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Cooperative Action of $Pt/\gamma\text{-}Al_2O_3$ Catalyst and $\gamma\text{-}Al_2O_3$ Diluent in the Hydrogenation of Benzene

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Benzene was hydrogenated with hydrogen in a flow reactor at 70–260°C over mechanical mixtures of 0.6 wt% $Pt/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$ as catalyst. When the alumina-supported Pt was diluted with alumina in the ratio of 1 : 20, the specific activity of the catalyst increased about fourfold. The results suggest that benzene hydrogenation occurs on both $Pt/\gamma\text{-}Al_2O_3$ and the diluent $\gamma\text{-}Al_2O_3$. The influence of the purity of reactants and $\gamma\text{-}Al_2O_3$ on the hydrogen spillover effects have been studied. $\gamma\text{-}Al_2O_3$ intentionally contaminated by Fe or coke gave lower conversions of benzene. Pretreatment with oxygen exerted a positive effect on the activity of catalysts. © 1987 Academic Press, Inc.

INTRODUCTION

The reality of spillover, defined as the combination of dissociative adsorption of hydrogen on the metal surface and migration of a not-yet-identified hydrogen species from the metal to the support or another phase, is no longer questioned. One can find experimental evidence of hydrogen spillover in many works, especially in those in which infrared spectroscopy (*1–6*), often combined with H–D exchange and temperature-programmed desorption (*7, 8*), were used. However, the important question that initiated much controversy concerns the extent of the real catalytic effects brought about by the migration of the hydrogen species. Hydrogenation of benzene is useful in the study of this problem.

An increase of catalytic activity in the hydrogenation of benzene in a pulse reactor was reported by Sancier (*9*) when he diluted Pd/Al_2O_3 with alumina ($\alpha\text{-}Al_2O_3$ content of 65% with the remainder principally $\delta\text{-}Al_2O_3$ and $\theta\text{-}Al_2O_3$). The percentage hydrogenation per 1 mg of Pd increased when increasing quantities of Al_2O_3 were added. Sancier approached a limiting factor of improvement of about 3 for a dilution of 200/1 (mass ratio). His interpretation was that hydrogen migrated to alumina and that it made the alumina surface active for benzene hydrogenation.

Vannice and Neikam (*10*) could not reproduce those results. They used a flow reactor and suggested that the data of Sancier (*9*) reflected primarily the limitations of a pulse reactor. In addition, they questioned the use of unpurified H_2 in Sancier's experiments. They suggested that alumina, used as a diluent, might act as a scavenger for impurities, according to the ideas of Schlatter and Boudart (*11*).

A few years later, Teichner *et al.* (*12*) reported that spillover hydrogen activated δ-alumina for the hydrogenation of benzene (as well as for other reactions). In their experiments, a basket containing the catalyst (metal on alumina) was separated from the δ-alumina after the treatment of the latter by spillover hydrogen had been carried out. This new type of experiment ruled out some proposed explanations of the cooperative action of a supported metal with the admixed particles of a support. It

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strengthened the idea that spillover hydrogen does indeed create catalytic centers on the surfaces of the admixed particles.

Recently, using a flow apparatus, Antonucci *et al.* (*13*) observed certain conspicuous effects in the hydrogenation of benzene over Pt/γ-Al$_2$O$_3$. The specific activity, referred to 1 mg of Pt, increased by a factor of more than 4 when the degree of dilution of the catalyst with γ-Al$_2$O$_3$ was 50/1 (volume ratio). The results indicated that the hydrogenation reaction occurred on the Pt/γ-Al$_2$O$_3$ and on the γ-Al$_2$O$_3$ diluent.

Although there are different opinions concerning the mechanisms, benzene hydrogenation on supported metal catalysts remains a good test reaction and can be used for studying the effects of hydrogen spillover. Basset *et al.* (*14*) confirmed that the hydrogenation of benzene over Pt/γ-Al$_2$O$_3$ is a "structure-insensitive" reaction according to the concept of Boudart *et al.* (*15*). The activity per platinum site does not depend on the complex used for impregnation (H_2PtCl_6 or $Pt(NO_2)_2(NH_3)_2$), Pt dispersion (12–67%), the surface of the alumina (105 and 330 m^2 g^{-1}), or the chlorine content of the catalyst (up to 0.5×10^{-3} ion g Cl$^-$ g^{-1}). The results of benzene hydrogenation indicated (*14*) that benzene and hydrogen are adsorbed on two adjacent platinum sites. The authors did not take into account the effect of dilution by γ-Al$_2$O$_3$.

