Low Temperature Photo enhanced CO_2 Reduction to CH_4 using Co-La/TiO_2 Catalysts

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The conversion of CO_2, a major constituent of greenhouse gases, to valuable fuels by sunlight is of significant interest due to the potential of using both light and heat from the sun to invoke sustainability in conventional energy-consuming chemical reactions.[1] In this study, with the intent of reducing thermal energy requirements as well as understanding the potential for light enhancement, the impact of visible light illumination on Co-La catalysts (loaded on TiO_2) for the CO_2 methanation reaction was examined. Specifically, Co with different La loadings on a TiO_2 support was exposed to white LED illumination under reaction conditions and the effect on catalyst activity and selectivity was investigated. In most cases light illumination delivered better catalytic activity over the temperature range 250-450°C. Of particular interest was the change in catalytic properties with the addition of La on TiO_2 support. In the case of Co_{10}-La_{10}/TiO_2, white light illumination (λ = 300-780 nm) lowered the activation energy by 20% and facilitated an 86% enhancement in CO_2 conversion (from 10% to 19% CO_2 conversion at 350°C). With different characterisations, it was revealed La promotion has potential to decrease crystallite size of Co, improved surface basicity and create more oxygen vacancies on the TiO_2 surface. Further detailed investigations with In-situ characterisations demonstrated the basic sites introduced by La played a pivotal role in enhancing CO_2 adsorption and its transformation to an intermediate specie susceptible to light enhancement. The absence of significant light enhancement on sample without La addition (Co_{10}/TiO_2) further validated the importance of La addition in this work and confirmed the observed light enhancement on La based samples was not invoked by photothermal heating.

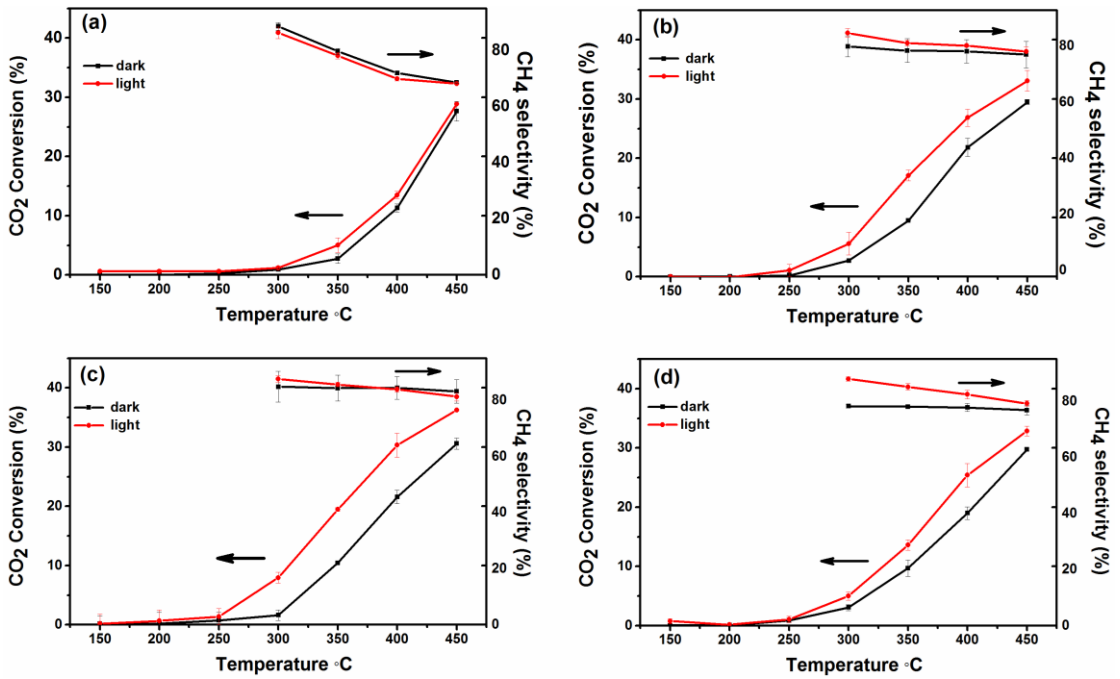

Figure 1: Catalyst activity and CH_4 selectivity with increasing temperature during CO_2 methanation by Co_{10}/La_x-TiO_2 where (x=0,5,10,15) (a) Co_{10}/TiO_2 (b) Co_{10}/ La_5-TiO_2 (c) Co_{10}/La_{10}-TiO_2 (d) Co_{10}/La_{15}-TiO_2. The black lines indicate thermal only conditions. The red lines indicate conditions with 0.5 W/cm^2 light illumination. In all tests, 45 mg of catalyst sample was used under $CO_2/H_2/N_2$= 1:4:1 at 24 mL/min. CH_4 selectivity was calculated relative to CO produced

References:

(1) Wang, Z.; Song, H.; Liu, H.; Ye, J. Coupling of Solar Energy and Thermal Energy for Carbon Dioxide Reduction: Status and Prospects. *Angew. Chemie Int. Ed.* **2019**.