



Preparation of Fe₂O₃-TiO₂ and its Photocatalytic Reduction of CO₂ to Methanol

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Fe₂O₃-TiO₂ nanoparticles were synthesized by sol-gel method and characterized by XRD, FTIR and UV-visible. The effect of the calcination temperature, the Fe₂O₃ composite light for the photocatalytic reduction of CO₂ to methanol was studied. Results showed that low recombination of Fe₂O₃ promote anatase type into rutile type and the high amount of composite inhibited the anatase type into rutile type. When the composite mass fraction of Fe₂O₃ was 1 %, the catalyst was calcined at 600 °C, catalyst dosage was 2.0 g/L, the flow rate of CO₂ was 200 mL/min, and the reaction time was 7 h, the reaction temperature was 90 °C, the reaction solution concentration of NaOH and Na₂SO₃ were 0.10 mol/L, the yield of methanol was as high as 319.42 μ mol/g. And exploring the mechanism of Fe₂O₃-TiO₂ catalyst photocatalytic reduction of CO₂.

Keywords: LaFeO₃-TiO₂, Photocatalysis, Reduction of carbon dioxide, Methanol.

INTRODUCTION

Extensive use of fossil fuels has led to widespread air rising levels of CO₂ gas which in turn aggravates the greenhouse effect, and attracted worldwide attention. At present, the resusing technology of CO₂ fixation is high cost, low yield, time-consuming, so it can not independently take up the task of handling CO₂¹⁻⁵. But making use of light catalyst for the photocatalytic reduction of CO₂ is considered the most promising method in solving the problem of greenhouse gas. In recent years, excellent optical properties of TiO₂ is widely used as a photocatalyst. Tan *et al.*⁶ showed that under UV irradiation, photocatalytic reduction of CO₂ to methane by TiO₂ happens, the conversion rate reached 200 parts per million. However, TiO₂ is a kind of wide energy gap with the ultraviolet part of the semiconductor and can only absorb sunlight, which limits the photocatalytic activity. The band gap of Fe₂O₃ is 2.2 eV, can absorb visible light. But the life of its light inspired photo-production electron hole is short and often has light corrosion, so the activity is limited. In view of this, the experiment tried to make two kinds of composite photocatalyst for the new efficient photocatalyst. Yang⁷ used TiCl₄ solutions and Fe(NO₃)₃ solution as raw material and ammonia water as precipitator, then made use of supercritical fluid drying method to prepare Fe₂O₃-TiO₂ composite powder. The research showed that its photocatalytic activity was superior to single phase of TiO₂ powders. But Yang *et al.*⁸ used FeCl₃ and TiOSO₄ as raw materials, made use of coprecipitation method to prepare Fe₂O₃-

TiO₂ composite powder. The result showed that the photocatalytic performance was inhibited. As a result, experiments used sol-gel method to prepare Fe³⁺ doped TiO₂ composite powders, studied the Fe³⁺ doping on structure and catalytic properties of powders. Then by photocatalytic reduction of CO₂ to characterize photocatalytic performance of the composite photocatalyst.

EXPERIMENTAL

All reagents were of analytical and were purchased from Shanghai Chemical Reagent Co., butyl titanate, ferric nitrate [Fe(NO₃)₃·9H₂O], glacial acetic acid, anhydrous ethanol, toluene, *etc.* deionized water for laboratory homemade.

Electronic precision balance (JA3003); Muffle furnace (KAJO6316); Magnetic stirrer; Thermostat drying oven (DZF-200); infrared spectrometer (VECTOR33); Uv-visible diffuse analyzer (SP - 1700); X-ray diffraction (XD-3); GC-MS (QP-5050A); homemade photocatalytic reactor.

Preparation of photocatalyst: Using sol-gel method to prepare Fe₂O₃-TiO₂, a certain amount of ferric nitrate was dissolved into deionized water, then added 5 mL of glacial acetic acid and 10 mL of ethanol in it to obtain liquid A. Measuring 17 mL of butyl titanate (C₁₆H₃₆O₄Ti) and dissolving it in anhydrous ethanol to get liquid B. Under vigorous stirring solution, A was dropwised in B, then stirring it for 5-10 min, making its aging, then placing it in the driving oven. At last, it was grinded and calcined in a muffle furnace for 6 h. Fe:Ti (mole ratio) were of 0.5, 1, 2 and 1 %, calcination temperatures

were 500, 600 and 700 °C, respectively. Then getting different amount of composite and different calcination temperature of catalyst.

Photocatalytic reduction of CO₂: A certain quality of the catalyst and Na₂SO₃, NaOH which were of 200 mL, 0.10 mol/L aqueous were added to the homemade annular reactor, stirring until frothy. Then a flow rate of CO₂ would pass into it. After 0.5 h, opening source (250 W mercury lamp of UV high pressure), and passing the cooling water into the jacket. After the reaction, the supernatant was centrifuged and extracted with toluene, then the yield of methanol was analyzed by GC-MS.

