Room temperature visible light oxidation of CO by high surface area rutile TiO$_2$-supported metal photocatalyst

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Abstract

Visible light-active rutile TiO$_2$ with a high surface area of 200 m^2/g was obtained by a low-temperature sol–gel synthesis, based on a long aging duration of a titania sol to stabilize the rutile phase. Decorated by an adequate amount of metallic nanoparticles, this non-doped TiO$_2$ displays high and stable performances for the on-stream room temperature oxidation of CO by visible light photocatalysis.
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1. Introduction

During the last decades, a growing part of the innovative research concerning the degradation of pollutants was notably focused on photocatalysis, in order to meet strict pollution abatement legislation required by environmental protection pressure [1–4]. Developing new high efficiency photocatalytic materials based on TiO$_2$ semi-conductor which is up to now the most efficient photocatalyst, is of immense importance for obtaining requested better performance processes and more generally for public health reasons.

The very low adsorption of CO on pure TiO$_2$ is highly detrimental to the CO photooxidation efficiency and could be overcome by supporting platinum particles onto UV-activated TiO$_2$ [5–7]. In addition, numerous research groups have reported that adding group VIII metals to polycrystalline TiO$_2$ increased the photocatalytic activity, by capturing in the platinum clusters the excited electrons from the TiO$_2$ conduction band [8–10]. Platinizing TiO$_2$ was generally reported not only to increase the photo-induced electron transfer rate by trapping the photo-generated electrons but also

to promote the CO adsorption by providing adsorption sites [11–14], CO being an accurate probe molecule for determining the platinum particle size on oxides by chemisorption. However, the electron capturing positive role of platinum clusters on TiO$_2$ remains subject to debate, since works performed on model surfaces at low temperatures at which the quenching of thermal reactions renders the electronic effects more visible, have reported that electron trapping in platinum clusters on TiO$_2$ (1 1 0) does not occur or is ineffective in enhancing the kinetics of photooxidation processes [15].

In parallel to non-photocatalytic CO removal using specially designed efficient oxide-supported Au nanoparticle catalysts, researches have been focused on the UV activation using commercial TiO$_2$ materials or well-defined TiO$_2$ surfaces [5–16]. Surprisingly no works have ever been reported for the gas phase CO oxidation by visible light activation. Since UV occupies only about 4% of the solar spectrum, transferring the activation mode from UV to visible light, as a first step towards the cheap, clean and renewable solar energy source, is nevertheless of high importance for sustainable development.

In parallel to the doping of anatase titania, visible light applications usually require semi-conductors with band gaps lower or equal to 3.0 eV, such as rutile TiO$_2$ (reported with a band gap of 3.0 eV or a band edge at λ = 413 nm) [17], thus ruling out the sole use of the conventional 3.2 eV band gap

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anatase phase. Rutile is usually reported to be less active than anatase as a photocatalyst [18–20]. Pure rutile phase is generally obtained by high temperature treatment of anatase, leading to a low surface area and low porosity material with large sintered TiO_2 particles. Different rutile synthesis methods including e.g. mist plasma evaporation, pulse magnetron sputtering and RF thermal plasma have been recently reported for powder and film growth [21–26], and a recent interest in rutile's photocatalytic applications is growing [27]. The synthesis of large amounts of small diameter rutile particles with an adequate and tunable porosity to allow a good accessibility of pollutants to the adsorption sites and a high surface area for dispersing metallic nanoparticles in the present case of CO removal or anchoring other oxides for coupled photocatalysts, remains of high interest.

2. Experimental

2.1. Photocatalyst preparation

The high surface area rutile synthesis consisted of a sol gel procedure in which the titanium isopropoxide (TIP, Fluka, purum) was first hydrolyzed under vigorous stirring by the addition of a 2 mol L^{-1} aqueous solution of hydrochloric acid (with a ratio of 14 mL of TIP per 23.5 mL of HCl solution). After 48 h of aging at room temperature of the hydrosol, polyethylenglycol (PEG-4000, 50 mg/mL of sol) used as porogen was introduced under stirring and the resulting mixture was dried at room temperature and further at 110 °C for 24 h, before calcination in air at 350 °C for 2 h (heating rate of 2 °C/ min).

