Photochemical Conversion of CO_2 into Methyl Alcohol Using SiC Micropowder under UV Light

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In our study, microparticles SiC powder was investigated as a catalyst for CO_2 photoreduction into methanol under UV light. The photochemical conversion of methanol was studied as function of time of exposition, the concentration and the grain size of the catalyst. The selectivity of the used catalyst to promote methanol formation was noticed. It was noticed also that the grain size and concentration have a great impact on the photochemical conversion of CO_2 to methanol. The best yield of methanol was achieved when a concentration of 0.75 M of SiC powder of 17 μm grain size and an exposure time to UV light of 2 h where assured. Maximum molar concentration of methanol achieved was under UV irradiation of 365 nm. Therefore, the catalytic property of silicon carbide has proved its efficiency in the photochemical conversion of CO_2 into alcohol thus far under UV light.

1. Introduction

To overcome the environmental problems related to greenhouse gas emissions and to fulfill the energy needs of future generations, research efforts are underway to develop sustainable and renewable energy sources, which are environmentally friendly [1]. CO_2 gas is one of the major contributors to the greenhouse effect and thus one of the primary causes of global warming. Therefore, the transformation of CO_2 into high valued products like methanol, hydrogen, and methane will be highly beneficial to the environment and the global climatic change [2, 3]. As an ideal green technology, photoreduction process which has been widely studied to purify water and air, has been adopted in the research field of CO_2 conversion [4, 5]. Most of previous work on the reduction of CO_2 by adapting photochemical process has been carried out using various catalysts semiconductors such as TiO_2 [6–8], WO_3 [9] or NiO [10]. The SiC is an indirect band gap semiconductor catalyst having a band gap energy ranging between 2.3 and 3.3 eV, depending on the various polytypes that exist. The band gap energy of 3C-SiC (β-SiC) is 2.35 eV and that of 4H-SiC (α-SiC) and 6H-SiC (α-SiC) are respectively 3.28 and 3.08 eV [11]. The α-SiC is the most commonly encountered polymorph; it is formed at temperatures greater than 1700 °C and has a hexagonal crystal structure (similar to wurtzite). The unique physical properties of SiC, associated to chemical inertness and high temperature stability, allow the superior performance of SiC devices in harsh environments such as required in catalytic applications. As a catalyst support, SiC has great applications in several important chemical reactions such as isomerization of linear saturated hydrocarbons, selective oxidation of hydrogen sulfide into elemental sulfur and photochemical reaction [12, 13].

The ultimate goal of this research is to use SiC microparticles for mass production of methanol from CO_2 transformation. Methanol is the most desired photoreduced product from CO_2, as it can be used as fuel directly. In this work, SiC microparticles powder was applied as a catalyst in the photoreduction of CO_2 into methanol in the presence of monochromatic UV irradiation. The relative merit of the different parameters such as catalyst dosage and irradiation duration in the production yield was investigated.

2. Experimental part

In order to investigate the effect of particle size and morphology on the photoreduction process of CO_2, two kinds of SiC powders were used in this study. SiC micropowder with the grain size of 7 and 17 μm size granules were used without any further processing. The CO_2 gas employed in the experiences was obtained by craftsmen from a yeast/liquid sugar mixture. Distilled water of very high purity was obtained from our plant. The photochemical reactions were performed in a glass reactor kept on a magnetic stirrer that constantly replenishes the catalyst in the path of radiation. Care has been taken not to let the water level to go very much higher than

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the level of the catalyst platform in order to have better interaction of radiation with the photocatalyst. A UV-LED lamp was used as illuminant. The UV-LED lamp was monochromatic with wavelength of 365 nm. Firstly, 100 ml distilled water was put into the glass reactor. Then, 0.075 mol of catalyst powder was added into above solution, then was tightly closed and checked for leaks up to 3 atm pressure. Before irradiation, ultrapure CO_2 was bubbled through the solution in the reactor for at least 24 h to ensure that all dissolved oxygen was eliminated and the irradiation lamp was turned on to start the photoreaction. The CO_2 gas was continuously bubbled through the above solution in the reactor during the whole irradiation. The irradiation time was 3 h. After a predetermined irradiation time, water samples were withdrawn from the reactor using syringe at 1, 2, 2.5, and 3 h, respectively, without opening the reactor and were subjected to FTIR analysis.

Ultrapure water is obtained from a Millipore Alpha-Q water purification system (18.2 MΩ; Millipore Corporation, USA). Morphology analysis was carried out with a scanning electron microscope (SEM) (PHILIPS SEM505). Optical measurements were carried out using an UV-vis-NIR spectrophotometer (Cary 500 Version 8, 01) in the wavelength range of 250–2500 nm. The X-ray diffraction (XRD) patterns were obtained by D8 Advance Bruker AXS diffractometer with a Ni filter and Cu K_α radiation ($\lambda = 1.54056$ Å). A thermo Nicolet Nexuswas spectrometer carried out in this work the investigation of different bonds present in the solution by the Fourier transform infrared spectroscopy (FT-IR).

