Zn－Cu－M(III) (M = Al, Ga) 層状複水酸化物光触媒を用いた二酸化炭素のメタノール化

Photo-catalytic Conversion of Carbon Dioxide into Methanol using Zinc-Copper-M(III) (M = Aluminum, Gallium) Layered Double Hydroxides

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Introduction Series of semiconductors formulated as $[Zn_{3-x}Cu_xM^{III}(OH)_8]^{+}_2(CO_3)^{2-}\cdot mH_2O$ (M = Al, Ga) layered double hydroxides (Zn-Cu-M^{III}-CO_3 LDH) were synthesized and applied for CO_2 conversion into CH_3OH under UV-visible light using H_2 as reductant.[1] CH_3OH selectivity was 68 mol% by the inclusion of Cu in the layers of LDH. In this session, the Cu site structure and its photocatalytic role was investigated.

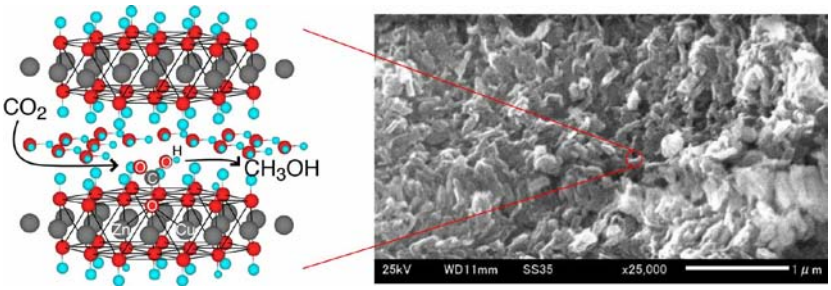
Experimental Section Zn-Cu-M^{III}-CO_3 LDH were synthesized by the co-precipitation of metal nitrates with Na_2CO_3 to maintain a pH value of 8. Cu, Zn, and Ga K-edge XAFS measurements for as-synthesized and in-situ catalysts were performed in transmission mode at 30–290 K.

Results and Discussion Spectrum pattern of Cu K-edge XANES for as-synthesized LDHs was nicely reproduced by the theoretically generated XANES for complete O_h layer structure model using FEFF 8.4. The Zn K-edge XANES pattern for the LDHs resembled that of Cu K-edge XANES.

On heating Zn-Cu-Ga-CO_3, post-edge peak intensity at 9016 eV decreased to 65%, suggesting the loss of interlayer H_2O and CO_3^{2-}. This behavior was supported by theoretical XANES spectra by FEFF 8.4 for $CuZn_{56}(OH)_{72}\cdot 38H_2O$ model and corresponding one to lose all of interlayer waters. Upon introduction of CO_2 at 290–523 K, the peak intensity increased back to 72–83% of as-synthesized one. This semi-reversible trend was observed only for the LDH samples containing Cu. Thus, the adsorption of CO_2 in the interlayer space of LDH on Cu sites was suggested, most probably to form HCO_3^- species on reaction with surface hydroxyl of LDH layers.

Further, in the Cu K-edge XANES measurements of Zn-Cu-Ga-CO_3 in CO_2 and H_2 under UV-visible light, the pre-edge peak at 8980 eV ascribed to Cu^{II} gradually decreased to 72% in 46 min and the intensity increased back to 79% at 5 min after the light was off. This Cu^{II}–Cu^{I} redox couple was provide the photo-generated electrons to hydrogen carbonate, formic acid, formyl, and formaldehyde intermediates to methanol.[1]

Reference
(1) Ahmed, *et al.*, *Journal of Catalysis*, DOI: 10.1016/j.jcat.2011.01.004 (2011).



Scheme 1. Structure and reaction intermediate of LDH photocatalyst to convert CO_2 into fuel.