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Synthesis and characterization of supported Pt and Pt alloys nanoparticles used for the catalytic oxidation of sulfur dioxide

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Abstract

Controlled pore glass silica (CPG) was used as support to prepare platinum-based catalysts using the wet impregnation method and DMSO or $CHCl_3$ as solvent. In all cases, the catalyst loading with the active phase was 2 wt%. The catalysts were tested for the SO_2 oxidation reaction at atmospheric pressure in the temperature range of 250–700 °C. The effect of doping the active metal with rhodium and palladium was also studied. The catalytic activities of the supported catalysts were found to follow the order Pt–Pd/CPG > Pt–Rh/CPG > Pt/CPG. A significant synergistic effect of the Pt–Pd alloy was observed compared with the SO_2 conversion efficiency of the individual metals supported on CPG. The effect of the solvent used in the impregnation step is also discussed with regard to the properties of the final product and to catalytic activity.

Keywords: Controlled pore silica; Platinum; Palladium; Rhodium; Catalyst; Sulphur dioxide oxidation

1. Introduction

Stricter legislative emissions control for the environment has led to the development of more efficient catalytic units in industry and vehicles. Released sulfur oxides are known to have a serious impact on the environment, and thus special attention has been given to eliminating or diminishing the emission levels [1].

Until the introduction of vanadium-based catalysts some five decades ago, platinum dominated the catalytic units involved in sulfur oxide conversion processes. The SO_2 oxidation reaction, the key step in the sulfuric acid production and flue gas desulfurization, was catalyzed by finely divided platinum metal particles deposited on asbestos and, later, on several types of silica. The wide use of platinum as the catalyst in such important industrial processes was responsible for the large turnover of the metal worldwide. Approximately 40% of the platinum produced in the Western world has been used in catalysis. In 1999, 28% of the total platinum demand was for catalytic processes, mostly by vehicle manufacturers. Difficulties in supply and cost limitations have stimulated the invention of substitutes.

Nowadays, stricter SO_2 emission control measures are prompting researchers to seek more efficient catalysts than those based on vanadium. This search has led back to platinum-based catalysts, as indicated by the increased attention in the recent literature [2–5]. Platinum catalysts supported on oxide carriers are advantageous over other types of catalysts used for the same catalytic process because they can be regenerated in situ in a two-step process. First, an oxidative gas stream is passed over the catalyst (e.g., using O_2 in the gas stream), and then the metal form is obtained in the reduction step [6–9]. The particles of the active phase may be redistributed, thereby regaining >95% of the original catalytic activity. Several methods have been proposed for this regeneration [10] and for the recovery of active metal from spent catalyst [11].

Controlled pore glass silica (CPG) is used to support platinum-based catalysts because it has well-defined surface characteristics. Controversial reports appear in the literature arguing on the use of silica as a support for platinum catalysts.

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In general, silica surfaces do not offer good stabilization of the active phase against sintering [12] and often result in low dispersion of the metal [13]. Nevertheless, silica surfaces appear to be in wide use worldwide, except in the U.S. Silica has some advantages as a carrier material, including its immunity to arsenic poisoning and temporary chlorine poisoning, extremely low surface oxygen mobility, and high conversion rates at high flow rates. In particular, the low surface oxygen mobility means that the catalyst may be very active even after prolonged low oxygen supply in the reacting gas, whereas vanadium-based catalysts show significantly decreased activity at these conditions [14].

Using rhodium alloyed with platinum maintains the hardness of the active phase on long exposure to high temperatures better than any other alloy of platinum. This property of rhodium has been attributed to its effect on suppressing the rate of recrystallization of the alloy under extreme conditions of temperature and reacting gases [15]. Furthermore, rhodium is considered to interact with O_2 molecules of the gas mixture and to increase its surface concentration at the solid/gas interface. With this mechanism, the SO_2 oxidation rate is enhanced.