3. Results and discussion

3.1. Conversion of CO_2 into methanol

Methanol has been widely targeted as product. It is formed by hydrogenation of CO_2 over wide range of catalysts. Methanol synthesis requires three equivalents of hydrogen per molecule of CO_2, two being incorporated into the product with the third being consumed in the production of the by-product, water. While CO_2 has low chemical activity, it is possible to activate it towards reaction through the use of catalysts, temperature and pressure. As carbon in CO_2 is in the oxidised form, many of the resulting reactions are reductions, either through the addition of hydrogen or electrons. While catalysts can play a significant role in reducing the activation energy and the total energy required for a reaction, it is likely that there will also need to be a considerable energy input to make it viable [6]. The ability of a semiconductor to undergo photoinduced electron transfer to adsorbed species on its surface is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbate. The relevant potential level of the acceptor species is thermodynamically required to be below (more positive than) the conduction band potential of the semiconductor [14]. The potential level of the donor needs to be above (more negative than) the valence

band position of the semiconductor in order to donate an electron to the vacant hole. The band edge positions of several semiconductors are presented in Fig. 1.
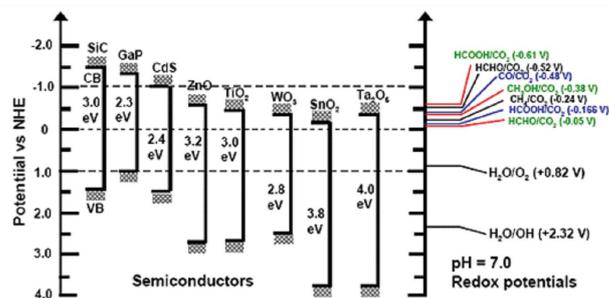
Fig. 1. Conduction band, valence band potentials, and band gap energies of various semiconductor photocatalysts relative to the redox potentials at pH 7 of compounds involved in CO_2 reduction [15].

As the potential of SiC conduction band looks more negative than those of other catalysts (Fig. 2), the reduction performance of photoelectrons in SiC will be much stronger. This is why granular SiC can easily be used as catalyst semiconductor to reduce CO_2, split water or degrade organic pollutants under UV light irradiation.

3.2. Characterization of catalyst semiconductor material

Before starting the photoreduction study, we have done some characterizations regarding the catalyst. Figure 2 shows the morphology of the 7 μm SiC microparticles, which is one of the three powder kind investigated in this study. We noticed that SiC as-received powder particles have sharp corners and are randomly fractured.

Fig. 2. The SEM morphology of as-received 7 μm average particle size SiC powder.

It is essential to identify the crystal structure of the actual SiC we used (hexagonal). The XRD of the powdered SiC with all the Miller indices labeled is shown in Fig. 3 and comparing our data with thus of JCPDS card #29-1128, it confirms the hexagonal structure.

Figure 4 depicts the diffuse reflectance spectrum where $(F(R)E)^{1/2}$ versus E is plotted and the band gap energy estimated is 3.05 eV approximately corresponds to
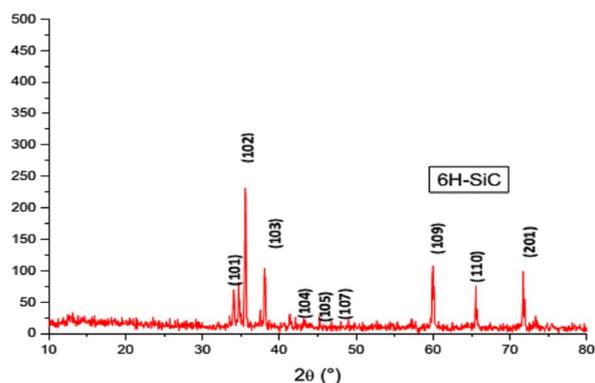
Fig. 3. X-ray diffraction pattern of 6H-SiC.
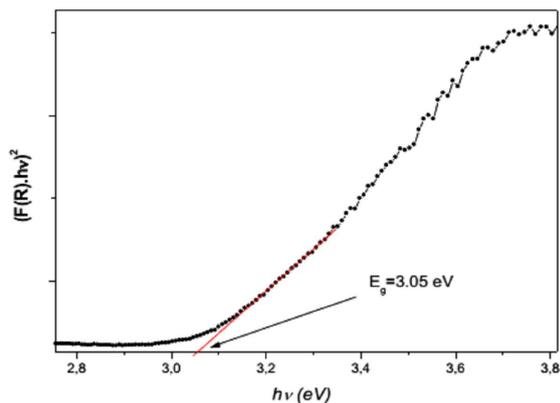
Fig. 4. Diffuse reflectance spectra of 6H-SiC powder, showing the band gap energy.

