

Coated Silica as Support for Platinum Catalyst

I. Coating of Silica with Alumina, Titania, and Lanthana

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Received January 11, 1990; revised January 3, 1991

Titania, lanthana, and alumina were coated on silica by the impregnation of silica with solutions of the corresponding salts, followed by drying and calcination. Threshold values for monolayer spreading of the three oxides were estimated by XRD and XPS, and the two methods gave consistent results. When a 2-dimensional close-packing model is used to calculate the amount of oxides needed to form a complete monolayer on the silica surface, the experimentally determined threshold coverage by titania is only about 30%, while alumina can cover up to 85% of the surface, and lanthana tends to be coated in excess of a monolayer. The results are discussed for each case. Though a decrease in surface area on coating was observed more or less in each case, the pore-size distribution pattern did not alter significantly, except in the case of lanthana coating, where a peak of large pores appeared. The distribution of the coating oxides throughout the pores of silica was practically uniform even with these simple coating methods, as verified by argon ion etching. Platinum deposition on the coated supports by impregnation was also uniform. Its electron binding energy is not significantly influenced by the monolayer coatings but appreciably lowered by lanthana coating. © 1991 Academic Press, Inc.

INTRODUCTION

Some SMSI oxides, such as titania, zirconia, and rare-earth oxides used as catalyst supports, often significantly affect the activity and selectivity of the catalysts, favorably in many cases (1-7). But such catalyst supports usually have some shortcomings such as lower stability and smaller surface area. Foger and Anderson (8) attempted to overcome such shortcomings by spreading titania in layers on alumina, and achieved some success.

The practice of employing a highly porous, physically strong, and chemically inert skeleton material as the base for constructing catalysts by the deposition of various components in layers, may be a good idea in developing the art of "catalyst architecture." Silica is a good candidate for such a skeleton material.

The method of depositing the adlayers on

the support has been varied (1, 8-12), but a simple method of spreading layers of compounds on porous supports has been used by Xie and co-workers (13-16). According to these authors, many compounds which can wet the support surface tend to spread spontaneously on support surfaces when heated in contact with the support at temperatures far below the melting points of the compounds, until a monolayer is reached. No multilayer or separate aggregates or crystallites will occur before monolayer coverage. Although the disappearance or absence of XRD patterns might not be a strong criterion for monolayer spreading (12), it is at least a reliable criterion for thin layers (at most 50 Å) and absence of large crystallites. It is also relatively simple and possibly acceptable for practical applications, where an exact monolayer is not strictly required. The uncertainty of this method can be further alleviated by employing an extrapolation procedure.

The present paper reports results ob-

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tained by coating silica with titania, lanthana, and alumina to a "threshold loading," which means the loading before the occurrence of detectable crystallites, in a simple manner similar to that employed by Xie *et al.*, and the use of such "monolayer"-coated supports for preparing Pt carrying samples (0.5%) of the sort usually used in catalytic oxidation or combustion. XRD was used for determining threshold loadings and XPS was used for characterizing the samples, and also for checking the threshold loading values found by the XRD method.

EXPERIMENTAL

Coating of Silica

Silica and purity of reagents. Mini-spherical silica containing Na 140 ppm and Fe 98.7 ppm, manufactured by Qindao Marine Chemical Product Factory (a popular product widely used in China as catalyst support, both in laboratories and chemical industry, especially favorable for fluidized bed use) was crushed to pass a 200-mesh screen, then boiled in 6 N HCl (AR grade) for 1–2 h, filtered, washed with distilled water to neutrality, dried at 393 K, and finally calcined at 773 K for 4 h. The BET area of the sample used for threshold loading determination was 398 m²/g after the above treatment, and that for catalyst preparation was 493 m²/g (pore volume 0.94 ml/g).

Unspecified chemicals used in this work were all AR grade (analytical reagents), which is a purity grade just next to the highest GR grade (guaranteed reagents), according to the grading system of purity used in China.

