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On the Influence of Sulfur on the Platinum/Iridium Bimetallic Catalysts in *n*-Hexane/Hydrogen 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 reactions of *n*-hexane and hydrogen have been studied over silica- and γ-alumina-supported monometallic and bimetallic Pt/Ir catalysts. Temperature-programmed reduction and X-ray diffraction clearly indicated alloy formation in the silica-supported catalysts. Changing the Ir content in the bulk of the catalyst resulted in a dramatic shift in selectivity due to the hydrogenolytic activity of Ir. However, after sulfurization all catalysts containing Ir showed a "Pt-like" behavior with respect to the selectivity. The increased yields of the sulfided Ir and Pt/Ir catalysts, when compared with the sulfided Pt catalysts, might be due to the relatively high dehydrogenating activity of Ir. © 1989 Academic Press, Inc.

INTRODUCTION

During the last 2 decades bimetallic catalysts, such as Pt/Ir (*1–4*), Pt/Re (*5–8*), and Pt/Sn (*9, 10*) have replaced the monometallic Pt (*11, 12*) catalysts in the naphtha reforming almost completely. The advantages of using bimetallic catalysts are the much longer lifetime of bimetallics (longer reforming cycles), improved gasoline yields, and a higher activity. Under comparable conditions only the Pt/Ir catalysts show a higher activity than the γ-alumina Pt catalysts. It has been reported that under industrial conditions Pt/Ir catalysts are about three times as active as Pt/Re and Pt catalysts.

In naptha reforming the lifetime of a catalyst is governed by the rate of deactivation. The metal surface of a working, industrial catalyst is covered to a large extent by blocking carbonaceous (*13*) deposits and sulfur (*14*). The addition of a second metal (Ir, Re, Sn) (*15*) and/or sulfur (*16–19*) improves the stability (the lifetime) of the catalyst which, for example, in the case of Ir (at reforming conditions), is assigned to a diminished amount of carbonaceous deposits (*20–24*) on the metal function (the amount of coke on the support (γ-alumina) of the sulfided catalyst increases but is of minor importance (*25*)). This has been clearly shown by TPO (temperature-programmed oxidation) studies (*25, 26*). Iridium is believed to decrease the formation of certain coke precursors due to its hydrogenolytic activity in a similar way as Pt/Re. When a catalyst is sulfided, a number of effects can take place. First, the free metal surface becomes diluted, resulting in the so-called "ensemble size effect" (*27–29*). Furthermore, the sulfurization can decrease the formation of carbonaceous deposits on the metal surface, again possibly due to the "ensemble size effect."

Bimetallic catalysts are also of interest in the view of the fundamental research ("which factors regulate the selectivity of metal catalysts?" is a very important question) and therefore a considerable volume of data has already been gathered on the alloys and bimetallics. Examples of these studies are listed below. However, as can be expected, not all questions have already been answered. In this article an attempt is made to answer those which stayed open. In particular an exact comparison of sulfur free and presulfided catalysts for a broad

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range of alloy (bimetallic) compositions was missing. The data obtained on this subject are presented below.

