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Titania-supported Pt and Pt–Pd nanoparticle catalysts for the oxidation of sulfur dioxide

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Abstract

Several types of titania (anatase) were used as supports for pure platinum and Pt–Pd bimetallic alloy catalysts. The preparation methods, normal wet impregnation technique and flame aerosol synthesis, obtained metal loadings of 2% by weight. The prepared catalysts were tested for SO_2 oxidation activity at atmospheric pressure in the temperature range 250–600 °C. The SO_2 to SO_3 conversion efficiency of the Pt–Pd alloy was significantly higher than that of the individual metals. The effects of the preparation method and the titania type used on the properties and activity of the resulting catalyst are discussed.

Keywords: Platinum; Titania; Catalyst; Nanoparticle synthesis; Sulfur dioxide oxidation

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1. Introduction

The catalytic oxidation of sulfur oxides followed by absorption are key processes in industrial waste treatment, affecting air pollution worldwide. Measures from the EU and EPA to decrease the release of sulfur oxides with the aim of achieving a cleaner environment have resulted in increased research efforts for developing more efficient catalysts and catalytic units [1]. Platinum-based catalysts are widely used in conventional exhaust gas cleanup and have proven stable and tolerant to the typical poisons of the combustion engine exhaust. Although much progress has been made on the well-known vanadium oxide systems used in industry [2–4], it is obvious that systems based on the platinum group metals may be more suitable for higher activity at lower temperatures. Until World War II, platinum dominated as catalyst in the sulfuric acid production industries, oxidizing sulfur dioxide (the key step in sulfuric acid production and flue gas desulfurization). This type of catalyst supported on oxide carriers has advantages over other catalysts used for the same catalytic process, because they can be regenerated in situ [5–10]. Synthesis of metal alloys is a common practice to improve the catalytic characteristics of monometallic catalysts [11–15]. Palladium, a platinum group metal, is thought to have relevant chemical properties and catalytic activity. The bimetallic alloy of the two metals has been tested as a catalyst for the SO_2 oxidation reaction, and the best conditions for improved catalytic performance have been investigated [16,17]. Such alloys have been tested in electrochemical fuel cells and in the exhaust gas treatment in car catalysts [18].

The use of noble metal-based catalysts is limited by their scarcity and high cost. Hence, improving their catalytic performance and decreasing their cost is important. The active phase in the final product should be highly dispersed and consist of nanoparticles. Achieving this depends on a number of factors, including the surface characteristics of the support, the nature of the metal precursors, the solvent, the rate of precursor salt formation, and more. The most commonly used support for platinum catalysts is silica, although tests with titania have shown that titania is a better support, because it is cheap, has

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better surface and electronic properties, is more acidic (very important for the specific reaction), and is resistant to steam and poisons in the gas mixture [19,20]. Although platinum-based catalysts supported on titania have been studied previously, improving their catalytic activity remains an important field for exploration. Catalytic properties depend on thermal treatment, doping, synthesis route, and surface characteristics of the carrier.

In the present work, we have investigated the effect of surface and morphological characteristics of several types of titania (anatase) as supports for platinum-based catalysts. We used two different preparation methods. The first method, which is based on impregnation, used acetylacetonate salts of the active metals as precursors and DMSO as the solvent. The activity of the bimetallic catalyst samples for the SO_2 oxidation reaction was compared with that of the respective pure metals. As an alternative method, the Pt/TiO_2 catalyst was prepared by a one-step flame synthesis method [21,22]. The following samples were investigated and compared for catalytic activity: wet impregnation of two commercially available titania samples, wet impregnation of flame-produced titania, and one-step synthesis of the supported noble metal in the flame with the same operating conditions as for pure flame-produced titania.

2. Experimental

2.1. Chemicals and gases

Two of the titania (anatase) samples used for catalyst preparation were commercial products (Alfa Aesar titanium (IV) oxide, anatase 99.9% and Millennium Co. TIONA-G5, anatase). Using the aerosol synthesis method, we prepared two titania (anatase) samples (T1 and T2, with specific surface areas of 57 and 98 m^2/g, respectively). For the formation of titania in flame, the Ti-isopropoxide complex was used to ensure high vapor pressure in the saturator.

The acetylacetonate salts of platinum and palladium ($Pt(acac)_2$ and $Pd(acac)_2$; Aldrich) were used as synthesis precursors for impregnation. Dimethyl-sulfoxide (DMSO), extra pure for chromatographic purposes (Aldrich) was used as a solvent. A catalyst sample, Pt/TiO_2, was prepared using the flame aerosol method by gas-phase decomposition of the Ti- and Pt-precursors [23].