Palladium belongs to the same group of elements as platinum, and thus some similarities in chemical behavior and possibly catalytic properties can be expected. A few hints in the literature concerning the platinum–palladium alloy used as a catalyst for the SO_2 oxidation suggest that the combination of the two metals may result in improved catalytic performance [16]. But this can be achieved only at a specific ratio of the two metals; an incorrect ratio can cause palladium to act as a poison of the pure platinum catalyst [17]. To date, no detailed work on this metal alloy and this reaction has been reported. Alloys of the two metals have been used as catalysts in electrochemical fuel cells and exhaust gas treatment in car catalysts [18].

In the present work, platinum-based catalysts supported on CPG silica were prepared using the acetylacetonate salts of the metals as precursors. Catalyst samples of pure platinum and with palladium or rhodium were prepared and characterized, and their activity for SO_2 oxidation was evaluated.

2. Experimental

2.1. Chemicals and gases

CPG, obtained from Sigma, was used as supporting material. Platinum acetylacetonate, $Pt(C_5H_7O_2)_2$ ($Pt(acac)_2$, Aldrich), was chosen as a precursor salt for the catalyst synthesis. Dopant solutions were prepared from the respective extra-pure solids (i.e., $Pd(acac)_2$ and $Rh(acac)(CO)_2$, Aldrich). Dimethylsulfoxide (DMSO; extra pure for chromatographic purposes; Aldrich) was used as a solvent of the acetylacetonate salts.

Commercial gases SO_2 (>99.99%), O_2 (99.8% + 0.2% N_2 and Ar), and N_2 (<40 ppm $O_2 + H_2O$) were used. All gases were dried through P_2O_5 columns before entering the synthesis gas cylinder flask.

2.2. Catalyst preparation

The CPG silica support material was allowed to interact with the $Pt(acac)_2$ solution in DMSO. The wet impregnation method was used for the synthesis. The platinum loading on the final product was chosen to be 2 wt%, as confirmed by combined TEM/EDAX and chemical analysis using atomic absorption spectroscopic (AAS). In the doped samples, CPG silica was coimpregnated in a solution with the platinum salt along with $Pd(acac)_2$ or $Rh(acac)(CO)_2$. The dopant content was meant to be 20% of the final alloy composition. The suspension was stirred for 3 days at 90 °C for equilibration, after which the solvent was evaporated and the solid material dried overnight at 110 °C. For sample reduction and calcination, the temperature was slowly (i.e., over 6 h) increased to 420 °C, kept stable at 420 °C for 3 h, and then slowly dropped to room temperature in 8 h.

Samples of pure palladium and rhodium supported on CPG were also prepared using the same method and tested for their catalytic activity.

In another preparation, chloroform was used instead of DMSO as the solvent of $Pt(acac)_2$ to support Pt on CPG (keeping the other experimental conditions the same). This sample was also examined and tested for catalytic activity.

2.3. Catalyst characterization

The metal particles supported on CPG were characterized by combined TEM, XRD, and chemical analysis (TEM-EDAX and AAS). For the microscopic examination (using a Philips EM 430 transmission electron microscope), a portion of the catalyst was ground in a mortar, suspended in ethanol, and dispersed by ultrasonication. A drop of the suspension was evaporated on a copper grid. Electron microscope pictures were taken at magnifications of ×400,000–×600,000. From the TEM pictures, the average size of the particles was measured (a mean of 80 particles) using image analysis software. (The electron microscope was calibrated with an internal standard of asbestos to avoid the common source of error in which the display magnification is higher than the pristine and thus the particles appear smaller.)

The chemical composition of the catalysts was confirmed by EDAX in situ analysis and by chemical analysis after dissolving the catalyst in aqua regia. Calibration curves were created using standard solutions of the metal (Merck). X-Ray crystallographic diffraction patterns of the catalysts were obtained (Philips PW 3710) using Cu-K_α radiation and Ni filter. To provide adequate count accumulation and sufficient resolution, the instrument operated at a scan rate of $0.04°/\text{min}$ with a 0.2° receiving slit.