We thought it timely to reexamine the cooperative effects of a supported metal with an admixed support. Incentive came from the stimulating results of Teichner and Pajonk and the interesting phenomena mentioned in a conference on spillover (*16*). On the other hand, many results obtained with other catalytic systems in our laboratory substantiate the idea that a spillover species arising from one phase can create and/or continuously modify catalytic centers situated on another phase, thus evoking a sort of remote control on those centers (*17–21*). Accordingly, one hypothesis for explaining the cooperation between supported metal and a support in benzene hydrogenation could be that catalytic centers are continuously created on the support by spillover hydrogen.

The aim of our work was to reexamine the results of Antonucci *et al.* (*13*) and to reconsider the objections against the idea that the dilution of a supported metal catalyst with a support might bring about the hydrogenation of benzene on the latter via hydrogen spillover.

We have investigated the influence of the purity of the gases (He, H$_2$) and benzene used as well as the effect of impurities intentionally introduced into γ-Al$_2$O$_3$ (Fe or coke deposits). We have also studied the influence of an oxygen pretreatment on the specific activity of diluted and nondiluted catalysts; the idea was that oxygen could remove possible support contaminations.

The hydrogen spillover effects were observed within the temperature range 70–150°C, which was broader than the one used by Antonucci *et al.* (70–100°C) (*13*).

EXPERIMENTAL METHODS

Catalyst and Reactants

A commercial γ-Al$_2$O$_3$ (Cyanamid, SN 5216) was used after being ground and sieved; the fraction of 100 to 200 μm was kept. The supported platinum catalyst was obtained by impregnation with chloroplatinic acid after calcination of the alumina at 500°C for 24 h (191 m^2 g^{-1}). $H_2PtCl_6 \cdot 6H_2O$ (0.159 g) was dissolved in distilled water and added to the flask with 10 g of γ-Al$_2$O$_3$. It was left in the dark for 7 days in order to obtain a uniform distribution of the Pt (*22*). The precursor thus obtained was dried at 65°C for 24 h and calcined in a flow of air for 24 h.

The prepared catalyst was diluted with γ-Al$_2$O$_3$ by being mixed in mass ratios of 3:5, 1:5, 1:7.5, 1:20, 1:40 and 1:95. Each mixture was obtained by shaking the flask until the catalyst particles appeared to be uniformly distributed in the diluent.

In the catalytic test, benzene (>99.5%)

from Merck, cylinder hydrogen (99.9997%), helium (99.9996%), and the mixture of helium (99.995%) + oxygen (99.995%) with 1% of O_2, from l'Air Liquide Belge were used.

In a second part of the experiments reported here, benzene and hydrogen were additionally purified. Benzene was distilled twice; the first distillation was carried out with Raney nickel in the boiling liquid. Hydrogen was passed through a Deoxo purifier and a molecular sieve dehydrator from Chrompack.

In some of the experiments, the γ-Al_2O_3 diluting the Pt/γ-Al_2O_3 catalyst was used as such (100–200 μm fraction, calcination at 500°C for 24 h). In other experiments, it was modified as follows:

(i) Preparation of γ-Al_2O_3 contaminated by coke. Two grams of γ-Al_2O_3 was heated for 6 h at 450°C in a stream of hydrogen 60 cm^3 min^{-1}) saturated with methylcyclopentane (MCP; >99% from Fluka A. G.). The MCP flow rate was 6 cm^3 h^{-1}. The same procedure was repeated the following day with helium instead of hydrogen.

(ii) Preparation of γ-Al_2O_3 containing 0.2 wt% Fe. For the impregnation, a portion of γ-Al_2O_3 was added to an aqueous solution of ferrous nitrate (Merck, p.a.) containing a calculated amount of Fe. The mixture was heated and stirred until dry, then heated overnight at 120°C and calcined at 450°C for 24 h. It was reduced with H_2 in the reactor after being mixed with Pt/γ-Al_2O_3.

