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The role of support and promoter on the oxidation of sulfur dioxide using platinum based catalysts

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Abstract

The catalytic oxidation of SO_2 to SO_3 was studied over platinum based catalysts in the absence and the presence of dopants. The active metal was supported on silica gel or titania (anatase) by impregnation. The activities of the silica supported catalysts were found to follow the order Pt–Rh/SiO_2 > Pt/SiO_2 > Pt–Al/SiO_2. For the samples supported on titania the respective order was Pt/TiO_2 > Pt–Rh/TiO_2 > Pt–Al/TiO_2. The size of the particles of the active phase, the presence of dopants and the purity of the catalyst were found to affect the catalytic performance. A careful selection of the pH of the impregnation solution and of the reduction temperature of the precursor salts resulted in a very active catalyst with average particle size of 1.7 nm.

Keywords: Silica; Titania; Platinum; Palladium; Rhodium; Catalyst; Sulphur dioxide oxidation

1. Introduction

Sulfur dioxide emission to the atmosphere is an increasing concern worldwide. In order to meet legislative demands to reduce release of SO_2, more efficient catalysts need to be developed. Platinum has been used as a catalyst for the oxidation of SO_2 in the industry of sulfuric acid production. Before the Second World War platinum was exclusively used in this process however, the immense requirements of sulfuric acid caused such a demand in platinum that resulted in difficulties in supply. Moreover, cost limitations and deactivation of the catalyst by e.g., arsenic compounds stimulated the invention of alternatives. Nowadays, the industrial use of platinum as a catalyst for the SO_2 oxidation – the key step in the sulfuric acid production and in catalytic flue gas desulfurization by the SNOX process – is essentially replaced by catalysts based on vanadium. However, the oxidation of SO_2 by platinum-based catalysts continues to attract interest [1–5]. This is mainly due to the fact that platinum particles can be redistributed and regain high catalytic activity whenever that drops as a result of prolonged use and exposure to O_2 [6] or chlorine gas [7]. Rhodium is a hardening agent of platinum alloys that maintain structural and textural characteristics even after long exposure at high temperatures. The contribution of Rh towards hardening of platinum alloys significantly exceeds the properties of any other metal alloyed with platinum. The use of the Pt–Rh alloy as a catalyst for the SO_2 oxidation is advantageous over other platinum based catalysts in terms of speed of activation, efficiency of conversion, duration of catalytic performance and stability at high temperatures [8]. Moreover, Rh strongly interacts with O_2 molecules and thus increases their surface concentration. This mechanism is responsible for enhancing the rate of the oxidation reaction. The idea of doping Pt with Al originated from electrochemical studies [9]. Although the formation of an alloy between Pt and Al is ambiguous, we will investigate if simple contact between the two metals would result in interesting catalytic properties.

Silica and titania were chosen to support the platinum particles. Silica has been reported to give insufficient stabilization of precious metal particles against sintering

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[10], and low dispersion of the active phase [11]. Nevertheless, it has some advantages, such as poisoning resistance against arsenic compounds, high conversion rates at high space velocities and extremely low surface oxygen mobility [12]. Especially, the low surface mobility of oxygen is very important because the catalyst is immunized against prolonged decreased oxygen content in the reacting gases; at such conditions the vanadium based catalysts undergo significant decrease in catalytic activity. Titania was chosen because it is one of most commonly used carriers in a variety of catalytic processes such as flue gas denitrification, hydrocarbon selective oxidation, CO hydrogenation, and NOx reduction with hydrocarbons [13–15]. The surface properties of titania, its poisoning resistance features and the strong metal support interactions, especially when the active phase is Pt, are additional reasons for the wide use of titania as a carrier [16].

In the present work, we investigated the Pt based catalysts supported on silica gel and titania (anatase). Catalyst samples were prepared in the presence of Rh and Al dopants and their activity was tested for the oxidation of SO_2.

