PHOTOCATALYTIC REDUCTION OF CO_2 TO METHANE

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Abstract
Photocatalytic reduction of carbon dioxide (CO_2) is a sustainable energy technology not only for emission control but also for the production of alternative fuels. In the present study Ti-mesoporous silica materials have been synthesized both with dried and calcined KIT-6, SBA-15-spherical silica at different Si/Ti ratios (200, 100, 50) and were characterized by BET and SEM analyses. The photocatalytic reduction experiments were conducted in an ad hoc designed Pyrex glass continuous flow reactor using CO_2 and water vapours as reactants in the presence of UV light to produce methane (CH_4) as the main desired product. Overall, Ti-KIT-6 (calcined) materials were superior in activity than Ti-KIT-6 (dried) materials. However, an opposite trend than Ti-KIT-6 was observed in the Ti-SBA-15-spherical, where Ti-SBA-15-spherical (dried) showed better methane production than Ti-SBA-15-spherical (calcined). It was found that the methane production was mainly dependent on the superior physical properties, structure connectivity and morphology of the KIT-6 and SBA-15-spherical mesoporous materials which provide better access to adsorb CO_2 and water to react. Ti-mesoporous molecular sieves exhibit high photocatalytic reactivity for the formation of CH_4, its reactivity being much higher than the commercial Degussa P25 powder titania photocatalyst. Moreover, Si/Ti ratio of 100 showed the highest methane production rate than Si/Ti ratios of 200 or 50, which indicates the importance of the specific Ti layer or dispersion on the respective mesoporous material.

Introduction

Global warming is a key challenge for the world which is mainly due to increasing level of greenhouse gases in the atmosphere. Carbon dioxide (CO_2) is the major contributor of this fact which arrives mainly from fossil fuel combustion [1]. Pre- or post-combustion CO_2 capture followed by compression and geological sequestration is one of those efforts made to reduce CO_2 emissions, but is energy intensive, hence costly. Therefore, preferable way to reduce CO_2 is to recycle it as a fuel feedstock with energy input from cheap and abundant sources (e.g. solar energy) [2].

Recently, photocatalysis technology to convert CO_2 into fuel has attracted the attention of many researchers and has become a promising application. It simply

uses ultraviolet (UV) and/or visible light as the excitation source for semiconductor catalysts, and the photoexcited electrons reduce CO_2 with H_2O on the catalyst surface and form energy-bearing products such as carbon monoxide (CO), methane (CH_4), methanol (CH_3OH), formaldehyde (HCHO), and formic acid (HCOOH) [3]. Photocatalysts such as TiO_2, CdS, ZrO_2, ZnO, and MgO have been investigated, and among them, wide band-gap TiO_2 catalysts (~3.2 eV) are considered the most convenient candidates in terms of cost and stability [3]. However, the design of highly efficient and selective photocatalytic systems for the reduction of CO_2 with H_2O is of vital interest [4]. It has been studied that the highly dispersed titanium oxide (Ti-oxide) catalyst anchored on porous Vycor glass, zeolites and some mesoporous silica materials exhibited a high and characteristic photocatalytic reactivity compared to bulk TiO_2 powder [5].
Therefore, in the present work, attention has been focused to prepare highly dispersed Ti-mesoporous silica materials within the novel KIT-6 and SBA-15-spherical for this application, with attractive physical properties, cavities and frameworks, in hydrothermal synthesis and utilized as photocatalysts in the photocatalytic reduction of CO_2 with H_2O to form CH_4. The results are also compared with the commercial Degussa P25 powder titania.

Experimental

KIT-6 mesoporous silica material was synthesized according to the procedure presented in [6,7]. The solid product obtained after the hydrothermal treatment was filtered, dried and/or calcined at 550 °C for 5 h so that it could be utilized further to prepare Ti-KIT-6 (dried or calcined).
SBA-15-spherical was obtained according to the procedure reported in [7,8]. The resultant precipitate was filtered, washed, dried and/or calcined at 550 °C for 5 h so that it could be utilized further to prepare Ti-SBA-15-spherical (dried or calcined).
The dried and calcined KIT-6, SBA-15-spherical were then treated with Titanium(IV) isopropoxide (98 %) at different Si/Ti ratios (200, 100, 50) followed by calcination to get Ti-mesoporous materials by following the proper procedure reported recently [9].
All the CO_2 photocatalytic reduction tests were performed in a Pyrex glass reactor. The procedure adheres to Italian regulations concerning the testing of photocatalysts, UNI 11247 [10]. The set-up shown in Fig. 1, includes a Pyrex glass reactor (transparent to UV light), connectors, mass flow controllers (Bronkhorst high tech), water bubbler, and a UV lamp (Osram ULTRA-VITALUX 300 W). This lamp emits a UVA mixture, ranging from 320 to 400 nm and UVB with 290-320 nm wavelengths, and it produces 13.6 and 3.0 W radiation, respectively; it is ozone-free and radiation is produced by a quartz burner and a tungsten wire filament, according to the manufacturer's specifications. The set-up also exploits CO_2 gas cylinder, a gas chromatograph (Varian CP-3800) equipped with a capillary column (CP7381) and a flame ionization detector (FID) with a patented ceramic flame tip for ultimate peak shape and sensitivity, which was used for the gas

analysis of the products. The reaction experiments were repeated twice and the results showed reproducibility with an error below 5 %.

