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Imaging of low temperature induced SMSI on Pd/TiO_2 catalysts

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Pd/TiO_2 catalysts were found to enter an strong metal support interaction (SMSI) state after reduction at temperatures as low as 473 K. This was identified as a significant loss in the CO uptake as monitored by low temperature FTIR. Electron microscopy provides direct evidence of the presence of ordered, reduced titanium oxide layers over palladium (SMSI state) for Pd/TiO_2 catalysts following reduction at temperature 623 K. The crystal phase was identified as Ti_4O_7 and this phase, once formed, was found to be stable even after exposure to atmospheric conditions.

KEY WORDS: low temperature induced SMSI; electron microscopy; low temperature FTIR; Ti_4O_7.

1. Introduction

Pd on TiO_2 catalysts have been extensively studied for use in a wide range of reactions such as selective hydrogenation of acetylene [1] and CO [2], hydrogenolysis [3], CO oxidation [4], photocatalytic degradation [5] and reforming of alcohols [6], and NO reduction [7].

More than 30 years ago, Tauster *et al.* [8,9] reported observing a significant suppression in H_2 or CO adsorption capacity by Pd/TiO_2 catalysts without an accompanying increase in crystallite size when the reduction temperature was increased to around 773 K. This suppression was ascribed to the catalysts having entered a particular physical state labeled as a strong metal support interaction (SMSI). Since then, SMSI has been used to label the modification of the adsorption ability of the metals from groups 8, 9 and 10, supported on partially reducible oxides such as TiO_2, after reduction at sufficiently high temperatures (generally ca. 773 K), although SMSI at lower temperatures has been reported using indirect methods [10,11]. The SMSI phenomenon can be explained either in terms of a decoration of the metal surface with partially reduced oxide entities [12,13] or as an electron transfer process between support and the dispersed metal [14,15]. Both of these scenarios lead to a decreased CO or H_2 chemisorbed on the metal, either due to a decrease in the number of accessible surface metal atoms or due to a change in electron density in the metal surface, which leads to a decrease in the metal and adsorbate bond strength.

Metal decoration by partially reduced species is the most common process for the formation of SMSI on Pd/TiO_2 catalysts. The chemical structure of the partially reduced titania was reported to be Ti_4O_7 [16,17] based on electron diffraction studies. This phase was detected on TiO_2 based catalysts after reduction at 773 K only in the presence of a noble metal. In general, the physical blocking of metal sites by a SMSI state is detrimental for catalyst performances [18], although several studies can be found where a system exhibiting SMSI has enhanced catalytic activity [10,11]. The apparent anomaly can be explained by the presence of an electronically enriched overlayer structure, and creation of appropriate metal-metal oxide interface sites [10,11,19] that have catalytic activity. The ability to determine when the catalyst is in a SMSI state is therefore a key parameter in selecting appropriate pretreatment conditions aiming to maximize the operational efficiency of the catalyst.

In this communication we report direct imaging of SMSI by electron microscopy of a powdered Pd/TiO_2 catalyst. Similar studies have been performed using single crystal systems [20,21] and model catalysts [22] but information is limited in the case of high surface area, powdered, supported catalysts although papers by Boyes and Gai [23] on Pt/TiO_2, Kę‘piński and Wolcyrz [24] on Pd/CeO_2 and the group of Datye [25,26] using Rh/TiO_2 should be mentioned. Nevertheless these studies were performed on catalysts reduced at higher temperatures (i.e. 773 K) than the one reported here (i.e. 623 K) and in general, the imaged titania overlayers detected under SMSI conditions showed no lattice fringe signals indicating that an amorphous rather than a Ti_4O_7 structured overlayer was present. The latter is therefore generally found in model systems or in those

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where the support was pretreated at high temperature to induce sintering.

2. Experimental

Monocrystalline titania anatase (93 m^2/g) was prepared by chemical vapour deposition method [27] and wet impregnated with $Pd(NO_3)_2 \cdot 2H_2O$ (Merck) to obtain a metal loading of 2. TiO_2 particles were produced by means of thermal decomposition of titanium isopropoxide vapour in a flow reactor. The product powder was then gradually annealed (10 K/min) to 870 K under high vacuum conditions ($P < 10^{-5}$ mbar) and treated in vacuum for 2 h. The resultant material was pretreated in a flow of 40mL/min of pure O_2 for a period of 5 h at 870 K before impregnation of Pd. The main objective of the procedure was to remove organic remnants and moisture. After this thermal treatment the support was impregnated with Pd salt using the wet impregnation method. A ratio of 10 mL water per gram of support was used and the weight of the salt was calculated in order to obtain a final weight percentage of noble metal of 2 in the catalysts. The resultant catalysts where then calcined at 723 K to remove nitrate and then gradually reduced (10 K/min) under in a flow of 50 mL/min of pure H_2 at different temperatures (298, 473 and 623 K) for 1 h.