2.4. Catalytic activity measurements

All catalytic activity experiments were performed in a fixed-bed reactor under atmospheric pressure and temperatures between 250 and 700 °C. In the experimental setup, the catalyst rests between two quartz wool plugs located at the bottom of a capillary U-shaped tubular microreactor cell of Pyrex glass. The reactor is inserted in a controlled temperature furnace in contact with a thermocouple for temperature detection. The gas flow was 30 mL/min in all activity tests (at ambient temperature and pressure) and was adjusted by a gas flow controller (Brooks model 5810). The composition of the gas mixture in the inlet stream was 10% O_2, 11% SO_2, and the balance N_2-simulated sulfuric acid synthesis gas, and it was kept constant over the course of the activity tests. No preheating device before the reactor was installed. Two series of tests were performed with catalyst loadings of 1.3 and 0.5 mg in the reactor.

The SO_2 concentration in the gas was monitored spectrophotometrically from the absorption peak at ca. 300.4 nm. The amount of SO_2 converted was determined from its depletion in the gas before and after passing the reactor. The absorption spectra were recorded by a modified Jasco V-570 UV/VIS spectrophotometer equipped with a 0.5-cm quartz cell using data acquisition software. The experimental setup was calibrated before and after each experiment to correlate the SO_2 partial pressure in the gas mixture with the measured absorbance. The gas was dried through columns of P_2O_5 before and after the reactor to remove traces of water.

3. Results and discussion

3.1. Catalyst characterization

The acetylacetonate salts used for catalyst synthesis decompose toward the pure metals at temperatures much lower than those used during reduction and calcination [19]. The temperature for reduction was chosen carefully, because at temperatures above 400 °C pure palladium slowly oxidizes to PdO_2, which decomposes to the metal form at ca. 700 °C.

In the present work we report on the use of DMSO as a suitable solvent of the acetylacetonate salts. Such salts are known to dissolve in conventional organic solvents (e.g., toluene, chloroform, etc.). DMSO has proven to be an excellent solvent of the acetylacetonate salts of platinum, palladium, and rhodium and to also have polar properties. The latter are very important because the solvent should be able to interact with the polar surface of the CPG silica and facilitate the penetration of the acetylacetonate precursor salts in the interior of the pores of the carrier. Furthermore, DMSO has relatively low surface tension (42.9 mN/m at 25 °C), approximately half of that of water at the same temperature [20]. This means that the solvent can more easily wet the pores of the carrier, and thus the dissolved salts can overcome wetting hindrances on entering into the cavities and can stabilize therein after reduction.

The use of acetylacetonate salts for the impregnation has been reported to give highly dispersed active phase in the final product. This was explained in terms of molecular migration of the precursor complexes on the surface of the support before decomposition to the pure metal form [21]. We speculate that fixation of the platinum acetylacetonates on an oxide support involves strong interactions and complexation between the platinum acetylacetonate salt and hydroxyl groups (–OH) on surface of the oxide support. The organic part of this complex is bulky; therefore, due to stereochemical limitations, these complexes have low surface concentration. This is probably the reason for the high metal dispersion and the formation of very small particles of the active phase.

