

REDUCTION AND OXIDATION OF Rh/Al₂O₃ AND Rh/TiO₂ CATALYSTS AS STUDIED BY TEMPERATURE-PROGRAMMED REDUCTION AND OXIDATION

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Summary

Careful preparation of Rh/Al₂O₃ catalysts leads to ultradisperse systems (H/Rh > 1.0). Temperature-programmed reduction (TPR) shows that these catalysts are almost completely oxidized during passivation. Identical preparation of Rh/TiO₂ catalysts leads to less disperse systems (H/Rh = 0.3), which exhibit two reduction peaks in TPR. These peaks are due to the reduction of small, well-dispersed Rh₂O₃ particles and of large, bulk-like Rh₂O₃ particles. In all cases reduction of Rh₂O₃ is complete above 450 K. TiO₂ is partly reduced by a metal-catalysed process above 500 K.

Introduction

Over the past years it has become clear that rhodium catalysts occupy a special position in the field of supported transition metal catalysts, because they are able to produce hydrocarbons as well as oxygenated products (alcohols, aldehydes, acids) from synthesis gas [1 - 10].

Various workers have tried to influence the selectivity and activity of the rhodium catalysts via special preparation [1, 2], additives [3 - 5] or mixed oxides [8 - 10], and where this succeeded at least two groups gave as the reason the presence of stabilized Rh⁺ on the surface [8, 10].

Some authors claimed the presence of isolated Rh⁺ sites in mono-metallic Rh catalysts on the basis of IR evidence (Worley *et al.* [11 - 13], Primet [14]), while others using electron microscopy found the Rh to be present as metallic rafts (Yates *et al.* [15]).

In all cases it seems obvious that the support plays an important role in either bringing or keeping the metal in a certain state of (non-)reactivity. A special example of such a metal-support interaction was discovered by Tauster *et al.* [16, 17] and is now known as Strong Metal-Support Interaction (SMSI): Supported metals such as Pt and Rh lose their capability for chemisorption of H₂, CO and NO if they have been reduced at high

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temperatures (e.g. 773 K) on supports such as TiO_2 and V_2O_3 . Normal chemisorption behaviour can be restored by oxidation at elevated temperatures, followed by low-temperature reduction, at for instance 473 K [16]. SMSI has been related to the occurrence of lower oxides of the support [18, 19], but the exact nature of the interaction still remains unclear.

Many of the above-mentioned phenomena involve one common property: The oxidation-reduction behaviour of supported Rh catalysts. We decided to study two systems, representative of many of those referred to above: 2.3 wt.% Rh/ Al_2O_3 and 3.2 wt.% Rh/ TiO_2 . Via sintering (see Experimental) we have induced a variation in particle size (dispersion) in order to examine the following questions:

- (i) How is oxidation-reduction influenced by particle size?
- (ii) Does particle size show any effect upon SMSI?

Before discussing the experimental techniques, we must introduce one last item: passivation. Since it is obvious that reduced systems cannot simply be stored in air, we passivate and stabilize them by applying a layer of oxygen on the metal particles in a controlled manner (see Experimental). Some authors have already examined the state of the catalysts after storage in air. Burwell Jr. *et al.* have used Wide Angle X-ray Scattering, Extended X-ray Absorption Fine Structure (EXAFS), hydrogen chemisorption and hydrogen-oxygen titration to characterize their supported Pt and Pd catalysts [20 - 23].

We will show that good insight in these matters can be gained via Temperature Programmed Reduction and Oxidation (TPR and TPO), supported by chemisorption measurements. TPR as a characterization technique was presented by Jenkins *et al.* in 1975 [24, 25] and has been used extensively in the past few years, as is seen from a recent review by Hurst *et al.* [26]. The technique allows one to obtain (semi)quantitative information on the rate and ease of reduction of all kinds of systems; once the apparatus has been built, analyses are fast and relatively cheap. We used an apparatus as described by Boer *et al.* [27], which enabled us to extend the analyses to TPO, and thus gather information about the rate and ease of oxidation as well.

