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The Influence of Sulfur and Carbonaceous Deposits on the Selectivity and Activity of Pt/Co Catalysts in Hydrocarbon Reactions

M. J. DEES AND V. PONEC

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

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The selectivity patterns in *n*-hexane/hydrogen reactions have been studied with silica and γ-alumina-supported Pt/Co monometallic and bimetallic catalysts. X-ray diffraction data of the silica-supported systems indicate that although alloys are formed, a part of Co stays out of the alloy particles observed by XRD. Changing the Co content in the bulk of the catalyst results in a dramatic shift in selectivity, due to the hydrogenolytic activity of Co. Also the activity and deactivation strongly depend upon the Co content. Presulfurization or coking of the bimetallic Pt/Co catalysts leads to a strong increase in the selectivity to isomerization when acidic sites are present. Experiments with pyridine confirm the acidic character of isomerization by γ-alumina. © 1989 Academic Press, Inc.

INTRODUCTION

Metal-based catalysts are widely used in the upgrading of naphtha. Because of the formation of carbonaceous deposits (coke) (*1–5*) the activity of the catalyst decreases during the reforming process and finally regeneration or replacement of the catalyst is necessary. The bimetallic catalysts such as Pt/Re (*6–9*), Pt/Ir (*10–13*), and Pt/Sn (*14–16*) show an increased stability and thus a much longer lifetime when compared with the monometallic Pt catalyst (*17, 18*). The addition of the second active component slows down the deterioration of the catalyst by coke deposits. Also the addition of sulfur (*13, 19*), or alloying of Pt with an inactive element (e.g., Sn) (*14–16*) can improve the stability of the catalysts.

It has been observed by Sachtler that sulfurization of Pt/Re catalysts increases the H/C ratio of hydrocarbon deposits on the metal surface (*20*). In the case of the bimetallic Pt/Ir catalyst, the Ir component is said to play an active role in preventing the deposition of coke by hydrogenolysis of the coke precursors (*21*). Temperature-programmed oxidation studies of coked Pt/Ir catalysts (*2, 22*) indeed revealed a decrease in carbonaceous deposits on the metal function when compared with the monometallic Pt catalyst. Given that Re and Ir can suppress coking (deactivation) of Pt, we now ask about the behavior of another metal with a similar hydrogenolytic activity—cobalt.

It is well known from the literature that Co, like Ir, Ru, Rh, and Ni, possesses a high hydrogenolytic activity which can be suppressed by coking (*23*) or by alloying (*24–26*). A zero selectivity to isomerization has been observed in the case of Co and Ni with several hydrocarbons such as *n*-hexane (*27, 28*), 2,2-dimethylpropane (*29*), 2,3-dimethylbutane (*28, 30*), 2,2-dimethylbutane (*27, 28*), and 2- and 3-methylpentane (*28, 31*). In contrast to these results, some isomerization of *n*-hexane over Ni has been reported (*32–34*). Aromatization by Co and Ni of 2-methylpentane and 3-methylpentane has also been observed (*35*) and is accompanied by side reactions which result in the formation of toluene. This has been demonstrated by Sárkány (*35*) who showed that Co and Ni, at low hydrogen/hydrocarbon ratios (about 2), can transform 2-methylpentane, 3-methylpentane, and 3-ethylpentane into toluene and ethylbenzene, respectively, while producing benzene simultaneously. According to

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Sárkány, the formation of benzene takes place via a CH_x addition–abstraction mechanism. The question is how is Co influenced in this respect by alloying with a metal which does not induce such a reaction?

Measurements by van Broekhoven and Ponec on methane/deuterium exchange reactions (*36*) indicate that Co and Ir, once metal–alkyl species are formed, quickly convert these species further to carbenes, carbynes, or carbides. Both Co and Ir prefer the formation of multiple bonds with the carbon atoms of hydrocarbons. Pt on the other hand shows a higher preference for single-bonded species and a low propensity to form multiple bonds (carbenes, carbynes, carbides). The excellent ability to form multiple bonds probably explains the high hydrogenolytic activity of Co and Ir. Can Pt in this respect modify Co in a similar way as an "inactive" metal would do?

Due to their successful applications, the Pt/Ir and Pt/Re bimetallic catalysts have already attracted much attention in fundamental research laboratories (*2–4, 9, 11–13*) and several theories have been formulated to explain the catalytic behavior of these bimetallics. Platinum–cobalt alloys (*37, 38*) offer a possibility of extending the verification of the existing ideas. Since the beneficial effect of Re or Ir on Pt is achieved in the sulfided state of the catalysts, this implies that not only should the fresh catalysts be studied, but also catalysts after a sulfur and/or carbonaceous layer deposition on their surfaces. Since the fresh and poisoned catalysts usually show different relative contributions of the metallic and acidic centers to the overall reaction, two kinds of support were investigated: an inert silica and acidic γ-alumina. The role of the acidic centers was then checked by using pyridine as a poison of the acidic centers.