EXPERIMENTAL

The catalysts investigated were prepared with varying Pt/Ir atomic ratios. Catalysts were prepared using the wet impregnation method, one set with a silica support (Merck, <230 mesh) and a second series of catalysts using a γ-alumina support (CK300, Cynamid/Ketjen). All catalysts contained 5.0 wt% of iridium and platinum together. The precursors, H_2PtCl_6 and $(NH_4)_2IrCl_6$ (Johnson Matthey Chemicals) 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 the evaporation of water at 373K, the catalysts were dried for 16 h at 383 K in air. The catalysts containing γ-alumina were calcined at 520 K for 4 h. Calcination at higher temperatures resulted, as has already been described previously (*30–32*), in the formation of large separated IrO_2 crystallites (catalytic experiments confirmed an increased "Ir-like" behavior in selectivity as well as activity). After reduction at 670 K for 5 h, the catalysts were sulfided using a thiophene/hydrogen (1/13) mixture at 570 K for 3 h. Removal of weakly bound sulfur and a partial removal of carbonaceous deposits was accomplished at 670 K for 16 h with hydrogen. A similar method has been described previously (*33*). Finally, all catalysts were (re-)reduced *in situ* for 5 h at 670 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 consists of a fixed bed, plug flow reactor, flow meters, filters for cleaning gases, an organic vapor saturator, and GLC analysis. A preset program was used to investigate all catalysts in an increasing followed by a decreasing temperature regime. The details have already 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 platinum catalyst at 320 K. Simultaneously, benzene was converted in cyclohexane. However, it has been established in separate experiments (with and without the second reactor) that practically no cyclohexane is formed without the use of a second reactor. The reactant gas mixture was analyzed using a GLC with automatic data collection, storage, and evaluation.

The overall conversion, α, is calculated by

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

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

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

where $k \cdot C_k^{j}$ denotes isomerization product k. The selectivities in hydrogenolysis and dehydrocyclization were calculated using analogous equations. The so-called multifission parameter M_{f} is defined as

$$M_{\mathrm{f}} = \frac{4C_2 + 3C_3 + 2C_4 + C_5}{C_1}.$$

A decrease of the parameter is an indication of an increase in multiple fission. To compare the performance of the presulfided catalysts also relative yields were evaluated and defined as the total conversion (conversion ranging from 0 to 1) times the respective selectivity, per gram catalyst.

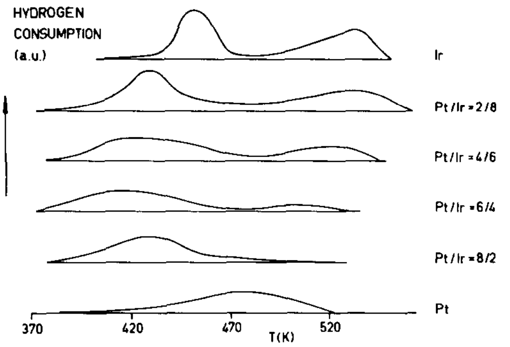

FIG. 1. TPR profiles of the silica-supported catalysts (dried at 380 K, 16 h).

To investigate the role of the support in the Pt/Ir catalysts a rather inert (silica) as well as an active (γ-alumina) support were used. To check the influence of a possible loss of sulfur and/or of coke formation, all catalysts were measured in an increasing, followed by a decreasing temperature regime. Experiments with pyridine were performed in order to distinguish between the catalytic activity of the metal and the support function. For this purpose small discrete amounts of pyridine were injected into the reactant mixture. The catalysts studied by X-ray diffraction (XRD) were all silica supported. The X-ray diffraction data of the catalysts were obtained on samples which were first reduced and subsequently exposed (slowly) to the ambient atmosphere. Thermal-programmed reduction (TPR) has been followed in a stream of a H_2/Ar mixture (5% H_2) with a temperature rise of about 5 K/min.

RESULTS

Typical results obtained by the use of TPR are shown in Fig. 1, for silica-supported catalysts (only the positions of the peaks are relevant). It can be seen immediately that the metals, platinum and iridium, influence each other upon reduction. The reduction of the bimetallic catalysts is achieved at a considerably lower temperature when compared to both the monometallic catalysts. A comparable shift in reduction temperature is observed when both metals are dispersed on γ-alumina which again indicates an interaction between both metals. Only the low-temperature TPR peak is relevant in this particular case. The high-temperature TPR peak which does not show a shift upon alloying is assigned to iridiumchloride or its combination with silica which is reduced less readily than the platinum compounds (*35*). Although these data might indicate the formation of bimetallic Pt/Ir clusters (alloys), it was nevertheless necessary to obtain further evidence. This has been achieved by X-ray diffraction of which the results are shown in Fig. 2. The data presented on the silica-supported catalysts in Fig. 2 show that the lattice parameter varies smoothly between Pt and Ir, in good agreement with the literature (*30, 36–38*). On the other hand, no diffraction data belonging to the pure metals have been observed. We consider it as a good indication that alloys have been formed in the whole concentration range. The γ-alumina-supported catalysts could not be investigated by X-ray diffraction because of the small metal particle size and the interference between the diffraction patterns of the metal particles and the support. Previously reported results on this subject (e.g., high-resolution electron microscopy (*39*) and X-ray diffraction (*40*)) are contradictory as far as a possible alloy formation is concerned. If the observed line broadening is ascribed entirely to the diminished particle size, the diffraction patterns indicate that all metals and alloys studied in

