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Synthesis of TiO_2 supported on activated carbon by MOCVD: operation parameters study*

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Abstract: A novel metallo-organic chemical vapor deposition (MOCVD) technique has been applied to the preparation of the photocatalytic titanium dioxide supported on activated carbon. The effects of various condition parameters such as carrier gas flow rate, source temperature and deposition temperature on the deposition rate were investigated. The maximum deposition rate of 8.2 mg/(g·h) was obtained under conditions of carrier gas flow rate of 400 ml/min, source temperature of 423 K and deposition temperature of 913 K. The deposition rate followed Arrhenius behavior at temperature of 753 K to 913 K, corresponding to activation energy E_a of 51.09 kJ/mol. TiO_2 existed only in anatase phase when the deposition temperature was 773 K to 973 K. With increase of deposition temperature from 1073 K to 1273 K, the rutile content sharply increased from 7% to 70%. It was found that a deposition temperature of 773 K and a higher source temperature of 448 K resulted in finely dispersed TiO_2 particles, which were mainly in the range of 10–20 nm.

Key words: MOCVD, Supported materials, Supersaturation, Titanium dioxide
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INTRODUCTION

Today titanium dioxide is an important photocatalytic material for wastewater treatment (Fujishima and Honda, 1972). Several practical problems arose concerning recovering when it was used as a powder suspension (Sopyan *et al.*, 1996), so studies to efficiently produce supported TiO_2 had to be conducted (Tsukasa *et al.*, 1996; Lei *et al.*, 1999).

The traditional methods for supported catalysts preparation are wet impregnation, precipitation, ion exchange and sol-gel method. Recently, metallo-organic chemical vapor deposition (MOCVD), an extensively used coating technology, was used to equip a support with active material in one step (Moene *et al.*, 1993; Serp *et al.*, 1995). Using MOCVD, many steps such as drying, calcinations and reduction, which critically affect catalyst performance in the traditional catalyst preparation, can be dispensed with. Moreover, MOCVD production of supported catalysts offers the following advantages (Hierso *et al.*, 2000): (1) the crystal structure of the active material is controllable; (2) the process is continuous; (3) a relatively simple apparatus is required.

Our previous work revealed that catalysts prepared by one step process showed higher catalytic efficiency in the degradation of phenol solu-

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tion than the two step one (Lei *et al.*, 1999). However, two fundamental aspects have not yet been fully investigated: (1) the role of experimental conditions such as source temperature, deposition temperature and carrier gas flow rate in deposition rate; (2) the influence of experimental conditions on the crystal structure and dispersion of TiO_2 particles, the characteristics of which usually govern the final properties of TiO_2. The present work mainly aims to investigate (1) and (2) in the process of supporting TiO_2 on activated carbon (AC) using the MOCVD method.

EXPERIMENTAL

Synthesis of TiO_2/AC photocatalysts

The MOCVD system is shown in Fig.1. TiO_2/AC was prepared by hot wall atmospheric pressure MOCVD using nitrogen as carrier gas and tetrabutyltitanate (TBOT) as the precursor. AC was boiled in 6 mol/L HNO_3 at 373 K for 60 min, and then washed with distilled water. AC (5.0 g, 40–60 mesh) was put into the quartz reactor, and dehydrated in a stream of dry nitrogen at 573 K for 3 h. Temperatures for MOCVD preparation were measured by the thermocouple inserted into the furnace (the reaction zone). After the reactor temperature stabilized, deposition was initiated by switching the precursor. At the end of deposition, the reactor was purged by nitrogen gas for about 10 min. The developed material was removed from the reactor without any further treatment. The details of the apparatus can be found elsewhere (Lei *et al.*, 1999).