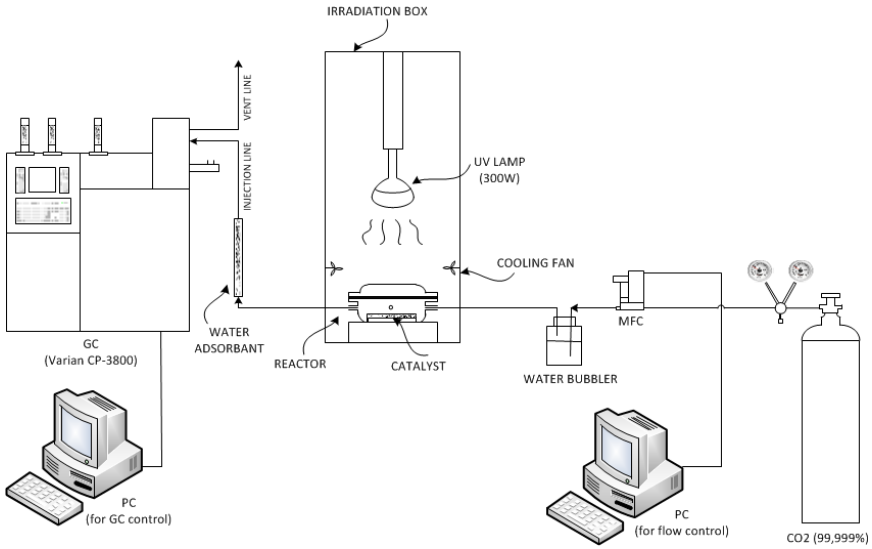

Figure 1. CO_2 photocatalytic reduction experimental set up.

Results and discussion

The physical and textural properties obtained by N_2 sorption of the mesoporous silica and Ti-mesoporous silica are shown in Table 1. Calcined KIT-6 and SBA-15-spherical have shown different and large surface areas, pore volumes and average pore diameters on the basis of their characteristics. However, a noticeable decrease was observed in the surface area and pore volume of the KIT-6 after Ti incorporation with different Si/Ti ratios both in dried and calcined samples. However, the average pore diameter was not changed significantly and remained uniform which might be due to 3-D pore structure of KIT-6 that managed to accommodate the Ti dispersion.

Moreover, unlike the Ti-KIT-6 case, in Ti-SBA-15-sperical, showed not only a decrease in surface area and pore volume but also in APD. However, dried samples showed comparatively less decrease in the physical properties which means Ti was easily accommodated by dried SBA-15-sperical and dispersed in the dried structure compared to the calcined rigid one-dimensional network.

Similar decreasing trend in the adsorption/desorption isotherms has also been noticed (not shown here) as was in the surface area, pore volume and average pore diameter. The scanning electron microscopy (SEM) results (not shown here) also confirmed the change in morphology of the mesoporous materials, especially in the Ti-SBA-15-sperical (calcined) samples, which showed bimodal morphology with grown particles. However, in case of Ti-KIT-6 the morphology before and after the

Table 1. Physical properties of Ti-KIT-6 and Ti-Spherical SBA-15 materials synthesized.

Samples	S_{BET}	PV	APD
[Ti-K-6(Dried) (Si/Ti=200)] Calcined	865	1.11	6.55
[Ti-K-6(Dried) (Si/Ti=100)] Calcined	767	0.80	6.48
[Ti-K-6(Dried) (Si/Ti=50)] Calcined	730	0.67	6.45
KIT-6(K-6) Calcined	772	1.04	6.49
[Ti-K-6(Calcined) (Si/Ti=200)] Calcined	726	0.95	6.45
[Ti-K-6(Calcined) (Si/Ti=100)] Calcined	700	0.85	6.40
[Ti-K-6(Calcined) (Si/Ti=50)] Calcined	684	0.73	6.41
[Ti-S-15(Dried) (Si/Ti=200)] Calcined	794	2.06	9.0
[Ti-S-15(Dried) (Si/Ti=100)] Calcined	776	1.90	8.8
[Ti-S-15(Dried) (Si/Ti=50)] Calcined	731	1.52	7.1
Spherical SBA-15(S-15) Calcined	638	1.62	10.1
[Ti-S-15(Calcined) (Si/Ti=200)] Calcined	591	1.36	7.3
[Ti-S-15(Calcined)(Si/Ti=100)] Calcined	481	1.17	6.1
[Ti-S-15(Calcined)(Si/Ti=50)] Calcined	403	1.15	5.9

S_{BET} (BET specific surface area in m^2/g); PV (cumulative pore volume in cm^3/g); APD (average pore diameter in nm)

Ti incorporation in all the samples was uniform. These results are also consistent with the BET results.