Experimental

TiO_2 (anatase, Tioxide Ltd, CLDD 1367, surface area $20 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.5 \text{ cm}^3 \text{ g}^{-1}$) and $\gamma\text{-Al}_2\text{O}_3$ (Ketjen, 000-1.5E, surface area $200 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.6 \text{ cm}^3 \text{ g}^{-1}$) were impregnated with an aqueous solution of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ via the incipient wetness technique to prepare a 2.3 wt.% Rh/ Al_2O_3 and a 3.2 wt.% Rh/ TiO_2 catalyst, as was established spectrophotometrically. The catalysts were dried in air at 355, 375 and 395 K for 2 h successively, followed by direct (pre)-reduction in flowing H_2 at 473, 773 or 973 K for 1 h. Prior to removal from the reduction reactor, the catalysts were passivated at room temperature by replacing the H_2 flow

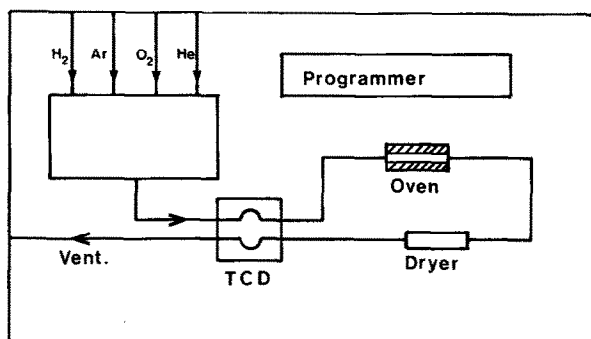


Fig. 1. Schematic representation of TPR-TPO apparatus.

with N_2 , and subsequently slowly adding up to 20% O_2 . The catalysts were then taken out of the reactor and stored for further use.

The TRP/TPO apparatus used is schematically represented in Fig. 1: a 5% H_2 -in-Ar or a 5% O_2 -in-He flow (300 ml h^{-1}) can be directed through a microreactor. The temperature of the reactor can be raised or lowered via linear programming. H_2 or O_2 consumption is monitored continuously by means of a thermal conductivity detector (TCD).

A typical reactor sequence is as follows (a similar sequence is followed during TPO):

- the passivated or oxidized sample is flushed under Ar flow at 223 K;
- Ar is replaced by the Ar/ H_2 mixture, causing at least an apparent H_2 consumption (first switch peak);
- the sample is heated under Ar/ H_2 flow at a rate of 5 K min^{-1} to 873 K;
- after 15 min at 873 K, the sample is cooled down at 10 K min^{-1} to 223 K;
- the reduced sample is flushed with Ar;
- Ar flow is replaced by the Ar/ H_2 mixture once more, now causing only an apparent H_2 consumption (second switch peak).

The switch peak procedure deserves some closer attention. The strong signal we call the first switch peak is mainly due to the displacement of Ar by Ar/ H_2 in the reactor, but in some cases real hydrogen consumption takes place, even at 223 K. Therefore we repeat the whole procedure after the TPR has been performed, when the catalyst has been reduced and cooled down to 223 K, and as a consequence is covered by hydrogen. Then we replace the Ar/ H_2 by pure Ar, resulting in a negative TCD signal. Subsequently we switch back to Ar/ H_2 . Since we do not expect any hydrogen consumption from the reduced hydrogen-covered sample at this time, the resulting second switch peak will be due solely to the displacement of Ar by Ar/ H_2 . Thus the difference between the first and second switch peaks reveals the real hydrogen consumption at 223 K, if there is any.

The reactions that might take place during TPO and TPR are:

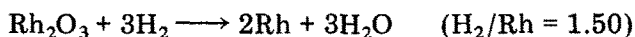
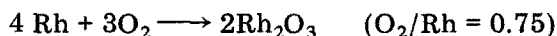


TABLE 1

Hydrogen chemisorption of Rh/Al₂O₃ (RA) and Rh/TiO₂ (RT) catalysts. LT: reduced in the apparatus at low temperature, HT: at high temperature, see text.

$T_{\text{pre-red.}}$	H/Rh		
	RA	RT(LT)	RT(HT)
473	1.70	0.37	0.08
773	1.53	0.29	0.05
973	1.23	0.12	0.01

The ratios express the hydrogen or oxygen consumptions in TPR or TPO, respectively, expected for reduction of bulk Rh₂O₃ or formation of this very material (apart from chemisorption of any kind).