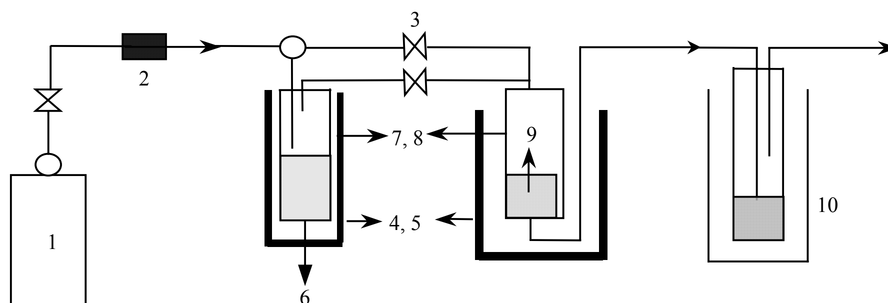
Characterization

The adsorption isotherms of nitrogen at 77 K were measured with an OMNISORP 100 instrument. Each sample was degassed at 623 K for at least 2 h until a pressure of 10^{-5} Pa was attained. The crystal structure of TiO_2 supported on AC was identified by XRD (Rigaku D/max 2550), performed over angular ranges of 2θ=10°–70°, scanned at a speed of 0.01 °/s and a step of 0.01°. The equipment was operated at 40 kV and 50 mA. The morphologies and particle sizes were investigated with TEM (JEM 2010), operated at 200 kV. The amounts of supported TiO_2 on activated carbon were determined, after dissolution, by complexation with hydrogen peroxide, according to the spectrophotometric method proposed by Snell and Ettre (1974).

RESULTS AND DISCUSSION

The effect of N_2 flow rate on the deposition rate is shown in Fig.2. It was found that the deposition rate increased with the increase of N_2 flow rate, and reached the maximum deposition rate [7.96 mg/(g·h)] at N_2 flow rate of 400 ml/min. This may be attributed to the evaporation of TBOT promoted by the high N_2 flow rate. However, when the N_2 flow rate further increased to 600 ml/min, the deposition rate decreased to 3.56 mg/(g·h). One possible reason was that the precursor concentration in the gas stream was strongly diluted.

Fig.3 depicts the effect of the source temperature on the deposition rate. When the source temperature increased from 348 K to 423 K, the



1–N_2 container; 2–Silica gel; 3–Valve; 4,5–Furnace; 6–TBOT; 7,8–Quartz tube; 9–AC; 10–Cold trap

Fig.1 Schematic diagram of MOCVD system

deposition rate increased from 0.84 mg/(g·h) to 7.26 mg/(g·h). It may be interpreted that the high source temperature resulted in the enhanced concentration of TBOT in the gas phase. However, the deposition rate nearly did not change when the source temperature increased from 423 K to 448 K. The possible reason was that the deposition process was mainly limited by the chemical kinetics; and that the deposition rate was independent of the source temperature. Therefore in the following studies the source temperature of 448 K was adopted.

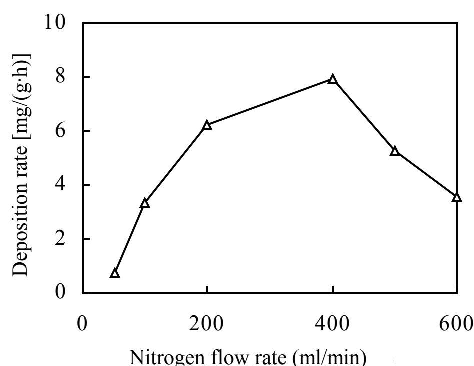


Fig.2 Effect of nitrogen flow rate on the deposition rate
Source temperature: 448 K; Deposition temperature: 973 K

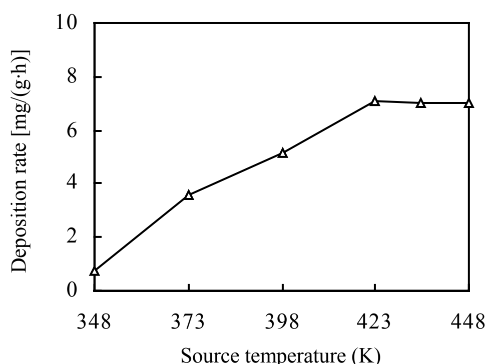


Fig.3 Effect of source temperature on the deposition rate
Deposition temperature: 873 K; N_2 flow rate: 400 ml/min

Fig.4 shows the effect of deposition temperature on the deposition rate. Almost no TiO_2 was observed when the deposition temperature was below 723 K, which indicated that TBOT was almost not decomposed (Zhang *et al*., 1998). From deposition temperature of 723 K to 1023 K, the deposition rate was in three stages as shown in a, b and c in Fig.4. An increase of deposition temperature from 753 K to 913 K (stage a) resulted in the rapid increase of deposition rate from 1.96 mg/(g·h) to 8.2 mg/(g·h). However, when the deposition temperature increased from 913 K to 1023 K (stage b), the deposition rate almost did not change. The deposition rate decreased from 8.2 mg/(g·h) to 5.26 mg/(g·h) when deposition temperature increased from 1023 K to 1200 K (stage c).

