

Sodium hexatitanate photocatalysts prepared by a flux method for CO₂ reduction with water

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Photocatalytic CO₂ reduction should be one of the desired methods for keeping the carbon cycle on the earth, and has been widely studied so far. In the present study, we prepared and characterized several Na₂Ti₆O₁₃ samples, and examined the photocatalytic performance of the Na₂Ti₆O₁₃ samples with Ag cocatalyst for the CO₂ reduction with water.

The Na₂Ti₆O₁₃ samples were synthesized by a flux method from Na₂CO₃ and TiO₂ powders as solutes by using NaCl as a flux salt. They were referred to as NT(NaCl, x), where the parameter x denotes the mol% of solute in the molten mixture at 1273 K. Another sample denoted to as NT(SS) was prepared by a solid state (SS) reaction at 1273 K, which corresponds to the case without using the flux ($x = 100\%$). The Ag cocatalyst of 0.1 wt% was loaded on them by a photodeposition method. Photocatalytic reaction was carried out in a specially designed quartz cell under a flow of CO₂ gas upon photoirradiation from a 300 W Xe lamp under ambient temperature and pressure. In the cell, 0.2 g of the photocatalyst powder was dispersed in 10 mL of water saturated with NaHCO₃. The amounts of products were determined by GC-TCD.

XRD profiles showed that all the prepared samples were assignable to Na₂Ti₆O₁₃ crystals without impurity phase. The SEM images revealed that the NT(NaCl, x) samples consisted of hexagonal rod-like crystals while the NT(SS) consisted of granular polyhedral-like particles.

All the Ag-loaded Na₂Ti₆O₁₃ samples exhibited the photocatalytic activity to produce CO, H₂ and O₂. Other product was not detected in this manner. The production of CO and H₂ should be through the CO₂ reduction and water splitting, respectively, which would take place competitively. During the initial period, the O₂ as the product from water oxidation was not detected, which might be quantitatively explained by photoadsorption on the surface, and it became to be observed after the continuous reaction for around 24 h. At the steady state, the reaction proceeded continuously with constant production rate on most of the samples. The CO production was not observed in the absence of the photocatalyst, CO₂, H₂O, or photoirradiation. Thus, it was confirmed that the CO₂ reduction proceed photocatalytically. The Ag cocatalyst drastically enhanced the photocatalytic CO₂ reduction so that it would be the important active sites for CO production.

The CO production rate varied with the samples as shown in Fig. 1. The Ag/NT(NaCl, x) samples exhibited higher activities than the Ag/NT(SS) sample. The size of the hexagonal rod-like crystals, width and length, were also plotted here. It is noted that there is a good relation between the CO production rate and the width of the rod-like crystals.

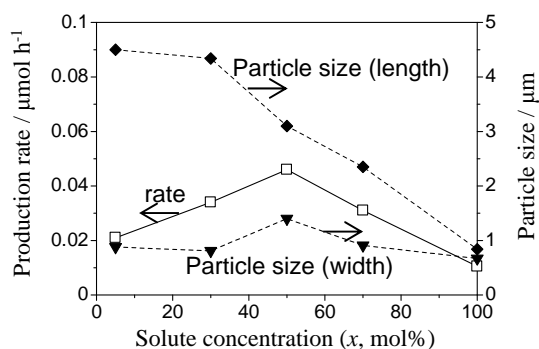


Fig. 1 Relationship between the CO production rate on the Ag/Na₂Ti₆O₁₃ samples at 24 h later and the average particle size of the polycrystals observed in the SEM images. The values at $x=100$ were of the NT(SS) sample.

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