Equipment and Procedures

The benzene hydrogenation reaction was carried out in a glass flow reactor (l = 20 cm, ϕ = 1 cm) fed from the top ("down flow"). The outlet was connected to a gas chromatograph (Intersmat IGC 120 DFL; FID detector) with a chromatographic column (l = 1.5 m, ϕ = $\frac{1}{8}$ in.) containing 10% CP Wax on Chromosorb WAW 100/120 mesh and kept at 95°C. The H_2 flow (F = 60 cm^3 min^{-1}) entered a saturator containing benzene at 28°C and then a condenser kept at 13°C. The composition obtained corresponded to a ratio H_2/C_6H_6 = 14.4 and was the same throughout all of our experiments, except in the series where the catalytic activity vs contact time expressed as W/F (g sec mol^{-1}) was studied.

The reaction temperature was measured by a Cr–Al thermocouple placed in a glass pocket inside the reactor.

Before the reaction, the catalysts were activated in two ways:

(i) Procedure P1, in which a helium flow of ca. 60 cm^3 min^{-1} was passed through at 120°C for 30 min and at 450°C for 30 min with, subsequently, a hydrogen flow of ca. 100 cm^3 min^{-1} for 3 h;

(ii) Procedure P2, in which a He + O_2 (1% O_2) flow of ca. 60 cm^3 min^{-1} at 300°C for 30 min was used, followed by a helium flow, as above, at 450°C for 30 min, and finally, the hydrogen flow at 450°C for 3 h.

The catalytic bed (catalyst + diluent, or catalyst alone) was kept constant and equal to 300 mg. In a part of the experiments, the extra top layer of 240 mg of γ-Al_2O_3 support was used.

The hydrogenation of benzene was studied in the 70 to 260°C temperature range (LHSV = 0.1 h^{-1}). The corresponding contact time is given at the beginning of the next section. Benzene and cyclohexane were practically the only organic components of the reaction mixture (>99 wt%). Benzene conversion (C, wt%) was calculated from the ratio between the corrected area of the cyclohexane peak and the total corrected areas of the benzene and cyclohexane peaks.

The catalyst deactivated slowly during the hydrogenation reaction. At 190°C, for example, a diminution of the benzene conversion by ca. 10% was observed after 6 h for a catalyst diluted at the 1 : 10 level. Usually, the experiments lasted under 2 h.

RESULTS

Preliminary Measurements

The pure 0.6 wt% Pt/γ-Al_2O_3-supported catalyst was very active in benzene hydrogenation. At temperatures nearing 110°C, conversions reached 100% and this did not change until 210°C was reached. The pure γ-Al_2O_3 was inactive in benzene hydrogenation in the whole range of reaction temperatures (70–260°C) studied.

In our work, the contact time defined as W/F (g sec mol^{-1}) has been chosen in order to yield easily observable differences between the various experiments. In all of them, a value of W/F of 1.46×10^6 g sec mol^{-1} was used.

The conversion of doubly purified benzene was examined as a function of the W/F value for a catalyst diluted at the 1 : 20 level. As cyclohexane is very weakly adsorbed, we should theoretically obtain a straight line for the plot of conversion vs W/F in the absence of heat and mass transfer limiting phenomena (*13*). The results have shown that, under our experimental conditions, this is nearly the case. The small deviation in our experiments does not impair the value of taking the benzene conversion as a measure of catalyst activity.

Experiments with Reactants Used without Special Purification

A first series of experiments was done with the reactants as received, according to procedure P1. These experiments concerned the possible role of γ-Al_2O_3 as a trap for catalyst poisons. All experiments presented in Fig. 1 were carried out with Pt/γ-Al_2O_3 and γ-Al_2O_3 in a proportion of 1 : 5. Benzene conversions were measured at various temperatures.

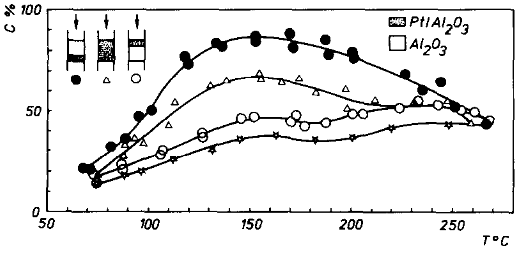

FIG. 1. Influence of reaction temperature and structure of catalytic bed on benzene conversion over 0.6 wt% Pt/γ-Al_2O_3 either undiluted (○, ●), diluted with γ-Al_2O_3 (1 : 5) (△), or diluted with glass fragments (☆).

