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CO_2 conversion into valuable fuels using chromium based supports

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Abstract

CO_2 utilization by direct catalytic conversion of CO_2 driven by solar energy is an attractive approach for producing alternative value added products suitable for end-use infrastructure. In order to fully harness the solar spectrum and increase photocatalytic activity and selectivity, Cr-TiO_2 based films were deposited on ceramic honeycomb monoliths with varying concentrations synthesized by sol-gel technique and dip coating route. The improved photocatalytic activity of the Cr-TiO_2 monoliths in the visible light region compared to pure TiO_2 can be attributed to increased visible light absorption and accessible active metal sites arising from the appropriate metal dispersion and loading amount.

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Keywords: CO_2 utlization; Photocatalysis ; Chromium; Monolith, Optical Fiber; Titanium dioxide

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1. Introduction

The need to meet global energy demand predicted to increase due to a rising global population has led to the development of different strategies by which alternative fuels can be produced from increasing CO_2 emissions. At present, utilization of CO_2 accounts for only approximately 2% of emissions and forecasts predict 700 megatons of CO_2/year could be mitigated [1]. Since CO_2 is a thermodynamically stable compound, its reduction must not consume additional energy or increase net CO_2 emissions. Renewable sources like solar energy provide readily available and continuous light supply required for driving this conversion process. Therefore, the use of solar energy to drive CO_2 photocatalytic reactions simultaneously addresses the aforementioned challenges, while producing sustainable fuels or chemicals suitable for use in existing energy infrastructure. CO_2 photocatalysis offers the

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possibility of utilizing captured CO_2 to synthesize energy rich and chemically useful products with the aid of semiconductor catalyst(s) under light irradiation and ambient conditions. Pure titanium dioxide (TiO_2) has been frequently used for UV induced photocatalysis due to its abundance, low cost and chemical stability. Conversely, its use for visible light induced photocatalysis is limited due to its large band gap; as it can only be activated by ultraviolet (UV) light which represents 2-5% of sunlight. In order to fully harness the solar spectrum and increase photocatalytic activity and selectivity, several studies have been conducted to modify the physicochemical properties of TiO_2 via the introduction of transitional metal ions [2-4]. When these metals replace Ti atoms in the substitutional sites, occupy the interstitial sites, or form aggregates on the surface of TiO_2, they can cause changes in the properties of TiO_2, where the band structures and properties of TiO_2 have been reported to be tailored by this process. These metals also serve as a source of charge-carrier traps which can increase the life span of separated electron hole pairs, and thus enhancing the efficiency and product selectivity for CO_2 photoreduction [2-3]. The textural properties and photoconversion efficiency can also be improved by anchoring photocatalysts onto supports. The deposition of TiO_2 based films on supports eliminates the need for post treatment separation, provides high surface area and mass transfer rate [3]. The use of interconnected three-dimensional structures like the honeycomb monolith containing parallel straight channels has been exploited for industrial processes due to its potentially high surface to volume ratio, easy of scale-up through an increase of its dimensions and channels, control of structural parameters (i.e. pore volume, pore size and surface area) etc. [4-5]. Photocatalytic studies conducted using the monolith as a support has identified low light utilization efficiency due to poor light distribution in the pores or channels of the honeycomb monolith as a major drawback associated with its use [6-9]. This drawback can be mitigated by threading the monolithic structures with optical fibers to eliminate limited light penetration through the internal channels of the monolith by acting as a light distributing guide. Doping of metal ions especially Cr in the lattice of TiO_2 can cause enhanced bathochromic shift from the UV region to longer wavelengths in the visible light region, and thus, improving its band width via the introduction of additional energy levels within the band gap of TiO_2 [10]. However, the influence of Cr doping on the performance of TiO_2 for photocatalytic reduction of CO_2 using monolithic structures has not been exploited. Until now, it remains unclear how the use of supports such as the ceramic honeycomb monoliths threaded with optical fibers influences the performance of Cr-TiO_2 for CO_2 reduction to fuels. Accordingly, the objective of this work is to understand the effect of these metal loaded photocatalysts on supports for CO_2 reduction. To gain this understanding, a series of single doped Cr-TiO_2 based monoliths synthesized by the improved sol-gel technique and dip coating method were tested in the internally illuminated monolith photoreactor system.

