

The Control of Metal Precursor Mobilities as a Variable in the Preparation of Supported Pt–Ru Bimetallic Clusters: The Use of Ruthenocene

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The preparation of silica supported Pt–Ru bimetallic catalysts using ruthenocene as the Ru precursor has been studied. The high volatility of ruthenocene requires the use of a sequential impregnation technique. A Pt/SiO₂ catalyst prepared by the impregnation of silica with H₂PtCl₆ · 6H₂O was impregnated with a solution of ruthenocene in benzene. The mobile Ru precursor phase was observed to diffuse across the support to surface Pt sites where it was rapidly reduced. The surface of the resulting bimetallic catalyst was enriched in Ru. A subsequent heat treatment resulted in diffusion of Ru into the bulk. When RuCl₃ · 3H₂O was used as the Ru metal precursor in this sequential impregnation technique, separate Pt and Ru particles were formed. This is explained in terms of the strength of metal precursor–support interactions. The hydrogenation of benzene and the hydrogenolysis of propane were used as catalytic test reactions in order to probe the presence of dual metal sites. The reaction rate for the hydrogenation of benzene was observed to go through a maximum at a surface composition of between 60 and 80% Pt. The hydrogenolysis of propane was consistent with a requirement of a Ru ensemble consisting of a small number of Ru surface atoms. © 1990 Academic Press, Inc.

INTRODUCTION

Historically the interest in bimetallic catalysts has focused on metallic combinations which are miscible in the bulk. The main reason for choosing this type of combination is the belief that metal–metal interactions are more likely to occur in miscible systems or in systems which have a small miscibility gap. More recently, it has been observed that metal–metal interactions are not limited to miscible systems (1). The notion that the two metals in a bimetallic catalyst should be thermodynamically miscible in the bulk has been found to be too restrictive. Furthermore, a thermodynamic model which correctly predicts the structure of bimetallics has little validity because: (1) the formation is kinetically and not thermodynamically controlled (2–5); (2) bimetallic

clusters can be formed from metals that do not form solid solutions (6, 7); (3) bulk phase diagrams cannot be applied to small particles with diameters of a few nanometers and; (4) interfacial free energies are not sufficiently well known to be used with any degree of confidence (8).

Pairs of metallic elements that are completely immiscible in the bulk, i.e., Ru–Cu (6) and Os–Cu (7), form bimetallic aggregates whose surface properties reveal extensive interactions between the two elements. This finding has opened up a very productive area of research.

In the preparation of supported bimetallic clusters, it has generally been thought that the metal which has the lower enthalpy of sublimation is preferentially enriched at the surface (9). Bimetallic clusters prepared from Group IB and Group VIII metals generally substantiate these claims. For example, supported bimetallic catalysts prepared

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by alloying either Ni or Ru with Cu have been shown to have surface compositions which are strongly enriched in Cu (1, 6, 10, 11). Recent studies by Wu *et al.* (12), using a Monte Carlo simulation method, have shown that for particles which have cubooctahedral symmetry, Cu atoms are preferentially located at sites which have low surface coordinations. These sites are identified with edges, steps, corners, and surface defects. The Ru atoms, on the other hand, are identified with high surface coordination sites such as terraces. Because Ru-Cu and Ni-Cu form endothermic alloys, Cu and Ru atoms are thermodynamically expected to form separate phases. The surface composition of these supported Ru-Cu bimetallic clusters has been experimentally determined by King and co-workers using solid-state NMR (13). These results are in good agreement with studies performed by Sinfelt (1) and Haller *et al.* (10), who suggest that supported Ru-Cu bimetallic clusters conform to a cherry model structure with an inner core consisting primarily of Ru and a peripheral skin consisting of Cu. Recent studies by Hong *et al.* (14), which make use of both EXAFS and ethane hydrogenolysis as a reaction probe, have found significant differences in the catalytic properties of the resulting Ru-Cu bimetallic clusters when different silicas are used as the supporting materials. According to these authors, these differences may, in some way, be linked to differences in the surface concentration of hydroxyl groups of the different silicas used.