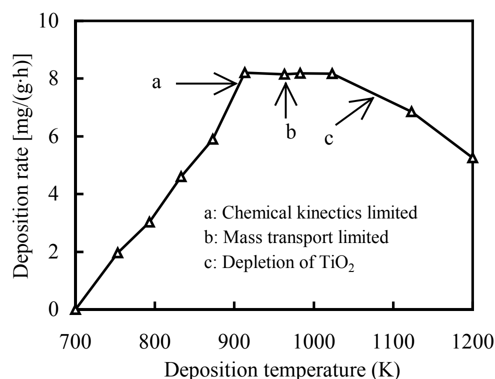


Fig.4 Effect of deposition temperature on the deposition rate Source temperature: 448 K; N_2 flow rate: 400 ml/min

In stage a, the deposition rate increased rapidly, which indicated that the rate-limiting mechanism was surface chemical kinetics, i.e., chemisorption, and/or chemical reaction, surface migration, lattice incorporation and desorption. These surface processes strongly depended on the deposition temperature. During this deposition process, Arrenius's law prevails (Choy, 2003):

$$\text{deposition rate}=A\exp(-E_a/RT)$$
$$\text{i.e. } \ln(\text{deposition rate})=-E_a/RT+\ln A$$

where A is a constant; E_a is the effective activation energy, kJ/mol; R is the gas constant; T is the absolute temperature of deposition.

Fig.5 shows the Arrenius plot, in region a, the logarithm of the deposition rate versus the reciprocal temperature curve. The slope of the line yields an effective activation energy of E_a=51.09 kJ/mol.

In stage b, the deposition temperature had no effect on the deposition rate. This was because the deposition temperature was so high that all active gaseous species could be decomposed entirely; so the deposition rate was limited by the mass transport.

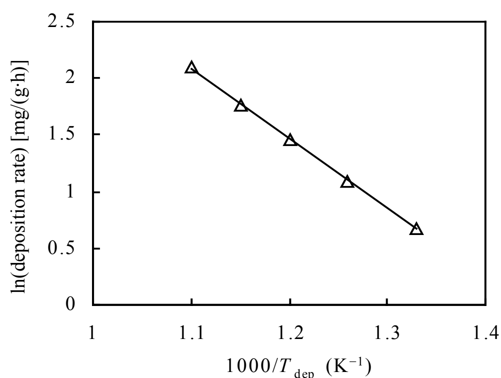


Fig.5 Arrenius plot of the deposition rate of MOCVD titania coating vs reciprocal temperature curve

At higher temperature (stage c), the deposition rate decreased with the increasing deposition temperature. This may be attributed to the depletion of reactants and/or increasing in the rate of desorption. Another possible reason was that the particles formed in the gas phase, adhered poorly to the support.

Fig.6 shows the XRD patterns of TiO_2/AC prepared by MOCVD. Anatase (2θ=25.3) was found during the MOCVD process at deposition temperature of 773 K, when rutile material (2θ=27.5) appeared at 1073 K.

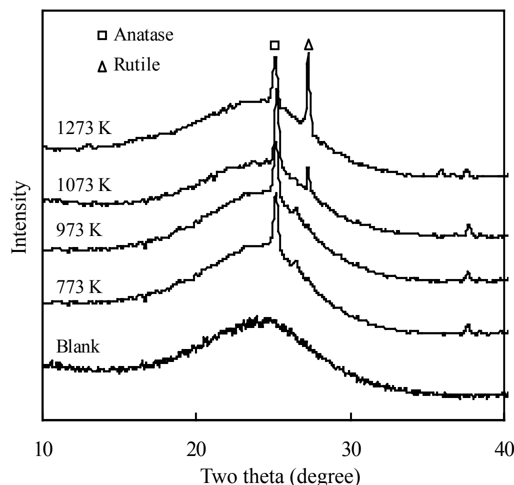


Fig.6 XRD patterns of the samples at various deposition temperatures

Fig.7 shows the increase in rutile content with deposition temperature. With the increase of deposition temperature from 1073 K to 1273 K, the rutile content sharply increased from 7% to 70%. Here rutile content is calculated with the following equation (Spur and Myers, 1957):

$$f_R = 1-(1+1.26 I_R / I_A)^{-1}$$

Where f_R is the fraction of rutile phase, I_R is intensity of (110) reflection of rutile, and I_A is intensity of (110) reflection of anatase.