Chemisorption measurements were carried out in a conventional volumetric glass apparatus after reduction of the passivated catalysts at 473 or 773 K in flowing H₂ for 1 h, followed by evacuation at 473 K for 1 h. After H₂ admission at 473 K, desorption isotherms were measured at room temperature. As desorption became noticeable only at pressures below 200 torr, we believe that the chemisorption value above that pressure is representative of monolayer coverage (*cf.* Crucq *et al.* [28]). The H/Rh values thus obtained for the various systems are presented in Table 1.

Results

Hydrogen chemisorption

The hydrogen chemisorption data as given in Table 1 were obtained for Rh/Al₂O₃ (RA) after reduction of the passivated catalyst at 473 K only, and for Rh/TiO₂(RT) also after reduction of the passivated catalyst at

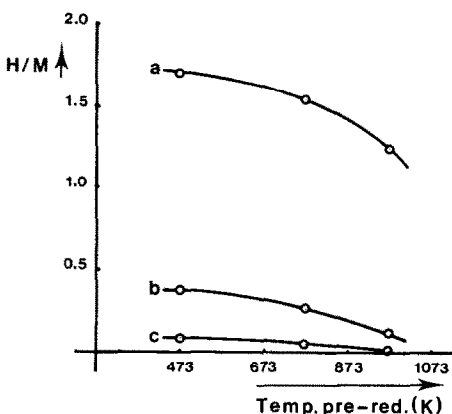


Fig. 2. Hydrogen chemisorption as a function of prereduction temperature: (a) Rh/Al₂O₃, reduced *in situ* at 473 K; (b) Rh/TiO₂, reduced *in situ* at 473 K; (c) Rh/TiO₂, reduced *in situ* at 773 K.

773 K, to induce SMSI behaviour. The catalysts will be denoted hereafter as RA 773 (Rh/Al₂O₃, pre-reduced at 773 K), RT 973 (Rh/TiO₂, pre-reduced at 973 K), etc. The results are represented graphically in Fig. 2, showing the values of H/Rh as a function of pre-reduction temperature (*i.e.* reduction prior to passivation; reduction prior to chemisorption was at either 473 or 773 K, as indicated). Values for Rh/Al₂O₃ range from 1.70 to 1.00, for non-SMSI Rh/TiO₂ from 0.37 to 0.12 and for SMSI Rh/TiO₂ from 0.10 to 0.01.

TPR and TPO of Rh/Al₂O₃

The TPR profiles of the passivated RA 473 and RA 773 catalysts are shown in Fig. 3a and b. The horizontal axis shows the temperature and the vertical axis the H₂ consumption (in arbitrary units).