EXPERIMENTAL

Two series of catalysts were prepared with varying Pt/Co atomic ratios using a wet impregnation method. One set of catalysts was prepared using silica as a support (Merck, <230 mesh) and a second series of catalysts using γ-alumina as a support (CK300, Cyanamid/Ketjen). The total metal loading of both series of catalysts was 5.0 wt%. The precursors H_2PtCl_6 (Johnson Matthey Chemicals) and $CoCl_2 \cdot 6H_2O$ (Merck) were dissolved in water, to which a small amount of concentrated hydrochloric acid was added (during the wet impregnation all solutions contained the same amount of chlorine). After evaporation of water at 373 K, the catalysts were dried for 16 h at 383 K in air. All catalysts containing γ-alumina as a support were calcined in air for 4 h at 520 K primarily to remove strongly held water at the surface of the support. Prior to the catalytic experiments, the deposition of coke, and the presulfurization, all catalysts were reduced in a flow of pure hydrogen for 5 h at 700 K. Coking of the catalysts took place at 700 K for 3 h (*n*-hexane/hydrogen = 1/16). The presulfurization was accomplished in a flow apparatus. A hydrogen flow passed through a saturator (at room temperature) containing thiophene, producing a thiophene/hydrogen (1/13) mixture, before entering the reactor with the reduced catalyst. The presulfurization took place for 3 h at 570 K. Removal of weakly bound sulfur and partial removal of carbonaceous deposits ("stripping") was accomplished at 670 K for 16 h in a pure hydrogen flow. A similar method has been described previously (*39*). Finally, all catalysts were (re-)reduced *in situ* for 5 h at 700 K prior to the catalytic experiments.

The experiments were carried out using an *n*-hexane/hydrogen (1/16) mixture, 1 bar total pressure, and a total flow of 10 ml/min. The apparatus used consisted of a fixed bed, plug flow microreactor, flow meters, filters for cleaning gases, and an organic vapor saturator. The gas mixture was analyzed with a GLC (Packard 438 A). A preset program was used to study all catalysts in an increasing then decreasing temperature regime, which was the same in all experiments. The details have been published previously (*34*). To convert all olefins into saturated hydrocarbons (to make separation by GLC and analysis easier) the reactant mixture passed a second reactor containing a silica-supported Pt catalyst at 320 K. The data collection, storage, and evaluation all took place automatically.

The overall conversion, α, is calculated by

$$\alpha = \frac{100 \sum_{i=1}^{n} i \times C_i^{\mathrm{p}}}{\sum_{i=1}^{n} i \times C_i^{\mathrm{p}} + n \times C_n^{\mathrm{f}}} \quad (\alpha \text{ in } \%),$$

where C_i^{p} is a product with i C atoms and C_n^{f} the feed with n C atoms. All measurements have been performed at $\alpha < 10\%$ to avoid secondary reactions as much as possible. The selectivity to isomerization is calculated according to

$$S_{\mathrm{iso}} = \frac{100 \sum_{k=1}^{n} k \times C_k^{i}}{\sum_{i=1}^{n} i \times C_i^{\mathrm{p}}} \quad (S_{\mathrm{iso}} \text{ in } \%),$$

where $k \times C_k^{i}$ denotes isomerization product k. The selectivities to hydrogenolysis and dehydrocyclization are calculated using analogous equations. The relative yields, Y, defined as the total conversion (conversion ranging here from 0 to 1) per gram catalyst times the respective selectivity, are calculated to compare the performances of the fresh and presulfided catalysts.

Both silica as well as γ-alumina-supported catalysts were studied to check the influence of the support. Some experiments were performed in which small discrete amounts of pyridine in nitrogen were injected into the feed. This kind of experiment enables one to distinguish between the catalytic activity of the metal and the support function of the catalyst in reforming reactions.

The average particle size of the catalysts was determined by electron microscopy. The silica-supported catalysts were investigated by X-ray diffraction.

RESULTS

All silica-supported catalysts have been examined by X-ray diffraction, after reduction by hydrogen at 700 K for 5 h, to obtain information on the alloy formation. Unfortunately, the γ-alumina-supported catalysts could not be investigated by X-ray diffraction due to the interference between the diffraction patterns of the metal and the support. The results of the silica-supported catalysts, which are shown in Fig. 1, indicate that alloys are formed indeed, but a part of the Co is not present in the alloy particles (seen by XRD). It is further observed in Fig. 2 that a diffraction peak due to unalloyed Co appears in none of the bimetallic systems studied here. Only the pure Co catalyst shows a diffraction pattern which corresponds to the *hcp* structure of Co (*43*).

There are several possible reasons why diffraction patterns like those in Fig. 2 should be observed with Pt/Co alloys:

(1) Co, which is not present in the alloy particles, remains unreduced (silicates, spinels).

(2) The missing Co (in alloys) is present as XRD-amorphous Co (metal).

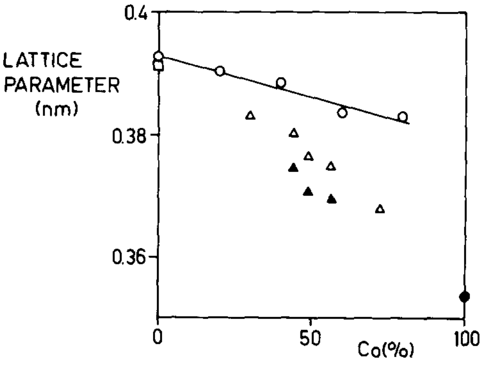

FIG. 1. Lattice parameter of the silica-supported catalysts (reduced at 700 K, 5 h) ○; △, ▲ lattice parameter of disordered fc cubic and ordered fc tetragonal alloys, respectively (*40*); □ lattice parameter of fc cubic Pt (*41*); ● lattice parameter of fc cubic Co (*42*).