FTIR spectra were recorded at 4 cm^{-1} resolution (100 scans) on a Bruker IFS 28. The catalysts were investigated after consecutive *in situ* reduction with 100 mbar of pure H_2 for 1 h, and evacuation of the cell for 30 min at the reduction temperature. Prior to reduction at 298 K, the catalysts was evacuated at 423 K for 1 h to remove traces of physisorbed water. Typical vacuum values obtained during evacuation were of the order of 2.0×10^{-7} mbar. Samples were pressed into self–supporting wafers Adsorption measurements were performed using 50 mbar of CO with the sample at 100 K.

A 200 kV analytical transmission electron microscope FEI Tecnia F20 S-TWIN with field emission gun, coupled with an EDAX UTW (Si) detector, Atomic-resolution HAADF Detector and Multiscan CCD Camera, was used. Electron transparent samples were prepared by immersing a copper grid coated with a carbon film into the powdered sample.

3. Results and discussion

Figure 1 shows an example of HAADF–STEM image of a conglomeration of grains and the Pd and Ti concentration measured along two lines A and B, for a catalyst which had been calcined at 723 K for 2 h and reduced in H_2 at 623 K for 1 h. The measurements were performed in order to determine Pd particles size as the HAADF signal increases due to the presence of thicker areas and/or heavy elements. EDX analysis was carried out to further confirm the identification of metal particles.

Line scan A crosses a Pd particle roughly 15 nm estimated from the diameter of the bright contrast ensemble which is assigned to the presence of Pd as the EDX analysis confirms. Line scan B crosses two particles of Pd one with roughly 10 and the other 20 nm which is in agreement with the size estimated from the EDX signal. From analysis of ca. 25 particles it was found that Pd ensembles have an average diameter between 10 nm and 20 nm.

Figure 2 shows FTIR spectra of CO adsorbed at 100 K. Bands centered at 2103 and 2084 cm^{-1} are assigned to linearly coordinated CO, whereas bands centered at 1995 and 1940 cm^{-1} are ascribed to multiply coordinated CO [10,28]. The low frequency tail on the band centered at 1940 cm^{-1} for sample reduced at 298 K would suggest a contribution from CO coordinated to Pd in three-fold hollow sites which is expected to give a band around 1850 cm^{-1}. The hydroxyl stretching region (3800–3300 cm^{-1}) and deformation region of adsorbed molecular water (ca. 1635 cm^{-1}) showed no appreciable differences between pretreatments and therefore it is assumed that under the test conditions, the water formed during reduction was completely removed during the evacuation step. Furthermore, the high vacuum conditions employed, ensured that a relatively clean surface free of other gaseous contaminants was obtained.

Spectra show a significant loss in intensity of both linear and bridging carbonyl components as the reduction temperature is raised from 298 to 473 K and then a further loss, particularly of the higher frequency component, on raising the reduction temperature to 623 K. The diminished adsorbate uptake following low temperature reduction is at odds with the standard procedure of reduction at 773 K in order to induce catalyst modification into a SMSI state. Note that the selected low adsorption temperature should ensure high surface coverage of available sites and compensate for weak adsorption processes resulting from any electronic modification to the Pd resulting from the onset of SMSI [10].

The decrease in the signal cannot be assigned to an experimental error. The band at ca. 2185 cm^{-1} due to CO adsorption on the support increased as the reduction temperature was raised as expected. Furthermore the energy passing through the sample remained constant for each measurement mainly as a consequence of the *in situ* pretreatment and measurement which prevented the need to move the sample. The other possible reason to explain a decrease in the CO uptake would be an increase in Pd particles size, although this is not expected given the mild reduction treatments involved [29]. Therefore, the results suggest a decrease in the number of available Pd surface atoms as a consequence of increasing the reduction temperature due to a partial decoration of metallic sites.

Low temperature FTIR experiments clearly indicate that the exposed Pd surface was decreased on increasing the reduction temperature due to increasing extent of

