# Heterogeneous $Cu/CeO_2$ catalyst for methanol synthesis by hydrogenation of dimethyl carbonate

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**Abstract:** We found that $Cu/CeO_2$ was an effective heterogeneous catalyst for hydrogenation of dimethyl carbonate (DMC) to methanol at low temperature of 433 K and low $H_2$ pressure of 2.5 MPa, giving 94% methanol yield based on the carbonyl of DMC. Characterization of $Cu/CeO_2$ catalyst by XRD, TEM, and XAFS showed that the size of Cu metal particle was subnanometer scale (<1 nm).

**Keywords:** Cu subnanoparticle, hydrogenation, methanol synthesis.

## 1. Introduction

Methanol is one of the most important chemicals because it is used as a starting material for various useful chemicals such as formaldehyde, dimethyl ether and acetic acid. Industrially, methanol is produced by hydrogenation of CO and $CO_2$ with $H_2$ over Cu-Zn-based catalysts.[1] However, the reaction typically requires severe conditions such as high temperature (523-573 K) and pressure (5-10 MPa). Recently, a new process for methanol synthesis from $CO_2$ at mild temperature was demonstrated by using Ru-based catalysts, where methanol is indirectly produced via formation of carbonate derivatives such as carbonates, carbamates and ureas from $CO_2$ and alcohols and/or amines.[2]

We have investigated $CeO_2$-catalyzed organic reactions, and have revealed that $CeO_2$ can activate $CO_2$ or esters on the surface of $CeO_2$.[3] Recently, we reported that formation of dimethyl carbonate (DMC) from $CO_2$ and methanol under mild reaction temperature can be promoted by the combination catalyst of $CeO_2$ and 2-cyanopyridine, giving 94% yield based on methanol.[4] We considered that $CeO_2$ catalyst in combination with hydrogenation-active metal species will be effective for the synthesis of methanol by hydrogenation of DMC at low temperature. In this study, we found that $Cu/CeO_2$ was an effective heterogeneous catalyst for hydrogenation of DMC to methanol under mild reaction conditions with high methanol yield based on carbonyl of DMC.[5]

## 2. Experimental

$CeO_2$ was prepared by calcining cerium oxide HS (Daiichi Kigenso, Japan) for 3 hours under air at 873 K. $Cu(x)/CeO_2$, where x means Cu amount (wt%), was prepared by impregnating the $CeO_2$ with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$. $M(1)/CeO_2$ catalysts (M=Pt, Ir, Au, Ni, Rh, Co, Pd, Ru and Ag) were prepared by the similar method using the corresponding precursors such as $(Co(NO_3)_2 \cdot 6H_2O$, $Pd(NH_3)_2(NO_2)_2$aq, $Ru(NO)(NO_3)_x(OH)_Y$aq, $AgNO_3$, $H_2IrCl_6 \cdot nH_2O$, $Rh(NO_3)_3$aq, and $[Pt(NH_3)_4] \cdot 3H_2O$. $Cu(1)/MO_x$ catalysts ($MO_x$=$ZrO_2$, MgO, $TiO_2$, $\gamma$-$Al_2O_3$, $SiO_2$, $SiO_2$-$Al_2O_3$) were prepared by impregnating each support with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$. All catalysts were calcined at 773 K for 3 h. Activity tests were performed in a 190 ml stainless steel autoclave with an inserted glass vessel. Before the reaction, the catalyst was dried at 473 K for 10 min under 2% $O_2/N_2$ flow. Standard reaction conditions were as follows: catalyst, 100 mg; DMC (anhydrous), 30 mmol; THF (anhydrous), 5 g; dodecane (an internal standard), 0.15 g; $H_2$, 8.0 MPa; 433 K; 4 h. The products in the gas phase and liquid phase were analyzed by GC with Porapak N and TC-WAX, respectively. Yield was calculated based on the carbonyl of DMC. $CH_3OH$/Cu ratio was calculated by the following equation; ($CH_3OH$/Cu ratio (mol/mol)) = (Produced methanol amount based on the carbonyl (mol))/(Total Cu amount (mol)).