Coating with titania. Weighed amounts of TiCl₄ were dissolved in anhydrous ethanol and added to dry silica prepared as above to a little more than incipient wetness. The mixture was heated at 333–353 K in a rotary evaporator and evaporated to dryness in a period of about 2 h. Distilled water was then added to the mass dropwise with shaking to more than incipient wetness. The mixture was then heated again in the same apparatus at a temperature a little below boiling to

drive off HCl and excess water in a period of 3 h, and then dried at 393 K, keeping the apparatus rotating at a rate of about 15 rpm. The sample was finally transferred to a muffle furnace and calcined for 5 h at 773 K in air.

Coating with lanthana. Aqueous solutions of lanthanum nitrate strongly acidified with HNO₃ were used to impregnate silica in a manner similar to that described above. The mixture was evaporated slowly in the rotary evaporator to dryness in 4 h, and further dried at 393 K. It was then heated in a muffle furnace at 623 K for 0.5 h to decompose the nitrate. The final calcination was carried out at 873 K for 8 h in air.

Coating with alumina. Alumina was coated onto silica in the same manner as in the case of lanthana, using aluminum nitrate instead.

Pure Supports

Gamma alumina was provided by Shanghai Molecular Sieve Factory, with a BET area of 261 m²/g. Lanthana was prepared by calcining lanthanum nitrate at 853 K for 8 h, BET area 7.1 m²/g. Titania was prepared by hydrolyzing TiCl₄, drying and calcining at 773 K for 5 h. Only anatase was detected by XRD in samples thus prepared, and the BET area was 28.3 m²/g.

Determination of Threshold Loading

Threshold loadings of titania and lanthana on silica were determined by plotting the residual crystalline phase of titania and lanthana respectively against the total amount of titania or lanthana loaded per gram of silica. Extrapolation of the straight line to zero residual crystalline phase gave the threshold value of the dopant for monolayer dispersion.

Alumina from thermal decomposition of the nitrate failed to give clear XRD patterns under calcining conditions used in this work. Therefore its monolayer loading threshold value was determined by repeated impregnation, which is discussed below.

Preparation of Platinum Catalysts

In a 100-ml round bottom flask, 7.4 g of a solution containing 3.38 mg of Pt per gram, prepared by dissolving chloroplatinic acid in 2 N HCl, was mixed with 0.30 g of monochloro-acetic acid dissolved in 10 ml distilled water. Five grams of previously prepared support was added and the flask was fixed to a rotary evaporator. The mixture was evaporated to dryness under rotary in 1–2 h, and then dried at 393 K in the same apparatus. The final calcination was carried out in a muffle furnace at 773 K for 4 h.

Physical Measurements

XRD measurements were carried out on a Rigaku Dmax-rA X-ray diffractometer, operating at 40 kV and 50 mA, using $\text{CuK}\alpha$ radiation filtered through a graphite monochromator, in a way of integrating scanning.

Specific surface areas and pore-size distribution were measured by low-temperature nitrogen adsorption on a Micromeritics Digisorb 2500 apparatus.

XPS studies were made on a Perkin-Elmer PHI 5300 ESCA SYSTEM apparatus, with $\text{MgK}\alpha$ (1253.6 eV, 250 W) radiation as the X-ray source. A PE-7500 computer was used for data processing. The energy scale was calibrated by $\text{Au } 4f_{7/2} = 84.0$ eV, and charge referencing was made with $\text{C } 1s = 284.6$ eV. The pass energy was 35.75 eV, and chamber vacuum was better than 10^{-8} Torr.

