atoms or by ionic species of the second metal.

Monometallic Pt clusters suffer drastic deactivation under severe conditions. This is demonstrated by the low activity of the cyclohexane conversion at 773 K, which is no higher than at 588 K. The deactivation is not only a simple blocking of the active sites, the selectivities for aromatization and hydrogenolysis change, too, with increasing reaction time (Figs. 3, 4). Therefore the working catalyst must be a Pt cluster which is continuously modified by carbonaceous residues. Considerable changes of selectivities of Pt by carbon or coke are known from other systems (20–22).

On appropriate bimetallic clusters the continuous deactivation is retarded. During the reaction they maintain higher activities and selectivities for aromatization for a longer time. This is evidenced by typical activity/time curves of mono- and bimetallic catalysts in Figs. 3 and 4. A consequence of the slower deactivation is again a maximum of activity as a function of the bimetal content. Small amounts of bimetal form active bimetal clusters, being less sensitive in deactivation; large amounts could block these clusters.

The observed maxima of activity (Figs.

2, 5, 6) therefore can be derived either from an inhibited hydrogenolysis or from a retarded deactivation. It is a question of whether both effects are really independent of one another. The hydrogenolytic splitting is normally connected with a deactivating deposition of coke. The simplest explanation would be that on bimetallic clusters the hydrogenolysis is inhibited and therefore the deactivating coke production is inhibited, too. The overall coke deposition has been determined gravimetrically, but no significant difference between mono- and bimetallic catalysts could be observed. It is possible that this method is too insensitive, detecting only the large amounts of "inactive" coke on the carrier, whereas those small amounts which really modify the metallic clusters remain undetected. Another independent possibility of a retarded deactivation is that a polycentric adsorption of poisoning intermediates is inhibited on bimetallic clusters. This would be in accordance with the conclusions of Masai et al. (8). They have investigated hydrogenations and dehydrogenations on silica-supported Pd–Sn and Ni–Sn catalysts and have found inhibiting and promoting effects of tin, too. They assume that tin lowers the adsorption of poisoning carbonaceous materials. Further experiments should be made in order to find a unique explanation of the retarded deactivation on bimetallic catalysts.

CONCLUSIONS

Additions of Pb or Sn have nearly the same influence on Pt/Al₂O₃ catalysts in dehydrogenation and dehydrocyclization.

Bimetallic catalysts can effect both positive and negative shifts of activity and selectivity.

As a rule the negative bimetal effect is connected with mild nondestructive reaction conditions, and the positive effect with severe destructive and deactivating reaction conditions.

Under severe conditions on bimetallic catalysts the aromatization is increased in comparison with Pt, whilst the hydrogenolysis is inhibited and the deactivation is retarded.

The variable activity of the bimetallic sites is explained by a model of twofold modified Pt clusters. Under mild conditions they are modified by the second metal, only. Under severe conditions they are modified by poisoning carbonaceous residues and additionally this modification is influenced by the second metal.

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