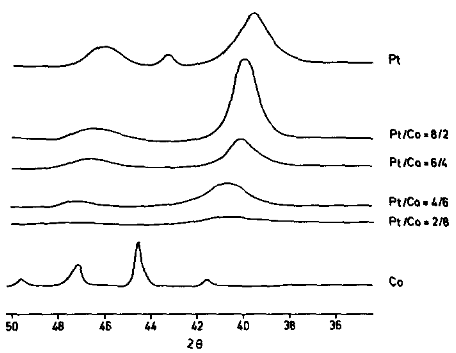

FIG. 2. Diffraction patterns of the silica-supported catalysts (reduced at 700 K, 5 h).

(3) The missing Co is present as a Co-rich, XRD-amorphous alloy.

According to a study by van 't Blik *et al.* (*44*) the reduction of an impregnated silica-supported Co catalyst (4.1 wt% Co) occurs in the relatively broad temperature range 273–600 K. Reduction of a γ-alumina-supported Co catalyst (4.44 wt% Co) occurred in the temperature range 443–653 K with a maximum rate at 543 K. According to Reuel and Bartholomew (*45*) a 75% reduction can be achieved with a silica-supported Co catalyst (3 wt% Co). The extent of reduction increases upon increasing metal loading. When the fraction of the metallic cobalt in some catalysts was determined by dissolving the metal in sulfuric acid and measuring the volume of the hydrogen evolved, the following results were obtained. The silica-supported Co system revealed a reduction of 81% and the silica-supported Pt/Co = 2/8 system showed a reduction of 84% (pure Pt does not dissolve). The comparable γ-alumina catalysts indicated reductions of 30% and 44% respectively with the standard reduction procedure at 700 K which is in good agreement with the literature (*45*, *46*). When a corresponding correction is made in Fig. 1, the experimental points obtained with the silica-supported Pt/Co catalysts shift in the direction of the massive Pt/Co alloys (triangles), but not far enough. Thus points (2) and (3) still have to be kept in mind.

If the observed line broadening is ascribed entirely to the diminished particle size, the diffraction patterns indicate that the silica-supported catalysts have an average particle size of about 5–7 nm. However, the diffraction pattern of the monometallic Co catalyst indicates particles of about 18 nm. Both silica- and γ-alumina-supported catalysts have been studied by EM (electron microscopy). The two series of catalysts showed particles of about 4–8 nm. The silica-supported monometallic Co catalyst showed particles of about 10–20 nm, again indicating that Pt influences (decreases) the particle size. EM also pointed out that the γ-alumina support was not visibly affected by the use of hydrochloric acid.

The H/*M* ratio of several silica-supported Pt/Co catalysts has been determined by hydrogen adsorption measurements (see Table 1). The hydrogen/Pt ratio has been obtained (at room temperature) at the equilibrium pressure of 0.1 Torr. Before chemisorption measurements, all samples were reduced *in situ* at 700 K for 5 h in a flow of pure hydrogen, evacuated, and subsequently cooled to room temperature under vacuum. The authors are aware of difficulties which arise when these or other similar (e.g., CO adsorption) data must be explained (chemisorption stoichiometry, crystal face population, etc.) and present

TABLE 1

Hydrogen Chemisorption (Volumetric Method) at 293 K and $P_{\text{equilibrium}} = 0.1$ Torr of the Silica-Supported Pt/Co Catalysts

Pt/Co	H/*M* ($\times 10^{-3}$)
100/0	80
60/40	22
20/80	14
0/100	0.2

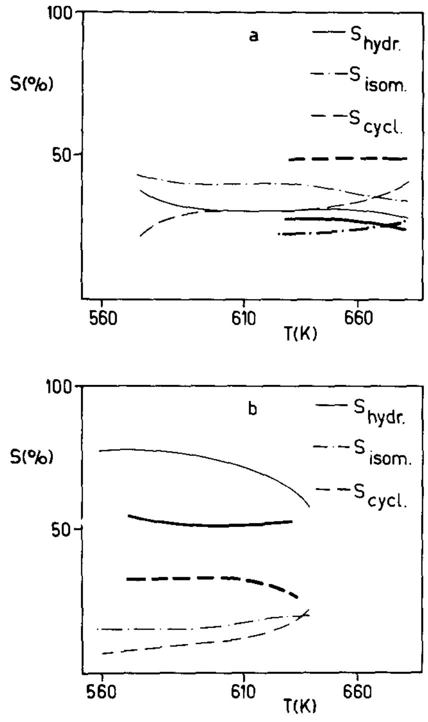

FIG. 3. Selectivity of silica-supported catalysts as a function of an increasing temperature regime: $S_{hydr.}$ (—), $S_{isom.}$ (- · · · -), $S_{cycl.}$ (- - -). The same for the decreasing temperature regime: $S_{hydr.}$ (—), $S_{isom.}$ (- · · · -), $S_{cycl.}$ (- - -); (a) Pt/Co = 8/2 (Pt-rich); (b) Pt/Co = 4/6 (Co-rich). Under (b) the selectivity to isomerization shows no change when the decreasing temperature regime is compared to the increasing temperature regime.

this table *only* for the sake of completeness of the characterization.