RESULTS

Threshold Loading of the Oxides on Silica

Titania on silica. As mentioned above, titania prepared in our experiments was purely anatase if the calcination temperature did not exceed 773 K. Residual anatase phase in samples of different titania loading on silica was evaluated from peak 200 of anatase ($2\theta = 48.14^\circ$), using peak 112 of standard α -silica ($2\theta = 50.2^\circ$) as reference. Calculations were made as follows (14):

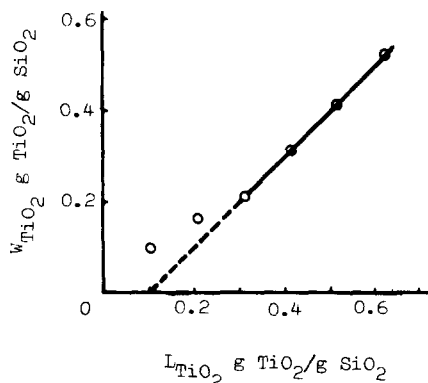


FIG. 1. Plot of residual TiO_2 crystalline phase W_{TiO_2} against TiO_2 loading L_{TiO_2} .

$$W_{\text{titania}} = \frac{I_{\text{titania}} X_{\alpha\text{-silica}}}{Y_{\text{silica}} (1 - X_{\alpha\text{-silica}}) I_{\alpha\text{-silica}} K_{\text{titania}}} \quad (1)$$

$$K_{\text{titania}} = \frac{I_{\text{titania}} X_{\alpha\text{-silica}}}{I_{\alpha\text{-silica}} X_{\text{titania}}} \quad (2)$$

where W_i is the residual crystalline phase of component i per gram of silica, X_i is the known wt% of i in the sample prepared for analysis, I_i is the relative intensity of the XRD peak chosen for component i , and Y_{silica} is the wt% of silica in the original sample.

The constant K_{titania} found by several calibration runs was 2.16, and values of W_{titania} obtained are plotted against L_{titania} (titania added g/g silica) in Fig. 1. Extrapolation of the straight line gives 0.12 g titania per gram of silica as the threshold value for monolayer spreading of titania on silica, corresponding to 0.030 g titania per 100 m² silica surface.

Lanthana on silica. The threshold value of lanthana monolayer coating was determined by XRD in the same manner as in the case of titania coating. A pure crystalline phase of A-lanthana was formed under the above mentioned conditions. The 102 peak of A-lanthana ($2\theta = 39.52^\circ$) was used for quantification, with reference to the 110 peak of a standard α -alumina sample ($2\theta = 37.8^\circ$). Some $\text{La}(\text{OH})_3$ might form by the

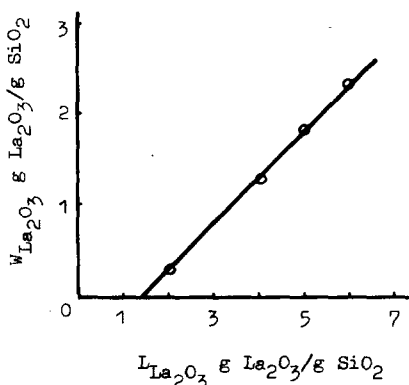


FIG. 2. Plot of residual La_2O_3 crystalline phase $W_{\text{La}_2\text{O}_3}$ against La_2O_3 loading $L_{\text{La}_2\text{O}_3}$.

hydrolysis of the nitrate during impregnation, and would not decompose even under temperatures higher than 853 K, thus interfering with the quantification of crystalline lanthana. This was avoided by acidifying the impregnating solution strongly with nitric acid.

Results obtained are plotted in Fig. 2. The threshold value found by extrapolation is 1.35 g lanthana per g silica, corresponding to 0.34 g lanthana per 100 m² silica.

Alumina on silica. Calcination of aluminum nitrate at below 873 K failed to give any XRD peaks, so the XRD method of evaluating monolayer coating was not applicable in this case. An alternative approach was attempted by repeated impregnation, filtration, and calcination. The amount of alumina loaded was monitored by the weight increase of the sample and Al^{3+} concentration changes of the impregnating solution. Results of the two ways of monitoring coincided.