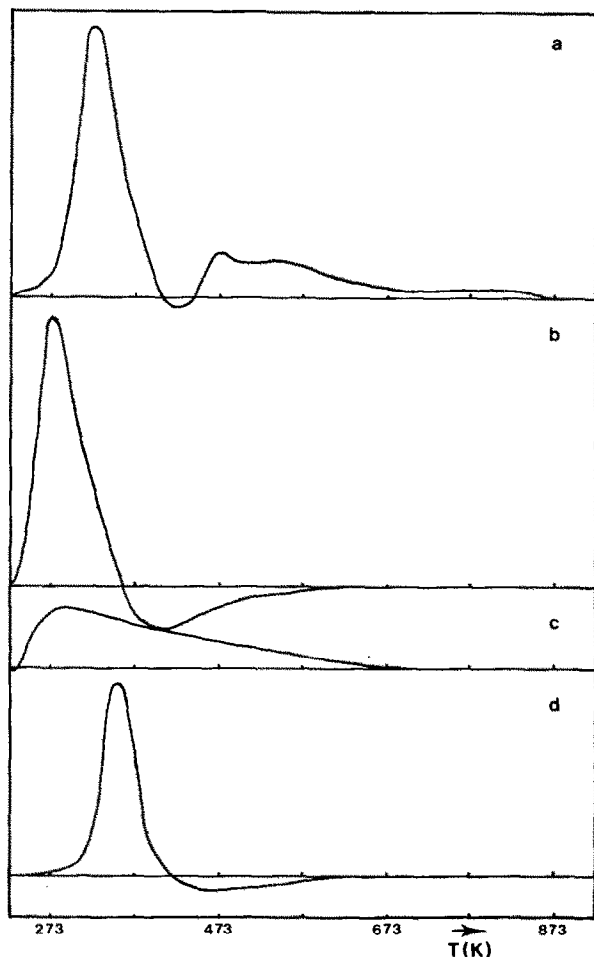


Fig. 3. 2.3 wt.% Rh/Al₂O₃ catalyst: (a) TPR of passivated catalyst, prerduced at 473 K; (b) TPR of passivated catalyst, prerduced at 773 K; (c) TPO following TPR of catalyst prerduced at either 473, 773 or 973 K; (d) TPR following TPO of catalyst prerduced at either 473, 773 or 973 K.

RA 473 shows a maximum H_2 consumption at 330 K, and some further reduction above 473 K. RA 773 shows a single consumption peak around 273 K, followed by desorption of H_2 . The pre-reduction had apparently been complete, and passivation of this ultradisperse Rh catalyst had led to dissociative oxygen chemisorption, but not full oxidation, since the net H_2 consumption amounted to 1.0 H_2 /Rh. Apparently the pre-reduction at 473 K of RA 473 had not been complete, and the oxygen chemisorbed on this system was harder to remove than from the others (RA 973 showed a TPR profile identical to that of RA 773).

The subsequent TPO, Fig. 3c, whose profiles were identical for all three systems, confirms these observations: O_2 consumption begins at 223 K, in the 'switch peak', continues when the temperature climb is started, reaches a maximum around 290 K, and then decreases very slowly towards higher temperatures.

Integration of the O_2 consumption signal proved difficult, due to the small sample sizes (typically 50 - 75 μmol of metal) and the small thermal conductivity of O_2 , but still amounted to a rather satisfying 0.6 - 0.7 O_2 /Rh (0.75 was expected, since chemisorbed H_2 was removed by heat treatment between TPR and TPO). The similarity of the TPO profiles of RA 473, RA 773 and RA 973 is in accordance with the fact that all these catalysts have been brought up to 873 K during the TPR run; it is not surprising to find that the TPR profiles of the completely oxidized systems (following TPO) are also identical (Fig. 3d). One single peak is observed around 360 K, corresponding to a hydrogen consumption of about 1.5 H_2 /Rh, which agrees with the reduction of Rh_2O_3 . Unsupported bulk Rh_2O_3 showed a reduction peak at 400 K in our apparatus, while oxidation of bulk Rh metal was only initiated above 870 K.

TPR and TPO of Rh/TiO₂

The TPR profile for the passivated RT 473 catalyst is shown in Fig. 4a. Its most striking feature is that the H_2 consumption already starts at 223 K in the 'switch peak', that is, as soon as H_2 /Ar is flushed through the reactor. Keeping in mind the much lower H/Rh value of this catalyst compared to the Rh/ Al_2O_3 series, we conclude that passivation here has caused only the formation of an outer layer of oxide on the relatively large metal particles. If the remaining metallic core could be reached by the hydrogen molecules, these molecules could dissociate and provide atomic hydrogen for easy reduction of the oxide layer at low temperatures. There is also some hydrogen consumption just above 473 K, as occurred for the corresponding Rh/ Al_2O_3 catalyst, indicating that also for Rh/TiO₂ the pre-reduction at 473 K was not complete. It is evident that the TiO₂ support can also be reduced, leading to H_2 consumption around 573 and 700 K. The H_2 consumption at 223 K amounts to about 0.4 H_2 /Rh.

The TPR profiles for RT 773 and RT 973 are similar, but since the Rh surface area decreases with increasing pre-reduction temperature (*cf.* Table 1) the amount of passivation oxygen also decreases, and thus so does