The catalysts were studied in the *n*-hexane/hydrogen reaction. The selectivities to hydrogenolysis, isomerization, and dehydrocyclization (the latter including benzene production) vary with temperature in a way which is illustrated by Fig. 3. In the range from 540 to 630 K, the silica- and γ-alumina-supported Pt-rich bimetallic catalysts present a rather constant selectivity and product distribution. However, a rapid deactivation due to carbonaceous deposits (during the experiment) occurs when the temperature rises above 630 K. The deposits result in a change in the selectivity pattern which is comparable to the changes observed when studying the Pt/Ir bimetallic systems (*47*). The selectivity to dehydrocyclization increases and the selectivity to isomerization decreases. The selectivity to hydrogenolysis shows only a slight decrease. The Pt-rich catalyst (Fig. 3a) shows a progressive poisoning at 685 K when held at this temperature. This leads to a change in selectivity as is indicated; the right end points of the curves do not coincide. The silica- and γ-alumina-supported Co-rich bimetallic catalysts show, at temperatures as low as 600 K, an even more pronounced deactivation during the experiment. However, the resulting change in the selectivity pattern is not the same as that observed for the Pt-rich bimetallic catalysts. Again, the selectivity to dehydrocyclization increases and the selectivity to hydrogenolysis decreases. The selectivity to isomerization remains constant in the case of the silica-supported catalysts, as is shown in Fig. 3b, and increases slightly in the case of the γ-alumina-supported catalysts. The latter is probably due to the acidic (isomerization) activity of the support which will be discussed below in more detail. It is obvious from the experiments that the presence of Co is responsible for the increased deactivation of the catalysts. Some coked Pt/Co bimetallic catalysts have been studied by X-ray diffraction but no evidence was found that the deactivation could be attributed to Co–carbide formation; however, this still does not completely exclude carbide formation in amounts undetectable by XRD. This is also true for the Co monometallic catalyst, which in contrast to all other (unpoisoned) catalysts showed an increasing activity with time.

The selectivities of the silica- and γ-alumina-supported catalysts are presented in Fig. 4, as a function of the bulk (atomic) percentage of Co. The unsulfided catalysts show a strong increase in the selectivity to hydrogenolysis and a decrease in the selectivities to isomerization and dehydrocyclization when the percentage of Co in the catalyst is increased. Both monometallic

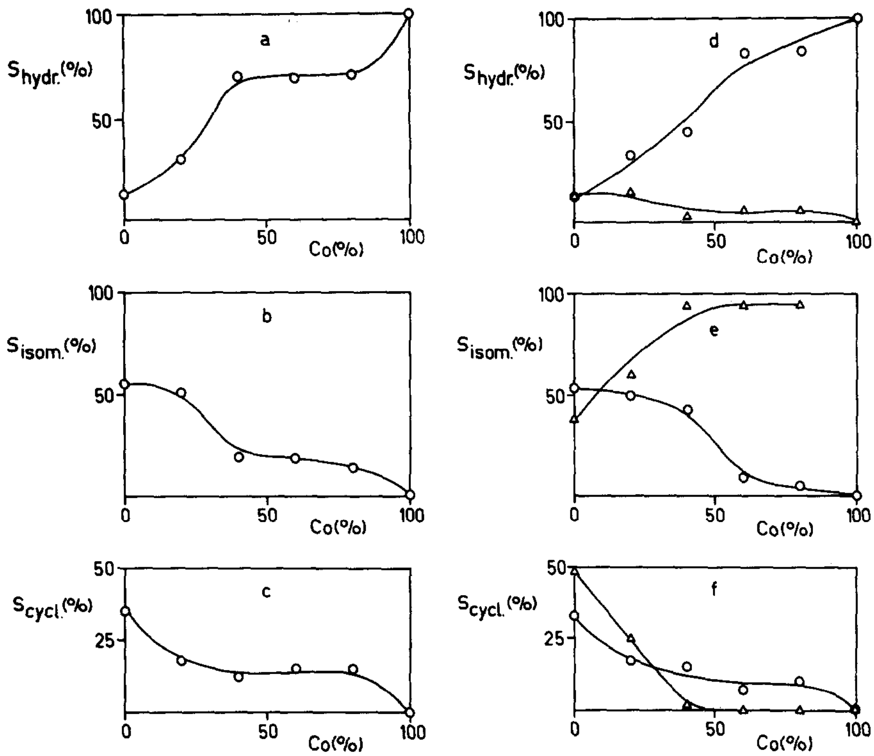

FIG. 4. Selectivities vs the Co bulk content of (O) unsulfided silica-supported catalysts (a–c). The same for (O) unsulfided and (△) presulfided γ-alumina-supported catalysts (d–f). (T = 620 K).

Co catalysts show a 100% selectivity to hydrogenolysis. However, the performance of the catalysts after the sulfurization is completely different. All silica-supported systems (except the sulfided monometallic Pt catalyst (*13*) which is not shown in Fig. 4) and the monometallic γ-alumina Co catalyst show no measurable activity in the sulfided state. The yields (per gram catalyst) observed with the γ-alumina-supported catalysts decrease by a factor of about 300 when compared with the unsulfided systems. The activity of the presulfided γ-alumina-supported catalysts shows a small increase during the experiments which can be attributed to a loss of sulfur. This loss of sulfur probably results only in an increase of the free metal surface but does not measurably affect the selectivity pattern. One can observe from Fig. 4 that the influence of sulfur on the Pt and Pt/Co systems, respectively, is rather different. When considering the γ-alumina-supported Pt and Pt-rich systems, sulfurization results in an increase in the selectivity to dehydrocyclization (mainly to methylcyclopentane), whereas the catalysts containing 50 at.% Co in the bulk (and more) do not form any cyclic products. The influence of sulfur and carbonaceous deposits (both are formed during the thiophene treatment) and of pure carbonaceous deposits on the product selectivities of a silica- and a γ-alumina-supported Pt/Co bimetallic catalyst, at 620 K, is shown in Fig. 5. The unmodified catalysts show a completely different product distribution. The silica-supported catalyst shows a rather small amount of multiple cracking, as one can see by comparing the selectivities to methane vs pentane and ethane vs butane, respectively. The γ-alumina-supported system shows a pronounced multi-