RESULTS AND DISCUSSION

FT-IR analysis: Fig. 1 shows the FT-IR results of the Fe₂O₃-TiO₂. According to the literature⁹, in a position near 3402 cm⁻¹ has a strong absorption, associating the molecule hydroxyl stretching vibration of O-H. The absorption peak near 1640 cm⁻¹ is bending vibration of absorbing moisture, the absorption peak near 1350 cm⁻¹ is stretching and bending vibration of C-H. The absorption peak near 1155 cm⁻¹ is stretching vibration of alcohol molecules' C-O-H. In addition, Ti-O bond vibrational peaks should be roughly at 800-450 cm⁻¹. Sharp peaks at 1087 cm⁻¹ can be O-Fe bond, who change the Ti-O-Ti structure. When it becomes Ti-O-Fe, defects appear in the crystal structure. Thus, TiO₂ and Fe₂O₃ co-occur with keys and generated Fe₂O₃-TiO₂ composite.

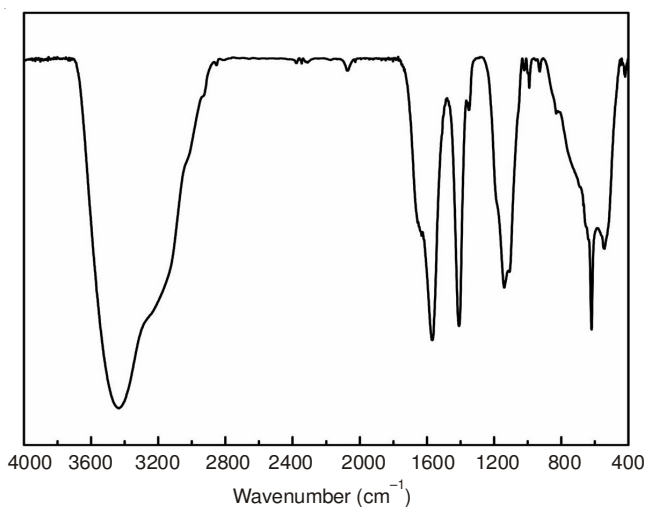


Fig.1. FT-IR of the Fe₂O₃-TiO₂ catalyst

DRS analysis: Fig. 2 is UV absorption spectra of pure TiO₂ and Fe₂O₃-TiO₂ composites which were calcinated at 600 °C and Fe₂O₃ composites were of 1 and 5 %. As can be seen from the figure, compared with the pure TiO₂, composite catalyst's spectral response range is broaden, leading to absorb the visible light better. Also, there are two absorption band edge, which can improve the activity of photocatalyst. TiO₂ is a wide band gap semiconductor and its bandgap energy is 3.2 eV. So its light use efficiency is relatively low and usually need ultraviolet light to excite electrons. However, the energy gap of Fe₂O₃ is 2.2 eV, adding the Fe₂O₃ can make the band crisscross, and effectively broaden the scope of absorbance, so as to better make use of light energy. Because of the significant

quantum size effect, the absorption band edge of Fe₂O₃-TiO₂ red shift significantly and for less than 300 nm uv absorption increases. Results show that the Fe₂O₃ and TiO₂ composite materials change electronic band structure, improve the optical response performance of the materials.

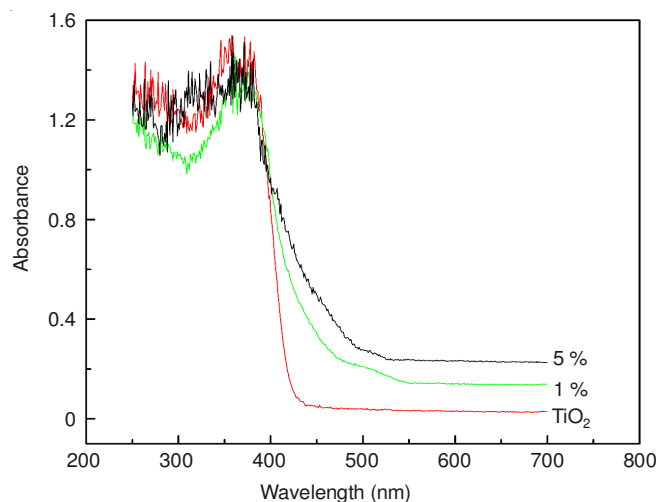
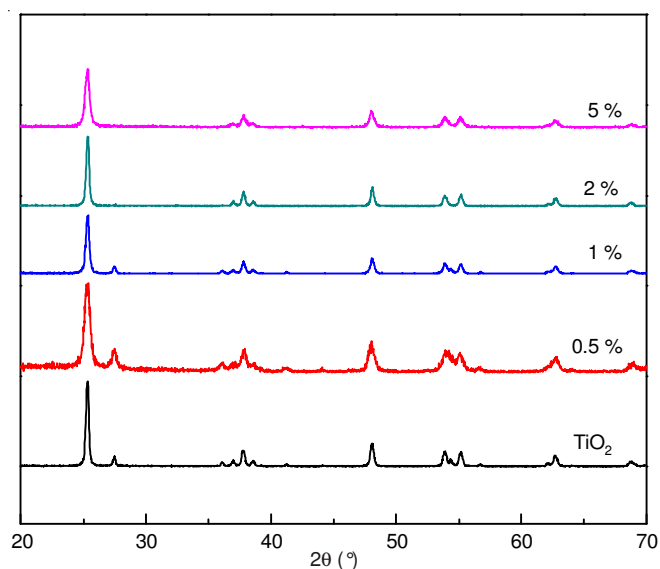