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 for the catalytic activity tests. All gases were dried through P_2O_5 columns before entering the synthesis gas cylinder flask.

2.2. Catalyst preparation

2.2.1. Wet impregnation

In all cases, the loading of the active phase was 2 wt%, as confirmed by TEM/EDAX and by chemical analysis using atomic absorption spectroscopy (AAS). Several titania anatase samples were chosen as support materials and were impregnated with $Pt(acac)_2$ solutions using the wet impregnation technique and DMSO as solvent. For the preparation of the bimetallic alloy samples, titania was coimpregnated in a solution with both the platinum and the palladium acetylacetonate salts. The desired content of the second metal was 20% on the final alloy composition. The suspension was stirred vigorously and maintained at 90 °C for 3 days to achieve equilibration, then the solvent was evaporated in a rotary evaporator, and the solid material was dried overnight at 110 °C. The sample was then reduced and calcinated at 420 °C, with the temperature slowly increased from room temperature to 420 °C over 6 h, then maintained at 420 °C for 3 h and finally decreased slowly to room temperature over 8 h.

2.2.2. Flame synthesis of pure TiO_2 support and Pt/TiO_2 catalyst

The setup for the aerosol synthesis of the pure titania (T1 and T2-TiO_2 preparations) and the catalyst sample of platinum supported on titania (T3-TiO_2) is shown in Fig. 1. The premixed flame with a central precursor jet is the same as that used by Hansen et al. [24]. Premixed methane and air react in a flat zone just above the arrestor plate. The arrestor is circular, 40 mm in diameter, and 5 mm thick and gives an even distribution of the methane/air mixture. The jet outlet in the center of the arrestor has a 1.27-mm inner diameter. The jet consists of nitrogen mixed with vapors of the precursors, i.e., Ti-isopropoxide, when only the titania was prepared, and Ti-isopropoxide along with $Pt(acac)_2$ in the case of direct, one-step catalyst preparation. The saturator for the solid $Pt(acac)_2$ in the

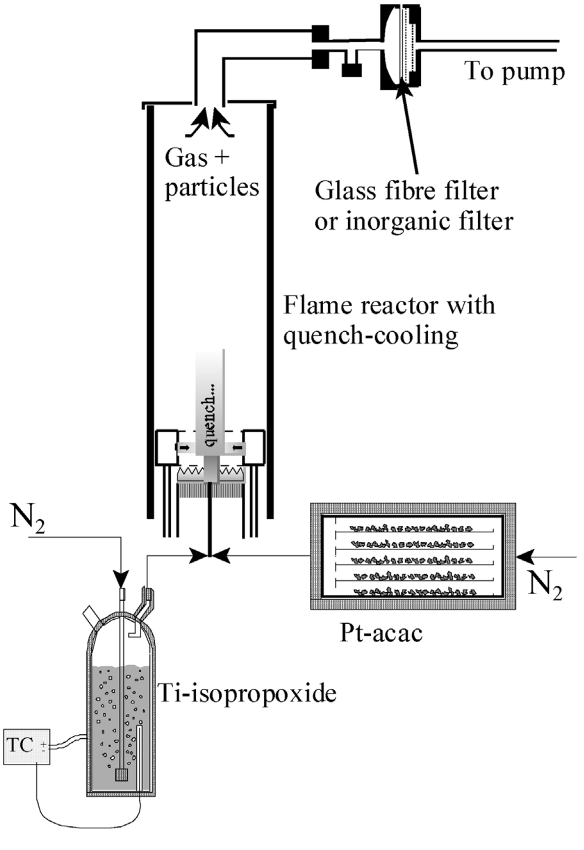


Fig. 1. Experimental setup for flame-aerosol synthesis of TiO_2 and Pt-doped TiO_2 particles (reproduced from Ref. [23]).