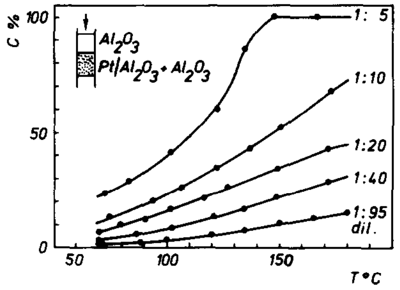

FIG. 2. Influence of reaction temperature on benzene conversion over 0.6 wt% Pt/γ-Al_2O_3 at various levels of dilution (1 : 5, 1 : 10, 1 : 20, 1 : 40 and 1 : 95) with γ-Al_2O_3. A layer of 240 mg of γ-Al_2O_3 was placed on top of the catalytic mixture.

In the experiments whose results are reported Fig. 1, γ-Al_2O_3 was placed on the top ("upstream"), on the bottom, or mixed with Pt/γ-Al_2O_3. Another experiment was done with the catalyst mixed with glass particles instead of γ-Al_2O_3. All conversion curves in Fig. 1 show one or two maxima. Usually, at temperatures higher than 150°C, the thermodynamic effect prevails and the conversion decreases (*13*). In Fig. 1, the highest conversion was reached when the γ-Al_2O_3 diluent was placed on the top (upstream). The lowest conversion was observed when the catalyst was mixed with an amount of glass particles (100 to 200-mg fraction equal to the one used with γ-Al_2O_3).

The results strongly suggest that one of the roles of γ-Al_2O_3 is to remove the impurities. It does this most efficiently when placed upstream. Glass is inefficient for that purpose.

In an additional series of experiments we observed γ-Al_2O_3 to have a positive role when placed above a catalytic bed. The experiments reported in Fig. 2 were done using 240 mg of γ-Al_2O_3 on top, with mechanical mixtures (300 mg) of Pt/γ-Al_2O_3 in various proportions.

Experiments with Purified Reactants

In this second series of experiments, we purified benzene and cylinder hydrogen as described under Experimental Methods. In addition, a pretreatment with O_2, according to procedure P2, was used.

Figure 3 presents results obtained under conditions similar to those of Fig. 1. The lowest conversion was observed when the catalyst was mixed with glass particles. The conversion level, however, was higher than in Fig. 1.

Figure 4 repeats benzene conversions vs temperature curves as a function of dilution of the catalyst with γ-Al_2O_3. Note that in this case, contrary to Fig. 2, no top purifying layer of γ-Al_2O_3 was used.

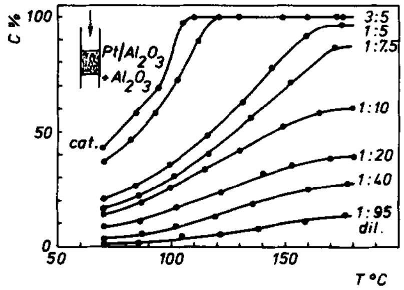

FIG. 4. Use of purified reactants and procedure P2. Influence of reaction temperature on conversion of benzene over 0.6 wt% Pt/γ-Al_2O_3 undiluted and at various levels of dilution (3:5, 1:5, 1:7.5, 1:10, 1:20, 1:40, and 1:95) with γ-Al_2O_3.

Experiments with Intentionally Added Impurities

Figure 5 indicates the influence of contaminants on the added γ-Al_2O_3 in the case of the catalyst diluted at the 1:10 level. In these experiments, the additionally purified reactants were used. In the case of curves A and D, procedure P1 was used whereas curves B and C were obtained by applying procedure P2 (with O_2).

The presence of coke deposited on γ-Al_2O_3 before mixing with Pt/γ-Al_2O_3 diminished benzene conversion (compare curves A and B). The decrease was much smaller in the case of the diluent contaminated by 2 × 10^3 ppm of Fe. A strong increase of benzene conversion (curve D) was observed in an experiment using a "purifying top layer" of 240 mg γ-Al_2O_3. This effect is strong at temperatures higher that 140°C because, in opposition to the results of Fig. 2, high-purity benzene and hydrogen were used here. This is discussed later.