Whatever its concentration, the platinum deposition (0.1– 0.5 wt.%) was performed onto the TiO_2-coated photoreactor, using an aqueous solution of H_2PtCl_6 (Strem Chem., >99%) with 2 mL per 100 mg of TiO_2. After drying at 110 °C for 1 h in air, the resulting photocatalyst coated on the reactor was oxidized at 350 °C for 1 h and finally reduced in flowing hydrogen at 400 °C for 1 h, both with heating rates of 5 °C/min. Palladium (0.3 wt.%) was co-impregnated using palladium nitrate ($PdNO_3·H_2O$, Strem Chem., >99.9%) dissolved into the platinum aqueous solution, before drying and final temperature treatments similar to that with pure platinum.

2.2. Characterization techniques

X-ray diffraction (XRD) measurements were carried out on a D-5000 Siemens diffractometer, in a $\theta/2\theta$ mode and using the $K\alpha_1$ radiation of Cu at 1.5406 Å.

The surface area and porosimetry measurements were carried out on an ASAP2010 Micromeritics using N_2 as adsorbant at liquid N_2 temperature. Before the N_2 adsorption, the material was outgassed at 200 °C for 1 h in order to desorb the impurities or moisture from its surface. The surface areas and pore size distribution were calculated by applying the B.E.T., B.J.H. and t-plot methods [28].

Thermal gravimetry analysis (TGA) was performed using a SETARAM thermo-analyser. The sample was placed in a platinum crucible and heated under a 50 mL/min 10% (v/v) O_2/ N_2 flow stream with a heating rate of 10 °C/min.

Scanning electron microscopy (SEM) was carried out on a JSM6700F JEOL microscope to provide information on the morphology.

The UV–vis absorption spectra of the materials were recorder on a Cary 100 Scan UV–vis spectrophotometer (Varian).

2.3. Photocatalytic CO oxidation

The photocatalytic oxidation of CO was carried out in a 300 mm length cylindrical concentric tubular Pyrex reactor made of two coaxial tubes 4 mm apart, between which the reactant mixture was passing through. Details concerning both reactor and device can be found in Ref. [29]. Rutile TiO_2 (440 mg) were evenly coated on the internal surface of the external tube, diameter 35 mm, by evaporating a rutile-containing aqueous slurry to dryness. The coated reactor was dried at 110 °C for 1 h in air, before the platinum deposition was performed as described in Section 2.1. CO (2000– 4000 ppmv) and 50% relative humidity were co-fed and balanced with air to 200 mL min^{-1}, 100 vol.% of relative humidity being defined as the saturated vapor pressure of water at 25 °C, which corresponds to about 24 Torr, i.e. about 3 vol.% relatively to the total atmospheric pressure. Before the photocatalytic reaction, the catalyst was first exposed to the polluted air stream with no illumination until dark-adsorption equilibrium is reached. Afterwards the UV illumination was switched on. The visible light source, a commercial 8 W daylight tube (400–800 nm), was located inside the internal tube. The reaction products were analyzed on-line by micro-gas chromatography allowing quantification of water, CO and CO_2.

3. Results and discussion

The synthesis of low-temperature rutile was performed easily by using a sol–gel synthesis for which a longer aging duration of the titania sol during the synthesis favors the rutile phase versus anatase, by a mechanism similar to that used for alumina, and consisting of dissolving and recrystallizing an oxide in its mother liquor in order to obtain a more stable crystalline phase [30,31] with a stabilization energy of 1.2– 2.8 kJ/mol compared to anatase. Appearance of rutile beside the anatase phase in the hydrosol occurred after few hours of aging whereas a 48 h aging totally suppressed the anatase phase, with pure rutile being observed. After calcination to remove the PEG porogen, pure rutile was observed by XRD, with crystalline domains of 11 ± 1 nm (Fig. 1).

The interest of using PEG was highlighted by surface area and porosimetry measurements. Fig. 2a shows the nitrogen adsorption–desorption isotherm of the high surface area rutile TiO_2 compared to that obtained for the PEG-free analogue (Fig. 2). The strong change in the isotherm pattern and hysteresis behavior evidenced the role of the PEG porogen during the rutile sol–gel synthesis. The rutile material synthesized using PEG had a high surface area of 196 $m^2 g^{-1}$ and a total pore volume of