Catalyst characterization studies performed on a series of supported Pt-Ru bimetallic clusters prepared by the coimpregnation of $\text{H}_2\text{PtCl}_6 \cdot m\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ have revealed major differences in both the surface composition and particle morphology of these particles (2-4). These differences are linked primarily to the nature of the supporting material. On silica, Miura *et al.* (2) have identified Pt-Ru bimetallic clusters which have a well-defined cherry-like structure and a core which is

strongly enriched in Ru. Furthermore, the Ru content of the core is not a strong function of catalyst composition for overall compositions below 75 at.% Pt. When alumina was used as the support, the Pt content of the Ru core was shown to increase monotonically with the overall concentration of Pt in the catalyst. Miura *et al.* (2) showed that when the supported Pt-Ru bimetallic clusters were prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as metallic precursors, the Pt phase was mobile with respect to the Ru surface phase. A model was developed in which Ru^{3+} was anchored to the surface during the initial pretreatment while $[\text{PtCl}_6]^{2-}$ migrated freely across the support, nucleating on the Ru surface sites. Because $[\text{PtCl}_6]^{2-}$ interacts more strongly with the surface of alumina than silica, the surface diffusion of the $[\text{PtCl}_6]^{2-}$ on alumina is more restricted. This restriction on surface diffusion results in a decrease in the surface enrichment of Pt. Ru-Rh and Ru-Ir silica supported bimetallic clusters prepared from the corresponding chlorides were found to have a homogeneous particle structure with little or no surface enrichment in either metallic component (3). It is noteworthy that like Ru, both Rh and Ir show little surface mobility during catalyst pretreatment. Presumably, this lack of surface mobility during the precursor state is linked to the cationic nature of the interaction between the metal precursor and the support. Because the interaction between $[\text{PtCl}_6]^{2-}$ and the support is anionic, and because it is also highly soluble in its water of hydration and the water formed as a result of the dehydroxylation of the support, its surface diffusivity is much higher than that observed for Ru, Rh, or Ir (3). Anhydrous RuCl_3 is nearly insoluble in water.

One of the goals that catalytic researchers engaged in preparative studies of supported bimetallic clusters should focus on is to tailor bimetallic catalysts to a well-defined surface composition. In particular, the control of variables which lead to the preferential surface enrichment of one

metal with respect to the other is important if the end result is to design a catalyst which can be used for a specific catalytic application. As already suggested, the choice of metal precursors which interact either strongly or weakly with the support and the method by which the precursors are pretreated appear to be the two most important variables.

To date we have been able to prepare Pt-Ru bimetallic catalysts which are surface enriched in Pt. This has been due to the more aggressive nature of the interaction between the Ru precursors and the support. In this paper we will report on the preparation of Pt-Ru/SiO₂ bimetallic catalysts which are surface enriched in Ru. In order to do this we have selected ruthenocene (bis-cyclopentadienyl Ru) as the Ru metal precursor. This compound interacts rather weakly with the support due to its high volatility. The metal precursor-support interactions are weak and the use of a nonpolar solvent decreases the net charge on the support.

Because the stability of the surface layer with respect to composition is also an important consideration in the preparation of bimetallic catalysts, a second aim in this study will be to measure changes in surface composition following high-temperature treatment. This study will first be performed using Pt gauze to which a layer of Ru will be added. If an exchange between surface Ru and bulk Pt atoms occurs, experiments aimed at extending this exchange study to include supported Pt-Ru bimetallic clusters will be performed. If this exchange occurs, the temperature at which it is observed becomes an important variable in catalyst preparation. Additionally, the importance of thermodynamic and kinetic surface enrichment effects can be sorted out.

EXPERIMENTAL

Materials. The silica support (Silbead N, 600 m²/g) was obtained from the Mizusawa Chemical Co., Japan. It was ground and

sieved to between 40 and 60 mesh before use. The resulting granules were sequentially washed with acetic acid (0.5 M), ammonia (0.5 M), and deionized water. Before use, the resulting silica was calcined at 500 C for 2 h.

Ruthenocene (Aldrich Chemical Co., research grade) was purified by sublimation. For the preparation of the standard coimpregnation catalysts, RuCl₃ · 3H₂O and H₂ PtCl₆ · 6H₂O (Soekawa Chemical Co., research grade) were used. For the preparation of the impregnated and coimpregnated catalysts, the ruthenocene was dissolved in benzene (Wako Chemical Co., research grade). All catalysts prepared from chlorided materials were subjected to a hot water wash to eliminate chlorine. The procedure has been described in detail elsewhere (15-17).

The carrier gas, 99.99% He (Showa Denko) was purified by passing it over a heated copper catalyst at 500 K backed by a molecular sieve, 5 Å. The purity of the carrier gas was confirmed by means of an O₂-CO titration technique. This method has been treated extensively in a previous paper (18).