2. Experimental

2.1. Sol-gel synthesis and dip coating of pure TiO_2 and Cr-TiO_2 based monoliths

Honeycomb ceramic monoliths with 177 channels were coated with SiO_2 sol and pure TiO_2 or Cr-TiO_2 sol with varying metal concentrations prepared by the controlled sol-gel method. SiO_2 sol was obtained from a mixture of ethanol (C_2H_5OH, Acros Organics), deionized water and tetraethyl orthosilicate ($Si(OC_2H_5)_4$, Acros Organics) in volume ratios of 2:1:2. The pH was adjusted to 2 using dilute hydrochloric acid (HCl, Fisher Scientific). After addition of polyethylene glycol (PEG, $(C_2H_4O)\ n.H_2O$, Acros Organics), the monoliths were submerged into SiO_2 sol for two repeated coating cycles of 30 minutes. The coated monoliths were then dried and calcined in a furnace at 973K for 3 hours. SiO_2 coated monoliths were then subsequently immersed in pure TiO_2 or Cr-TiO_2 sol prepared using n-butanol, acetic acid, titanium (IV) butoxide and fixed amount of chromium (III) nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$, Acros Organics) as precursors. The TiO_2/SiO_2 or Cr-TiO_2/SiO_2 coated monoliths were dried and calcined at 150 °C and 500 °C, respectively to burn off organic compounds and complete crystallization. Side glowing optical fibers were used as light distribution guides.

2.2. Characterization

The diffraction pattern of the Cr-TiO_2 based monoliths were determined by using the Hiltonbrooks X-ray powder diffractometer. Ultraviolet-visible spectroscopy (UV-Vis, Varian Cary 300) was used for the measurement of the band gap, threshold wavelength, and the absorbance of ultraviolet light as a function of the transmittance. The band gap energy (E_g) of the catalysts was estimated using the standard equation, which is based on the relationship between frequency (c/λ) and photon energy ($E_g = 1240/\lambda$). The morphology and elemental composition of the nanoparticles were evaluated by transmission electron microscopy (TEM, JEOL 2100F). Chemical and electronic states of the elements present in the catalysts were detected by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra). All binding energies were charge corrected to the internal standard of carbon (1s, 285 eV).

2.3. CO_2 photocatalytic reduction

Photocatalytic reduction of CO_2 in gaseous phase was evaluated in a cylindrical Pyrex glass reactor containing the catalyst-coated supports (honeycomb ceramic monoliths threaded with optical fibers) [8]. The monolith threaded with approximately 177 side glowing optical fibers was placed in a parallel manner such that light irradiated through the quartz window of the reactor could be transmitted along the internal channels of the monolith. Total influx (68.35mW/cm^2) of visible light measured at different positions of the assembled photoreactor was supplied by a halogen lamp (500 W). The reactor was purged with helium (He) gas to check for leakage and contamination prior to the continuous supply of CO_2 gas flow saturated with water vapor if no leak was detected. Extracted gas samples were identified and analyzed after 4 hours of visible light irradiation using the mass spectrometer (MS, Hiden Analytical) equipped with capillary, quadrupole mass analyzer (HAL 201-RC) and Faraday/Secondary electron multiplier (SEM) detectors.

3. Results and Discussion

3.1. Monolith characterization

All diffraction peaks for pure TiO_2 and Cr-TiO_2 based monoliths can be indexed to the tetragonal anatase phase TiO_2 which was confirmed by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) Card File No.21-1272. Chromium peaks in its metal or oxide phase were not observed even at the highest doping ratio of 2wt%, due to the high dispersion of chromium species in TiO_2 structure. A red shift and enhancement of the light absorption properties towards the visible light region was observed for all the Cr-TiO_2 based monoliths when compared with the spectrum of pure TiO_2 monolith (3.1eV). The optical properties of TiO_2 were tuned towards the visible light by the substitution of Ti^{4+} by Cr^{3+} ions. The incorporation of Cr ions in the TiO_2 matrix is responsible for the shift towards the visible light region due to the charge transfer transition from the 3d orbitals of Cr species to the TiO_2 conduction band. The tailings observed in the absorption band of Cr-TiO_2 samples have been reported to be assigned to Cr doping creating additional energy levels (Cr 2p level) and oxygen vacancies within the band gap of TiO_2 [11]. Absorption spectra of the resulting Cr-based TiO_2 photocatalysts showed increased shift in the visible light with increased Cr doping concentration. The band gap energies of the Cr-based catalysts were within the range of 2.12-2.94eV, with the largest red shift occurring for the 2wt% Cr-TiO_2 sample. The binding energies of the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ core levels at 576.5eV and 586.3eV are characteristic of chromium (III) oxide for all Cr-TiO_2 monoliths, respectively (Wagner *et al.* (2007)). This indicates that Cr species exist predominantly in the TiO_2 lattice sites in the form of Cr^{3+}. These values are consistent with the binding energies of Cr $2p_{3/2}$ measured for Cr doped TiO_2 [11-12].