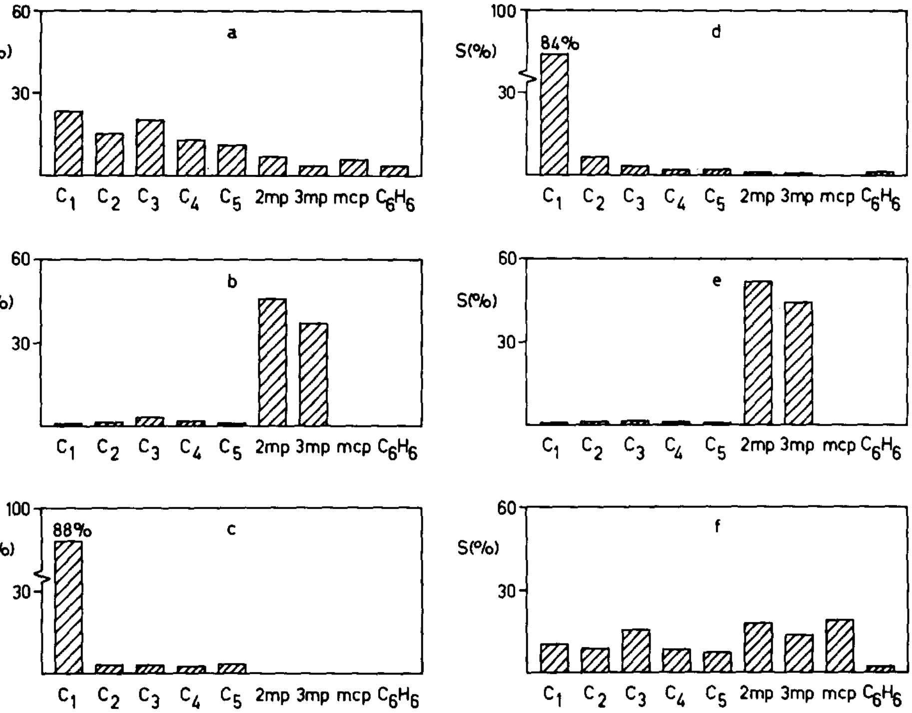

FIG. 5. Product selectivities of silica and γ-alumina-supported catalysts (Pt/Co = 4/6, T = 620 K): (a) unsulfided, silica-supported; (b) a mixture of the presulfided silica-supported catalyst with acidic γ-alumina support; (c) coked, silica-supported; (d) unsulfided γ-alumina-supported; (e) presulfided γ-alumina-supported; (f) coked γ-alumina-supported.

ple cracking leading to a high selectivity to methane (84%). An explanation for this enhanced "Co-like" character of the γ-alumina-supported catalyst is not at hand. One might argue that Co in the alumina-supported catalysts is alloyed less than that in the silica-supported systems.

With the silica-supported system, the influence of sulfur on the product distribution could not be studied because of the complete absence of activity after the standard sulfurization procedure. Therefore, we decided to mix the "inactive" presulfided silica-supported system with an equal amount (weight) of fresh and acidic γ-alumina. The product distribution of this mixture and the resulting yields are fully comparable to those obtained when using the presulfided γ-alumina-supported catalyst. Both systems result in an almost pure selectivity to isomerization (2 and 3 mp). This experiment is a good indication that acidic activity plays an important role even at relatively low temperatures. The role of the silica-supported sulfided Pt/Co system obviously is the formation of dehydrogenated hydrocarbons.

The deposition of coke at an elevated temperature (700 K) demonstrates a striking difference between both bimetallic systems (the total activity at 620 K of both coked catalysts was nearly the same). The silica-supported catalyst shows a dramatic shift to hydrogenolysis (severe multiple cracking, which could be due to unalloyed Co or a Co-rich, XRD-amorphous alloy), whereas coking of the γ-alumina-supported system induces a shift to the isomerization and cyclic products. It has been confirmed by an experiment in which pure hydrogen flowed past the coked catalyst that the high selectivity to methane of the silica-sup-

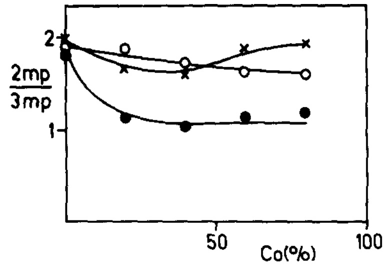

FIG. 6. 2/3 mp ratio ($T = 620$ K) vs Co bulk content: (×) unsulfided silica-supported catalysts; (○) unsulfided γ-alumina-supported catalysts; (●) presulfided γ-alumina-supported catalysts.

ported system was not due to the removal of the previously deposited coke during this experiment.