The CO used was research grade (99.9% purity) and was purchased from the Takachito Chemical Co., Japan. The H₂ was obtained from the Skowa Denka Co., and had a purity of 99.99%.

Adsorption experiments. The adsorption of CO and H₂ was performed using the dynamic pulse adsorption method (19, 20). Surface composition measurements were performed using a selective O₂-CO titration method (2). In this technique, advantage is taken of the fact that the titration of a monolayer of chemisorbed oxygen on Pt using CO(g) to a CO₂(g) end point is complete for a CO/O₂ titration ratio of 4.0. For Ru, the corresponding end point in the titration is obtained for a CO/O₂ ratio of 1. The large difference in titration ratios can be used to obtain an average surface composition of the bimetallic catalysts. The validity of the technique has been checked using

quantitative infrared (21) spectroscopy and temperature-programmed desorption (22).

Surface analysis. In several experiments, Ru was deposited on the surface of a sample of Pt gauze by sublimation. Surface analysis of the resulting Pt-Ru gauze was carried out using electron microprobe analysis (EPMA, Shimadzu EMX-SM), and XPS (ULVAC PHY ESCA 558 UP).

Catalytic experiments. The hydrogenation of benzene and the hydrogenolysis of propane were performed in a flow reactor at ambient pressures. The reactant gas mixtures $\text{H}_2/\text{C}_6\text{H}_6 = 10/1$ or $\text{H}_2/\text{C}_3\text{H}_8 = 4/1$ were passed over the catalyst bed (200–500 mg of catalyst) at a flow rate of 50–100 ml/min. The hydrogenolysis of propane was carried out at 380–490 K and the hydrogenation of benzene was performed at 300–430 K. Conversions were maintained below 20% in order to minimize undesirable heating effects.

RESULTS

The Preparation of Ru/SiO_2 from $\text{Ru}(\text{C}_5\text{H}_5)_2$. The preparation of a Ru/SiO_2 catalyst by impregnation from a benzene solution of ruthenocene [$\text{Ru}(\text{cp})_2$] was attempted. The resultant catalyst was dried at 298 K and then reduced in H_2 at 600 K for 3 h. Analysis of the resulting catalyst by X-ray fluorescence showed that approximately 90% of the Ru was lost during reduction. Apparently, the sublimation of ruthenocene occurs at a temperature which is below the reduction temperature of Ru. Additionally, the dispersion of the Ru which was retained by the silica was very low (<1%).

Because of these results and because of the high volatility of ruthenocene, the direct gas-phase deposition of Ru from a ruthenocene precursor directly onto the silica substrate was tried. The apparatus used in this deposition is shown schematically in Fig. 1. It consists of an electrically heated pyrex tube. A predetermined weight of ruthenocene was held in place using quartz

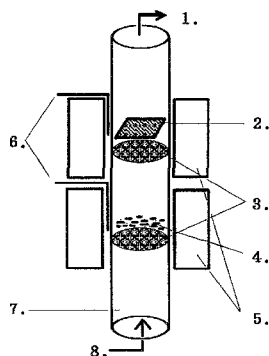


FIG. 1. Apparatus used for the vapor-phase deposition of $\text{Ru}(\text{cp})_2$ on silica or Pt gauze: (1) hydrogen outlet; (2) substrate (Pt gauze or SiO_2); (3) quartz wool; (4) $\text{Ru}(\text{cp})_2$ powder; (5) electric furnaces; (6) thermocouples; (7) pyrex tube (10 mm o.d., 50 cm length); (8) hydrogen inlet.

wool. The silica substrate was placed immediately downstream of the quartz wool. The deposition of ruthenocene onto the silica substrate was carried out in flowing H_2 at a flow rate of 5–10 ml/min. Using this method, we succeeded in preparing a Ru/SiO_2 catalyst which had a total metal loading of 0.26 mmol of Ru/g of catalyst (2.6 wt% Ru). About 85% of the ruthenocene could be deposited in a H_2 flow at 360 K using this technique. The ruthenocene deposited on the surface was subsequently decomposed in flowing H_2 at 500 K. The Ru metal dispersion of the resulting Ru/SiO_2 catalyst was much too low (2–3%). These results are in sharp contrast to those reported by Kitajima *et al.* (23), who were able to obtain unit Ru dispersion using Ru cyclooctatriene as a Ru precursor on an alumina substrate. Presumably, this is due to the high volatility of ruthenocene which does not interact significantly with the hydroxyl groups of the silica support. As ruthenocene migrates across the support, the most likely method of reduction occurs when the metal precursor comes into contact with a Ru particle which can activate H_2 . For this reason, crystallite size is large, resulting in a low Ru dispersion. In contrast, Ru (cyclooctadiene, cyclooctatriene)

interacts strongly with an alumina support leading to high dispersion.