Fig. 2. UV absorption spectra of pure TiO₂ and Fe₂O₃-TiO₂ catalysts

X-ray diffraction analysis: Fig. 3 shows the XRD spectra of pure TiO₂ and Fe₂O₃-TiO₂ with different amount of composition, they are all calcined at 600 °C. The pure TiO₂ calcined at 600 °C is in anatase phase, which is the main body. However, the diffraction peak intensity of the 0.5 % iron compound of the rutile phase TiO₂ is greater than the pure TiO₂. Because of the introduction of Fe₂O₃ promote anatase phase's transition to rutile phase. The 0.64 Å ionic radius of Fe³⁺ can easily enter the lattice of TiO₂ and instead of Ti⁴⁺ (0.68Å) and through increasing crystal oxygen vacancy to reduce the strain energy of anatase to rutile. However, the diffraction peak intensity of rutile is weakened with the increase of Fe₂O₃ concentration, when the composite volume reaches 2 %, the diffraction peak almost disappear. Because the introduction of Fe³⁺ promotes the contact between the TiO₂ particles and hinders the transport of Ti⁴⁺ and O²⁻ between particles and rearrangement. But the anatase's phase turning into rutile phase must go through Ti-O bond cleavage and Ti⁴⁺ bond rearrangement, so big amount of composite could suppress anatase phase getting rutile phase^{10,11}. This suggests that the low composite amount of Fe₂O₃ promotes anatase phase getting rutile phase and the high amount of composite inhibits the anatase phase getting rutile phase.

Fe₂O₃-TiO₂ catalyst's photocatalytic reduction of CO₂: Figs. 4 and 5 shows that photocatalytic performance of the composite calcined at different temperatures and different amount of Fe₂O₃-TiO₂ produce effects similar to La₂O₃-TiO₂, first increased and then decreased. When the calcination temperature is 600 °C, the composite volume is 1 %, the yield of methanol is highest. Because Fe³⁺ as be the photo-generated electron-hole shallow potential capture trap, reducing the recombination probability of electrons and holes. With composite increased, Fe³⁺ becomes recombination center of electrons and holes, the photocatalytic activity is reduced or even disappear. Meanwhile, the energy gap of Fe₂O₃ is smaller than

Fig.3. XRD spectra of pure TiO₂ and Fe₂O₃-TiO₂ catalyst

that of TiO₂, so the wavelength of light absorption is higher. So, after the formation of the three-phase heterojunction structure, photo-generated electrons transfer easily from the surface of TiO₂ to the surface of Fe₂O₃, reducing the surface electron density of TiO₂, namely reducing the photo-generated electron-hole recombination rate, so as to improve the photocatalytic activity of Fe₂O₃-TiO₂. Therefore, under the condition of 1 % compound and 600 °C calcinated, catalyst can not only guarantee the anatase phase accounts for large proportion and can achieve the effect of mixed crystal, so it has best catalytic activity.