Comparison of Fig. 5 with Fig. 4 indicates that the benzene conversions are similar for both series of experiments, although two different experimental procedures were adopted. It is only in the case of the 1:5 mixture that a more marked difference is observed.

DISCUSSION

We first evaluate the magnitude of the synergetic effects which take place when Pt/γ-Al_2O_3 and γ-Al_2O_3 are in contact.

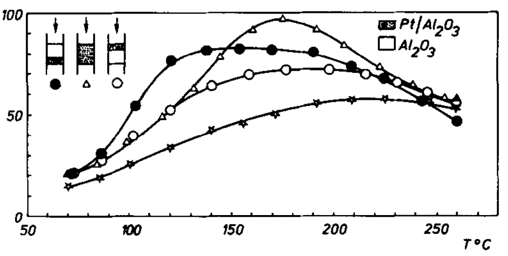

FIG. 3. Use of purified reactants and procedure P2. Influence of reaction temperature and the structure of catalytic bed on benzene conversion over 0.6 wt% Pt/γ-Al_2O_3 either undiluted (○, ●), or diluted with γ-Al_2O_3 (1:5) (△), or diluted with glass balls (☆).

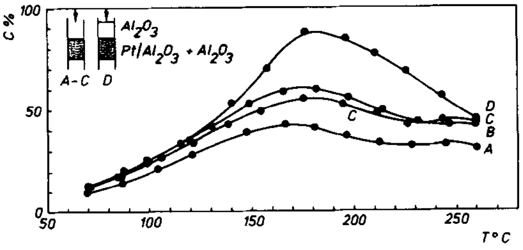

FIG. 5. Use of purified reactants and procedure P1 (curves A and D) and procedure P2 (curves B and C). Influence of reaction temperature on conversion of benzene over 0.6 wt% Pt/γ-Al_2O_3 diluted 1:10 with γ-Al_2O_3 covered by carbonaceous deposit (A), pure γ-Al_2O_3 (B), 0.2 wt% Fe/γ-Al_2O_3 (C), or pure γ-Al_2O_3 + the top layer of 240 mg of γ-Al_2O_3 (D).

Thereafter, we concentrate on three main subjects: the influence of reactant impurities or γ-alumina contaminations on benzene hydrogenation, the possible origins of the synergetic effects, and the additional information which our work can provide on the hydrogenation reaction on a catalyst consisting of a noble metal and a support.

Quantification of the Synergetic Effects

The first series of experiments, where a top layer of γ-Al_2O_3 is necessary for the elimination of impurities, cannot reflect correctly the cooperation between Pt/γ-Al_2O_3 (catalyst) and γ-Al_2O_3 (diluent) so we focus our attention on the second series of experiments (see Experiments with Purified Reactants).

Figure 6 is a plot of the conversion vs catalyst/(catalyst + Al_2O_3) mass ratio. In the absence of any cooperative effect, conversion should vary linearly. The increase of conversion with respect to the straight line corresponds to a synergetic effect. Figure 6 shows that there is noticeable synergy in the catalyst + Al_2O_3 mechanical mixtures. The activity of the mixtures was always higher than the value calculated on the basis of the individual components. More precisely, let us take the individual weights of each component of the catalyst mixture present in a given experiment. The conversion was higher than the addition of the conversion due to the same quantity of Pt/γ-Al_2O_3 alone plus that due to Al_2O_3 alone. The nondiluted Pt/γ-Al_2O_3 gives a conversion of 100% between 110 to 210°C and therefore can be a good reference for the synergy curves below 110°C only. The curves presented in Fig. 6 indicate that mixtures have about 150% of the activity of the individual components taken separately.