406 nm of wavelength. This band gap energy is closer to the band gap energy of the SiC of polytype 6H-SiC [16, 17]. This justifies the use of 365 nm (3.47 eV) UV light as incident radiation for 6H-SiC in our study which is capable of promoting the electron from the valance to conduction band and thereby triggering photoreduction process.

3.3. FTIR analysis

IR spectroscopy provides a powerful tool in the identification of species and interpretation of their structure and morphology, since the IR spectra are highly sensitive to the product temperature, composition, and mixing ratio of the molecular components, which are all linked to the intermolecular interactions. Methanol has attracted a lot of attention in both computational and experimental studies of hydrogen bonding and mixing in liquids, particularly with water. It is well known from laboratory and computational physical chemistry investigations that both methanol and water form strong hydrogen bonds both as pure constituents and in mixtures, interact strongly with one another. Hydrogen bonding causes shifts in the vibrational frequencies of the functional groups that they are associated with and it is therefore possible to glean much about the structure and morphology of condensed form of molecules from their

infrared spectra. In methanol, the vibrational spectra of the C–O, O–H, and the C–H stretch are sensitive to the interaction between nearest neighbours. The O–H stretch has been used extensively to study hydrogen bonding between H_2O and CH_3OH in dimers, matrix isolation and in clusters, however, in the bulk condensed and liquid phases. As the broad absorption bands due to the O–H stretching frequencies of both CH_3OH and H_2O overlap, the study can pose a problem. Even if this overlapping exists, it can be distinguished from each other at a certain concentration.

3.3.1. Mechanism of methanol formation over SiC catalyst

We specify that our study did not focus so much on the quantification of the methanol spectra, but on what this spectra can inform us about the usefulness of the photoreduction process of CO_2 in the formation of methanol, expected to be obtained by using SiC μm-sized particles as catalyst. Hence, the methanol formation was checked on the basis of changes in the hydrogen bonding resulting from mixing the two molecules, H_2O and CH_3OH, as a function of CH_3OH formation in H_2O. The observation of Fig. 5 confirms the formation of the methanol.
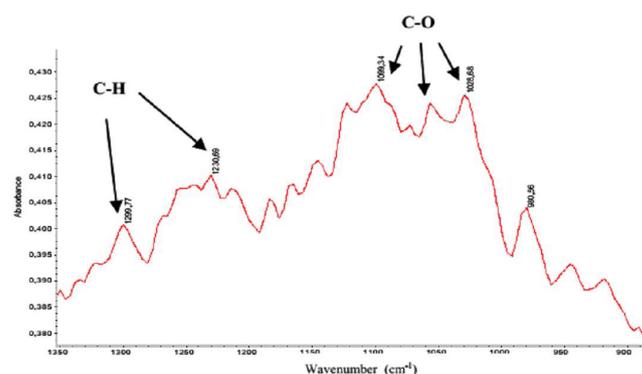
Fig. 5. FTIR spectra of a water sample taken from a reactor containing SiC powder of 7 μm average grain size.

3.4. Parameters influencing the photoreduction process

We investigated the influence of some parameters, like the concentration of the catalyst, the grains size as well as the time of exposure to the UV light, on the photoproduction of the methanol by degradation of the CO_2 gas. The monitoring results of the methanol formation were tracked by mean of the band OH in the IR spectra made after every experiment.

3.4.1. Influence of the grain size of the SiC micropowder

The grain size of the SiC micropowder was the first parameter to study its influence on the phototransformation of methanol by reduction of CO_2 gas. Thus, we compared two types of SiC micropowder, one with average grain size of 7 μm and the other one of 17 μm. The IR spectra of the two samples taken from their corresponding reactors are presented in Fig. 6.
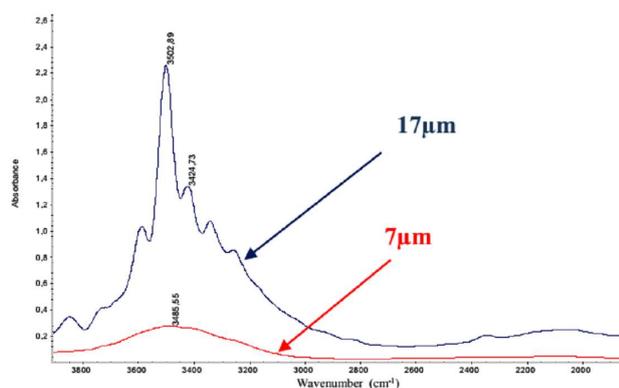
Fig. 6. FTIR spectra of samples taken from reactors containing SiC powder with average grain size of 7 μm and 17 μm.