2. Experimental

2.1. Chemicals and gases

Silica gel 100, SiO_2, (Merck) and titania (anatase), TiO_2, (Alfa Aesar Chemicals, >99.99%) were used as supports. The specific surface area of silica and titania are 290 and 53 m^2/g, respectively as measured by the triple point BET method. The average pore size is 100 and 250 nm for silica gel and titania, respectively. Platinum chloride, $PtCl_4$, (H. Drijfhout & Zoon's, Amsterdam, The Netherlands) was chosen as a precursor salt for the synthesis. Dopant solutions were prepared from the respective extra pure solids, i.e., $RhCl_3{\cdot}3H_2O$ (Aldrich), and $AlCl_3{\cdot}6H_2O$ (Merck) using deionized water. We have chosen the chloride salts of the respective metals because they are very soluble in water.

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 in the catalytic activity tests. All gases were dried through P_2O_5 columns.

2.2. Catalyst preparation

The silica gel contained up to 0.01%Zn, which is suggested to have a poisoning effect on platinum catalysts used in the SO_2 oxidation process [17]. To remove Zn, silica gel particles were suspended in 1 M HCl solution and allowed to equilibrate for 2 h at 60 °C under continuous stirring and ultrasonication. Then the particles were filtered and washed through a 0.22 μm filter. The process was repeated three times and finally the particles were dried overnight at 100 °C. After treatment, Zn could not be detected by chemical and EDAX analysis. The Zn-free silica gel was impregnated with the $PtCl_4$ solution aiming at 2 wt.% loading with the active phase. This was confirmed by combined TEM/EDAX and chemical analysis. In the doped samples, the silica gel was suspended and coimpregnated in a solution, which contained the precursor chloride salts of Pt and Rh or Al. The content of the dopant was meant to be 10% of the total metal content of the catalyst. After equilibration for 2 days at 50 °C the solvent was slowly evaporated in a rotary evaporator and the solid material was dried overnight at 110 °C. Then the sample was reduced at 500 °C with formier gas (90%N_2, 10%H_2). The temperature increased stepwise (i.e., each step was 1 h at 100, 200, 300, and 400 °C, and 3 h at 500 °C). Then, the catalyst was allowed to cool to room temperature under continuous formier gas flow.

Two series of silica-supported catalysts were prepared keeping the pH of the impregnation solution above (i.e., pH 7) and below (i.e., pH 1) the point of zero charge (p.z.c.) of silica gel, which is at pH 2.7. The pH was adjusted by adding 0.01 M NaOH or 0.01 M HCl. To test the effect of the reduction temperature on the catalytic activity, the catalyst sample prepared from a solution with pH 1, was divided in two parts that were reduced with formier gas at 500 and 700 °C, respectively.

Titania anatase, TiO_2, was also impregnated by a $PtCl_4$ solution with pH 6.7, which is slightly higher than the p.z.c. of the surface (i.e., at pH 6–6.5). In the doped samples, the dissolved $PtCl_4$ and one of the $RhCl_3$ or $AlCl_3$ salts were coimpregnated in the titania particles. The final composition of the dopant in the total metal content of the catalyst was 10%. After impregnation the sample was dried overnight and the precursor salts were reduced to the active metal by formier gas at 500 °C (as before the temperature was increased stepwise).

2.3. Catalyst characterization

The size of the platinum particles supported on silica or titania was measured by transmission electron microscopy, TEM, (Philips EM 430) using an image analysis software (average of ca. 80 particles). The microscope was calibrated using an internal standard (asbestos lines) to avoid the common source of error, where the display magnification is higher than the real and hence, the particles appear smaller.

Thermogravimetric–differential thermal analysis, TGA–DTA, (Mettler TGA cell) and temperature-programmed reduction, TPR, experiments were carried out using formier gas as reducing agent (gas flow 110 ml/min). The set-up was coupled with a mass spectrometer to analyze the composition of the gas outlet. Before analysis all samples were kept overnight under vacuum to remove adsorbed surface water and other molecules. The samples were heated with a rate of 1.5 °C/min and a step at 300 °C for 1 h, before reaching the maximum at 650 °C.

X-ray powder diffraction patterns (Philips PW 3710, Cu Kα radiation, scan rate 0.04°/min) of the catalyst were recorded to analyze the crystallographic characteristics of the active phase.

2.4. Catalytic activity test

The experimental set-up used for the catalytic activity tests consisted of a U-shaped capillary reactor made of Pyrex glass, which was placed in a temperature-controlled furnace. The synthesis gas passed through the catalyst bed, which was located between two plugs of quartz wool. The temperature in the furnace was measured with a thermocouple in contact with