3.2. CO_2 photocatalytic reduction

The photocatalytic activities of Cr-based catalysts coated on the monolith threaded with optical fibers were evaluated for CO_2 photoreduction after 4 hours of visible light irradiation. As shown in Figure 1, the product rates of methanol and hydrogen steadily increase with higher metal concentration to give an optimal ratio of 1wt%Cr-TiO_2. The production rate of methanol and hydrogen over the 0.1wt%Cr-TiO_2 monolith was lower when the monolith was used as a sole support without optical fibers compared to the sample where the optical fibers were threaded in the channels of the monolith. When the monolith is used as a sole support, not all immobilized photocatalyst may be activated due to limited light distribution arising from the catalyst coated on the outer surface absorbing most of the light and light intensity decaying rapidly along the opaque channels of the monolith. Doping of Cr improves the photocatalytic activity due to the dopant facilitating the light absorption of TiO_2 towards the visible light region. All the Cr-TiO_2 photocatalysts show improved product rates when compared to pure TiO_2 where no product formation was observed. The improved photocatalytic activity of the Cr-TiO_2 monoliths in the visible light region compared to pure TiO_2 can be attributed to increased visible light absorption and accessible active metal sites arising from the appropriate metal dispersion and loading amount. Decreased product rates were also observed for the subsequent higher doping ratios under visible light. This result could be due to the coverage of the surface of TiO_2 with increased metal ions which inhibited interfacial charge transfer due to insufficient amount of light energy available for activation of all the catalyst particles [9].

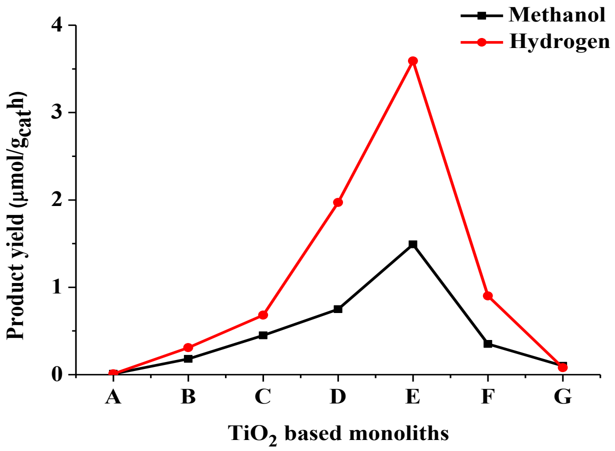

Fig. 1. Effect of Cr doping on TiO_2 based monoliths threaded with optical fibers for CO_2 photocatalytic reduction under visible light irradiation. ((A) TiO_2, (B) 0.1wt% Cr-TiO_2 with no optical fibers, (C) 0.1wt% Cr-TiO_2, (D) 0.5wt% Cr-TiO_2, (E) 1wt% Cr-TiO_2, (F) 1.5wt% Cr-TiO_2 and (G) 2wt% Cr-TiO_2; C-G were tested with optical fibers)

4. Conclusions

Sol gel derived Cr-TiO_2 immobilized onto monolithic structures threaded with optical fibers were studied under visible light irradiation. The photocatalytic activities of Cr-TiO_2 based monoliths with various doping concentrations were evaluated for CO_2 reduction after 4 hours of visible light irradiation. The optical properties of TiO_2 were tuned towards the visible light with increased Cr concentration when compared to pure TiO_2. The incorporation of Cr ions in the crystal lattice of TiO_2 improved the photocatalytic activity in the visible light with optimal doping concentrations of 1wt% when compared to pure TiO_2. Conversely, high Cr concentration was detrimental to visible light photocatalytic activity due to the Cr species acting as multiple trap sites and thus facilitating electron-hole recombination.

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