The weight of alumina loaded onto a definite weight of silica, by repeating the cycle of impregnation with fresh aluminum nitrate solutions followed by suction filtration and calcination, increased with the number of cycles but leveled off rapidly, as shown in Fig. 3. The asymptotic value of alumina loading may be approximated by the result of the third cycle, which gave 15.6% or

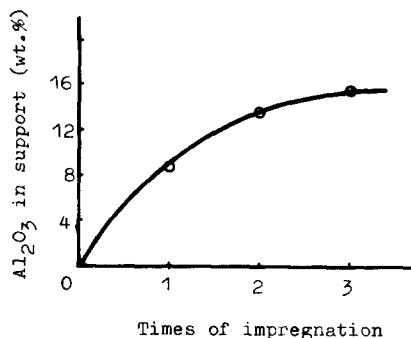


FIG. 3. Amount of Al_2O_3 coated on SiO_2 against times of impregnation.

0.185 g alumina per g silica, or 0.046 g alumina per 100 m² silica.

This phenomenon of limited deposition was verified by subjecting γ -alumina to the above cycles. There observed practically no weight increase at the end of the first cycle.

Checking of threshold loading by XPS. Strohmeier *et al.* (17) described in their paper on Cu/alumina surface characterization that on plotting Cu/Al atomic ratio found by XPS and ISS against Cu content, the ratio increased linearly with increasing Cu content at first and leveled off beyond 9–10 wt% Cu. They attributed the linear part to surface monolayer spreading of Cu. Plots of Ti/Si, Al/Si, and La/Si found by XPS in this work against the corresponding loadings are given in Figs. 4 to 6. The points scattered considerably with high loadings due to the onset of inhomogeneity and segregates on the

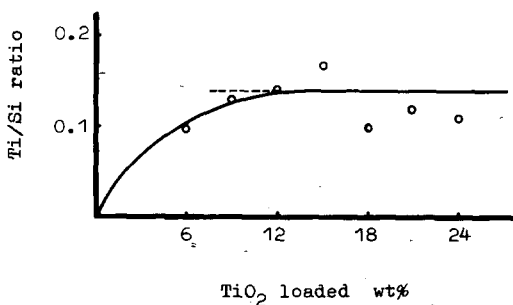


FIG. 4. Plot of surface Ti/Si ratio against TiO_2 loading on SiO_2 .

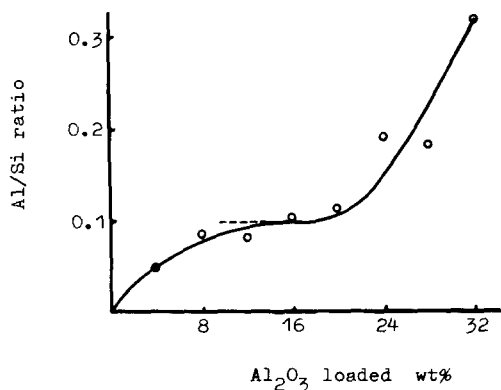


FIG. 5. Plot of surface Al/Si ratio against Al₂O₃ loading on SiO₂.

surface, and go upward in the cases of lanthana and alumina coating. A similar upward trend has been observed by Kohler *et al.* for CuO/SiO₂ (18), and by Chen *et al.* for Li/alumina (19). Chen attributed it to the formation of over layers after full coverage. This is possible in the case of our lanthana coating.

Taking the tangential point of the levelling off part in Figs 4 to 6 as the monolayer threshold, the threshold loadings are: 0.030 g, 0.040 g, and 0.22 g per 100 m² silica surface, for titania, alumina, and lanthana