Alloy particles were well supported on CPG even after ultrasonication of the sample during preparation for the TEM analysis. Often platinum particles supported on the surface of silica were removed from the carrier by ultrasonication [13]. Image analysis of the TEM pictures of the catalyst samples revealed that the average size of the Pt, Pt–Pd, and Pt–Rh particles were 2.5, 2.2, and 2.7 nm, respectively (Figs. 1a–1c). As may be seen from the pictures, the platinum particles are distributed finely over the surface of the carrier despite the general perception of silica's poor supporting properties. The fact that such nanosized particles were synthesized was attributed to the selection of the precursor salts, the DMSO solvent, and on the surface characteristics of the support. CPG silica has an average pore diameter of 7.5 nm (with a relatively narrow pore size distribution); therefore, small crystals of the precursor phase that grow in the pores are narrowed by the cavity walls. During reduction, the organic part of the precipitated precursor salt is removed and the pure metal particles, which are catalytically active, remain hosted in the pore cavity of the carrier. The acetylacetonate salts were formed inside the pore cavities of the support. Evidence of this appraisal comes from the TEM image analysis that showed no particles larger than the size of the pores; if particles had grown on the surface of the carrier, they should be significantly larger than the pores (this was the case when $CHCl_3$ was used as a solvent of the acetylacetonate salts).

The structure and the properties of platinum nanoparticles were extensively discussed by Poltorak and Boronin [22]. Assuming that the platinum clusters have the same octahedral structure as in the bulk metal, we can calculate the number of atoms of the platinum crystallites supported on CPG. From our data, after linear regression we can calculate that each of these nanoparticles with a projected diameter of ca. 2.5 nm and hemispherical shape consists of ca. 60 platinum atoms (with an interatomic distance between the platinum atoms of 0.2775 nm and a unit cell volume with ccp symmetry of 0.06 nm^3). If we assume a two-dimensional particle on the surface of the carrier, then each particle is formed by only 10 Pt atoms. These calculations are somehow arbitrary, because it has been argued that the physical and crystallographic properties of nanoparticles are often different than those observed in bigger crystals [23].

XRD analysis of the final catalyst showed no peaks that could be assigned to the precursor salts. The XRD patters of the alloyed catalysts resembled those of the pure Pt catalyst. This is common in cases where the dopant concentration in the alloy is low and when the active phase consists of nanoparticles with an average size of 2 nm.

3.2. SO_2 oxidation catalytic tests

Good dispersion and small particle sizes are often found in catalysts characterized by high activity. This hypothesis was tested for the catalysts prepared in this work. The composi-