In order to study the stability of Ru–Pt films, the vapor phase deposition of ruthenocene on the surface of a Pt gauze (100 mesh) was performed. The deposition of ruthenocene on the surface of the Pt gauze was studied at 450 K in flowing H_2 using the apparatus described in Fig. 1. The deposition temperature of 450 K was found to be optimal. At temperatures in excess of 450 K, the deposition of ruthenocene occurred nonselectively on the quartz wool, the pyrex tube, and on the Pt wire gauze. At temperatures below 450 K, reduction of the ruthenocene precursor did not occur on the Pt surface and the ruthenocene was preferentially deposited downstream of the Pt gauze.

The results of the Ru deposition for periods of 1 and 6 h at 450 K are shown in Fig. 2. Prior to the deposition of Ru, the electron probe microanalysis (EPMA) spectrum shows that only Pt is present (Fig. 2A). Exposure of the Pt gauze to ruthenocene in the presence of flowing H_2 for 1 h shows the appearance of a Ru signal (Fig. 2B). The Ru signal increased following exposure of the Pt gauze to ruthenocene for 6 h (Fig. 2C).

The corresponding wide-angle XPS spec-

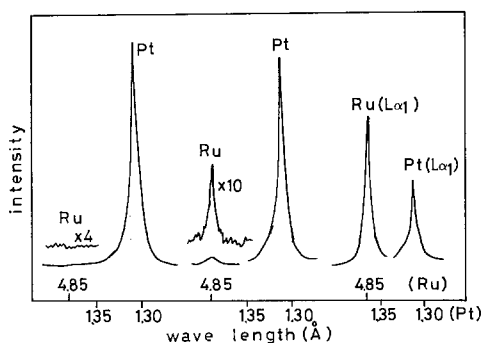


FIG. 2. The effect of $Ru(cp)_2$ treatment time on the deposition of Ru atop Pt gauzes as studied using electron microprobe analysis (EPMAW): (A) before deposition of Ru; (B) 1-h exposure to $Ru(cp)_2$; (C) 6-h exposure to $Ru(cp)_2$.

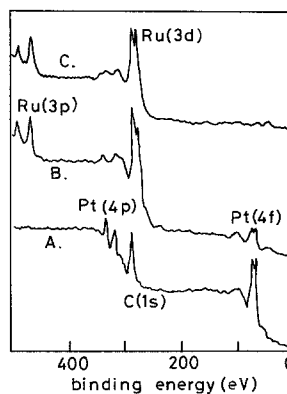


FIG. 3. The effect of $Ru(cp)_2$ treatment time on the deposition of Ru atop Pt gauzes as studied using XPS: (A) before deposition of Ru; (B) 1-h exposure to $Ru(cp)_2$; (C) 6-h exposure to $Ru(cp)_2$.

tra of the surface of the Pt gauze are shown in Fig. 3. Following exposures of the Pt gauze to ruthenocene in flowing H_2 at 450 K for periods of 1 and 6 h, respectively, the XPS peaks corresponding to $Ru(3d)$ and $Ru(3p)$ increased with a concomitant decrease in the intensity of the $Pt(4f)$ peak. These results, which are shown in Fig. 3B and 3C, are consistent with the deposition of a Ru film on the surface of the Pt gauze.