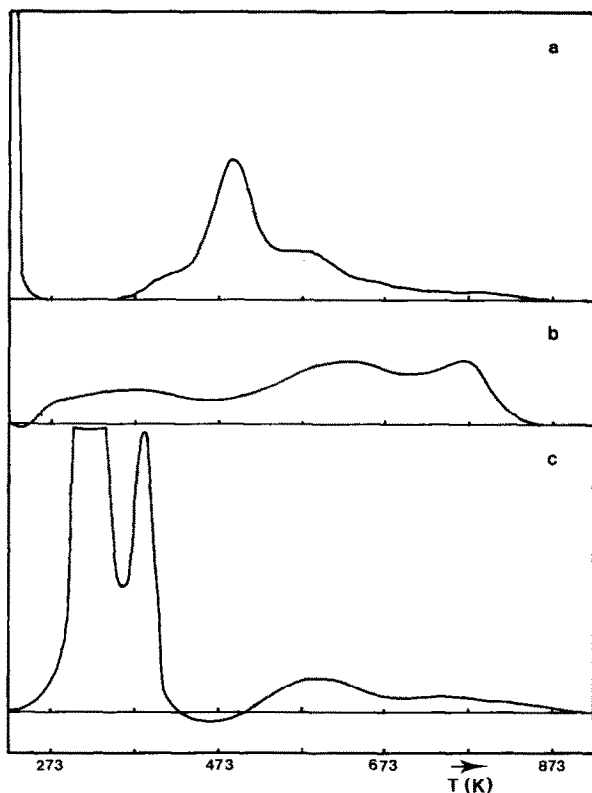


Fig. 4. 3.2 wt.% Rh/TiO₂ catalyst: (a) TPR of passivated catalyst, prereduced at 473 K; (b) TPO following TPR of catalyst prereduced at either 473, 773 or 973 K; (c) TPR following TPO of catalyst prereduced at either 473, 773 or 973 K.

the H₂ consumption at 223 K in the TPR profiles. The consumption just above 473 K has also disappeared as a consequence of the higher pre-reduction temperature.

Figure 4b shows the TPO profile of the reduced RT catalyst. The three TPO profiles of RT 473, 773 and 973 are alike: three 'areas' of oxygen consumption appear, which we attribute respectively to chemisorption (which is the only phenomenon on Rh/Al₂O₃), corrosive chemisorption and complete oxidation. We will come back to these assignments in the subsequent Discussion.

The TPR profiles of the oxidized samples of the RT series are again identical (Fig. 4c) and show two clearly divided H₂ consumption maxima, at 325 and 385 K. Consumption in the first peak is about 1.3 H₂/Rh and in the second one about 0.3 H₂/Rh. Taken together, the H₂ consumptions are close enough to the expected value of 1.5 H₂/Rh to attribute them both to reduction of Rh₂O₃. The peak at 385 K is assigned to bulk-like Rh₂O₃ particles (note that the peak maximum for unsupported Rh₂O₃ is at 400 K), and that at 325 K to a better-dispersed Rh₂O₃ phase. Furthermore, the

possibility of some support reduction taking place here as well, in advance of the support reduction around 573 and 700 K, cannot be excluded.

Discussion

Hydrogen chemisorption has been used through the years by many workers to characterize metal surfaces [7, 9, 10, 14, 16, 20 - 23, 29, 30]; when attempts were made to calculate metal surface areas from hydrogen chemisorption data, a hydrogen-metal stoichiometry of one was used. On the other hand, if CO was involved, some authors [31] chose a stoichiometry of one, while others [14] mentioned higher stoichiometries.

We feel that if it is accepted that a metal atom such as Rh can adsorb two or more CO molecules, then the idea of the same atom adsorbing more than one hydrogen atom should not be excluded. Thus although our experimental H/Rh results exceed unity, we think they are real (Table 1), and that the hydrogen chemisorbed does not exceed a monolayer (*cf.* Crucq *et al.* [28]), and is entirely bound to the metal. We did not try to distinguish between so-called 'reversible' and 'irreversible' adsorption, because we believe that in the thermodynamic sense there is no such distinction. In following the procedures that lead to that supposed distinction, one merely encounters the physical restrictions of the experimental apparatus, such as pumping speed and conductivity of the capillary tubing [28].

As described in the Experimental Section, we admitted hydrogen at 473 K. This was done simply to accelerate adsorption and did not effect the ultimate amount of adsorption, as was verified by measuring the adsorption isotherms at room temperature*. This leaves us with chemisorption values above unity, and therefore, like some other authors [21, 30], we find it impossible to calculate a particle size or a dispersion from these data, since there is no particular stoichiometry value to prefer. We imagine these Rh particles could be raft-like, as suggested by Yates *et al.* [15] (although they were dealing with only 0.5 wt.% Rh/Al₂O₃), where the edge atoms could have the possibility of adsorbing more than one H atom.