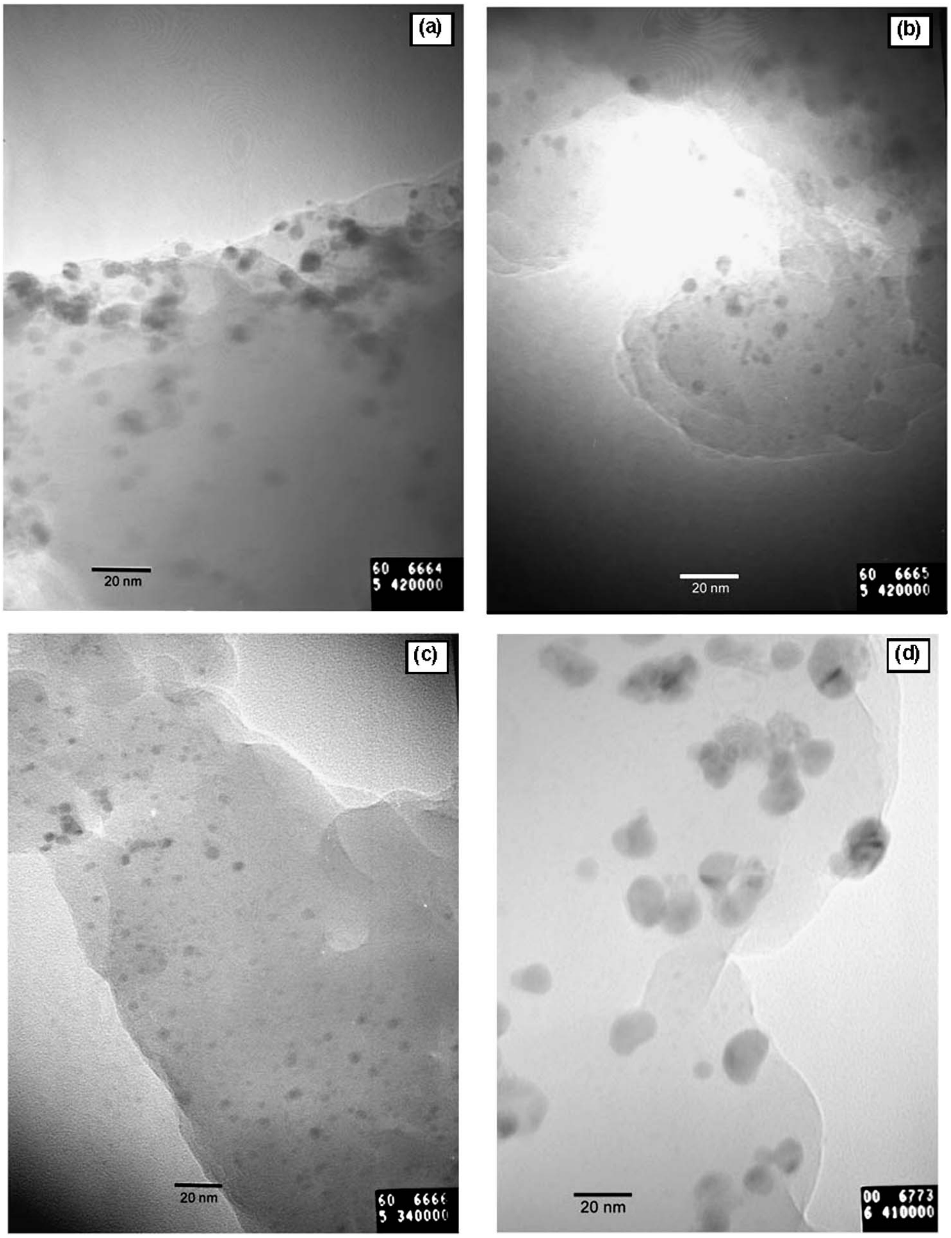

Fig. 1. TEM pictures of platinum based catalysts supported on CPG silica: (a) Pt/CPG, (b) Pt–Pd/CPG, (c) Pt–Rh/CPG, using DMSO as a solvent of the precursor salts, and (d) Pt–Pd/CPG alloy catalyst after impregnation in $CHCl_3$.

tion of the reacting gases was kept constant in all catalytic activity tests. The activity was measured over a wide temperature range of 250–700 °C. The maximum catalytic activity was observed in this range, with activity decreasing on further temperature increases. Blank experiments were also performed in an empty reactor and in the presence of unsupported CPG silica. In both cases the conversion observed was negligible and within the limits of the experimental error of the detection method. This indicates that SO_2 and O_2 do not spontaneously react in the gas phase under the experimental conditions used.

Pure Pd catalysts are susceptible to poisoning from SO_2 in the gas mixture, and Pt renders the sample resistant [24]. It is anticipated that there is an optimum ratio between the two metals in the alloy leading to the highest catalytic activity. Far from this ratio, the catalyst will suffer from poisoning and relatively low activity. Preliminary data show that the optimum Pt:Pd ratio is close to 5:1, and thus we used this ratio for the synthesis of the bimetallic catalysts.

The composition and catalytic activity of the samples tested, along with the experimental conditions, are summarized in Table 1. The Pt-based catalysts supported on CPG were very active for SO_2 oxidation even at very low loadings of catalyst with the active phase and of the reactor with the catalyst. Furthermore, the space velocity was quite high, suggesting that the contact time for conversion of the SO_2 molecule on the catalyst surface is very short (i.e. ca. 0.002 s). The length of the catalyst bed inside the reactor was ca. 2 mm.