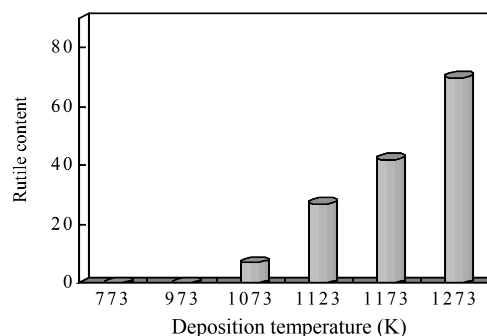


Fig.7 Effect of deposition temperature on the rutile content

TEM micrographs of samples prepared by MOCVD are shown in Fig.8. Numerous TEM micrographs were used to obtain particle size distribution histograms of TiO_2/AC samples given in Fig.9 clearly showing that the dispersion of sample b was better than that of sample a. A possible explanation was that a higher source temperature (448 K) would produce a high supersaturation ratio, which greatly favored the nucleation rate in comparison with the particle growth rate, and so resulted in numerous small particles much more dispersed (Hierso *et al*., 2000).

For sample c, the particles were mainly in the range of 10–20 nm and more dispersed, which proved that the coating had been quite improved. At deposition temperature of 773 K, heterogeneous reaction may occur at the gas-solid interface where the anchoring sites were surface groups (such as hydroxyl) of the support. Therefore the produced TiO_2 firmly adhered to the support, as easily seen in Fig.10a. When the deposition temperature was higher (973 K), homogeneous reaction would also occur. The pyrolysis of TBOT in the gas phase would result in the pregrown TiO_2 unit, which was the growth site. So the particles were only slightly

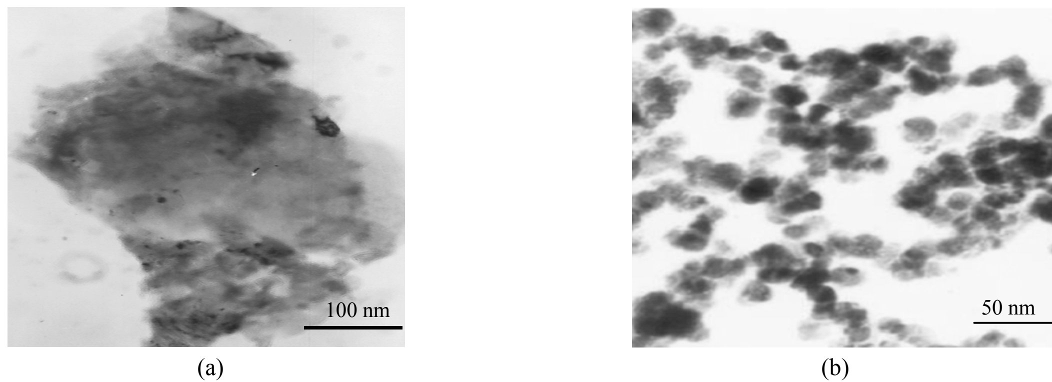


Fig.8 TEM microographs of TiO_2/AC samples
(a) 398 K; (b) 448 K

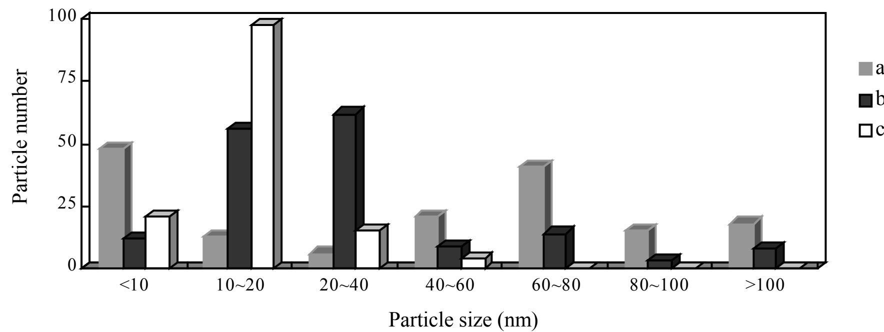


Fig.9 Particle size distribution of TiO_2/AC samples: source temperature/deposition temperature of sample a, b and c were 398 K/973 K, 448 K/973 K and 448 K/773 K respectively