design of Jensen et al. [25] is a small thermostatted steel box with five 85-cm^2 stainless steel trays with layers of powdered $Pt(acac)_2$. The concentration of the precursor in the nitrogen carrier gas is determined by the temperature of the saturator. To prevent condensation of the precursor in the transport tube, the temperature of the tube from the saturator to the burner was kept approximately 20 °C higher than that in the saturator. The liquid Ti-isopropoxide was kept in a bubble bottle, in which the second stream of nitrogen became saturated with the Ti-precursor. The temperature of the bubble bottle was controlled by a temperature controller connected to a thermocouple inserted in a glass tube extending into the bottle. The burner was equipped with a quench-cooling ring above the arrestor [24], which was used for rapid cooling of the flame product gases. To avoid contact with air, the flame reactor was kept in a quartz-tube shield open only at the top. The quench-cooling ring was cooled internally with liquid water to avoid overheating of the metal. The circulated cooling water was preheated to 50 °C to prevent condensation of water from the combustion gas on the cooled surfaces inside the reactor. All flow rates were measured by a calibrated rotameter. In all experiments, the flow rates of methane and air to the burner were held at 0.62 and 9.87 l/min, respectively, and the nozzle outlets of the quench-cooling ring were fixed at 17 mm above the arrestor plate. The product gas was drawn through a 1.0-µm pore size filter by a vacuum pump to collect the particles. The entire setup was placed in a hood.

2.3. *Catalyst characterization*

The specific surface area of the titania samples was determined by nitrogen adsorption using the triple-point BET adsorption isotherm [26]. All samples were outgassed overnight at 120 °C under vacuum to ensure a clean surface free from preadsorbed species and water.

The metal particles of the active phase supported on the various titania samples were characterized by combined TEM-EDAX, XRD, and chemical analysis. For the microscopic examination (TEM; Philips EM 430), a small portion of the catalyst was ground in a mortar, then suspended in ethyl alcohol and dispersed by ultrasonication. A drop of the suspension was evaporated on a copper grid. Electron microscope images were obtained at different enlargements between 410,000 and 600,000. The average size of the platinum particles was measured from the TEM pictures using image analysis software (a mean of 80 particles). The electron microscope was calibrated with an internal standard of asbestos to avoid the common source of error where the display magnification is higher than the real magnification and the particles appear smaller. The chemical composition of the catalysts was tested by EDAX in situ analysis and by chemical analysis (AAS) after the catalyst material was dissolved in aqua regia. X-Ray crystallographic diffraction patterns of the catalysts were obtained with a Philips PW 3710 using Cu-K_α radiation and a Ni filter. To provide adequate count accumulation and sufficient resolution, the instrument was operated at a scan rate of 0.04°/min with receiving slit of 0.2°.

2.4. *Catalytic activity*

All measurements of catalytic activity were performed in a fixed-bed reactor system operated at atmospheric pressure over the temperature range 250–700 °C. In all cases, the reproducibility of the activity measurements was better than 10%. The catalyst was fixed between two plugs of quartz wool at the bottom of a capillary U-shaped tubular Pyrex microreactor cell. The reactor was inserted in an oven regulated by a temperature controller. The gas flow of the reactants was maintained at 30 ml/min using a flow meter (Brooks 5810). In all activity tests, the concentration of the gas mixture in the inlet stream was 10% O_2 and 11% SO_2 balanced with N_2, simulating sulfuric acid synthesis gas. The catalyst loading was kept constant at 0.5 mg, which corresponds to a ca. 2-mm long catalyst bed. Additional activity tests were performed with different amounts of catalyst to assess the effect of loading on the catalyst performance. The reactants were not preheated before entering the reactor.

The concentration of SO_2 in the gas mixture was monitored continuously with a spectrophotometer using the UV absorption peak at ca. 300.4 nm. The SO_2 conversion was determined from the concentration change in the gas mixture 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. The experimental setup was calibrated before and after each experiment, and calibration curves were constructed to correlate the SO_2 partial pressure in the gas mixture with the measured absorbance. All gas streams were dried through columns of P_2O_5.

3. Results and discussion

3.1. *Catalyst characterization*

In all preparations, using both the liquid and aerosol synthesis methods, the acetylacetonate salts of platinum and palladium provided the source of the respective metals. These precursors are advantageous for flame synthesis because they have a high vapor pressure, a prerequisite for this method. The salts should evaporate at relatively low temperatures (preferably below 200 °C) before being carried to the flame reactor by the nitrogen carrier gas. For the liquid method, the wet impregnation technique was used, with DMSO as the solvent. The acetylacetonate salts are known to dissolve in conventional organic solvents, but DMSO has proven to be an excellent solvent with adequate properties. First, it has very good polar properties. This is a critical factor, because the solvent must interact with the polar surface of titania and facilitate the penetration of the acac salts into the pores of the carrier. Second, DMSO has low surface tension (42.9 mN/m at 25 °C) [27], allowing the solvent to readily enter the pores of the support and the dissolved salts to crystallize into the cavities, in which the metals can stabilize after reduction. In the past, other solvents have been used for the acetylacetonate salts, including chloroform (unpublished data) and methanol [28], but the particles formed were relatively big.

