Reaction Mechanism of DMC Formation from CO_2 and Methanol over CeO_2(111): A DFT Study

Toshiyuki Sugiyama,[1] Akira Nakayama,[2] and Jun-ya Hasegawa[2]
[1]*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[2]*Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan*
*E-mail: nakayama@cat.hokudai.ac.jp, hasegawa@cat.hokudai.ac.jp

From the viewpoint of green sustainable chemistry, the direct conversion of CO_2 to valuable chemical products has attracted increased attention. The direct synthesis of dimethyl carbonate (DMC) from CO_2 and CH_3OH is one of the important processes in this regard. It has been reported that CeO_2-based catalyst is effective for this reaction[1]. In this study, we theoretically investigate the reaction mechanisms of DMC formation over CeO_2 by the density functional theory (DFT) calculations.

The adsorption structures of CO_2 and CH_3OH on CeO_2(111) are first investigated, and the three and two stable structures are determined (Figs 1 and 2). The first step of the reaction involves the formation of methyl carbonate from adsorbed CO_2 and CH_3OH. Several pathways are determined from respective adsorption structures, and we found that the pathway starting from CO_2 (A3) and CH_3OH (B1) provides the lowest activation energy for the formation of methyl carbonate, where the dissociated methoxy group attacks the molecularly adsorbed CO_2.

The methyl carbonate reacts with another CH_3OH, resulting in the formation of DMC. The two reaction mechanisms are investigated for this step (Fig. 3). In the first mechanism, methoxy species generated by a proton dissociation using the base site on CeO_2 attacks a carbon atom of the adsorbed methyl carbonate, and then DMC and water molecules are formed. In the second mechanism, the surface oxygen atom attacks the carbon atom forming the C-O bond, and then the OH group in the resulting intermediate dissociates. After this step, the methoxy species on the surface attacks the carbon atom of the intermediate, and then the DMC molecule is formed.

We have located the stable and transition state structures along these pathways, and the potential energy profiles are obtained. The details of the reaction mechanisms and the roles of the acid-base sites on CeO_2 surface are discussed in the session.

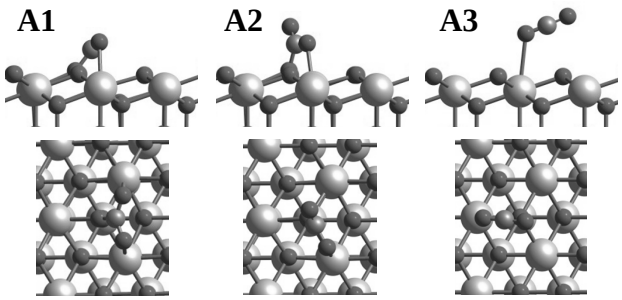

Fig.1 Adsorption structure of CO_2 on CeO_2 surface.

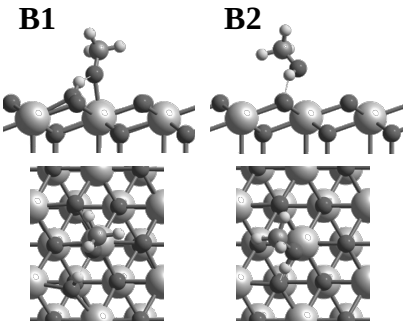

Fig. 2 Adsorption structure of CH_3OH on CeO_2 surface.

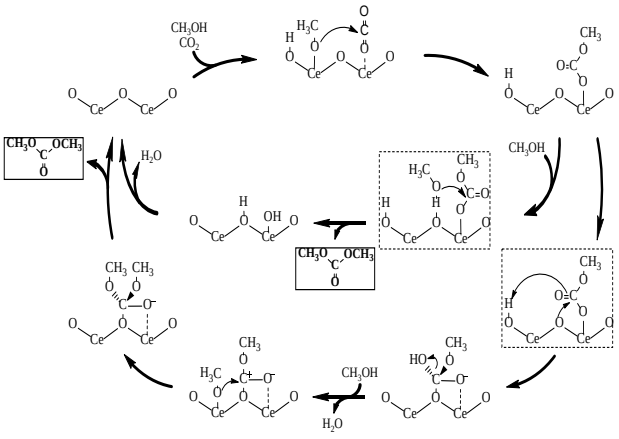

Fig. 3 Reaction mechanism

REFERENCE

[1] Honda, M.; Tamura, M.; Nakagawa, Y.; Sonehara, S.; Suzuki, K.; Fujimoto, K.; Tomishige, K. *ChemSusChem* **2013**, *6*, 1341–1344.