The conversion of SO_2 was calculated from the difference between the moles of SO_2, n_{SO_2}, before and after passing

Table 1
Catalytic activities of the platinum based catalysts supported on CPG silica. Feed gas 11% SO_2, 10% O_2 and 79% N_2, flow rate 30 mL/min. Loading with the active phase 2 wt%

Catalyst	Reactor loading (mg)	Max. activity			Space velocity ($\times 10^6$ h^{-1})
		TOF (mol SO_2 conv./(mol s))	% Conversion	Temp. (°C)	
Pt/CPG	1.9	3.8	32	480	0.36
Pt–Pd/CPG	1.3	11.3	66	510	0.46
Pt–Rh/CPG	1.9	6.9	58	540	0.56
Pd/CPG	1.3	2.2	22	650	0.50
Rh/CPG	1.3	1.3	13	650	0.53
Pt/CPG	0.5	8.9	20	510	1.30
Pt–Pd/CPG	0.5	23.4	52	550	1.20
Pt–Rh/CPG	0.5	15.6	35	550	2.10
Pd/CPG	0.5	3.1	13	650	1.20
Rh/CPG	0.5	2.4	10	650	1.25
Pt–Pd/CPG–$CHCl_3$	0.5	17.3	38	600	1.30

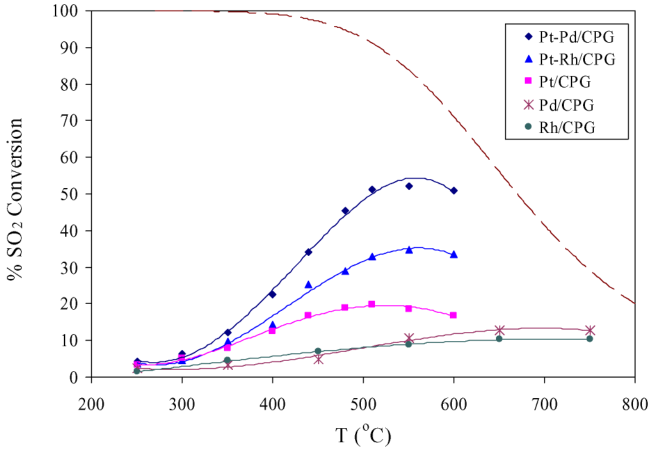

Fig. 2. Conversion of SO_2 over pure and alloyed platinum catalysts supported on CPG silica. Loading with the active phase 2 wt%, catalyst loading of the reactor 0.5 mg. Space velocities and TOF are shown in Table 1. The dashed line represents the calculated equilibrium conversion for the oxidation of SO_2 to SO_3 with O_2 (11% SO_2, 10% O_2, balance N_2, total pressure 1 atm).

through the catalyst bed in unit time, using the following equation:

$$(\%\ \text{Conversion}) = \frac{n_{SO_2,\text{before}} - n_{SO_2,\text{after}}}{n_{SO_2,\text{before}}} \times 100.$$

The activity in terms of turnover frequencies (TOFs), calculated as mol of SO_2 converted per mol of the active phase in the reactor in unit time, are given in Table 1. The conversion of SO_2 to SO_3 is plotted as a function of the reaction temperature in Figs. 2 and 3. These plots show the dependence of the oxidative conversion of SO_2 on the reaction temperature. The presence of a dopant in the catalyst sample resulted in significant enhancement of the catalytic activity. The conversion of SO_2 for pure platinum catalysts and promoted with palladium or rhodium is shown in Fig. 2. In all cases, the catalytic activity dropped after reaching a maximum. The temperature of maximum conversion depends on a number of factors, including gas flow rate, catalyst loading with the active phase, and reactor loading with the catalyst. Further increase of the temperature resulted in lower conversion. After reaching the maximum activity, subsequent temperature decrease and reheating led to 5–10% lower catalytic activity, depending on the platinum alloy composition, compared with those observed from the initial temperature increase. This may be explained in terms of a sintering effect of the particles of the active phase at high temperatures. The metal particles mounted on the surface of the carrier may recrystallize and the platinum atoms consisting the nanoparticle may rearrange in such a way to change the structure of the active phase. This process renders the catalyst less active for the reaction, because the interatomic distances on the surface of the metal or of the alloy also change. Furthermore, at temperatures above 600 °C and under an oxidative environment, oxidation of the platinum sublayers is possible when the active phase consists of nanoparticles [25]. This process results in decreased catalytic activity.