Undoubtedly, the difference is clear, for the same quantity of SiC powder, the O–H band observed in the case of the photocatalytic treatment with a powder having an average grain size of 17 μm is clearly superior to that obtained in the case of the treament using a powder of average grain size of 7 μm. Definitely, the catalytic property of SiC is surface dependent (intervenes the surface of the SiC microparticles constituting the powder).

3.4.2. Influence of the concentration of SiC powder

According to the observation of IR spectra obtained for each concentration of SiC powder (Fig. 7), we noticed that the photoreduction of the CO_2 is sensitive to the quantity of the catalyst and that the latter presented an optimum for a concentration of SiC equal to 0.75 M.
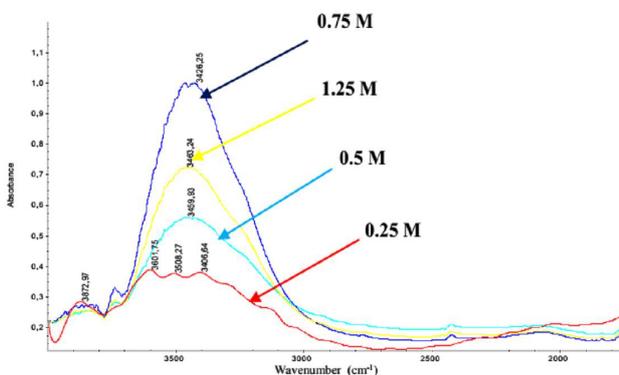
Fig. 7. FTIR spectra of water samples taken from reactors containing different amount of the catalyst of 17 μm average grain size.

It is worth noticing that a pair of competitive reactions (i.e. photoreduction and photooxidation) exists, generally, in the photochemical process. It can be found from Fig. 8 that, at the very beginning of the process, the photoreduction rates might be faster than that of photooxidation because of the low concentration of methanol produced. Indeed, after a certain level of methanol concentration is reached, the concentration of methanol starts decreasing, which is possibly due to the existence of catalytic oxidation of methanol over SiC microparticles with

positive V_B position [13]. Consequently, when methanol is produced in a substantial amount, it supposed to be adsorbed on the surface of the catalyst and then undergoes oxidation processes. This assumption was proposed according to phenomenon observed and explained by other groups [18].

3.4.3. Influence time exposition to UV light

We also followed the photoproduction of methanol according to the time of exposure to the UV light using the SiC powder of average grain size of 17 μm and 1 g of weight. The various IR spectra obtained are given in Fig. 8.
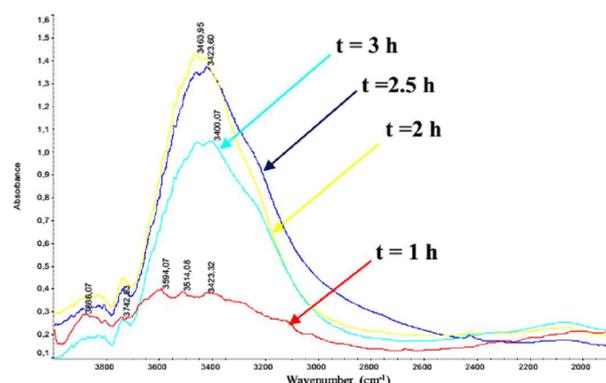
Fig. 8. FTIR spectra of water samples taken at different exposition time from a reactor containing 0.25 M of the catalyst with average grain size of 17 μm.

There also, the reaction reaches its maximum for a time of exposition to the UV light of 2 h, then decreasing as the time increased. Furthermore, a light shifting of the O–H band towards the red is observed with the increase of the exposition time. We think that, here also, the phenomenon of the pair competitive reactions is at the origin of this variation.

4. Conclusion

In summary, this work was a real approach to an artificial photosynthesis of methanol, driven by UV energy, using water and CO_2 as the starting materials and SiC as catalyst. Our investigations revealed that, for this kind of process, there are some critical factors to be satisfied for ensuring an efficient photoconversion of CO_2, like catalyst dosage, UV exposure duration, and particle size. With the knowledge that UV radiation only contributes less than 4% to the whole solar spectrum and 43% of the solar energy lies in the visible light region, we are convinced that we found a co-catalyst which can absorb visible light became unavoidable condition. We were able to finalize that, fulfilling a core/shell structure by coating the SiC particles with another semiconductor which absorb in the visible range, could enhance the catalytic activity of SiC microparticles. The development of such SiC based artificial photosynthesis is a promising route to either a renewable fuel or valuable chemicals.

Acknowledgments

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