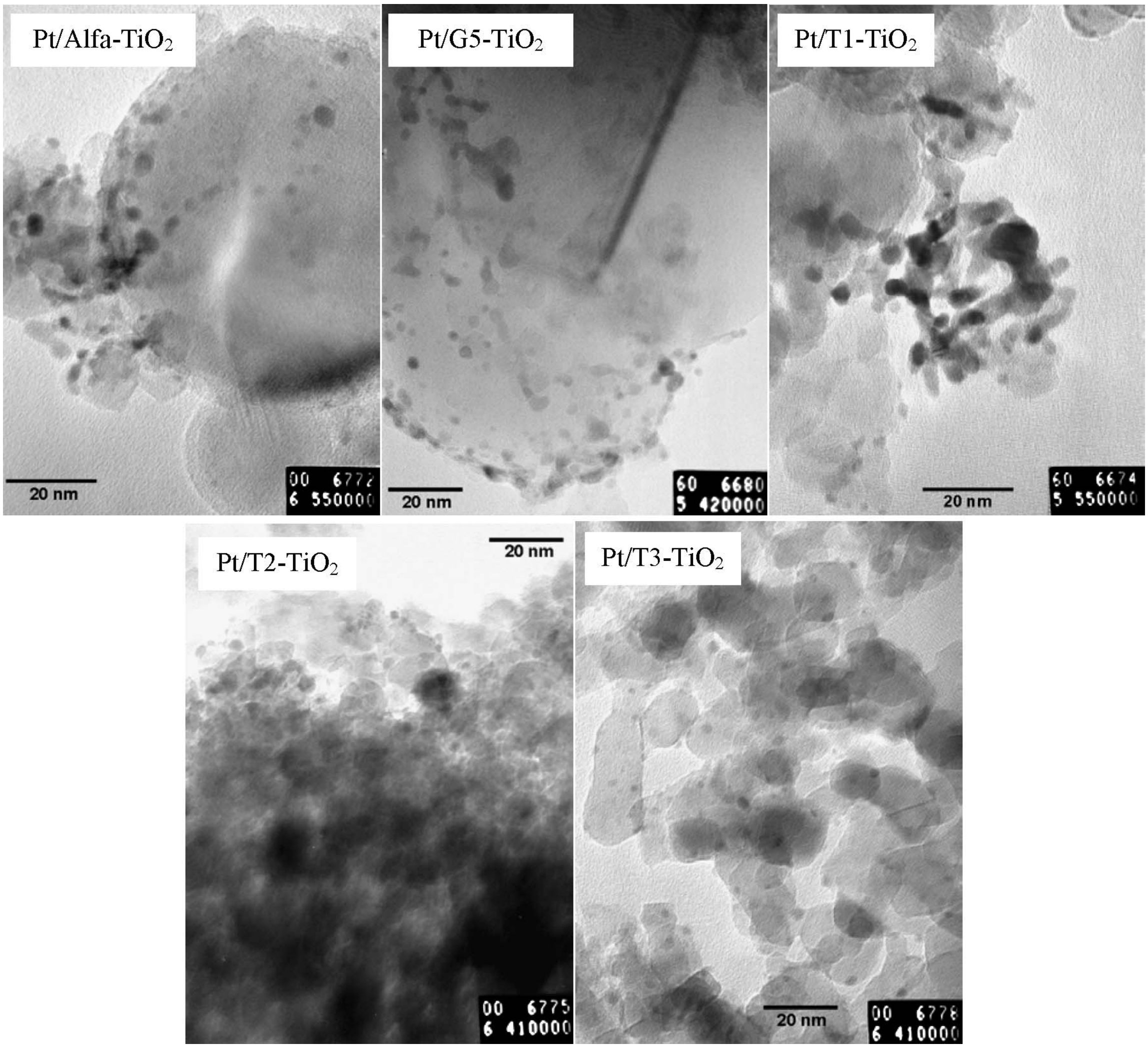


Fig. 2. TEM pictures of platinum nanoparticles supported on different titania samples. In all cases the particles are homogeneously distributed on the surface of the support and the particle size is 2 nm or less.