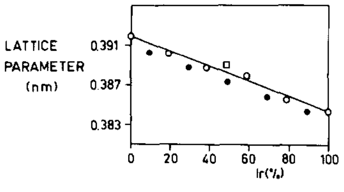

FIG. 2. (○) Lattice parameter of the silica-supported catalysts; (●) average values for the alloys quenched from homogeneous solid solutions (*36*); (□) average value determined from positions of a number of diffraction lines (*30*).

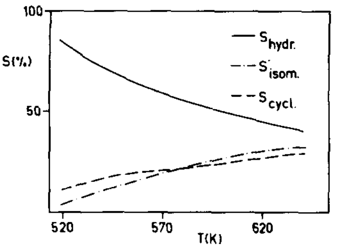

FIG. 3. Selectivity of a silica-supported catalyst (Pt/Ir = 8/2) as a function of an increasing temperature regime.

this paper had an average particle size of about 5 nm. A study of some samples by electron microscopy showed particles of the same size.

The selectivities to hydrogenolysis, isomerization, and dehydrocyclization (the latter including benzene) vary with temperature in a typical way which is illustrated by Fig. 3. In the range from 470 to 670 K, the selectivity to hydrogenolysis decreases while that to isomerization and dehydrocyclization increase with increasing temperature. However, when the selectivities are determined in the decreasing temperature regime (following the increasing temperature regime), the selectivity to hydrogenolysis remains the same when compared to the increasing temperature regime, whereas the selectivity to isomerization decreases and that to dehydrocyclization increases. The total conversion shows deactivation of the catalyst upon decreasing temperature, due to carbonaceous deposits. The presulfided catalysts preserve their activity as well as their selectivities when the decreasing temperature regime is compared to the initial, increasing, temperature regime. The selectivities vary when the content of iridium is changed, as is demonstrated in Fig. 4. Iridium is a very active catalyst for hydrogenolysis (*41–43*) so that it is not surprising that even at a small bulk concentration of Ir the effect on the selectivities is observable (although the surface concentration of Ir is most likely always smaller than the bulk concentration (*44, 45*)). However, the influence on the selectivity of Ir is so strong that it might even indicate that, in spite of good mixing, the alloys contain a small amount of unalloyed Ir which escapes detection by XRD. That could also explain why the effect of Ir is even more pronounced on γ-alumina-supported catalysts