It is worthwhile mentioning that in the case of the Pt/Co bimetallic systems, the sulfurization process strongly influences the ratio of 2 and 3 mp. As shown in Fig. 6, the unsulfided silica- and γ-alumina-supported catalysts feature ratios between 1.6 and 2, which are the values commonly found with Pt (*48*). However, the presulfided γ-alumina-supported catalysts (as well as the mixture which has been discussed in relation to Fig. 5) show 2/3 mp ratios near unity. This can all be explained by the fact that the ratio of 2 and 3 mp is governed by the type of isomerization. The isomerization with the sulfided catalysts obviously results from the catalytic activity of the acidic γ-alumina.

The yields of various products obtained with the presulfided γ-alumina-supported catalysts vary with the Co content as demonstrated in Fig. 7. As one can observe, all yields show a rapid decrease with the increasing percentage of Co in the catalysts. The presulfided monometallic Co catalyst did not show any activity at all. The yield of the isomerization products is almost constant in the region from 40 to 80 at.% Co. It is obvious from Fig. 7 that the yields of the cyclic and hydrogenolyzed products observed with the presulfided catalysts are mainly due to the surviving catalytic activity of Pt, as they all rapidly decrease with an increasing Co content.

The presence of an acidic activity has been checked by experiments in which pyridine is injected (2–4 ml of a saturated pressure of pyridine in a nitrogen flow at 298 K) into the reaction mixture, to poison the acidic centers. The dosing of pyridine was repeated until almost no further change in activity or selectivity was observable. The results of these measurements are shown in Fig. 8.

As can be observed with both catalytic systems studied (presulfided monometallic Pt and presulfided bimetallic Pt/Co = 4/6, both supported by γ-alumina), the addition of pyridine results in deactivation. In the case of the monometallic Pt system, isomerization and dehydrocyclization are suppressed most, whereas hydrogenolysis is less affected. However, with the bimetallic Pt/Co system both isomerization and hydrogenolysis are affected in the same manner during the experiment described (no formation of cyclic products at all). This might indicate that with this catalyst a part of hydrogenolysis can also be catalyzed by the support. It is obvious that mainly the metal activity of Pt is responsible for dehydrocyclization. The degree of deactivation as a result of the addition of pyridine shows large differences. The activity of the monometallic Pt catalyst decreases by a factor of about 3 in contrast with the bimetallic Pt/Co system which loses almost all its activity.

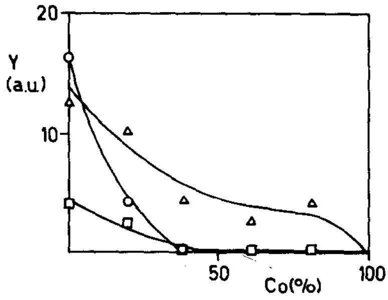

FIG. 7. Yields vs Co bulk content of the presulfided γ-alumina-supported catalysts ($T = 620$ K): (△) isom.; (○) cycl.; (□) hydr.

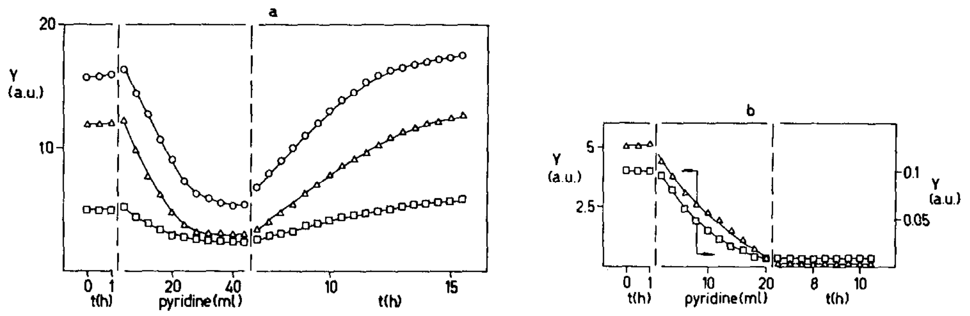

FIG. 8. The yields with presulfided γ-alumina-supported catalysts ($T = 620$ K) vs time-on-stream (h). During the experiments, pyridine was injected into the feed: (△) isom.; (○) cycl.; (□) hydr. (a) Monometallic Pt; (b) bimetallic Pt/Co = 4/6.

The most pronounced difference between both systems is the complete recovery of activity and selectivity of the presulfided Pt catalyst and the enduring deactivation of the bimetallic system. This indicates that acidic activity plays a very important role in the sulfided bimetallic Pt/Co system. The same behavior (i.e., no recovery of activity) has been observed for the sulfided Pt/Re system (*49*). On the other hand, the presulfided Pt catalyst resembles the presulfided Pt/Ir system (*13*); both systems show a complete recovery of activity and selectivity when the dosing of pyridine is stopped.

DISCUSSION

The X-ray diffraction data indicate a partial alloy formation of the silica-supported Pt/Co catalysts. However, with an increasing percentage of Co, only a small decrease of the lattice parameter is observable. Nevertheless, no XRD evidence is found for the existence of unalloyed particles, neither of Pt nor of Co. The problems encountered here have already been mentioned in the context of Figs. 1 and 2, and little can be added. Inspection of Fig. 5 reveals that a coked silica-supported Pt/Co catalyst shows a remarkably high selectivity to methane as one would expect of pure Co (multiple cracking). This might indicate that some unalloyed Co or Co-rich particles are present. However, an infrared study of adsorbed carbon monoxide on Pt–Co mono- and bimetallic systems did not reveal the existence of these particles (*47*).