Image analysis of the TEM pictures of the catalyst samples showed that the average size of the particles was about 2 nm. Fig. 2 shows TEM pictures of the different titania samples supporting particles of pure platinum and platinum alloyed with palladium. These pictures show the fine surface distribution of platinum on the carrier. Formation of such small particle sizes can be attributed not only to the surface characteristics of the supporting material, but also to the choice of the precursor salts. As shown in Table 1, the average particle size of the supported metal depends on the surface characteristics of the titania sample used. Small crystals of the precursor phase grow in the narrow cavities. During reduction, the organic part of the originally precipitated precursor salt was removed and the pure metal, which is catalytically active, remains hosted in the pore cavity of the carrier. This process gives rise to strong interaction of the metal particles with the support after reduction. The metal particles of the active phase supported on titania were well immobilized on the surface of the carrier and were not dislodged even after ultrasonication during the TEM analysis. It has been reported that platinum particles supported on other supports were removed by ultrasonication [29]. No sign of particle aggregation on the support was observed, confirming the strength of the anchoring of the platinum particles and alloys on titania as previously suggested for other metals and alloys supported on silica [30].

Table 1
Source and properties of the titania (anatase) samples and the prepared catalyst

Titania sample	Titania preparation method	Surface area (m^2/g)	Catalyst preparation method	Particle size of the active phase (nm)
Alfa-TiO_2 (Alfa Chemicals)	Wet	53	Impregnation	1.9
G5-TiO_2 (Millenium Co.)	Wet	340	Impregnation	2.0
T1-TiO_2	Aerosol synthesis	57	Impregnation	2.5
T2-TiO_2	Aerosol synthesis	98	Impregnation	2.3
T3-TiO_2	Aerosol synthesis	100	Aerosol synthesis	1.9

The acetylacetonate salts gave high dispersions of the active phase. Previously, this has been attributed to molecular migration of the precursor on the surface of the support before decomposition [31]. The process may also involve strong interactions and complexation between the platinum acetylacetonate and the surface hydroxyl groups (–OH) of the oxide support. The organic part of the precursor salt is bulky, and thus such complexes have low concentrations on the surface of the support. This might be the reason for the high metal dispersion and for the size of the nanoparticles formed. After impregnation, the precursor was transformed to the metal during the reduction process. The acetylacetonate salts used for the catalyst preparations decompose to the pure metals at lower temperatures than those used during the reduction and calcination step [32]. The residual acetylacetonate groups were removed from the system in the form of CO_2 and H_2O with no further contamination of the catalyst.

In the flame-produced catalyst, the TiO_2 particles were formed by combustion of the Ti-isopropoxide and the decomposition of the Pt(acac)$_2$, resulting in Pt atoms that are oxidized in the hot, oxygen-rich environment of the flame. Subsequently, the gaseous Pt species collide with the aggregated titania particles, thus forming the catalyst in a single step.

The X-ray diffractograms of the catalyst showed no peaks that could be assigned to the precursor acetylacetonate salts or to the Pt–Pd alloy. The latter was due to the low content of the second metal and to the extremely small size of the particles [33]. Nanosized particles affect the intensity of the peaks mostly by microabsorption. Powder X-ray diffraction could not confirm alloy formation with particles <4 nm [33,34]. Moreover, the spectra were complicated due to the presence of titania (titanium dioxide, anatase, JCPDS card file 83-2243) with many strong peaks that often overlap with the weak peaks of the active phase.

Good dispersion and small particles of the active phase are often characterized by high catalytic activities. Moreover, the use of titania as a support with well-known physicochemical properties and surface characteristics is expected to give good catalytic performance. These hypotheses were tested for the prepared samples.

3.2. SO_2 oxidation catalytic tests

Pure Pd catalysts are susceptible to poisoning when SO_2 is present in the gas mixture. Pt makes the catalyst resistant to sulfur poisoning [35]. Preliminary experiments and catalytic activity tests revealed that the best-performing catalyst for SO_2 oxidation had a Pt:Pd ratio of ca. 5:1. This composition was used for the synthesis of the bimetallic catalysts.

The SO_2 oxidation tests were performed in a microreactor at atmospheric pressure, and the activities were measured over a wide temperature range (250–700 °C). When the catalyst mass in the reactor was increased above 1.0 mg, the conversions were $>70\%$, but this led to significant uncertainties in the spectrophotometric measurements due to oleum production. Blank experiments performed in the empty reactor and in the presence of pure titania showed no detectable SO_2 conversion, suggesting that the reaction between SO_2 and O_2 did not occur at the experimental conditions used. A typical spectrophotometer measurement, shown in Fig. 3, represents the SO_2 depletion from the feed gas after passing through the catalyst. Table 2 summarizes the catalytic activities and experimental conditions. As this table shows, all catalysts were very active for SO_2 oxidation at very low reactor loading and low catalyst loading with the active phase. Furthermore, the space velocities were very high, suggesting that the contact time necessary for the conversion of SO_2 over the catalyst surface is extremely short (i.e., ca. 0.001 s).