The Ru film deposited on the surface of the Pt gauze was heat treated at 600 and 900 K in flowing H_2 . The corresponding XPS spectra are shown in Fig. 4. Heat treatment at 600 and 900 K for 3 h shows the reappearance of the $Pt(4f)$ band together with a concomitant decrease in the intensity of the $Ru(3p)$ band. The corresponding EPMA spectra confirmed that the Ru was not lost by evaporation. It is apparent that this heat treatment results in the diffusion of surface Ru atoms into the bulk according to the reaction



The stepwise impregnation of Pt/SiO_2 . An attempt was made to prepare Pt–Ru/ SiO_2 bimetallic particles by the deposition of ruthenocene on the surface of a Pt/ SiO_2 catalyst by a procedure which was identical

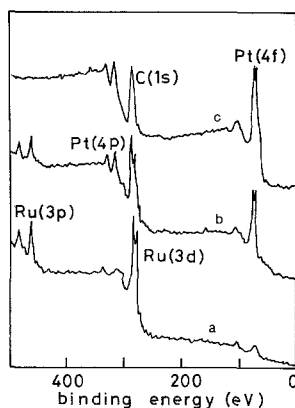
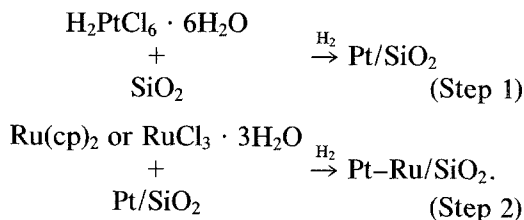


FIG. 4. The effect of heat treatment in H₂ flow on the XPS spectra of Pt gauze covered by a thin layer of Ru. (a) Before heating; (b) treatment in H₂ for 1 h at 600 K; (c) treatment in H₂ for 3 h at 900 K.

to that used in the preparation of the Ru/Pt gauze. Unfortunately, this method did not result in the formation of Pt-Ru bimetallic particles. Only Pt and very large Ru particles were formed.

The preparation of supported Pt-Ru/SiO₂ particles was easily accomplished by employing a stepwise impregnation technique. In this method, a Pt/SiO₂ catalyst was prepared by the impregnation of SiO₂ with H₂PtCl₆ · 6H₂O followed by drying at room temperature and reduction in H₂ at 600 K. The Pt metal loading of this catalyst was 0.3 mmol/g (5.8% by wt). The resulting Pt/SiO₂ catalyst was then impregnated with

either a benzene solution of ruthenocene or an aqueous solution of RuCl₃ · 3H₂O. Schematically, this preparation technique can be represented as follows:



Following the stepwise impregnation of Pt/SiO₂ with the benzene solution of ruthenocene, the catalyst was dried at room temperature. The temperature was then slowly increased in flowing H₂ from room temperature to 453 K (×2 K/min). It was subsequently reduced at 600 K for 3 h followed by evacuation at 600 K for 0.5 h. When the catalysts were prepared by the stepwise impregnation method, more than 90% of the Ru was retained on the surface of Pt/SiO₂.

The results of the surface composition measurements performed using the O₂-CO titration method are shown in Table 1 as a function of Ru metal loading. The total metal dispersion, the number of surface atoms in mmol/g and the total number of metal particles are also shown in Table 1. As the metal loading was increased, the total number of Pt surface atoms was ob-

TABLE I

Structure of Ru-Pt/SiO₂ Catalysts Prepared by the Stepwise Impregnation of Pt/SiO₂ with Ru(cp)₂

Amount of Ru(cp) ₂ (mmol/g)	Dispersion (%)	Surface comp. ^a Ru/Pt (%/%)	Number of surface atoms Ru/Pt (μmol/g)	Number of metal particles 10 ¹⁶ /g-SiO ₂
0.038	30.3	0/100	0/90.0	9.90
0.115	27.3	7.8/92.2	13.9/85.7	8.42
0.174	26.1	31.6/68.4	34.9/75.6	9.56
0.227	24.7	59.6/40.4	77.6/52.7	9.75
0.227 (750 K)	26.4	19.4/80.6	27.0/112	11.9
0.227 (900 K)	26.7	23.6/76.4	33.2/107	23.3

^a Measured using the O₂-CO titration method as in Ref. (2).

served to decrease (Column 4, Table 1). However, the total number of metal particles remained constant to within the experimental error of the measurements. This observation suggested that the Ru did not form separate particles but that the bimetallic particles were formed as the result of surface migration of the ruthenocene to a Pt particle where its ligand was most likely reduced by the presence of H₂ chemisorbed on the surface of Pt. This is, therefore, consistent with a proposed bimetallic assisted reduction process (4).

The bimetallic catalyst, which had a Ru metal loading corresponding to 0.227 mmol of Ru/g of catalyst (2.3 wt% Ru), was heat treated in flowing H₂ at 750 and 900 K for 3 h. The total number of surface Pt atoms decreased (Column 4, Table 1). However, the total number of metal particles remained roughly constant (Column 5, Table 1). The corresponding surface composition showed a sharp drop in Ru (Column 3, Table 1). The observation that the total number of particles remains constant, as a result of this heat treatment, strongly suggests that the surface-bulk phase compositional changes are occurring within each particle and not as the result of the formation of separate Ru and Pt particles.