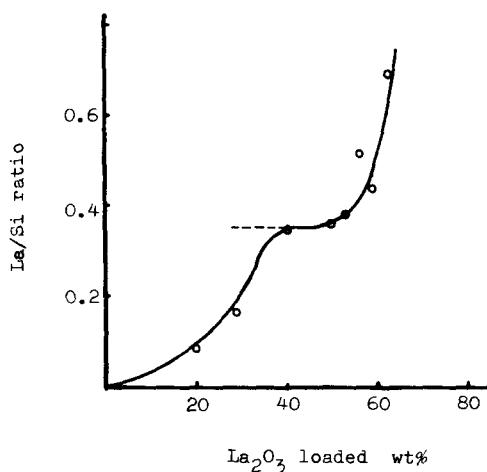


FIG. 6. Plot of surface La/Si ratio against La₂O₃ loading on SiO₂.

coatings, respectively. Comparing with the values found by the XRD method, the agreement is fairly good. The threshold value of lanthana on silica found by XRD quantification is apparently too high.

Pore Size Distribution of Silica before and after Coating

The process of coating as mentioned above caused appreciable decrease in surface area relative to the original silica. A separate set of experiments were made to assess the effect. The following percentage reductions in BET surface area were found: 2.6, 35.6, and 76.5% for titania, alumina, and lanthana coating, respectively. Doubts about the structure alteration of silica by hydrolysis during the coating process, which was usually carried out in a strongly acidic medium, were raised except in the case of titania coating. Therefore the pore-size distribution patterns of the coated samples and the uncoated silica, plotted as percentage of maximum pore volume vs average pore diameter, were compared as shown in Fig. 7. A blank test for strong acid action, simulating the condition for lanthana coating (30 ml 20% HNO₃ plus 2 g silica and evaporated to dryness in 4 h), was conducted and the pore distribution of the product is also shown in that figure.

Only minor differences are observed between all the curves, except that a relatively high peak appears at 475 Å and pores below 40 Å disappear for lanthana coating (Fig. 7c). As other features are not seriously altered and the 475 Å peak is absent in the blank test sample (Fig. 7e), it is not likely a result of silica hydrolysis, but rather a feature of segregated lanthana, or secondary pores created by particle aggregation with overdosed lanthana as the glue. Therefore the possibility of silica deterioration through hydrolysis in the course of coating operation can be considered as insignificant if not totally excluded. The surface area reduction might be caused mainly by the clogging of mesopores at the mouths (not filled up), and the less chance of clogging for larger pores

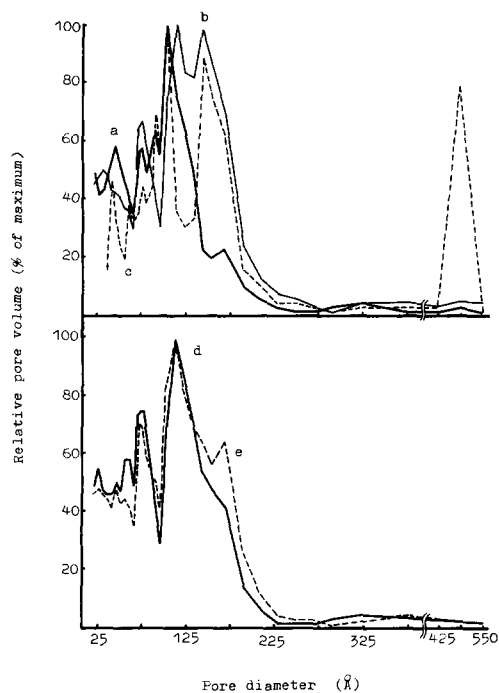


FIG. 7. Pore distribution of coated and uncoated silica supports. (a) 12% titania on silica; (b) 16% alumina on silica; (c) 40% lanthana on silica; (d) HCl washed and calcined silica (see text); (e) 30 ml HNO_3 + 2g SiO_2 evaporated to dryness in 4h.

might be offset at least partially by its greater contribution to pore volume. The percentage pore volume reduction for the three coated samples are: 2.1, 31, and 72.3%, respectively, being very similar to the area reductions given above.