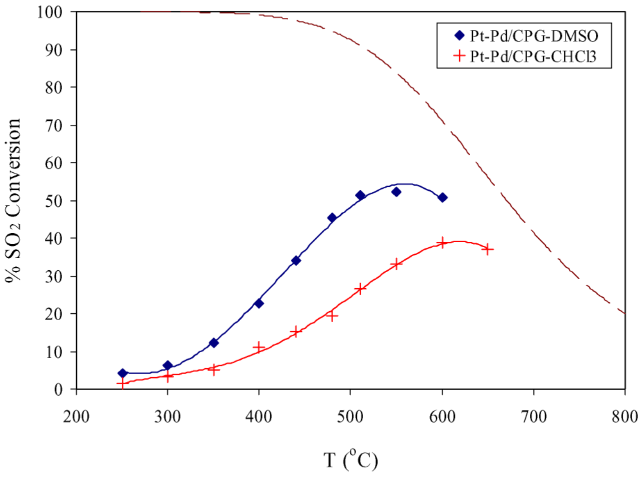

Fig. 3. Conversion of SO_2 over Pt–Pd bimetallic catalysts supported on CPG silica using the same preparation method and DMSO (◆) or $CHCl_3$ (+) as a solvent. Loading with the active phase 2 wt%, catalyst loading of the reactor 0.5 mg. Space velocities are shown in Table 1. The dashed line is the calculated equilibrium conversion for the oxidation of SO_2 to SO_3 with O_2 (11% SO_2, 10% O_2, balance N_2, total pressure 1 atm).

The experimental data given in Table 1 indicate that, depending on the composition of the alloy, the catalysts tested showed maximum activity at different temperatures in the following order: $T_{\text{Rh/CPG}} > T_{\text{Pd/CPG}} > T_{\text{Pt–Rh/CPG}} > T_{\text{Pt–Pd/CPG}} > T_{\text{Pt/CPG}}$. This series suggests that the Rh catalyst is the most resistant to structural and morphological changes. The temperature of maximum activity depends on the carrier, composition of the reactants, physical properties of the metals and alloys, and oxidation resistance of the active phase. The pure palladium (Pd/CPG) and rhodium (Rh/CPG) catalysts had maximum activity at higher temperatures compared with the platinum–palladium alloyed (Pt–Pd/CPG) and pure platinum catalysts.

The maximum activity of the catalysts tested shows a different trend: Pt–Pd/CPG > Pt–Rh/CPG > Pt/CPG > Pd/CPG > Rh/CPG. The platinum–palladium alloyed catalyst, which showed the highest activity, was 50% more active than the platinum–rhodium alloy, 160% more active than the pure platinum catalyst, and 300% more active than the palladium catalyst. This finding indicates that a synergistic effect resulted from bringing platinum and palladium in close contact in the alloy for the catalytic reaction studied. The electronic configuration of the supported metals and alloys and the still-uncertain mechanism of SO_2 oxidation over Pt-based catalysts conceal the interpretation of the observed series of activities.