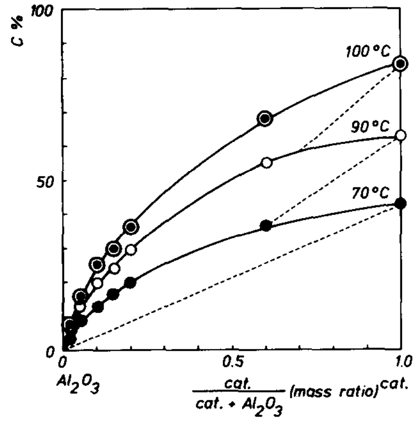

FIG. 6. Synergy curves for the 0.6 wt% Pt/γ-Al_2O_3 system at different temperatures: 70°C (●); 90°C (○); 100°C (◉).

The synergetic effects in the 70–100°C temperature range are presented in Fig. 7A in a different manner. For that, we define the specific activity ratio R_1 as

$$R_1 = \frac{\text{conversion on diluted catalyst}}{\text{conversion on Pt/}\gamma\text{-Al}_2\text{O}_3} \text{/mg Pt}$$

Figure 7 shows that this ratio varies from 1.5 to 4.0 for dilutions 3 : 5 and 1 : 20, respectively.

In order to make a similar comparison of the specific activities at temperatures ranging from 70 to 150°C, we calculated another ratio, R_2, obtained from the equation

$$R_2 = \frac{\text{conversion on diluted catalyst}}{\begin{array}{c}\text{conversion on diluted}\\ \text{catalyst in } 1:5\end{array}} \text{/mg Pt,}$$

where the catalyst diluted at the 1 : 5 level was taken as the reference. As seen in Fig. 7B, R_2 varies from 1.1 to 1.7 for dilutions 1 : 7.5 and 1 : 20, respectively.

Ratios R_1 and R_2 are independent of the reaction temperature for dilutions not exceeding 1 : 20. The behaviour of the catalyst in the case of the dilutions 1 : 40 and 1 : 95 is explained later.

The changing of the reference in R_2, in comparison with R_1, obviously diminishes the values of the specific activity ratio. Nevertheless, R_2 is always higher than 1. The converging indications obtained with R_1 and R_2 show that, in the 70–150°C temperature range, the activity of 1 mg Pt

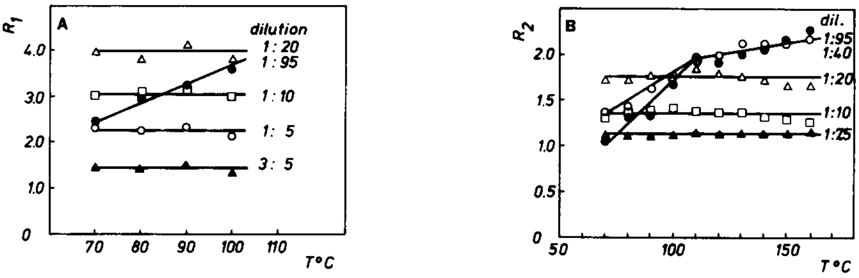

FIG. 7. Specific activity ratios R_1 (A) and R_2 (B) vs temperature at various levels of dilution (R_1 and R_1 defined in the text).

increases with dilution over a very large range of benzene conversions (see Fig. 4).

Role of Contaminations

Previous experiments concerning the effect of admixed alumina on catalytic activity led to suspicion that some type of contamination was involved. Our present results clearly show that the synergetic effect indeed depends on the purity of reactants and the contamination of the alumina. Thus discussion of the problem of impurities present in both the feed and the alumina is appropriate.

Figure 1 shows that benzene conversion depends on the position of the added alumina with respect to the catalyst. The lowest activity was observed when the layer of Pt/γ-Al_2O_3 was in the top level, that is, directly exposed to the reactant stream. This strongly suggested that alumina when mixed, or when reacting first with the feed (on top), had indeed a purifying effect. Extensive purification of reactants, when carried out independently, also distinctly increased benzene conversion, as shown in Fig. 3 in comparison with Fig. 1. The comparison is particularly instructive where the curves corresponding to mixtures (Δ) are concerned. In Fig. 1, a maximum conversion of about 65% is attained, whereas values in excess of 95% are noticed when purified reactants are used. The experiments with glass particles, instead of alumina, show that the effect depends on adsorptive properties, i.e., the removal of impurities, and not with phenomena due to the flow dynamics in the bed.

