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Novel nanostructured-TiO_2 materials for the photocatalytic reduction of CO_2 greenhouse gas to hydrocarbons and syngas

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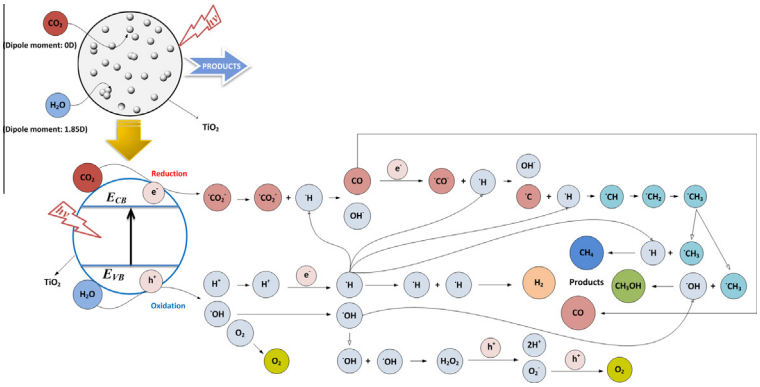
HIGHLIGHTS

- Novel nanostructured-TiO_2s were used for CO_2 reduction to hydrocarbons and syngas.
- Meso. TiO_2 showed a higher production and better reaction kinetics and stability.
- There was competitive adsorption of CO_2 and H_2O vapors on surface of the catalyst.
- UV light, H_2O/CO_2 ratios and catalyst shapes were optimized to improve products.
- Partial saturation of active adsorption sites and O_2 produced caused deactivation.

GRAPHICAL ABSTRACT



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ABSTRACT

In the current work an attempt has been made to synthesize novel high surface area nano-TiO_2 materials (titanium dioxide nanoparticles/TNPs and nanostructured or mesoporous titanium dioxide using KIT-6 silica template/Meso. TiO_2) in order to establish the photocatalytic reduction of CO_2 greenhouse gas in the presence of H_2O vapor to produce hydrocarbons and syngas. The synthesized materials have been characterized through N_2-adsorption/desorption, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and ultraviolet–visible (UV–Vis) spectroscopy analysis techniques. The TNPs consists of an average 11 nm of TiO_2 particles, shows a higher surface area of 151 m^2/g than the commercial Aeroxide P25 TiO_2 (53 m^2/g), and also demonstrates an enhanced adsorption capacity. However, the Meso. TiO_2 has shown a higher surface area (190 m^2/g) and mesoporosity (4 nm pores) than the TNPs and Aeroxide P25 TiO_2, as confirmed by the characterizations. In the reaction, the TNPs with the enhanced adsorption capability, due to the high surface area and smaller nano-sized particle morphology, showed a higher syngas (CO, H_2) production than the commercial Aeroxide P25 TiO_2. However, the novel Meso. TiO_2 showed more hydrocarbons (CH_4, CH_3OH) and a higher syngas production together with better reaction kinetics and stability due to its better characteristics than the commercial Aeroxide P25 TiO_2. The key parameters that affect the activity have been optimized to increase fuel production. The reaction mechanism indicates competitive adsorption of CO_2 and H_2O vapors on the catalyst surface. The key parameters including the UV light source and UV intensity, H_2O/CO_2 ratios and catalyst shapes influence the catalytic performance, and therefore, these parameters have been optimized to increase the fuel products. Partial saturation of the active adsorption sites and the oxygen produced are the possible causes of the

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deactivation, however, the catalysts can be regenerated quickly through a simple evaporation technique.

1. Introduction

Carbon dioxide (CO_2), a primary greenhouse gas that is caused by human activities, and which is mainly obtained from fossil fuel combustion, plays a significant role in global warming [1,2] and is currently considered a key challenge throughout the world. Moreover, owing to the great increase in human activities, there is a consequent increase in the energy demand. Because of the shortage and restrictions on the use of fossil fuels, great efforts have been made to develop alternative energy resources [3].

Converting CO_2 to valuable fuels or useful chemicals is one of the best ways of preventing a rise in temperature due to the greenhouse effect and of solving the energy crisis [4–6]. This process turns CO_2 from an undesired waste into a valuable and cheap carbon source feedstock that could replace fossil fuels. In this context, many researchers have tackled this issue. Currently, several methods are being studied to reduce CO_2, including photovoltaic cells, photoelectrochemical cells, direct photocatalytic reduction using molecular catalysts and photocatalytic reduction through water [6]. The photocatalytic conversion of CO_2 with H_2O seems to be a promising technique when appropriate energy sources, such as UV and/or visible light used as excitation sources for semiconductor catalysts, since the photoexcited electrons reduce CO_2 with H_2O on the catalyst surface to produce energy-bearing products such as methane (CH_4), methanol (CH_3OH), carbon monoxide (CO), formic acid (HCOOH), and formaldehyde (HCHO) [1,7–16]. Several photocatalyst oxides and non-oxides, such as TiO_2, CdS, ZnS, SiC, WO_3, Fe_2O_3, ZrO_2, ZnO_2, and MgO_2, have been used extensively for photocatalytic reduction [7]. However, wide band-gap TiO_2 photocatalysts (3.2 eV) are considered the most convenient candidate for this application, due to this environmentally friendly material which shows a good oxidation power, strong resistance to chemicals and photocorrosion, non-toxicity, a low operational temperature, low cost, and significantly low energy consumption, all of which have led to relevant applications for fuel production [3,17]. However, low photocatalytic CO_2 conversion and product selectivity are two aspects that still need to be tackled. Therefore, the designs of highly efficient photocatalysts and selective photocatalytic systems for the reduction of CO_2 with H_2O are of vital importance for the industrialization of this process.