Another important question is the surface composition of the bimetallic systems. All data presented in this paper clearly indicate that even a relatively small amount of Co has a strong influence on the performance (activity and selectivity) of the catalyst, irrespective of whether the catalyst is presulfided or not. This behavior probably indicates that the metal surface is enriched in Co, which, indeed, can be expected if the segregation is a purely enthalpy-driven process. Some segregation certainly can be expected in the alloy particles as large as those used in our experiments. If for any (kinetic) reason no segregation takes place, the selectivity patterns could also be explained by assuming the presence of unalloyed Co or of Co-rich alloys.

The deactivation of the catalysts by carbonaceous deposits shows a strong correlation with the amount of Co in the system. An increasing amount of Co implies an enhanced deactivation whereas the selectivity is also influenced. Thus, in this respect Co clearly differs from Re and Ir. It is also interesting to note that Pt/Co alloys differ from pure Co in this respect. The striking difference in the product selectivity between both coked catalysts, as described in the context of Fig. 5, indicates the importance of the nature (mainly the acidity) of the support.

The sulfurization of the γ-alumina-supported catalysts results in a shift from metal- to acid-catalyzed isomerization (and hydrogenolysis), increasing with an increasing amount of Co. This is confirmed by the experiment in which pyridine was injected into the feed. With the presulfided monometallic Pt catalyst the metal-like reactions still prevail. On the other hand, the presulfided Pt/Co catalysts mainly show an acid-like activity.

The increase in activity during the experiments with the presulfided catalysts (probably due to a loss of sulfur) has also been observed with the presulfided Pt/Ir (*47*) and the presulfided Pt/Re system (*50*).

The 2/3 mp ratio is another good indication for the "metallic" or "acid site" isomerization. Previously reported results on Pt/*n*-hexane demonstrate that metal-like isomerization can be preceded by the formation of a five-membered ring (*48*) (methylcyclopentane-like intermediates). Opening of the ring intermediate results in a 2/3 mp ratio of about 2. As is demonstrated in Figs. 5 and 6, the acid-catalyzed isomerization of (dehydrogenated) *n*-hexane shows a 2/3 mp ratio of about 1, in favor of an acid-catalyzed mechanism.

No dehydrocyclization (aromatization) is observed with *n*-hexane and our silica/γ-alumina-supported Co catalysts. The selectivity to this reaction of the Pt/Co catalysts is low and can be ascribed to Pt.

Finally, a few words about the comparison of the bimetallic systems studied up to now in our laboratory: Pt/Re (*49*), Pt/Ir (*13*), and Pt/Co. Common to all three systems is that the element added to Pt, when unsulfided, prefers hydrogenolysis and does not deactivate as fast as pure Pt during hydrocarbon reactions. The first of the features manifests itself also in the bimetallic catalysts: in all three cases, the sulfur-free bimetallics show a lower isomerization and dehydrocyclization and a higher hydrogenolytic selectivity. The addition of Ir increases, in a broad range of alloy composition, the total activity of the catalyst (per gram) by a factor of about 3 when compared with the monometallic Pt catalyst. The monometallic Ir catalyst is far more active than the monometallic Pt catalyst. On the other hand, the addition of Co or Re to Pt decreases, in a broad range of alloy composition, the total activity by a factor of about 8. The second feature, an improved deactivation behavior due to the addition of a second metal to Pt, manifests itself only in the case of Ir and Re. The Pt/Co bimetallic catalysts deactivate more severely when compared with the monometallic Pt system.

In view of the practical application of such catalysts, it is also necessary to study the catalysts which have been modified by a reaction with a sulfur-containing feed (thiophene). In the sulfided state the catalysts mentioned show some similarities, but also some important differences. First, it is common to all of them that presulfurization of the catalysts, as described in this paper, strongly suppresses the total activity (per gram) by a factor ranging from 100 to 300 (deactivation, by the described standard sulfurization: Pt/Ir < Pt/Re < Pt/Co). The activity (hydrogenolysis, isomerization, and dehydrocyclization) of the presulfided catalysts is measurable (under our conditions) starting at a temperature of about 570 K, which is significantly higher (about 60 K) than that of the unsulfided systems. The sulfurization mainly suppresses the reactions which can be ascribed to the metallic surface. As a result, the acidic site activity is the one which survives the sulfurization best and this leads to a high isomerization selectivity. The sulfided metals themselves do not play the role of acidic centers, since sulfided, silica-supported Pt/Re and Pt/Co bimetallic catalysts do not show any (hydrogenolysis, isomerization, and dehydrocyclization) activity, in contrast to the sulfided, silica-supported Pt/Ir bimetallic systems which still show activity, attributed to preserved activity of the metal site. After the addition of γ-alumina to a sulfided silica-supported Pt/Co catalyst (Fig. 5b), one observes isomerization which is due to the acidic sites as the ratio 2/3 mp indicates.