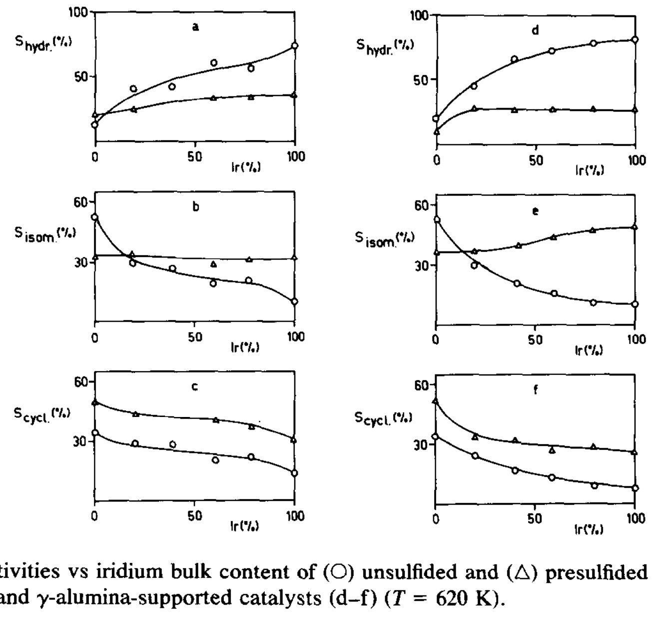

FIG. 4. Selectivities vs iridium bulk content of (○) unsulfided and (△) presulfided silica-supported catalysts (a–c) and γ-alumina-supported catalysts (d–f) (T = 620 K).

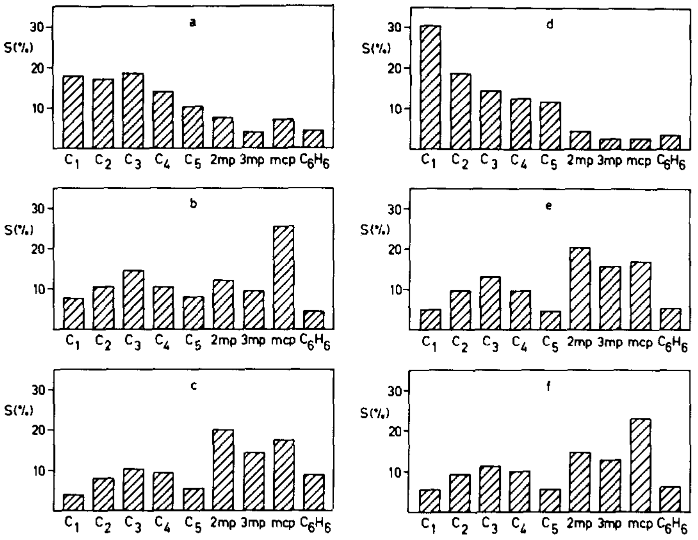

FIG. 5. Product selectivities of silica- and γ-alumina-supported catalysts (Pt/Ir = 4/6, T = 620 K): (a) unsulfided silica supported; (b) presulfided silica supported; (c) physical mixture of the sulfided silica-supported catalyst and calcined γ-alumina (520 K, 4 h); (d) unsulfided γ-alumina supported; (e) presulfided γ-alumina supported; (f) presulfided γ-alumina-supported catalyst, treated with pyridine.

when compared to silica-supported catalysts.

Modification of the catalyst by the thiophene/hydrogen treatment, which leads to sulfurization of the surface and probably to deposition of carbonaceous deposits, changes the activity and selectivity (when compared to sulfur free catalysts) of the catalysts in a dramatic way. It is interesting to note that sulfur not only suppresses the total hydrogenolysis, but also changes the character of hydrogenolysis as can be seen in Fig. 5. Modification by sulfur suppresses the terminal and multiple hydrogenolysis (methane) more than the internal fission (e.g., propane). This is also documented by the parameter of fission M_f. Modification by sulfur results in more "Pt-like" catalysts, as can be seen in Fig. 6. Modification of the catalyst by the thiophene treatment is also beneficial for the isomerization and dehydrocyclization selectivities. The thiophene treatment causes a suppression by a factor of about 100 of the total activity of all catalysts. In general, the bimetallic catalysts are about three times more active than the Pt catalysts and about three times less active than the Ir catalysts.

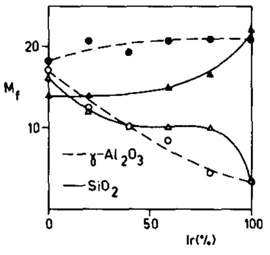

FIG. 6. Multifission parameter, M_f, vs iridium bulk content (T = 620 K): (△) unsulfided silica supported; (▲) presulfided silica supported; (○) unsulfided γ-alumina supported; (●) presulfided γ-alumina supported.