The structures of the bimetallic catalysts prepared by the sequential impregnation of Pt/SiO₂ with an aqueous solution of RuCl₃ · 3H₂O are shown in Table 2. The number of Pt surface atoms remained roughly constant (Column 4, Table 2) while the number of Ru surface atoms increased. Additionally, there was a sharp drop in metal dispersion as the Ru metal loading was increased. These results strongly suggest the simultaneous formation of large monometallic particles coupled with a smaller number of bimetallic particles. In order to verify these observations, the hydrogenolysis of propane and the hydrogenation of benzene were studied over both series of catalysts. The respective rates were compared to those obtained for a series of Pt-Ru/SiO₂ bimetallic catalysts prepared by standard

TABLE 2

Structure of Ru-Pt/SiO ₂ Catalysts Prepared by the Stepwise Impregnation of Pt/SiO ₂ with RuCl ₃ · 3H ₂ O			
Amount of RuCl ₃ (mmol/g)	Dispersion (%)	Surface comp. ^a Ru/Pt (%/%)	Number of surface atoms Ru/Pt (μmol/g)
0	30.0	0/100	0/90.0
0.093	24.5	2.9/97.1	2.9/93.3
0.135	24.0	4.0/96.0	4.2/104
0.269	18.9	11.2/88.8	12.1/95.7

^a Measured using the O₂-CO titration method as in Ref. (2).

coimpregnation methods and the rates obtained over a mechanical mixture consisting of Pt/SiO₂ and Ru/SiO₂.

The hydrogenation of benzene. A substantial synergistic effect in the turnover frequency for the hydrogenation of benzene was observed on both the bimetallic catalysts prepared by coimpregnation and those prepared by the sequential impregnation of Pt/SiO₂ with Ru(cp)₂ (Fig. 5). The maximum TOF occurred over both series of bimetallic catalysts at a surface composition

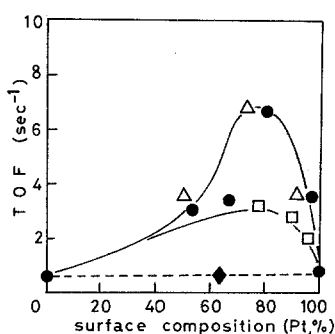


FIG. 5. Change in the TOF of benzene hydrogenation as a function of Ru-Pt surface composition corresponding to catalysts prepared by the following methods: (Δ) stepwise impregnation of Pt/SiO₂ using Ru(cp)₂; (●) coimpregnation using H₂PtCl₆ · 6H₂O and RuCl₃ · 3H₂O; (□) stepwise impregnation of Pt/SiO₂ using RuCl₃ · 3H₂O; (◆) mechanical mixture of Ru/SiO₂ and Pt/SiO₂. H₂/C₆H₆ = 10/1, T = 350 K. Flow rate 110 ml/min.

which corresponded to between 60 and 90% Pt. The TOF exceeded that observed over the monometallic Pt/SiO₂ or Ru/SiO₂ catalysts by nearly an order of magnitude. This synergistic effect for the hydrogenation of benzene has been observed before and has been attributed to the formation of strongly bound, dehydrogenated C₆H_x intermediates on the surface of Pt. These strongly adsorbed C₆H_x intermediates result in the poisoning of surface sites responsible for the hydrogenation of benzene (24). The presence of adjacent dual metal sites apparently results in a decrease in the number of strongly bound dehydrogenated C₆H_x intermediates. This leads to an increase in the reaction rate by nearly an order of magnitude. A much smaller synergistic effect was observed over the bimetallic catalysts prepared by the sequential impregnation of Pt/SiO₂ with RuCl₃ · 3H₂O, suggesting the presence of a large number of monometallic Ru/SiO₂ particles. Synergism was not observed when the hydrogenation of benzene was studied over the physical mixture.