'Sintering' of these particles (H/Rh decreases from 1.7 to 1.0 upon reduction at 973 K) would then mean that the number of edge atoms decreases, for example by forming rafts or even (hemi)spherical particles. Still we are dealing with ultradispersed systems. We estimate that in all cases the Rh particle size does not exceed 10 Å.

For the RT series the H/Rh values as established after 473 K reduction are much lower, which was to be expected considering the difference in surface area between Al₂O₃ and TiO₂ and the similar metal loadings. Here also we see a decrease in the H/Rh values as a result of an increase in pre-reduction temperature. But in this case this is simply due to growth of the

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metal particles, resulting in a decreased metal surface area. The H/Rh values after 773 K reduction show evidence for SMSI behaviour. The values are small, however, and of the order of magnitude of the experimental error. Therefore we cannot at this point draw any conclusion about a relationship between SMSI behaviour and particle size. We expected this to be difficult, since both particle growth and increasing SMSI behaviour lead to less hydrogen chemisorption, and the limits of experimental accuracy might thus prohibit a distinction between the two effects.

It is evident that RT 773 and RT 973 must have been in the SMSI state after pre-reduction, but they showed normal chemisorption behaviour after the passivation and re-reduction at 473 K in the chemisorption apparatus. This means that the passivation, following the pre-reduction, must have destroyed the SMSI state.

Our TPR and TPO results also prove that passivation is rather drastic. For small metal particles on Al_2O_3 , TPR of the passivated samples differs from that of the oxidized ones only in the position of the peak, that is, in the ease of reduction. From the shape of the TPO pattern, we can deduce that the effect of a long passivation time (such as storage in air) approaches that of a real oxidation. But it is very clear that no matter what the initial state of the Rh, passivated or oxidized, reduction is complete above 400 K.

Worley and coworkers studied the oxidation state of Rh on various supports, beginning with various Rh precursors, via IR absorption experiments after CO adsorption [11 - 13]. Apart from IR absorptions attributed to CO adsorbed on metallic Rh, some absorptions were found which were attributed to CO adsorbed on isolated Rh^+ sites. For 2.2 wt.% Rh catalysts, these isolated Rh^+ sites were found to be more abundant for Al_2O_3 than for TiO_2 as support [13], and more abundant for RhCl_3 than for $\text{Rh}(\text{NO}_3)_3$ as precursor [12, 13]. The authors concluded that the poorest reduction of Rh (their reductions were carried out at 673 K) occurs when using Al_2O_3 as a support and RhCl_3 as a precursor. From the TPR evidence presented here, we conclude that the systems studied by Worley *et al.* must have been completely reduced prior to admission of CO, and therefore we prefer another explanation. The best dispersion of metallic Rh particles is obtained on Al_2O_3 , and starting from RhCl_3 . Upon CO adsorption, the smaller particles break up and create the isolated dicarbonyl species that were attributed to Rh^{+1} by Worley *et al.* EXAFS proof for this explanation is published elsewhere [32].

Our findings for Rh/ TiO_2 agree very well with the results published by Burwell *et al.* for Pd and Pt on SiO_2 and Al_2O_3 [20 - 23]. Upon passivation, the larger metal particles create an oxide 'skin', the formation of which can almost literally be seen in the TPO of Rh/ TiO_2 (Fig. 4b). The small metal particles on Al_2O_3 show only one tailing chemisorption peak, but for Rh/ TiO_2 oxygen chemisorption is followed at higher temperatures by corrosive chemisorption and finally, around 700 K, by complete oxidation. Apparently oxygen diffusion through the oxide layer is a strongly hindered process. Attribution of the intermediate temperature region of oxidation