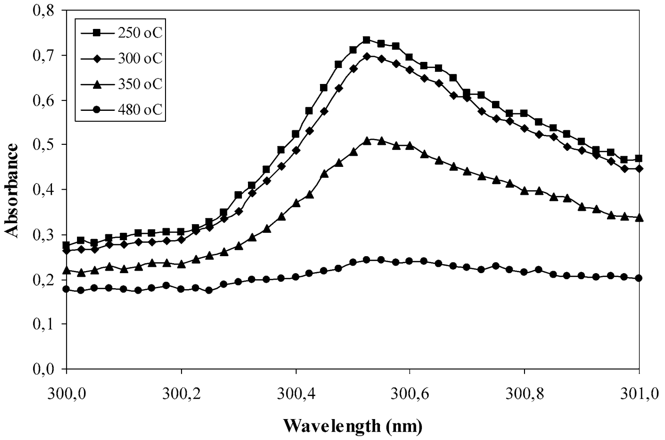
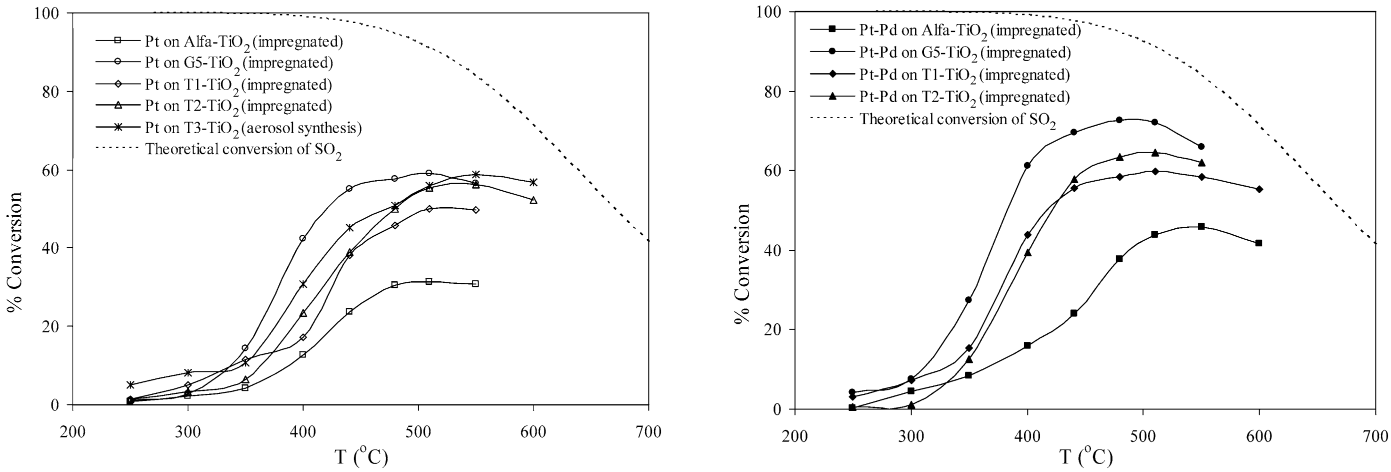


Fig. 3. SO_2 depletion from the synthesis gas mixture over 0.5 mg of the Pt–Pd/G5-TiO_2 catalyst, from spectrophotometric measurements.

The conversion of SO_2 was calculated from the difference in the number of moles, n, of SO_2 before and after passing the catalyst bed (Table 2). The catalytic activity was also expressed in terms of the turnover frequencies (TOFs), calculated as mol of SO_2 converted per mol of the total amount of the active phase in the reactor per unit time. The conversion of SO_2 to SO_3 as a function of the reaction temperature, T, is plotted in Fig. 4 for the different catalysts synthesized; in all cases, catalyst loading with the active phase and the reactant gas flow rate were kept constant at 2% w/w and 30 ml/min, respectively. The presence of palladium in the catalyst produced significant changes in the catalytic activity. This is illustrated in Fig. 4, which shows the activity of the platinum catalysts unpromoted and promoted with palladium. In all catalysts, catalytic activity decreased after reaching a maximum at 490–540 °C. The temperature of maximum activity depends on such factors as gas flow rate, catalyst loading with the active phase, and reactor load. Further increases in temperature led to lower conversions. When the temperature was slowly decreased from 650 °C to room temperature, the measured activities were lower than those obtained during the temperature increasing process. The activity decreased by between 5 and 10%, depending on the composition of the catalyst. This could be due to an increase of the particle size of the active phase as a result of sintering of the particles at high temperatures. The isolated particles on the surface of the carrier may also recrystallize, thereby changing the structure of the active phase. This process may make the catalyst less active, because interatomic distances of the metal or of the alloy are very important in interfacial phenomena such as catalysis. Furthermore, at temperatures above 600 °C, the active phase, which consists of nanoparticles, is susceptible to oxidation from the reactants and thus affect the catalytic properties [36]. Another explanation could be due to a change in the struc-