The purification role of γ-Al_2O_3 is indisputable. The observed phenomenon, however, exhibits an additional complexity. Pretreatment with oxygen is also beneficial. The results of Fig. 2 (unpurified reactants, protecting layer, procedure P1) and Fig. 4 (purified reactants, no protecting layer, procedure P2) practically coincide for the dilution level of 1 : 10 or more. The conclusion is that contaminants on the γ-Al_2O_3 (organic molecules adsorbed during storage, present as traces in He, H_2, etc.) interfere with the purifying role of that adsorbent. An additional explanation of the effect of the oxygen pretreatment might be that the pretreatment oxidizes the surface of platinum, bringing about a uniform surface state before and after H_2 reduction, thus improving the catalyst. However, the major role of O_2 is certainly linked to the removal of surface contaminants. Figure 5 indeed shows that a carbonaceous deposit on γ-Al_2O_3 diminishes benzene conversion.

Another role of alumina contamination has been invoked, namely, that common alumina impurities, e.g., iron, might possess a strong catalytic hydrogenation of their own (*23*) (although the alumina was subjected to a special treatment in those experiments). This was the reason for the experiment involving the introduction of ferrous nitrate (2×10^3 ppm Fe) into the diluent of the supported Pt catalyst. Figure 5 shows a slight diminution of benzene conversion (curve C). The effect is small, and possibly of the same order as the experimental error at temperatures lower than 150°C. The experiment indicates that the catalytic role of iron, reduced by molecular hydrogen or by spillover hydrogen, is negligible.

Origin of the Synergy between Pt/γ-Al_2O_3 and γ-Al_2O_3

The previous discussion shows that catalytic experiments can be conducted under conditions in which contamination is eliminated to a level where it has no more influence on catalytic activity. Figures 2 and 4 indicate that conversion is not proportional to the quantity of Pt/γ-Al_2O_3 used. The presence of γ-Al_2O_3 enhances that activity. There is, indeed, a real synergy as indicated in the first reports in the literature on the behaviour of mixtures of hydrogenation catalysts with alumina. Figure 6 and, especially, Fig. 7 quantify this synergy as the mathematical interpretation of the first section of this discussion. This synergy takes place within a very wide range of temperatures (70–150°C) and dilution levels (3 : 5 to 1 : 40). The percentage conversion per milligram of platinum approached a limit of improvement corresponding to a factor of about 4, for a dilution of 1 : 20.

In a general way, synergy between two phases in catalytic systems may have the following origins: (i) *bifunctional* catalysis; (ii) formation of more active *compounds* between both phases; (iii) regeneration of *active sites* on one phase of spillover species emitted by the other phase ("remote control"); (iv) reaction of *spillover hydrogen,* produced on one phase, with a reactant adsorbed on the other phase *(21)*.

It is difficult to imagine that a bifunctional mechanism could operate in benzene hydrogenation, especially involving as one category of centers, those which do not activate hydrogen (on alumina). The formation of compounds is not relevant to our case: no new compounds can be formed between the γ-alumina of the support and that of the diluent!

It is more difficult to rule out remote control. One cannot imagine that spillover hydrogen acts by removing contaminating species on active centers: our best experiments are done under conditions where this elimination has already taken place, and this would suggest that active centers exist on γ-Al_2O_3. However, in view of the proposal which we make below that mechanism (iv) operates, we do not rule out that some remote control may be superimposed on (iv). Indeed, we could imagine that spillover hydrogen in addition to reacting with benzene on γ-Al_2O_3 (mechanism (iv)) continuously eliminates contaminations (remote control (iii)) which would interfere with (iv). However, this is an unnecessary complication at the present stage of the investigations.

We aim to show that the last explanation (iv), in addition to being the only plausible one in our system, also accounts satisfactorily for the details of the observed phenomena.

In essence, a reactive hydrogen species (spillover hydrogen) formed on one phase (Pt) spills over to react with benzene adsorbed on the other phase; i.e., γ-Al_2O_3. As Al_2O_3 is used as a support, this assumption has already been made but without being really substantiated. The use of separate γ-Al_2O_3 particles in our case, and the important effects observed, constitute convincing proof.

We may remark in passing that this conclusion makes easily understandable the fact that procedure P2 (pretreatment of the catalyst by O_2) contributes to the enhancement of the synergetic effect. Indeed, if the Pt surface is purer, it will produce more spillover hydrogen.