There is a very interesting difference in the isomerization activities of the sulfur-modified catalysts. Iridium, or iridium-rich alloys show after sulfurization an isomerization activity which is strongly dependent on the support being used, as is shown in Fig. 7. This evoked the suspicion that the isomerization activity difference between the silica- and alumina-supported catalysts is due to the acidic isomerization on γ-alumina. This suspicion has been proven justified by the results of experiments in which

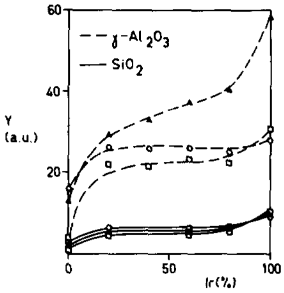

FIG. 7. Yield vs iridium bulk content of the presulfided silica- and presulfided γ-alumina-supported catalysts (T = 620 K): (△) isom.; (○) cycl.; (□) hydr.

pyridine was injected in discrete amounts (2 ml of saturated pressure pyridine at 373 K) into the stream of the reaction mixture. As can be seen in Fig. 8, isomerization is suppressed most when pyridine is added, as one would expect if a substantial part of isomerization results from acidic (γ-alumina) activity. It is interesting to note that poisoning of both metallic and acidic functions is reversible to a greater extent. This is different from the results obtained with γ-alumina-supported Pt/Re bimetallic catalysts (*46*). Close inspection of Fig. 5 reveals the following interesting fact. When a physical mixture of a silica-supported catalyst (60 wt% Ir) with metal free γ-alumina is prepared, the mixture shows the same selectivity in the sulfided state as the corresponding γ-alumina-supported catalyst. Vice versa, when a presulfided catalyst with γ-alumina as a support is treated by pyridine, the selectivity pattern is the same as with the silica-supported analog. This illustrates the important contribution of acidic centers in the reactions with sulfided catalysts. This contribution of acidic centers is overshadowed by the high metal activity when unsulfided catalysts are monitored in the temperature range 470–670 K, but it becomes more important when the catalysts have been presulfided. It is certainly even more important under industrial conditions where the operation temperature is about 700 K.

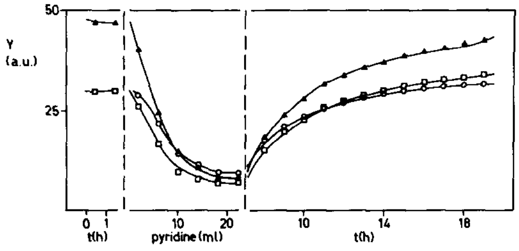

FIG. 8. Yield of a presulfided γ-alumina-supported catalyst (Pt/Ir = 2/8, T = 620 K) vs time-on-stream (h). During the experiment, pyridine was injected into the feed (total amount: 22 ml): (△) isom.; (○) cycl.; (□) hydr.

DISCUSSION

When working with bimetallic/alloy catalysts one has to obtain some information on (a) alloy formation and (b) surface composition. As far as the first problem is concerned, the data strongly indicate that alloy formation indeed occurred when silica is used as the support: TPR shows mutual influence of the metals on each other, XRD data show a smooth, linear variation in the lattice parameter when the composition of the catalyst alters, and the same is true for the selectivity parameters. In the case of the γ-alumina-supported catalysts only the mentioned TPR experiments might give an indication of alloy formation. On the other hand, the information on surface composition is, in general, less conclusive. There are already data available on the surface composition of bulk powder materials but there is no information on the powders we have been using. In the graphical presentation of our data, the parameters measured (yields, selectivities, etc.) are plotted as a function of the bulk composition. Figure 9 shows a comparison of two selectivity curves: one showing the selectivity to hydrogenolysis of the silica supported catalysts as a function of the bulk composition, the other as a function of the surface composition, assuming it is the same as in the alloys studied by Kuijers *et al.* (*44*). However, for the purpose of this paper the uncertainty involved is of no crucial importance. All data on selectivity show a rather