The catalytic activity of the palladium-doped sample is remarkably high even at very small reactor loadings. This catalyst gave a maximum of 52% SO_2 conversion with an extremely high space velocity of $1.2 \times 10^6\ h^{-1}$. Notably, such conversion was observed over 0.01 mg or ca. 5×10^{-5} mol of the active phase. The conversion increased when the amount of the catalyst in the reactor increased, but this also resulted in lower activity in terms of TOF. Therefore, when the reactor was loaded with higher amounts of catalyst, not all of the catalytically active phase was actually exposed to the reactant gases, even though the flow rate was relatively high. At higher loading of the reactor with the catalyst, the conversion reached very high values, making the analysis of SO_2 concentration problematic with the detection system used. The effect was more pronounced at high temperatures, where high conversions were observed. The amount of SO_3 produced from the reactor was high, and SO_3 was condensed at temperatures lower than that of the reactor setting. The condensation occurred in the tubes of the gas outlets and resulted in the production of pure oleum.

The temperature of the maximum activity shifted to lower temperatures when the loading of the reactor increased. This finding, given in Table 1, is in accordance with the experimental observations of Holmes et al. 70 years ago for unpromoted platinum catalysts supported on "chalky" silica gel [26].

The oxidation of SO_2 to SO_3 is very exothermic; hence at high temperatures, the equilibrium shifts to the side of the reactants and low conversion is expected (Figs. 2 and 3, dashed line). Using the composition of the synthesis gas mixture, the calculated SO_2 converted at equilibrium is 99.98% at 270 °C. At 400 °C, the equilibrium conversion decreases to 99.1%, and at 470–550 °C, where most of the activity maximums are observed for the catalyst samples tested in this work, it drops rapidly from 95.6 to 83.8%. As shown in Fig. 2, the catalytic conversion of SO_2 was low at 270 °C but with very low loading of the reactor and of the catalyst with the active phase. The activity was remarkably high when the temperature reached 400 °C. Presumably, apart from sintering of the particles of the active phase at temperatures above 600 °C, the decreased catalytic activity observed in this temperature range may also be due to thermodynamic factors which take over the kinetics.

Using spectroscopic techniques (e.g., XPS, HREELS, NEXAFS), it has been previously shown that during the reaction, oxygen preadsorbs on the Pt {111} surface at temperatures significantly lower (i.e., 450 °C) than that required for extensive adsorption of SO_2 [27]. This is in line with the catalytic activity data presented in Table 1, which show maximum conversion at around 500 °C.

The effect of the solvent used for the synthesis was also evaluated. Keeping all the experimental conditions the same and changing the solvent from DMSO to chloroform (the most common solvent for the acetylacetonate salts) gave a Pt–Pd bimetallic catalyst with larger particles and lower activity. Although the dispersion of the particles was good (probably as a result of using the acetylacetonate salts of platinum and palladium), the average particle size was ca. 9 nm (as calculated by image analysis of the TEM pictures shown in Fig. 1d). The Pt–Pd alloy catalyst in chloroform had 52% lower activity compared with the respective catalyst prepared using DMSO as a solvent (Fig. 3; Table 1).

4. Conclusion

Pure platinum-based catalysts were tested and their activities for the catalytic oxidation of SO_2 were evaluated. CPG silica is a suitable carrier when the surface characteristics need to be well defined. The prepared catalysts had an average particle size of ca. 2.5 nm and showed high activity for SO_2 oxidation. The catalysts were prepared from the acetylacetonate salts of platinum, palladium, and rhodium. The latter, used as dopants, produced significantly improved catalytic properties. The Pt–Pd alloy gave the highest conversion at very low reactor loading and a relatively low (i.e., 2 wt%) active-phase loading of the support. The calculated space velocities were high, pointing to a very short (i.e., 0.002 s) contact time between the reacting molecules and the catalyst surface. Maximum activity was observed at about 500 °C, depending on the catalyst composition. Further temperature increases led to a drop in activity due to sintering of the particles of the active phase and thermodynamic equilibrium limitations.

DMSO was found to an advantageous solvent not only because it dissolves the acetylacetonate salts of the metals, but also because it has polar properties and low interfacial tension, thus interacting well with the polar surface of the carrier. Following the same experimental procedure but using a conventional organic solvent, such as $CHCl_3$, for the acetylacetonate salts gave a catalyst with lower activity.

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