Propane hydrogenolysis. The hydrogenolysis of propane was studied over the bimetallic catalysts prepared by coimpregnation using H₂PtCl₆ · 6H₂O and RuCl₃ · 3H₂O and those prepared by the sequential impregnation of Pt/SiO₂ with a solution of Ru(cp)₂ in benzene. The results show that the TOFs as a function of surface composition are comparable over both series of catalysts (Fig. 6). The curve shows a $y = x^n$ ($n \sim 3$) dependence, suggesting a Ru surface ensemble requirement. This is in good agreement with a previous study on propane hydrogenolysis in which the poisoning of Ru surface sites by chlorine was studied (17).

DISCUSSION

This study shows that a reversal in the surface enrichment of one metal with respect to the other can be accomplished by selecting metal precursors which interact, more or less strongly, with the support. In previous studies (2-4) it was shown that

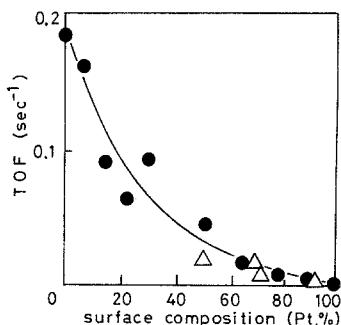
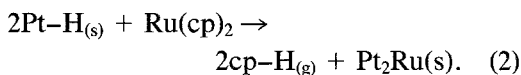


Fig. 6. Change in the TOF of propane hydrogenolysis as a function of Ru-Pt surface composition corresponding to catalysts prepared by the following methods: (△) stepwise impregnation using Ru(cp)₂; (●) coimpregnation using RuCl₃ · 3H₂O and H₂PtCl₆ · 6H₂O. H₂/C₃H₈ = 4/1, T = 420 K. Flow rate 50 ml/min.

when H₂PtCl₆ · 6H₂O and RuCl₃ · 3H₂O were used as metal precursors, cationic Ru species interacted strongly with the silica support and PtCl₆²⁻ diffused freely over the support to nucleate on the Ru surface sites. In this study we have achieved a reversal of this behavior by first preparing a Pt/SiO₂ catalyst followed by sequential impregnation using Ru(cp)₂. In this case Pt is anchored to the support and the highly mobile Ru(cp)₂ precursor diffuses rapidly over the support, nucleating on the surface of the Pt surface sites. We suggest that the presence of H₂ is an important requirement for the formation of bimetallic particles. Apparently, hydrogen which is chemisorbed on the surface of Pt, can react rapidly with the ligands of the Ru precursor. This results in the reduction and nucleation of the Ru on the surface of the Pt. This reduction can be represented by the following chemical equation:



When a Ru precursor such as RuCl₃ · 3H₂O which interacts more strongly with the support is used, the surface mobility of the Ru surface species is decreased. This results in the formation of only a small number of bimetallic particles and a large

number of monometallic particles. When coimpregnation methods are used, surface diffusion is less restricted. This results in the formation of bimetallic particles which are generally enriched in the metal whose precursor interacts more weakly with the support.

It is important to note that even though kinetic effects during pretreatment appear to predominate, thermodynamic effects cannot be excluded. The diffusion of Ru into the bulk was observed to occur readily when Pt gauze covered by a Ru layer was heat treated at 600 K. Similar results were observed by Bowman and Sachtler (25) when Pt and Ru films which had been sequentially deposited were exposed to high temperatures. The supported bimetallic catalysts prepared by the sequential impregnation of Pt/SiO₂ with Ru(cp)₂ were reasonably stable at 600 K. However, heat treatment at 750 and 900 K resulted in the depletion of Ru from the surface layer followed by diffusion into the bulk.

The hydrogenation of benzene over supported bimetallic clusters is an excellent test reaction to probe the formation of dual metal sites. When the hydrogenation activity is different on the corresponding component monometallic catalysts, a synergistic effect is often observed when the reaction is carried out on the bimetallic clusters. This synergism appears to be maximized when the number of dual metal sites is high. For a physical mixture this synergism is essentially zero.

CONCLUSIONS

The following important conclusions emerge from this study:

(1) The use of a mobile metal precursor with respect to a second metal precursor which is strongly attached to the support results in the surface enrichment of the more mobile metal surface species.

(2) The presence of hydrogen is important in promoting the nucleation of the more mobile species on the surface of the strongly bound metal species.

(3) Heat treatment results in a thermodynamic rearrangement of the metal components within Pt–Ru films. This rearrangement was also observed within individual bimetallic particles at temperatures in excess of 750 K. This implies that thermodynamic effects cannot be excluded.

(4) The hydrogenation of benzene is very sensitive to the presence of dual metal surface sites.

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