XPS Studies of Pure Oxides and Coated Silica Loaded with Pt

Results of the electron binding energies of the cations in different samples are listed in Table 1. At least two peaks for Pt $4f_{7/2}$ were observed in most of the cases, but only the strongest one is given in Table 1. A weaker peak around 71 eV accompanying the stronger one is probably a sign of partial reduction of Pt^{4+} during calcination. In samples containing Al, the Pt $4f$ peak was masked by Al $2p$, so that the BE for Pt $4d_{5/2}$ was recorded instead, although it is rather

weak for samples with <1% Pt and harassed by noises.

It can be seen that in samples coated with monolayer alumina and titania, Pt $4f_{7/2}$ gives practically the same BE as that in the case of pure silica. But the influence of lanthana is significant, as revealed by the considerable lowering of BEs of Pt $4f$ and Si $2p$ in samples containing lanthana. This effect of lanthana on Pd has been observed by Fleisch *et al.* (20). The authors proposed that the Pd surface might be partly covered by patches of LaO_x making the Pd negatively charged. This is also possible in our case for Pt. The LaO_x patches might have formed during the process of preparation rather than or in addition to latter migration, because our samples were to be used in catalytic combustion experiments, and were not subjected to hydrogen reduction, and all the samples examined were freshly prepared. The influence of dispersed lanthana seems to be more pronounced than that of its bulk state. All the dispersed oxides seem to have slightly higher BEs for their cations. The low BE values for Si $2p$ in the alumina-coated sample and for Pt $4d_{5/2}$ in Pt/ Al_2O_3 cannot be readily explained at present, and therefore no discussion is attempted.

Sputtering with an Ar^+ beam operating at 3 KV and 20 μA , effecting an etching rate of about 30 $\text{\AA}/\text{min}$, was used to characterize the homogeneity of coating and Pt deposition. The results are shown in Fig. 8. The distribution of Pt and the coating oxides is in general basically uniform. This does not mean that the coating cations have penetrated into the bulk of silica lattice, but rather that the foreign cations are spread on the interior surfaces of silica.

DISCUSSIONS

The original purpose of this work was to create monolayer coatings of oxides on a silica skeleton, so as to make catalyst supports of high surface area and good abrasion resistance, and yet with surface chemical properties resembling those of the coating

TABLE I
Electron Binding Energies of the Cations (eV)

	Pt 4f _{7/2}	Pt 4d _{5/2}	Si 2p	Al 2p	Ti 2p _{3/2}	La 3d _{5/2}
Pt/SiO ₂	74.6	314.8	104.4			
Pt/Al ₂ O ₃	^a	313.1		74.6		
Pt/TiO ₂	74.4				458.2	
Pt/La ₂ O ₃	73.8					834.3
Pt/Al ₂ O ₃ /SiO ₂	^a	314.8	103.1	74.8		
Pt/TiO ₂ /SiO ₂	74.6		104.2		458.6	
Pt/La ₂ O ₃ /SiO ₂	72.5		102.8			834.7

^a Masked by Al 2p.

oxides. But the problem is actually complicated and the idea of monolayer coating merits further discussion.

Monolayer Dispersion of Titania

Fransen *et al.* (12) has set forth five criteria for the presence of a monolayer on the carrier surface of their Mo oxide catalyst. Roozeboom *et al.* (21) added another two, when studying their vanadia catalysts. The criterion used by Xie *et al.* (13), based on XRD detection of crystallites, was considered the weakest one by Scholten (in discussion of Ref. (12)). Nevertheless, if the purpose of a monolayer coating were only to provide a modified, covered support surface for further preparation, then the methodology of using XRD may be made on a pragmatic basis. Therefore, it was chosen in this work to determine the threshold monolayer loadings. Such a choice is further justified by checking with XPS surface composition measurements, although it is also not an accurate method.