Hydrothermally synthesized Ti-containing zeolites (TS-1, Ti–Beta) and mesoporous molecular sieves (Ti–MCM, Ti–HMS, Ti–FSM) have been subjected to the photocatalytic reduction of CO_2 with H_2O [11]. Fig. 2(a) shows production rate of the CH_4 formation which is originated from the unique properties of the charge transfer excited state, i.e., $(Ti^{3+}–O^{-})^*$ of the tetrahedrally-coordinated titanium oxide species within the silica frameworks. It can be seen that Ti-KIT-6 (calcined or dried)(Si/Ti=100) shows the highest activity in its category which is due to the combined contribution of the high dispersion state of the Ti–oxide species and the large pore size with a 3-dimensional channel structure. Similarly, Ti-SBA-15(dried)(Si/Ti=100) which has very large pore size but one-dimensional pore structure, also presents the highest CH_4 formation. These results also show that the above mentioned optimized photocatalysts gave superior activity than the commercial Degussa P25 as shown in Fig.2. Moreover, the results are comparable with literature reported for TiO_2 as photocatalyst [12] or Ti-zeolites as well as Ti-MCM-41 [11,13] for this application.

Higher activity of Ti-oxide species prepared within the ordered silica frame works was revealed by Ti-dispersion [11]. Fig. 2(a) and (b) show that at different Si/Ti ratios (200, 100, 50), the Ti-dispersion is always expected to be different, finally

leading to different Ti-layers. The optimum Ti-layer (layer 2 at Si/Ti=100) showed the highest CH_4 production rate.

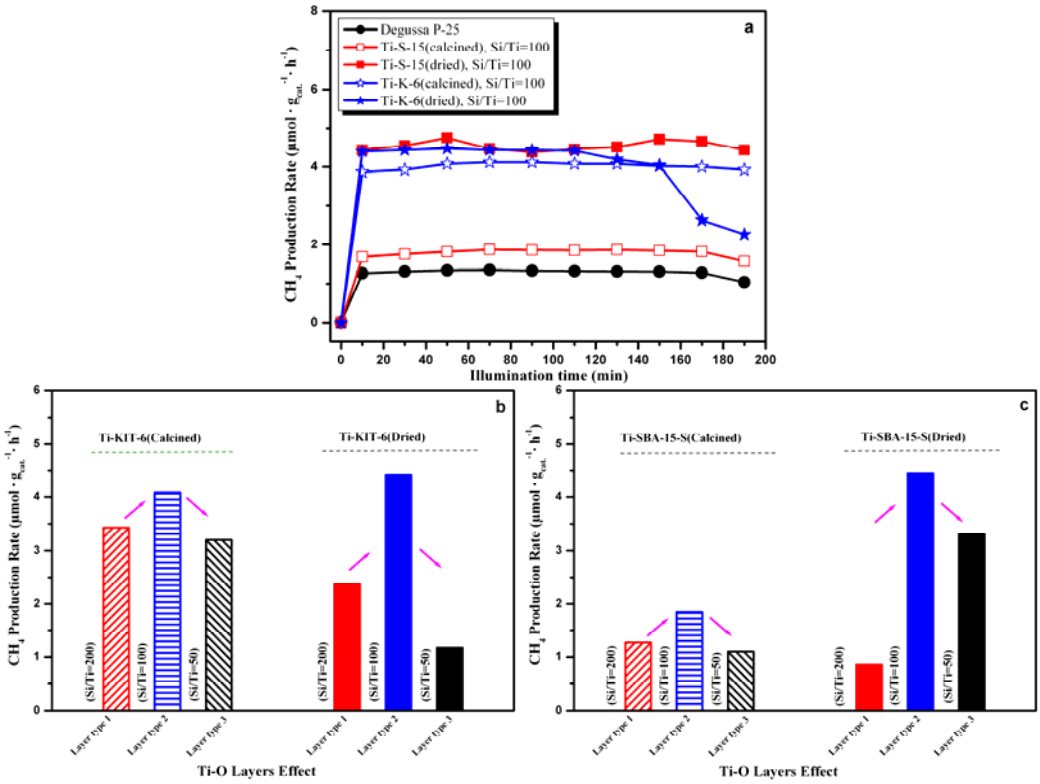

Figure 2. Activity results for CO_2 photocatalytic reduction at 40 °C: (a) methane production comparison by optimized photocatalyst from each category, (b) effect of Ti-layers on methane production in Ti-KIT-6, and (c) effect of Ti-layers in Ti-SBA-15-spherical photocatalysts after 2 h of reaction time.

Conclusions

Ti-mesoporous silica (KIT-6, SBA-15-S) with different Si/Ti ratios (200, 100, 50) synthesized revealed that Ti-KIT-6(both dried or calcined) as well as Ti-SBA-15-S(dried only) at Si/Ti=100 followed by calcination showed the maximum CH_4 formation than at other conditions, which are also much higher than commercial Degussa P25 powder titania. It is due to superior physical properties of these mesoporous materials as well good dispersion of Ti-species. The results suggest that these novel mesoporous molecular sieves (KIT-6, SBA-15-S) containing highly dispersed Ti–oxide species are promising candidates as effective photocatalysts for reduction of CO_2 to CH_4 and indicate their suitability to be further optimized in future research.

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