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REFERENCES

1. Davis, S. M., Zaera, F., and Somorjai, G. A., *J. Catal.* **77,** 439 (1982).
2. Barbier, J., *in* "Proceedings, 4th International Congress on Catalyst Deactivation, Antwerp, 1987" (B. Delmon and G. F. Froment, Eds.), Vol. 34, p. 1. Elsevier, Amsterdam, New York, 1987.
3. Margitfalvi, J., Göbölös, S., Tálas, E., Hegedüs, M., and Szedlacsek, P., *in* "Proceedings, 4th International Congress on Catalyst Deactivation, Antwerp, 1987" (B. Delmon and G. F. Froment, Eds.), Vol. 34, p. 147. Elsevier, Amsterdam, New York, 1987.
4. Lieske, H., Sárkány, A., and Völter, J., *Appl. Catal.* **30,** 69 (1987).
5. Barbier, J., Churin, E., Marecot, P., and Menezo, J. C., *Appl. Catal.* **36,** 277 (1988).
6. Kluksdahl, H. E., US Patent 3,415,737 (1968).
7. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63,** 112 (1980).
8. Winter, W. E., and Markley, G. E., US Patent 4,440,628 (1984).
9. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **99,** 126 (1986).
10. Sinfelt, J. H., US Patent 3,953,368 (1976).
11. Ramaswamy, A. V., Ratnasamy, P., and Sivasanker, S., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976," Vol. 2, p. 855. The Chemical Society, London, 1977.
12. Rasser, J. C., Beindorff, W. H., and Scholten, J. J. F., *J. Catal.* **59,** 211 (1979).
13. Dees, M. J., and Ponec, V., *J. Catal.* **115,** 347 (1989).
14. Burch, R., and Garla, L. C., *J. Catal.* **71,** 360 (1981).
15. Dautzenberg, F. M., Helle, J. N., Biloen, P., and Sachtler, W. M. H., *J. Catal.* **63,** 119 (1980).
16. Beltramini, J., and Trimm, D. L., *Appl. Catal.* **31,** 113 (1987).
17. Haensel, V., US Patent 2,479,109 (1949).
18. Haensel, V., US Patent 2,479,110 (1949).
19. Barbier, J., and Marecot, P., *J. Catal.* **102,** 21 (1986).
20. Sachtler, W. M. H., private communication.
21. Carter, J. L., McVicker, G. B., Weissman, W., Kmak, W. S., and Sinfelt, J. H., *Appl. Catal.* **3,** 327 (1982).
22. Barbier, J., Corro, G., and Zhang, Y., *Appl. Catal.* **13,** 245 (1985).
23. van Senden, J. G., van Broekhoven, E. H., Wreesman, C. T. J., and Ponec, V., *J. Catal.* **87,** 468 (1984).
24. Ponec, V., and Sachtler, W. M. H., *J. Catal.* **24,** 250 (1972).
25. Sachtler, W. M. H., and van Santen, R. A., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 22, p. 69. Academic Press, New York, 1977.
26. Burch, R., and Mitchell, A. J., *Appl. Catal.* **6,** 121 (1983).
27. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58,** 268 (1979).
28. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **19,** 101 (1970).
29. Boudart, M., and Ptak, L. D., *J. Catal.* **16,** 90 (1970).
30. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58,** 260 (1979).
31. Paál, Z., and Tétényi, P., *Nature (London)* **267,** 234 (1977).
32. Anderson, J. R., and MacDonald, R. J., *J. Catal.* **19,** 227 (1970).
33. Anderson, J. R., MacDonald, R. J., and Shimoyama, Y., *J. Catal.* **20,** 147 (1971).
34. Ponec, V., and Sachtler, W. M. H., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 1, p. 645. North-Holland, Amsterdam, 1973.
35. Sárkány, A., *J. Catal.* **89,** 14 (1984).
36. van Broekhoven, E. H., and Ponec, V., *J. Mol. Catal.* **25,** 109 (1984).
37. Zyade, S., Garin, F., Hilaire, L., Ravet, M. F., and Maire, G., *Bull. Soc. Chim. Fr.,* 341 (1984).
38. Zyade, S., Garin, F., and Maire, G., *New J. Chem.* **11**(5) (1987).
39. Parera, J. M., Beltramini, J. N., Querini, C. A., Martinelli, E. E., Churin, E. J., Aloe, P. E., and Figoli, N. S., *J. Catal.* **99,** 39 (1986).
40. Martin, D. L., *Trans. Metall. Soc. AIME* **212,** 478 (1958).
41. Goldschmidt, H. J., and Land, T., *J. Iron Steel Inst. London* **155,** 221 (1947).
42. Luo, H. L., and Duwez, P., *Canad. J. Phys.* **41,** 758 (1963).
43. Hofer, L. J. E., and Peebles, W. C., *J. Amer. Chem. Soc.* **69,** 893 (1947).

44. van 't Blik, H. F. J., Koningsberger, D. C., and Prins, R., *J. Catal.* **97,** 210 (1986); van 't Blik, H. F. J., and Prins, R., *J. Catal.* **97,** 188 (1986).
45. Reuel, R. C., and Bartholomew, C. H., *J. Catal.* **85,** 63 (1984).
46. Chin, R. L., and Hercules, D. M., *J. Phys. Chem.* **86,** 360 (1982).
47. Dees, M. J., unpublished results.
48. Gault, F. G., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 30, p. 1. Academic Press, New York, 1981.
49. Rek, P. J. M., den Hartog, A. J., and Ponec, V., *Appl. Catal.* **46,** 213 (1989).
50. Rek, P. J. M., den Hartog, A. J., and Ponec, V., unpublished results.