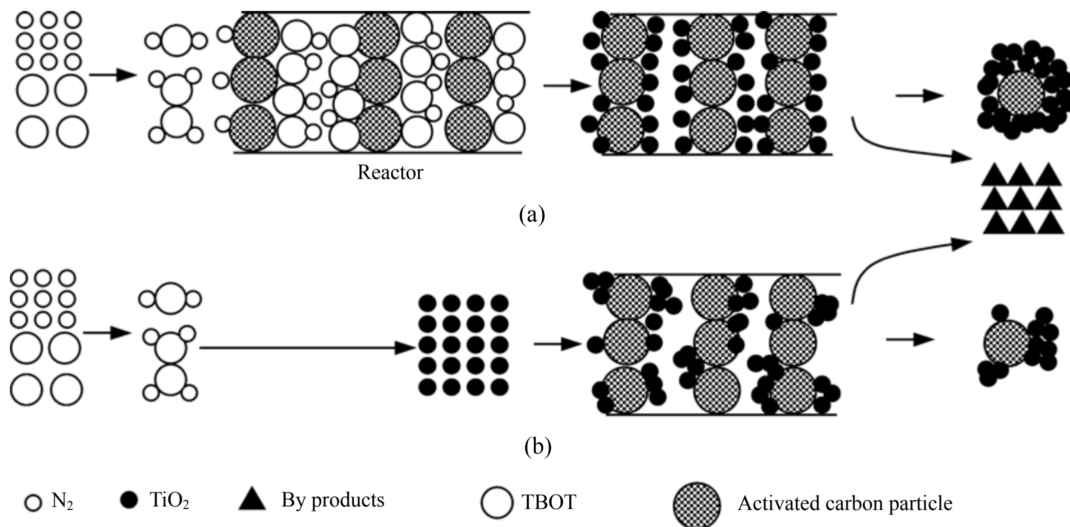


Fig.10 Schematic drawing of the key MOCVD steps (a) the heterogeneous MOCVD process; (b) the homogeneous MOCVD process

dispersed, as shown in Fig.10b (Choy, 2003; Zhang and Griffin, 1995).

Table 1 depicts the BET area of the samples with different loading rate. It was worth noting that there was no huge decrease in the specific surface area of all the samples, which was usually important

Table 1 BET area of the sample

Deposition temperature	Blank AC	773 K			973 K		
Loading rate (%wt)	0	4.3	10.6	21.8	4.3	10.6	21.8
BET (m^2/g)	731.4	678.4	635.0	532.4	622.3	516.7	462.9

for supported catalysts to provide the sufficient capacity of adsorption. It could also be observed that the specific surface area of the samples prepared at 973 K were smaller than that of the samples prepared at 773 K, which suggested that the texture of AC was less affected by the process at the latter deposition temperature. This can be attributed to the fact that TiO_2 particles produced at 773 K were smaller and highly dispersed.

CONCLUSION

TiO_2/AC catalysts were developed by MOCVD method and the effects of various condition parameters such as carrier gas flow rate, source temperature and deposition temperature on the deposition rate were examined. The maximum deposition rate of 8.2 [mg/(g·h)] was obtained under conditions of a carrier gas flow rate of 400 ml/min, a source temperature of 423 K and deposition temperature of 913 K. For the chemical limited process (753 K−913 K), Arrhenius equation for the deposition rate as a function of the deposition temperature yielded an effective activation energy E_a of 51.09 kJ/mol. XRD results showed that TiO_2 deposition in the temperature ranges 773 K to 973 K was only in anatase phase and that rutile appeared at 1073 K. With the increase of deposition temperature from 1073 K to 1273 K, the rutile content sharply increased from 7% to 70%. It was found that high source temperature (448 K) was beneficial to the dispersion of the supported TiO_2 especially in the process of the heterogeneous process (deposited at 773 K), and the particles were mainly 10 to 20 nm. The structure and texture of the support were maintained well after MOCVD process, especially when the TiO_2 particles were finely dispersed.

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