Table 2
Catalytic activities of the platinum based catalysts supported on titania. Feed gas composition 11% SO_2, 10% O_2 and 79% N_2, flow rate 30 ml/min, catalyst loading 2%

Catalyst	Reactor loading (mg)	Max. activity, TOF ($mol_{conv.\,SO_2}$/ ($mol_{active\ phase}$ s))	Max. activity (% conversion)	Temp. of max. activity (°C)	Space velocity (h^{-1})
S-Pt-21 (Pt/Alfa-TiO_2)	0.5	14.0	31	510	4,000,000
S-Pt-11 (Pt–Pd/Alfa-TiO_2)	0.5	20.6	46	550	4,500,000
S-Pt-19 (Pt/G5-TiO_2)	0.5	26.5	59	510	2,000,000
S-Pt-13 (Pt–Pd/G5-TiO_2)	0.5	32.6	73	480	2,000,000
S-Pt-14 (Pt/T1-TiO_2)	0.5	22.5	50	510	3,000,000
S-Pt-15 (Pt–Pd/T1-TiO_2)	0.5	26.8	60	510	3,000,000
S-Pt-23 (Pt/T2-TiO_2)	0.5	25.2	56	550	1,500,000
S-Pt-24 (Pt–Pd/T2-TiO_2)	0.5	28.9	65	510	1,500,000
ST-Pt-25 B (Pt/T3-TiO_2)	0.5	27.5	59	550	1,500,000
S-Pt-11 (Pt–Pd/Alfa-TiO_2)	1.6	10.9	78	480	1,400,000
S-Pt-13 (Pt–Pd/G5-TiO_2)	1	15.9	71	510	1,000,000
S-Pt-14 (Pt/T1-TiO_2)	1.5	9.7	65	510	1,000,000
S-Pt-15 (Pt–Pd/T1-TiO_2)	1.2	13.4	72	510	1,250,000



(a) (b)

Fig. 4. Conversion of SO_2 over pure (a) and alloyed (b) platinum catalysts supported on titania. Space velocities are shown in Table 1. The broken 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). The reproducibility of the catalytic activity measurements was better that 10%.

ture of titania from anatase to rutile; the latter is more stable at elevated temperatures.

As shown in Table 2 and Fig. 4, the platinum-alloyed catalysts supported on titania showed maximum activity at lower temperatures compared with those of pure platinum catalysts. For a given carrier, the temperature of maximum activity depends on the physical properties of the metals or the alloys, and also on the oxidation resistance of the active phase at the reaction conditions. Furthermore, the temperature of maximum activity shifts to lower temperatures with increasing reactor loading. This result, shown in Table 2, is in line with the experimental observations of Holmes et al. [37] 70 years ago for unpromoted platinum catalysts supported on silica gel substrates.

The palladium-alloyed platinum catalysts were 17–49% more active than the pure platinum catalysts prepared with the same method and having approximately the same particle size of the active phase. From this, we may conclude that a synergistic effect results from combining the two metals. The electronic properties of the supported metal and the alloy, the nature and physicochemical characteristics of the carrier, and the still-uncertain mechanism of SO_2 oxidation over Pt-based catalysts should be taken into consideration when interpreting the observed activities.

The catalytic activity of the palladium-doped platinum catalyst was remarkably high even at the very small reactor loadings used. The conversion of SO_2 reached 73% at high space velocities of 2–4.5 × 10^6 h^{-1}. It is noteworthy that such conversion was attained over 0.01 mg or ca. 5 × 10^{-5} mol of the active phase. The conversion increased with increasing amount of catalyst in the reactor, but this also resulted in lower activity in terms of TOFs. Consequently, in the case of high reactor loading, not all of the active phase in the reactor is exposed to the reactant gases.