The Beijing University group (13–16) postulated an apparently oversimplified model of two-dimensional close packing monolayer of O²⁻ ions on carrier surface for monolayer spreading of any oxide. The difference between different oxides lies only in the number and position of the cation. If the ionic radius of O²⁻ is taken to be 1.40 Å, the area of one TiO₂ unit corresponds to that occupied by the parallelogram inscribing two O²⁻ ions, which is $1.36 \times 10^{19} \text{ m}^2$. A monolayer calculated by this method should have 0.098 g titania per 100 m² silica. The experimental value 0.030 is only 30.6% of full coverage. If the reduction in surface

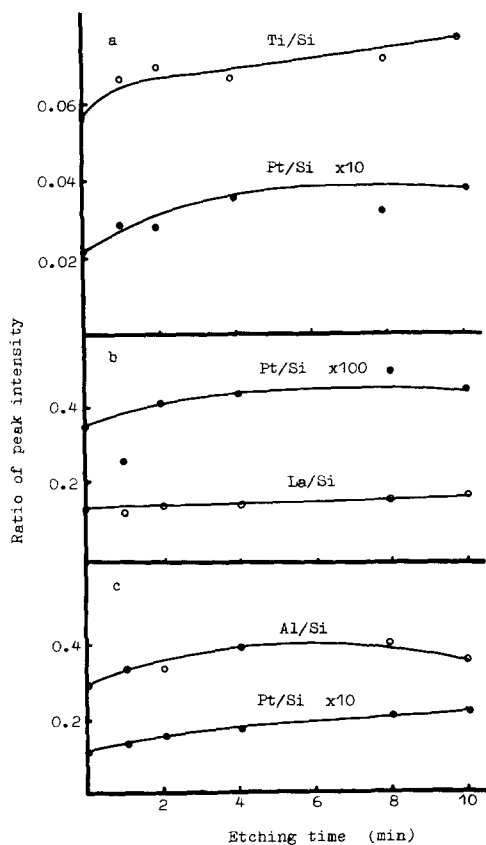


FIG. 8. Sputtering profiles of Pt catalysts on coated supports. (a) Pt/TiO₂/SiO₂; (b) Pt/La₂O₃/SiO₂; (c) Pt/Al₂O₃/SiO₂.

area, which amounts to about 2–8% is taken into account, the coverage still does not exceed 34%. Liu *et al.* (16) obtained by this method a 27% coverage of silica by MoO₃, roughly close to our result for TiO₂/SiO₂. There may be operational, topographical, and chemical reasons for this incomplete coverage. But the most important one might be chemical in nature. The lattice patterns of the coating oxide and the skeleton are not identical, so the coating shall neither grow on the surface according to the skeleton lattice, nor form a lattice of its own crystals, but adapt to the surface environment, forming a "surface phase oxide structure" (SPO), a term used by Murrell *et al.* (22) recently to describe their dispersion of silica on alumina. In addition, surface functional groups might also play an important role, especially OH groups which might be responsible for the binding of TiCl₄ to the surface. The coverage would then be limited by the number of OH groups and steric hindrance. The observed coverage corresponds to 4.5 OH groups per 100 Å², if one TiCl₄ is bound to silica through two OH groups, which is a reasonable value (23).

With respect to the monolayer calculation, some authors used crystallographic parameters to estimate the area occupied by a unit of the coating oxide. For example, Fransen *et al.* (12) cited a value of 15.4 Å² for a MoO₃ unit, and Roozeboom *et al.* (21) used 10.3 Å² for VO_{2.5} calculated from the 010 plane of V₂O₅ crystal. The monolayer threshold values calculated from these figures are much larger and the discrepancy between theoretical and experimental values will be much greater than those calculated from Xie and Liu's model, which gives 20.4 Å² for MoO₃ and 17.0 Å² for VO_{2.5}. Although theoretically less sound (24), the latter model seems practically more preferable.

Dispersion of Alumina

When the two-dimensional close-packing model was applied to the coating with alu-

mina, the monolayer loading calculated should be 0.083 g alumina per 100 m² surface. The experimental value of 0.046 corresponds to 55% coverage. For the value of 0.040 found by XPS, the coverage is only 48%. If the reduction in surface area mentioned above is taken into account, the coverage might amount to 75–85%, much closer to a complete monolayer than in the case of titania coating.

