Spectroscopic insights into the deactivation and regeneration of active species over Co/TiO_2 in continuous CO_2 photocatalytic reduction reaction to CH_4

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Abstract: TiO_2-based photocatalysts (bare, Pt and Co promoted ones) were evaluated in a continuous gas phase CO_2 reduction under UV-light irradiation. Co/TiO_2 showed superior catalytic activity, particularly towards CH_4 formation. *In situ* DRIFTS studies under dark and irradiation conditions suggest the pivotal roles of bicarbonate species at the catalyst surface as the active species leading to CH_4 and H_2 production.

Keywords: Photocatalysis, Co/TiO_2, CO_2 reduction, DRIFTS, catalyst regeneration, bicarbonates.

1. Introduction

The increasing rate and amount of carbon dioxide emissions in the atmosphere represents the main cause of the global warming. CO_2 transformation into useful chemical compounds such as methane and methanol offers possible paths to utilize emitted CO_2 and mitigate the greenhouse effect.[1] CO_2 is a thermodynamically stable molecule and an energy input is required to active and convert it. For this aim, special attention has been given to make use of the solar radiation as a sustainable energy source. However, most photocatalytic systems show low conversion efficiency, and there is an increasing need of developing materials with high response to sunlight in the UV and visible light ranges.

TiO_2 is the most widely used and investigated photocatalyst.[2] The creation of Schottky barrier by metal doping has been employed as the strategy to improve TiO_2 photocatalytic activity and to control product selectivity. Pt is the most common promoter and some other transition metals such as cobalt are gaining increasing attention because of their abundance and absorption in the visible region.[3]

The vast majority of literature reports in the photocatalytic CO_2 transformation describe the reactions performed with the catalyst in aqueous solution. However, CO_2 photoreduction in solution is generally limited because less energy is required to reduce water (0 V vs RHE at pH 0) than to reduce CO_2 (-1.49 V vs RHE at pH 0), and CO_2 presents low solubility in water. Consequently, the reduction of water is favored over CO_2 reduction and performing the reaction in gas phase is an alternative approach to overcome this limitation.[4] To date, mechanistic aspects of the photocatalytic CO_2 reduction remain unclear and we would like to tackle them with our investigations by relating the surface species with the catalytic activity, thus by means of *in situ* spectroscopy.[5]

2. Experimental

Photocatalysts (Pt/TiO_2 and Co/TiO_2) were prepared by wetness impregnation method (0.2 wt% metal loading) and calcined in air at 350 °C for 3 h. Photocatalytic tests were performed using 100 mg of catalyst under the flow of CO_2 gas (4.5 mL min^{-1}) saturated with H_2O vapor (at 40 °C) for 4 h with a 400 W high-pressure Hg lamp (UV-Technik) at 150 °C using a home-made reaction setup equipped with a reactor with a quartz window. The effluent gas composition was continuously monitored by an online MS and a microGC.[6] *In situ* DRIFTS study of the surface species formed over the catalysts was performed under the identical conditions as that of the catalytic tests using a commercial cell placed in a Praying Mantis accessory (Harrick Scientific). An optical fibre-based light source (250 W high-pressure Hg lamp, UV-Consulting Peschl) was used as the irradiation source for *in situ* DRIFT study to locally focus the light on the samples.

3. Results and discussion

Figure 1a shows the amounts of CH_4 and H_2 produced in the photocatalytic tests with TiO_2, Pt/TiO_2 and Co/TiO_2. Metal promoters (Pt or Co) obviously enhanced the catalytic activity in both CH_4 and H_2 production. Comparing the Pt and Co promoted catalysts, Co/TiO_2 showed higher CH_4 production and lower H_2 production, thus improving the selectivity towards CH_4. CH_4 and H_2 concentrations in the effluent stream reached a maximum after 30 min of irradiation and then decreased exponentially for the three materials (not shown here), showing a clear catalyst deactivation.