## 3. Results and discussion

Hydrogenation of DMC to methanol was investigated using $CeO_2$-supported 1 wt% metal catalysts ($M(1)/CeO_2$) and metal oxide supported 1 wt% Cu catalysts ($Cu(1)/MO_x$). As for $M(1)/CeO_2$ catalysts, $Cu(1)/CeO_2$ showed high conversion (11%) and high selectivity to methanol based on the carbonyl of DMC (81%), however other catalysts exhibited low conversion (<5%). Therefore, Cu is suitable metal species over $CeO_2$ in this reaction. As for $Cu(1)/MO_x$ catalysts, $CeO_2$, $ZrO_2$, MgO, and $TiO_2$ supported catalysts showed high selectivity to methanol. Among them, $Cu(1)/CeO_2$ exhibited high activity. On the other hand, $Al_2O_3$ and $SiO_2$-$Al_2O_3$ supported catalysts showed higher conversion than other catalysts, however, the selectivity to methanol was very low. Therefore, the combination of Cu and $CeO_2$ is the most effective for the reaction.

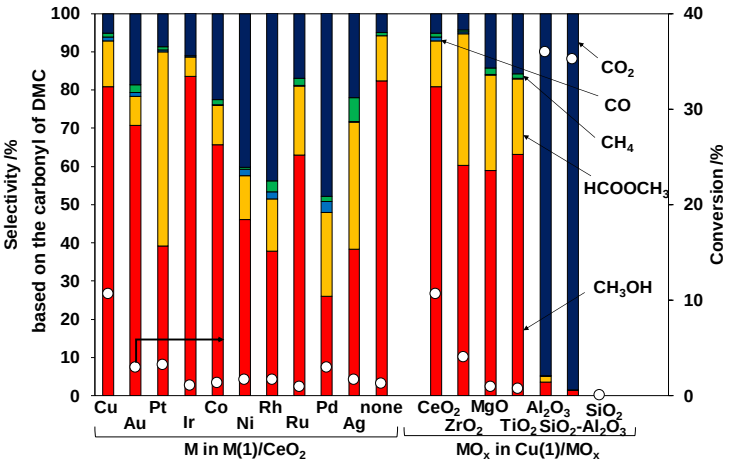


**Figure 1.** Methanol synthesis by hydrogenation of DMC over various catalysts. Conditions: catalyst, 100 mg; DMC, 30 mmol; THF, 5 g; $H_2$, 8 MPa; 433 K; 4 h.

The effect of Cu loading amount was investigated using $Cu(x)/CeO_2$ (x= 0-5) catalysts. The conversion and selectivity to methanol increased with increasing Cu amount up to 2 wt% and 0.5 wt%, respectively. $CH_3OH$/Cu ratio (mol/mol) was highest at 1 wt% Cu loaded $CeO_2$ ($Cu(1)/CeO_2$). Therefore, $Cu(1)/CeO_2$ is the most effective catalyst for the reaction.

Time-course of hydrogenation of DMC using $Cu(1)/CeO_2$ to methanol was studied. The reaction proceeded smoothly to reach 100% conversion after 24 h, which gave 94% yield of methanol based on the carbonyl of DMC, and the TON based on total Cu amount reached 224. Moreover, the effect of $H_2$ pressure using $Cu(1)/CeO_2$ was investigated in the rage of 2.5-9.5 MPa. The conversion and selectivity to methanol gradually decreased with decreasing $H_2$ pressure, however, these changes were very small. Therefore, the catalyst can be used at low $H_2$ pressure.

$Cu(x)/CeO_2$ catalysts (x = 0-5) were characterized by XRD, TEM, and XAFS. In $Cu(1)/CeO_2$ catalyst after the reaction, Cu species such as CuO, $Cu_2O$, and Cu metal were not observed by XRD and TEM analysis. Coordination number (CN) of Cu-Cu shell in $Cu(1)/CeO_2$ measured by EXAFS was 5.5, which was much smaller than that of Cu foil (12). Based on the results of TEM and EXAFS analysis, the size of Cu species will be very small and subnanocluster scale.

## 4. Conclusions

We demonstrated that heterogeneous $Cu/CeO_2$ catalyst is effective for hydrogenation of DMC to methanol under mild reaction conditions. The methanol yield based on the carbonyl of DMC and TON based on total Cu amount reached 94% and 224, respectively. The size of Cu species on $CeO_2$ was subnanocluster by various analyses such as XRD, TEM and XAFS.

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