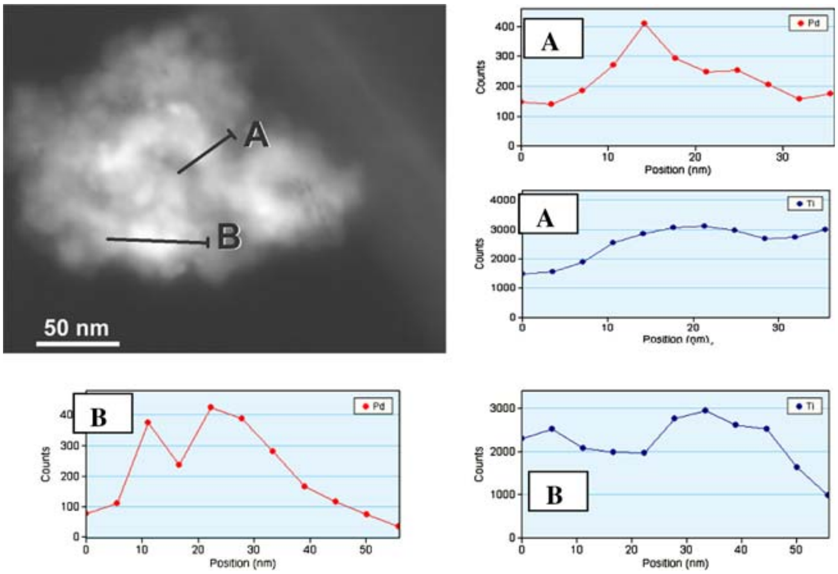

Figure 1. High angle annular dark field (HAADF) image and energy dispersive X-ray (EDX) line profiles of Pd/TiO_2 catalyst collected from a conglomerate of small grains.

decoration, however from the FTIR alone, it is not possible to deduce the identity of the species covering the Pd surface. Transmission electron microscopy provides a potential means to identify these species.

Electron diffraction was performed in order to identify any crystal phases which were present in the vicinity of the Pd crystallites after reduction. The technique is ideal for determine crystal structure because is very sensitive and virtually non-destructive, enabling determination of structures with low sample volume present on the catalysts upon reduction.

Figure 3 shows a typical SAED pattern collected over a grain conglomerate with an area of ca. 2 μm. In the diffraction pattern, weak diffraction spots from Pd (111) and Pd (002) were detected. In addition to signals from Pd there are the strong spots from anatase, (101), (004), (105), (211), and (213) crystal faces. Ti_4O_7 diffraction spots result from the (0−21), (−104) and (221) planes [30]. The ring pattern simulation in the upper left corner of the figure was generated by rotating the SAED spots around the centre of the pattern and drawing the intensities around a closed circle. The relative weakness of the Ti_4O_7 signals is related to the small quantity of this phase within the total sample volume.

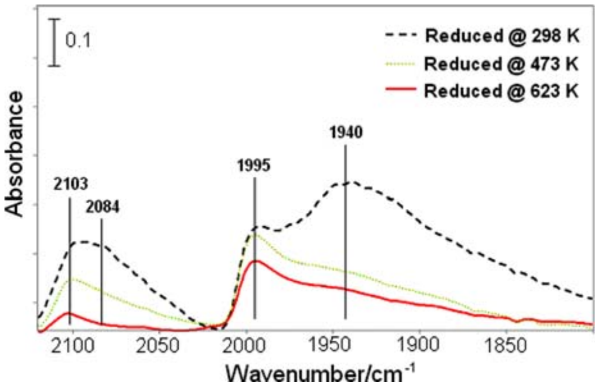

Figure 2. Low temperature FTIR spectra following exposure to CO.

Ti_4O_7 could only be detected on the SAED pattern when Pd was present since no evidence was found for Ti_4O_7 in SAED collected over small areas where Pd was absent. The result clearly indicates that on one hand Ti_4O_7 is formed due to reduction procedure and not by interaction of the sample with the electron beam and on the other hand that their location must be in the vicinity of Pd suggesting the involvement of hydrogen spilled over in their formation.

Figure 4 shows HRTEM micrographs of a Pd particle after reduction at 623 K and may be considered as representative of the whole catalyst surface. The figure is dominated by the Pd particle with a diameter ca. 15 nm and the lattice fringes of 0.35 nm related to the anatase grains showing (101) planes. The other lattice fringes indicated in the micrographs correspond to partially reduced titania (Ti_4O_7), showing (0−21) planes with $d_{(0-21)}$ = 0.52 nm, (221) planes with $d_{(221)}$ = 0.28 nm and (120) planes with $d_{(120)}$ = 0.43 nm. Areas of partially reduced titania can be found on the support and over the metal, consistent with results of Logan *et al.* [25] for Rh/TiO_2. However whereas an amorphous layer was reported for Rh/TiO_2 [25] here the layer covering the metal and support is crystalline since its lattice fringes are well resolved.