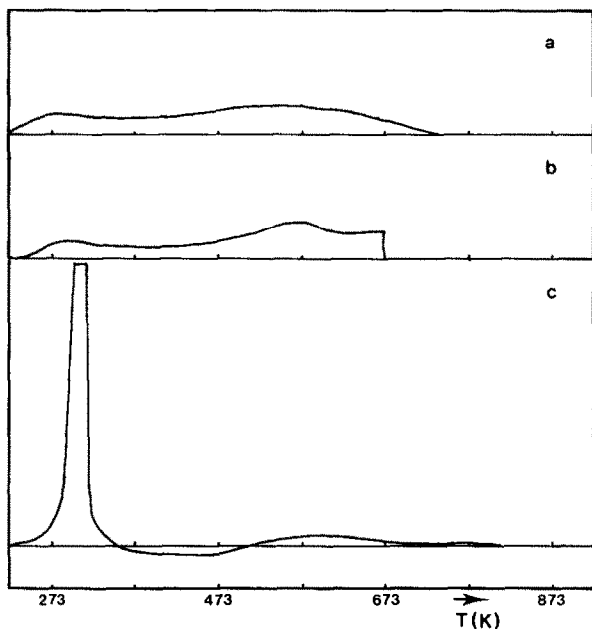


Fig. 5. (a) TPO of a reduced 3.0 wt.% Rh/SiO₂ catalyst; (b) TPO up to 673 K of a reduced 3.2 wt.% Rh/TiO₂ catalyst; (c) subsequent TPR.

to corrosive chemisorption is supported by our TPO results using 3 wt.% Rh/SiO₂ (Grace Silica, S.P. 2.-324, 382, 290 m² g⁻¹), shown in Fig. 5a. This TPO exhibits two oxygen consumption areas, one around 273 K which is due to oxygen chemisorption, and one around 500 K due to corrosive chemisorption. All of the Rh on SiO₂ is in a well-dispersed form (H/Rh = 0.4), as was confirmed by the subsequent TPR of this Rh/SiO₂ catalyst, which showed only one H₂ consumption maximum at 335 K. This peak corresponds to that of the first reduction peak observed for Rh/TiO₂ at 325 K (*cf.* Results). The oxidation peak around 700 K in the TPO of Rh/TiO₂ is attributed to the formation of rather large, bulk-like Rh₂O₃ particles whose reduction is observed as a separate H₂ consumption maximum at 385 K in the TPR (Fig. 4c).

That the large particles both oxidize and reduce at a higher temperature than the small particles has been proven by a rather simple experiment, shown in Fig. 5b and c. The TPO is first run with a reduced Rh/TiO₂ system up to 673 K. Subsequently TPR is performed which demonstrates that the reduction peak at 385 K has completely disappeared. Thus the fraction of Rh which reduces at 385 K oxidizes above 673 K, and vice versa.

That one can distinguish between a well-dispersed phase and a bulk-like phase of Rh₂O₃ on TiO₂ has been noted before by Yao *et al.* [33], although these authors used Al₂O₃ as a support and had to oxidize for 12 h at 973 K to create the bulk phase.

The fact that part of the TiO_2 support is being reduced as well, in a metal-assisted process, is in agreement with findings for Pt/TiO_2 [34, 35]. Reoxidation of the support does take place during TPO, since O_2 consumption exceeds the expected O_2/Rh value of 0.75 in all cases, but is apparently hidden in the TPO profile by the stronger O_2 consumption due to the Rh oxidation.

Conclusions

The 2.3 wt.% $\text{Rh/Al}_2\text{O}_3$ catalyst proved to be ultradisperse, with H/Rh values ranging between 1.7 and 1.0. The catalyst behaved accordingly in TPR and TPO: easy reduction and rapid oxidation were observed to such an extent that passivation led to almost complete oxidation.

The 3.2 wt.% Rh/TiO_2 catalyst was much less disperse (H/Rh 0.37 - 0.12) and showed evidence of two distinct forms of Rh (and Rh_2O_3), appearing as two reduction peaks in TPR (reductions of well-dispersed and bulk-like Rh_2O_3) and three oxidation areas in TPO (oxygen chemisorption and oxidative chemisorption of well-dispersed Rh, and complete oxidation of bulk-like Rh).

Investigation was begun of the influence of particle size upon oxidation-reduction behaviour, but we were not able yet to establish a relationship between SMSI behaviour and particle size. All Rh/TiO_2 samples could be brought into the SMSI state.

We shall continue this search by varying the dispersion, the metal content and the reduction procedure.

This investigation has shown unambiguously that the TPR-TPO technique is a very powerful tool for distinguishing the various ways in which oxygen can react with a metal, and thus allows a careful analysis to be made of the state of dispersion of the metal on the catalyst.

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