Dispersion of Lanthana

The monolayer loading for lanthana calculated by Xie's model is 0.27 g lanthana per 100 m² surface. The experimental value of 0.34 found by the XRD method is 26% higher than the calculated. Liu *et al.* observed similar results (15), and attributed the surplus to manipulation losses during impregnation. This was unlikely in our case.

We note from XRD the easy formation of La(OH)₃ by the hydration of lanthana by moisture in air. If it enveloped lanthana crystallites or covered some parts of the surface lanthana layer, the XRD method will give a monolayer loading value higher than actually needed. This is very probable because Rosynek and Magnuson (25) found that lanthana absorbed water at 298 K forming La(OH)₃ even when the water vapor partial pressure was <10 Torr, and Fleisch *et al.* (20) found that La(OH)₃ transformed to a mixture of La(OH)₃, LaO(OH), and La₂O₃ after heating at 873 K for as long as 17 h.

Reduction in surface area was exorbitant in this case, amounting to 76–86% of the original. The coating is obviously not monolayer, and may consist of several layers of oxide, hydroxide, and oxyhydroxide. The presence of a large amount of OH groups may provide active sites for multilayer growth. The value of 0.22 g lanthana/100 m² silica found by XPS corresponds to 81% coverage and is therefore more reasonable. But the excessive reduction in surface area suggests that the actual coverage is far in excess of 100%. The possibility of silica

structure destruction by hydrolysis has been discussed above. If not excluded, it should not be predominant.

In cases of coating by pure oxides, the amount of oxide present in excess of that needed for a monolayer coverage will go into normal crystallite growth of its own, instead of adding to the SPO layer to form multilayers, because normal crystal growth is energetically more favorable than the growth of multilayers following a strained SPO pattern. But before monolayer completion, the "wetting" energy of the surface by the dopant may make the formation of a SPO layer compete favorably with the formation of crystallites and multilayers, so that the latter processes would not occur. These may explain the "spontaneous monolayer spreading of certain catalytic components over carrier surfaces" reported by Xie and co-workers (13-16).

Another complication in the case of the lanthana sample is that it may redissolve during the preparation of Pt catalysts by impregnation with strongly acidic H_2PtCl_4 , and then redeposit together with Pt, as Kieffer *et al.* (2) had proposed in impregnating La promoted silica with Rh salt solution. The two species are intermingled instead with Pt on top of lanthana in our case, causing the encapsulation or embedding of Pt by lanthana.

The Pt loaded samples prepared in this work are to be tested as combustion catalysts, which will be reported in another paper (Part II of this work), together with further characterization with H_2 chemisorption and TPD of H_2 (26).

CONCLUSION

Uniform coatings of titania, alumina, and lanthana can be formed on silica by impregnation with solutions of their salts (plus hydrolysis in the case of titania), followed by calcination. The deposits of alumina and titania are monolayers of more or less imperfect coverage, while lanthana forms

multilayers or aggregates. Threshold monolayer loadings can be determined by XRD quantification of the crystalline phase which appears after the completion of monolayer, employing an extrapolation procedure, or by XPS surface analysis. The two methods give consistent results. In the case of lanthana, the situation is complicated by its easy hydration and the redissolution of the coating when used in further preparation.

Platinum deposited on the coated supports has a uniformity similar to that of the coating oxides. The electron binding energies of both Pt and Si are lowered appreciably by the lanthana coating, but not significantly influenced by alumina and titania.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China. XPS studies were financed by the United Test Centre of Zhong Guan Cun District of Beijing. Assistance in experiments with XRD by Mr. Jian Liang, and support for the revision work by Prof. Z.-Y. Guo, are also gratefully acknowledged. Finally, helpful comments have been made by the reviewers, and some of these were followed in the revision work.

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