The SMSI state genesis has been attributed to support reduction at high temperature, normally 773 K [8,25,31], due to H_2 spilled over from the metal. This activated hydrogen facilitates the formation of partially reduced support species, which can then migrate and 'decorate' the metal. HRTEM images (Figure 4) show

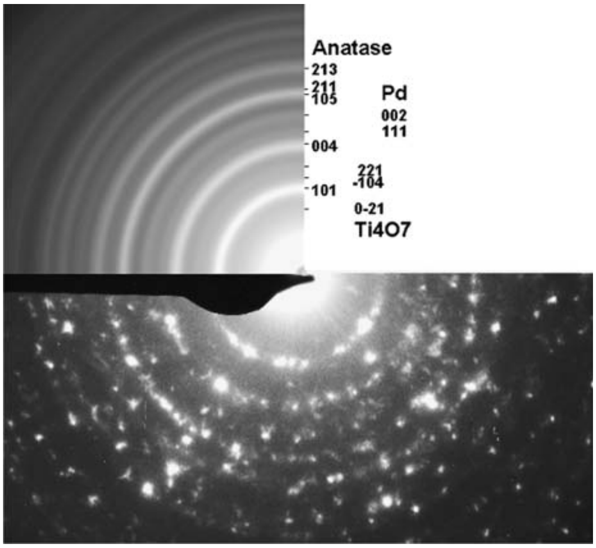

Figure 3. Selected area electron diffraction pattern (SAED) of Pd/TiO_2.

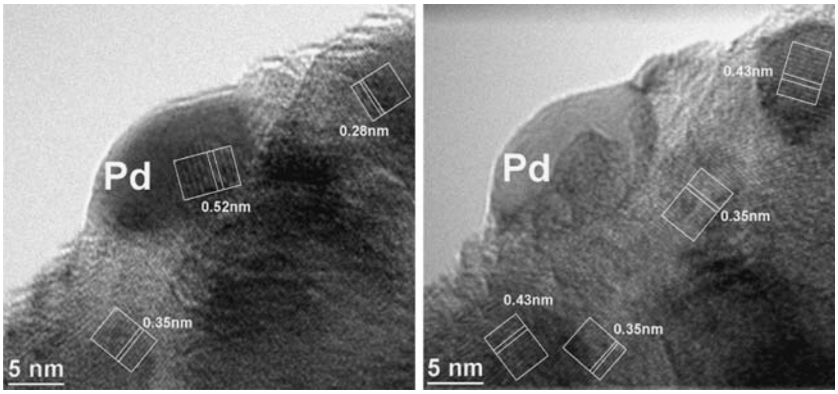

Figure 4. High resolution TEM micrographs showing Pd/TiO_2 and the presence of Ti_4O_7 $d_{(0-21)} = 0.52$ nm, $d_{(221)} = 0.28$ nm and $d_{(120)} = 0.43$ nm) on the metal and support. The images depict the same conglomerate under different focussing conditions in order to reveal the crystalline structure of individual grains.

lattice fringes related to Ti_4O_7 dispersed throughout the support and on the palladium suggesting an initial step involving support reduction followed by the migration of the mobile Ti_4O_7 species to the metal thereby confirming the postulated mechanism.

The present data is consistent with previous reports in terms of the final state and the observation of decorated metal particles. However, the present study is unique as it shows for the first time the presence of reduced support phases even for catalyst reduced at 623 K, some 150 K lower than the standard pre-treatment condition employed leading to detection by TEM. Additionally, FTIR results suggest some decoration even after 473 K reduction, leading to loss of CO uptake. One might argue that this reduced phase is a consequence of sample exposure to the electron beam. From the HRTEM data it is difficult to discard the formation of reduced titania as a result of electron beam exposure. However, the presence of Ti_4O_7 type species was only detected when Pd was present as with the non evasive SAED, which strongly suggests that the Ti_4O_7 type species are a consequence of the interaction of the support with the H_2 dissociated on the noble metal.

Details in Figure 4 also suggest that the decoration of metal sites by $TiOx$ occurs *via* indiscriminate encapsulation rather than by a preferential decoration of specific Pd facets. There are suggestions that decoration begins preferentially at extended terrace type facets [32]. A further point to note is the stability of the reduced overlayer. As no attempt was made to prevent contact of the samples with air between the pre-treatment and the measurements, the Ti_4O_7 phase that is formed is clearly stable in air. This finding is consistent with results of Braunschweig *et al.*[26] for Rh/TiO_2 where the pre-SMSI state was only completely restored after overnight oxidation at 773 K.

The detection of a low onset temperature for which SMSI is induced is extremely relevant, in particular with reference to reactions believed to be sensitive to the metal-reduced metal oxide interface such as crotonaldehyde hydrogenation where a drastic increase in selectivity upon reduction of the catalysts at 773 K is ascribed to the formation of SMSI state [33,34]. A better awareness of the onset of this state may allow better tuning of pretreatment conditions to optimize catalyst performance.

4. Conclusion

SMSI occurs for Pd/TiO_2 at temperatures of 623 K and below, much lower than previously observed by TEM. The process involves migration of a partially reduced, stable, form of titania, as Ti_4O_7, which travels from the support to the metal surface and leads to a non-selective decoration of Pd particles without change in the crystallinity of this phase. Implications are that selection of the most appropriate pretreatment conditions to optimize catalyst selectivity on the basis of a particular metal-support interface arrangement may require closer attention to the onset of low-temperature induced SMSI.

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