Various approaches are currently being adopted to synthesize more efficient TiO_2-based materials for this application. These include synthesis of the uniform single-phase titania crystalline structure, band-gap modification of the UV-activated TiO_2 particles, surface cocatalyst deposition to catalyze redox reactions, the use of a sensitization effect to harness visible light, and enhancing nanofabrication techniques to obtain a better control of the size and morphology [18]. The latter approach seems to be more promising as it offers several advantages over the others. Nanostructuring, in particulars, helps to improve the charge-separation and transport properties and increases the available surface area of photocatalysts [19].

Mesoporous silicas [20,21], due to their combination of good accessibility, uniform pore size and high surface area, are interesting candidates for the nanocasting technique to produce various nano-replica materials [22]. KIT-6 (Korea Advanced Institute of Science and Technology-6) has a 3-dimensional (gyroid cubic Ia3d) pore structure and a large pore size, and it has already received the attention of many researchers for different applications [20,23]. Therefore, in the present work, an attempt has been made to synthesize the large surface area and high adsorption capacity of nanostructured or Mesoporous TiO_2 (Meso. TiO_2) by means of a KIT-6 silica template. TiO_2 nanoparticles (TNPs) with a large surface area and high adsorption capability were obtained with the sol-gel method using a Vortex reactor. These materials were utilized in this study to photocatalytically reduce CO_2 with H_2O vapors to produce hydrocarbons (CH_4, CH_3OH) and syngas (CO, H_2), and the results have been compared with the best available Aeroxide P25 TiO_2 material on the market. The key factors that affect the catalytic activity have been optimized to increase fuel production. The mechanism pathways followed to obtain these fuel products and the deactivation and regeneration of the catalysts are discussed.

2. Experimental

2.1. Synthesis of the materials

The TNPs was synthesized in the laboratory using a vortex reactor (VR; the VR is a passive mixer characterized by a small volume of about 0.5 mL, whose mixing time can be tuned by changing the flow rates of the inlet solutions) using the sol–gel method as reported in our previous work [24]. The mesoporous silica material (KIT-6) was obtained according to the procedure that has been shown in a recent work [20]. After a hydrothermal treatment, the obtained solid product was filtered, dried and/or calcined at 550 °C for 5 h, and then utilized as a template to prepare Meso. TiO_2. The Meso. TiO_2 (using KIT-6 replication) was obtained according to the procedure reported in [25], but KIT-6 was used instead of SBA-15 as the silica template, and Titanium (IV) isopropoxide (TTIP, Sigma Aldrich, 98%) was used as the TiO_2 precursor. The commercial Aeroxide P25 TiO_2 was purchased from Avonik industries and was used for reference purposes in this work.

2.2. Characterization of the materials

The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}), pore volume (PV) and average pore diameter (APD) were measured on the powder materials, which had previously been outgassed at 150 °C using a Micromeritics FlowPrep 060, USA (sample degas system), by means of N_2 sorption at 77 K on a Micromeritics Tristar II, USA (surface area and porosity) instrument.

The X-ray diffraction (XRD) patterns were recorded in order to determine the different polymorphs, on an X'Pert Phillips diffractometer using Cu Kα radiation, under the following conditions: 2θ = 10–90°; 2θ step size = 0.02. The small-angle X-ray diffraction (SAX) patterns of the materials were recorded on a Phillips instrument at 2θ = 0.2–3.5°. The morphology and mesoporous structure of the samples were observed by means of a Leo Supra 55 field emission scanning electron microscope (FE-SEM, Zeiss Merlin). The ultraviolet–visible (UV–Vis) spectroscopy diffuse reflectance spectra were recorded using a Varian model Cary 500 spectrophotometer with a suitable quartz cell for measuring powders.

The total UV light intensity was measured by Field Master Power Meter Head from Coherent (Auburn, CA, USA) with a sensor of 3 cm inner diameter and capacity to measure from 10 mW to 100 W.

2.3. Structured catalytic reactors

In order to have a viable application, the TiO_2 photocatalyst cannot be used in powder form but needs to be shaped into a