Highly Concentrated CO Evolution for Photocatalytic Conversion of CO_2 by H_2O as an Electron Donor

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The reduction in human-induced emissions of CO_2 from automobiles, factories, power stations, etc., over the next 15 years is currently one of the most important issues facing the planet. The Intergovernmental Panel on Climate Change (ICPP) warned that temperature change has to be controlled lower than 2 degrees Celsius relative to average temperature before the Industrial Revolution by the end of century. It has also warned that if no action is taken to deal with the rate of CO_2 emissions, this will result in grave consequences for the planet, leading to sea surface elevation and desertification. We should therefore attempt to develop industrial processes using CO_2 as a feedstock in order to build a sustainable society in the near future.

We previously reported that the several oxides such as ZrO_2, MgO, and Ga_2O_3 show activity in the production of CO from the photocatalytic conversion of CO_2 in the presence of H_2 and CH_4. Linear CO_2 molecules adsorbed on the surface of the solid bases are converted into unique structures, such as bicarbonate and carbonate species possessing lattice oxygen atoms. We believe that the process involves the capture and distortion of CO_2 upon adsorption on a solid base through activation by photoirradiation. Unstable CO_2 species adsorbed onto the surface can then be reduced by electrons with protons derived from H_2O ($CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$). It is well-known that the catalytic sites are easily poisoned by H_2O. If H_2O does function as the electron donor, then it is important to obtain a stoichiometric ratio between the amount of O_2 evolved and the amount of CO_2 reduced. Moreover, the reduction of H^+, released from H_2O molecules, usually competes with CO_2 reduction when several heterogeneous materials are used as photocatalysts for the reduction of CO_2 with H_2O. Generally, the production of H_2 via the reduction of H^+ is the dominant pathway. Therefore, to achieve high selectivity in the photocatalytic conversion of CO_2 with H_2O, the electrons generated through the oxidation of H_2O must be controlled to selectively. These days, We found that $ZnGa_2O_4/Ga_2O_3$,[1, 2] $La_2Ti_2O_7$,[3] SrO/Ta_2O_5,[4] $ZnGa_2O_4$,[5] $ZnTa_2O_6$,[6] and $Sr_2KTa_5O_{15}$[7] with the modification of Ag cocatalyst exhibit good conversion of CO_2 and high selectivity toward CO evolution for the photocatalytic conversion of CO_2 by H_2O as an electron donor. The selectivity toward CO evolution (%) = $100 \times \boldsymbol{R}_{CO} / (\boldsymbol{R}_{CO} + \boldsymbol{R}_{H2})$ where $\boldsymbol{R}_{CO}$ and $\boldsymbol{R}_{H2}$ was formation rates of CO and H_2, respectively. An isotope experiment using $^{13}CO_2$ and mass spectrometry clarified that the carbon source of the evolved CO is not the residual carbon species on the photocatalyst surface, but the CO_2 introduced in the gas phase. In addition, stoichiometric amounts of O_2 evolved were generated together with CO over all the photocatalysts as shown above.

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