Catalytic activity is affected by the preparation method and carrier used. From the data presented in Table 2 and the sample characteristics given in Table 1, clearly the catalytic activity depends not only on the particle size of the active phase, but also on the surface characteristics of titania. High specific surface area of titania facilitates the dispersion of the active phase, and, moreover, the pore diameter plays a significant role in decreasing the size distribution of the particles. The precursor salts grow in narrow cavities, and their crystal size is limited by the pore walls. After heat treatment, the precursor salt decomposes and the bulky acetylacetonate part is removed, leaving very small crystals of the active phase anchored on the carrier surface. From the observed activities of the catalysts and the fact that the average particle size of the active phase is nearly the same in all preparations (i.e., ca. 2 nm), we can conclude that the activity depends on the surface area of the support. Platinum catalysts supported on G5 titania showed the highest activity. Surface analysis of G5 titania demonstrated that the pore size distribution is 2–50 nm. Therefore, small pores and high specific surface area of the carrier result in catalysts with improved activity. This finding is in line with previous reports on catalysts for the oxidation of NO_x and hydrocarbons [38,39].

The Pt/T3-TiO_2 catalyst, prepared by the one-step aerosol method, gave remarkably high activity even though the surface area of titania was low (i.e., three times less) compared with G5 titania. Keeping in mind the methodology and the general principles of the aerosol synthesis method, a very high dispersion of the platinum particles would be expected. Fig. 3 shows the fine dispersion of the Pt particles obtained by simultaneous decomposition of Ti and Pt precursors in the flame. The flame-produced Pt/T3-TiO_2 is the most active catalyst among the monometallic platinum catalysts in terms of TOFs (Table 2). Its activity is high and comparable to that of some of the Pd-promoted bimetallic catalysts. Strobel et al. recently produced catalysts of platinum supported on alumina in a spray flame unit, in which a liquid precursor containing both platinum and alumina precursor was sprayed and combusted in a flame to give the supported noble metal catalyst. These authors also reported a high activity for their samples compared with traditionally impregnated samples, due to the open structure of the aggregated, dendritic structure of the material produced by the gas-phase route [39].

Thermodynamic studies on the oxidation of SO_2 to SO_3 show that the reaction is exothermic, which means that at high temperatures, the equilibrium shifts to the side of the reactants. Therefore, the conversion decreases when the temperature is increased (see the broken line in Fig. 4). Based on the composition of the gas mixture used in the present work (i.e., 11% SO_2, 10% O_2, balance N_2, total pressure 1 atm), the calculated SO_2 conversion to SO_3 at equilibrium is 99.98% at 270 °C. The equilibrium conversion decreases to 99.1% at 400 °C and drops rapidly from 95.6 to 83.8% at 470–550 °C, the range in which most of the activity maximums were observed in the present work. In the presence of an active catalyst, the kinetic factors prevailed over the thermodynamic factors. As shown in Fig. 4, the catalytic conversion of SO_2 over the catalysts tested was very small at 270 °C. However, keeping in mind the 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. The low activities of the catalysts observed at temperatures above 600 °C may also be due to thermodynamic factors that take over the kinetics.

4. Conclusion

Titanium dioxide, anatase, is the most favorable carrier for Pt-based catalysts because of its good surface properties and resistance to poisoning. In this work, Pt and Pt–Pd catalysts were tested and their activities for the oxidation of SO_2 to SO_3 were discussed with regards to different titania supports. The catalysts were prepared by impregnation using the acetylacetonate salts of Pt and Pd as precursors. Pd is a proven promoter of the Pt catalyst. Using DMSO was found to be advantageous for the synthesis, because DMSO is a good solvent of the acetylacetonate salts and has polar properties and low interfacial tension, promoting good interaction with the polar surface of titania. The average particle size of the active phase was between 1.9–2.5 nm, and the samples demonstrated remarkably high activities for SO_2 oxidation at high space velocities (up to $4.5 \times 10^6\ h^{-1}$); the contact time required for conversion over the catalyst surface was about 0.001 s. The Pt–Pd alloy showed the highest activity at very low loading of the reactor and at relatively low (i.e., 2%) loading of the support with the active phase.

Maximum activity was observed at temperatures between 490–540 °C depending on catalyst composition, but a further increase in temperature led to a decrease in activity, probably as a result of sintering of the particles of the active phase and also because the reaction becomes limited by chemical equilibrium.

The method used to synthesize the titania used in catalyst preparation affected the catalytic performance of the final product. G5 titania gave the most active catalyst after impregnation. Comparing the activities of the samples containing only platinum showed that the aerosol synthesized catalyst had remarkable catalytic performance. Consequently, this method may prove useful in work aimed at improving other important metal- or metal oxide-based catalysts.

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