Hydrogen species cannot migrate beyond a certain distance which, however, depends on the textural properties of the solid mixture and the operating conditions. Figure 7A shows that the specific activity depends on the degree of dilution and increases up to a dilution of 1 : 20. This activity decreases in more diluted systems. Lower values of the R_1 and R_2 ratios are observed at 70–100°C for 1 : 40 or 1 : 95 dilutions.

This latter phenomenon cannot be explained by the limited extent of the spread of spillover species. Once a sufficient quantity of γ-Al_2O_3 diluent is present, all available spillover hydrogen can spread on γ-Al_2O_3 and react. The hydrogen spillover production "machinery" of Pt works at full capacity. Adding more γ-Al_2O_3 can not do more for that "full capacity" production and would therefore serve no purpose. (Incidentally, the same reasoning would hold for the production of spillover hydrogen for remote control.) The only phenomenon which could interfere negatively with benzene conversion is necessarily some sorption occurring on *non-H-irrigated* pure γ-Al_2O_3. The simplest hypothesis is to take into account the adsorption–desorption of benzene and/or possible migration of benzene on the surface of γ-Al_2O_3, which would act as a bypass, thus subtracting some benzene molecules from contact with the active surfaces (Pt and H-covered γ-Al_2O_3).

These explanations are consistent with the observed effects of temperature. Surface migration is an activated process. An increase in reaction temperature provokes higher mobility of adsorbed species. One could thus explain why the participation of spillover hydrogen in the hydrogenation (reaction on γ-Al_2O_3) increases particularly above 110°C (see Fig. 7B). This effect is clear for the 1 : 40 dilution; it becomes progressively less so as dilution increases, in view of the foregoing arguments.

Insight into Detailed Mechanism

In order to justify these views, we calculated Arrhenius plots from the measured rates of benzene hydrogenation between 70 and 150°C. The results for undiluted catalyst and for various diluted samples all show an equal slope up to the 1 : 20 dilution level. The curve for the 1 : 95 dilution level shows a change of slope which may be due simply to underestimation of conversion values characteristic of the 1 : 95 dilution, especially below 110°C (see Figs. 2 and 4).

Comparing our results with those of Antonucci *et al.* (*13*), we find many similarities. In both studies, remarkable synergetic effects have been observed in the hydrogenation of benzene. As an explanation of the results, spillover hydrogen as the agent changing the catalytic properties of γ-Al_2O_3 was proposed. In both studies, also, there are some unexplained effects, for example, in the dependence of specific activity ratio vs temperature for the highest level of dilution. We observed that the R_1 ratio changed with the reaction temperature at the 1 : 95 dilution, while Antonucci *et al.* (*13*) found that ratio to be temperature-independent up to a ratio of 1 : 100.

Antonucci *et al.* (*13*) proposed an interesting mechanism in which three types of reactions between hydrogen and benzene are postulated: (1) reaction on the Pt surface; (2) reaction between spillover hydrogen and benzene adsorbed on γ-Al_2O_3; (3) reaction between spillover hydrogen and benzene from the gas phase. This mechanism seems valid in view of our results.

CONCLUSIONS

The hydrogenation of benzene was studied over Pt supported on γ-alumina. The role of the purity of reactants and diluent was described. In one series of experiments, pro analysi reactants were used as such, and in the second series specially purified reactants and pretreatment with O_2 (to additionally clean γ-alumina) were used.

γ-Alumina intentionally contaminated with carbon deposits gives a lower degree of conversion. In the case of Fe-doped γ-alumina, only negligible effects on conversion were observed.

Various mechanical mixtures of Pt catalyst and γ-alumina showed a remarkable synergy, that is, conversions over mixtures were always higher than over individual mixture components taken alone.

The effect was explained by the existence of spillover hydrogen which migrates onto the surface of the γ-alumina diluent and hydrogenates adsorbed benzene.

We believe our present results to be important in that they prove a phenomenon which had been reported conclusively only rarely hitherto.

Generally, the results of Antonucci *et al.* (*13*) were confirmed. The mechanism of benzene hydrogenation with the participation of Pt as well as γ-alumina surfaces was demonstrated.

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