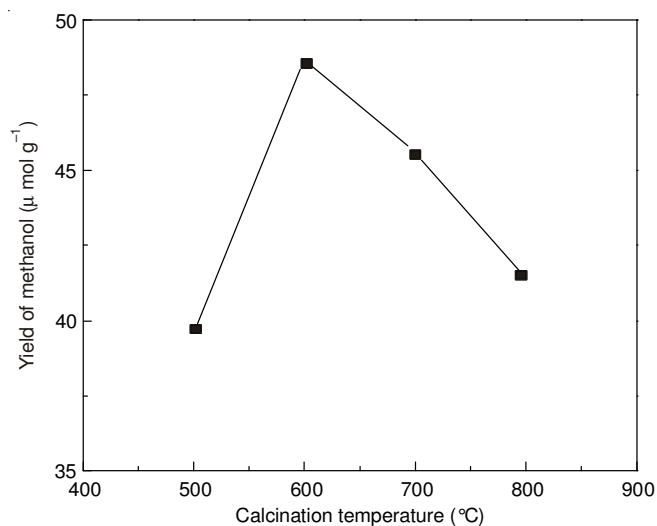
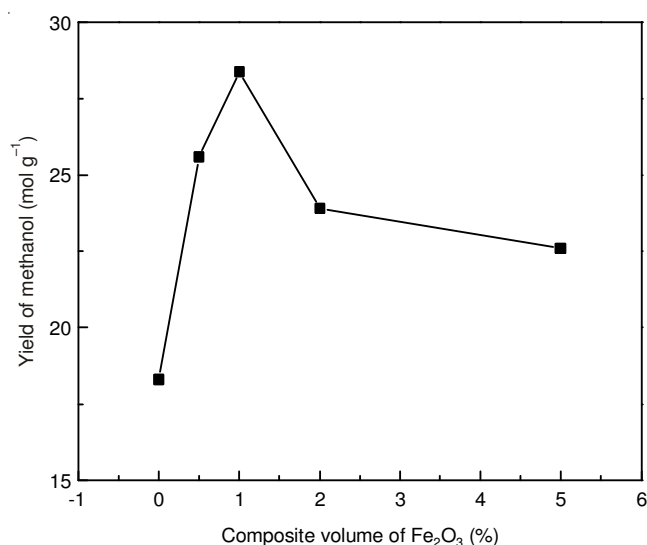
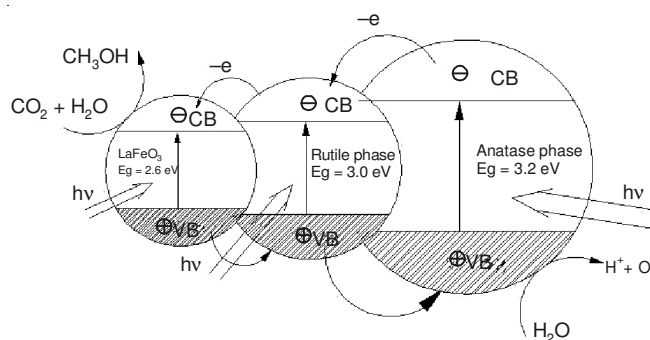


Fig. 4. Calcination temperature on the yield of methanol

Mechanism: When the Fe₂O₃-TiO₂ composite catalyst is in UV irradiation, the electronic of anatase TiO₂ valence band will take transition to the conduction band, then transfer to rutile phase or conduction band of Fe₂O₃. And the electron of rutile TiO₂ conduction band will continue to transfer to the conduction band to Fe₂O₃, it effectively increases the efficiency of electron-hole separation. At the same time, under visible light irradiation, photo-generated electron excitations of the

Fig. 5. Composite volume of Fe₂O₃ on the yield of methanol

TiO₂ rutile phase will also be transferred to the conduction band of Fe₂O₃, thus effectively prevent photo-carrier recombination. Fe₂O₃ can absorb more visible light, and produce photo-generated electron-hole, which can further increase the generated carriers number of the sample under visible light. Also three phases have high crystallinity, which is conducive to the charge transport, and provide the conditions for the separation of the electron-hole [12]. Thus the composite catalyst formed by heterogeneous structure of anatase, rutile phase of TiO₂ and Fe₂O₃ phase has wide scope response high peak, and can be effective implementation of the photocatalytic reduction of CO₂. The reaction mechanism is shown in Fig. 6.

Fig. 6. Mechanism of Fe₂O₃-TiO₂ catalyst's photocatalytic reduction of CO₂

Conclusion

Using sol-gel method to prepare Fe₂O₃-TiO₂ nano composite catalyst with butyl titanate, ferric nitrate be raw materials. The composite of the catalyst effectively inhibited the phase transformation of TiO₂ and made the catalyst form TiO₂ anatase, rutile and Fe₂O₃ three-phase heterojunction structure.

The absorption band of the added to Fe₂O₃ composite materials red shift, resulting the emergence of two absorption band, broadening the range of the light response. Fe₂O₃-TiO₂ composite catalyst enhanced the absorption of ultraviolet light and at the same time could be capable of absorbing a visible light, make full use of light source, improve the performance of the photocatalytic reduction of CO₂.

When the composite mass fraction of Fe₂O₃ was 1 %, the catalyst was calcined at 600 °C, catalyst dosage was 2 g/L, the flow rate of CO₂ was 200 mL/min, and the reaction time was 7 h, the reaction temperature was 90 °C, the reaction solution concentration of NaOH and Na₂SO₃ were 0.10 mol/L, the yield of methanol was as high as 319.42 μmol/g.

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