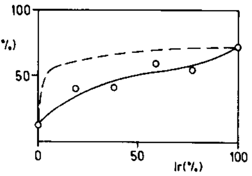

FIG. 9. Selectivity to hydrogenolysis of the silica-supported catalysts vs the iridium content in the bulk (O) and the iridium content at the surface according to Kuijers *et al.* (*44*) (---).

smooth change with the percentage Ir in the bulk. The unsulfided catalysts dispersed on silica show a quite similar selectivity pattern between 20 and 80 wt% Ir in the alloy. This is in accordance with the fact of Pt surface enrichment, which causes an almost constant surface composition in the above-mentioned alloys. The enrichment is most pronounced with bulk materials, but it decreases with decreasing particle size. This similarity is not found when the unsulfided γ-alumina-supported catalysts are investigated. One can observe a sharper increase in the selectivity to hydrogenolysis and a sharper decrease in the selectivities to isomerization and dehydrocyclization with the increasing bulk percentage Ir. This might be due to the possible existence of unalloyed Ir particles, as has already been mentioned above. However, after the catalysts have been presulfided, the selectivity patterns of both silica and γ-alumina-supported catalysts show a remarkable resemblance. Both series of catalysts undergo a dramatic drop in the selectivity to hydrogenolysis which is most probably due to a decrease in the ensemble size of free surface metal atoms (the so-called ensemble size effect is due to the change in availability of ensembles of contiguous sites of active metal atoms required for a given reaction to occur). As a consequence, sulfurization increases the selectivities to isomerization and dehydrocyclization. The above-described sulfur treatment converts the bimetallic and monometallic Ir catalysts in such a way that they tend to resemble the monometallic Pt catalysts. This is true when one compares the selectivities, but the yields obtained (Fig. 7) are strongly dependent on the bulk percentage of Ir and this is true whether the catalysts are silica- or γ-alumina supported. All yields but one show a constant value between 20 and 80 wt% Ir in the catalysts. The yields of isomerization products obtained by γ-alumina-supported catalysts show in the same region an increase with an increasing bulk concentration of Ir. This tendency is not observed when using the silica-supported catalysts. This is explained by the bifunctionality of the alumina-supported catalysts, which manifests itself also at the rather low temperatures applied here. Comparison with the results of the pyridine experiments clearly shows the influence of the isomerization activity of the acidic centers of γ-alumina. Experiments in which pyridine doses have been injected in the feed clearly show that for the alumina-supported catalysts isomerization is affected most and is thus most likely to be related to the acidic centers of alumina. The same behavior has been observed with sulfided Pt/Re catalysts. However, Pt/Ir catalysts differ from the latter ones in one essential aspect. Poisoning of the acidic activity is irreversible with Pt/Re but to a high extent reversible with Pt/Ir catalysts. This is probably related to the fact that the Ir-sulfide is much more active in the hydrogenolysis of nitrogen or sulfur containing compounds than Pt or Re (*47*). The Ir-sulfide is able to supply effectually more hydrogen (ads.) (more than Pt-sulfide or Re-sulfide) for the removal of pyridine adsorbed on alumina (via hydrogen spillover). This indicates that hydrogenolysis and dehydrocyclization preferably take place on the metal.

Finally, the results listed above, e.g., the TPO experiments described in the literature, clearly indicate that sulfided Pt/Ir bimetallic catalysts show a superior performance when compared to the sulfided monometallic Pt catalysts. Actually, in the case of the sulfided γ-alumina-supported catalysts, the monometallic Ir catalyst showed the best performance due to the combination high activity–high selectivity (especially to isomerization). Again a possible explanation could be the higher dehydrogenating activity of sulfided Ir catalysts when compared with sulfided Pt catalysts (*47*). It can be expected that at higher temperatures the alloys can combine an almost "Pt-like" low selectivity to hydrogenolysis with an increased selectivity to dehydrocyclization and aromatization (the extent of the reaction which increases most with increasing temperature). This is probably accompanied by an improved resistance to self-poisoning.

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