To further investigate chemical species formed at the catalyst surface leading to CH_4 production and the nature of deactivation, *in situ* DRIFTS were performed using Co/TiO_2 during the dark time and under UV irradiation, both under the flow of CO_2 saturated with water (Figure 1b). During the dark time (Figure 1b, **1**) Co/TiO_2, Pt/TiO_2 and TiO_2 showed similar features of surface species, with an initial formation of bicarbonate species and then their transformation to carbonate species as evidenced by the spectral features in 1350-1700 cm^{-1}. Within the first irradiation cycle (**1+UV**), the reduction (i.e. consumption) of bicarbonate bands at 1400 cm^{-1} was observed, while carbonate bands became gradually more prominent (ca. 1560 cm^{-1}) in exchange. The spectral features remained unaltered during the subsequent dark time and another irradiation cycle, indicating that the surface covered with the carbonate species are the “deactivated” state of the catalyst. Catalytic tests with CO_2 gas saturated with methanol+water showed that the activity could be recovered with more stable CH_4 and H_2 production (the results not shown). *In situ* DRIFT spectra under such conditions (Figure 1b, **2** and **2+UV**) interestingly shows that especially under irradiation condition the spectral features of bicarbonate species were restored.

This study suggests that the H atoms bound to carbonates, thus forming bicarbonates, play important roles in determining the photocatalytic activity of the TiO_2-based materials. The consumption of bicarbonates likely leads to the formation of carbonate species that block active sites, causing an irreversible surface deactivation under the condition of catalytic runs. Further studies are underway to understand the role methanol on the intermediate species formed during the CO_2 photoreduction, as well as the effects of metal promoters.

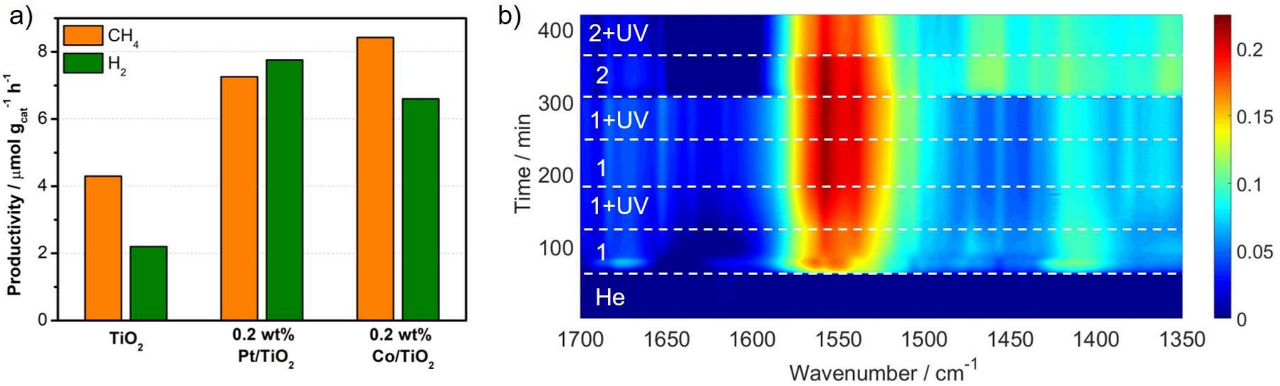

Figure 1. a) CH_4 (orange) and H_2 (green) production obtained from photocatalytic CO_2 reduction in the presence of H_2O vapor with TiO_2, Pt/TiO_2, or Co/TiO_2. b) *In situ* DRIFT spectra of Co/TiO_2 under He, stabilization with water-saturated CO_2 under dark (**1**), subsequent 1 h irradiation (**1+UV**), the repeated cycle with CO_2 saturated with methanol/water under dark (**2**), and subsequent 1 h irradiation (**2+UV**).

4. Conclusions

Reduction of CO_2 to CH_4 was successfully achieved more efficiently over Pt/TiO_2 and Co/TiO_2 than over TiO_2 under UV light. Especially, Co/TiO_2 showed a favorable reactivity for CH_4 production. DRIFTS studies elucidated the possibility of surface regeneration by the addition of methanol, and the importance of OH groups, increasing the formation of surface bicarbonate active species which directly influenced the catalytic performance.

References

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