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# Carbon Dioxide Conversion to Methanol over Size-selected Cu<sub>4</sub> Clusters at Low Pressures

Cong Liu<sup>a,‡</sup>, Bing Yang<sup>a,‡</sup>, Eric Tyo<sup>a</sup>, Soenke Seifert<sup>b</sup>, Janae DeBartolo<sup>b</sup>, Bernd von Issendorff<sup>c</sup>, Peter Zapol<sup>a,\*</sup>, Stefan Vajda<sup>a,d-f,\*</sup> and Larry A. Curtiss<sup>a,\*</sup>

<sup>a</sup> Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave. Lemont, IL 60439, USA;

<sup>b</sup> X-ray Science Division, Argonne National Laboratory, 9700 S. Cass Ave. Lemont, IL 60439, USA;

<sup>c</sup> Physikalisches Institut, Universität Freiburg, Stefan-Meier-Straße 21, 79104 Freiburg, Germany;

<sup>d</sup> Nanoscience and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave. Lemont, IL 60439, USA;

<sup>e</sup> Department of Chemical and Environmental Engineering, School of Engineering & Applied Science, Yale University, 9 Hillhouse Avenue, New Haven, CT 06520, USA;

<sup>f</sup> Institute for Molecular Engineering, University of Chicago, 5801 South Ellis Avenue Chicago, Illinois 60637, USA

## Supporting Information Placeholder

**ABSTRACT:** The activation of CO<sub>2</sub> and its hydrogenation to methanol is of much interest as a way to utilize captured CO<sub>2</sub>. In this work we investigate the use of size-selected Cu<sub>4</sub> clusters supported on Al<sub>2</sub>O<sub>3</sub> thin films for CO<sub>2</sub> reduction in the presence of hydrogen. The catalytic activity was measured under near-atmospheric reaction conditions with a low CO<sub>2</sub> partial pressure, and the oxidation state of the clusters was investigated by *in situ* grazing incidence X-ray absorption spectroscopy. The results indicate that size-selected Cu<sub>4</sub> clusters are the most active low-pressure catalyst for catalytic CO<sub>2</sub> conversion to CH<sub>3</sub>OH. Density functional theory calculations reveal that Cu<sub>4</sub> clusters have a low activation barrier for conversion of CO<sub>2</sub> to CH<sub>3</sub>OH. This study suggests that small Cu clusters may be excellent and efficient catalysts for recycling of released CO<sub>2</sub>.

The industrial process of methanol (CH<sub>3</sub>OH) synthesis from syngas (CO, CO<sub>2</sub> and H<sub>2</sub>) is carried out at high pressures (10 to 100 bar) using a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst<sup>1</sup>. Due to increasing emission of CO<sub>2</sub> from fossil fuel combustion and other anthropogenic activities, this catalytic system has also become the focus of interest for obtaining sustainable CH<sub>3</sub>OH by hydrogenation of captured CO<sub>2</sub> (CO<sub>2</sub> + 3H<sub>2</sub> → CH<sub>3</sub>OH + H<sub>2</sub>O)<sup>2,3</sup>. Efforts have been made to modify and improve the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst<sup>3-5</sup>. Nevertheless, the high pressure required for achieving a quality yield of CH<sub>3</sub>OH using these catalysts brings a great challenge for reducing the energy input and cost for this process. Also, effective catalysts are in need for alternative feed streams with lower CO<sub>2</sub> concentrations. Thus, developing an effective low-pressure catalyst for CO<sub>2</sub> reduction to CH<sub>3</sub>OH is highly attractive.

Recently, size-selected subnanometer transition metal clusters have received considerable attention in catalysis,

because of their unique electronic and catalytic properties, which differ from bulk metal surfaces and larger nanoparticles. Although a number of computational and experimental studies have been focused on catalytic and electrocatalytic CO<sub>2</sub> reduction to fuels on various metal clusters<sup>6-8</sup> and larger nanoparticles<sup>9-13</sup>, there is a paucity of research on CH<sub>3</sub>OH synthesis from CO<sub>2</sub> and H<sub>2</sub> on size-selected non-precious metal clusters. Previously, we have successfully synthesized subnanometer metal clusters with narrow size distributions on thin film support materials (e.g., Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>), and these materials have shown great potential in the catalytic conversion of small molecules.<sup>14-16</sup> In this contribution, we report on Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> clusters as an effective catalyst for the reduction of CO<sub>2</sub> to CH<sub>3</sub>OH at a low CO<sub>2</sub> partial pressure (0.013 atm), with a higher activity than those of recently developed low-pressure catalysts.

Cu<sub>4</sub> clusters were synthesized using size-selected cluster source,<sup>17</sup> which enables single-size mass selection with atomic precision without fragmentation.<sup>18</sup> The Cu<sub>4</sub> cluster was chosen based on preliminary density functional (DFT) calculations indicating they are active for methanol formation. By soft landing, 7 ng of Cu<sub>4</sub><sup>+</sup> clusters were deposited onto a three monolayer amorphous Al<sub>2</sub>O<sub>3</sub> thin film prepared by atomic layer deposition (ALD) on top of the native oxide of silicon wafer (SiO<sub>2</sub>/Si(100)). The detailed description of the preparation method can be found in the previous report.<sup>17</sup> Previous studies have also shown that such a film can keep a variety of clusters from sintering under reaction conditions.<sup>15,16,19</sup> All samples were exposed to air after synthesis and oxidized copper clusters were identified in the subsequent characterization. The catalytic testing and grazing-incidence X-ray absorption near edge structure (GIXANES) measurements of Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> clusters were performed in a home-built reaction cell<sup>14,20,21</sup> which allows for X-ray scattering off the sample surface at a grazing incident angle ( $\alpha_c = 0.18^\circ$ ) (Details see SI). All measurements were carried out

under *in-situ* conditions with 20 sccm flow of 1% CO<sub>2</sub> and 3% H<sub>2</sub> gas mixture carried in helium at a total pressure of 1.25 atm.

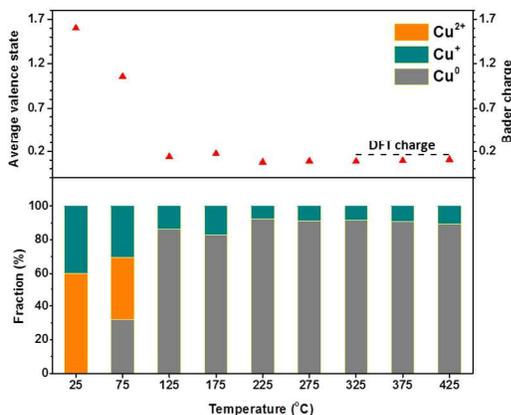


Figure 1. Oxidation state of Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> clusters at different temperatures under *in-situ* catalytic reaction conditions (3% H<sub>2</sub>, 1% CO<sub>2</sub> and 96% He, 1.25 atm): a) Average valence state of Cu<sub>4</sub> clusters. The inserted dashed line indicates the calculated charge from DFT for comparison. b) Linear combination fit (LCF) results of XANES spectra using bulk Cu foil, Cu<sub>2</sub>O and CuO powder as reference materials.

The characteristic GIXANES features at the Cu K-edge<sup>22</sup> reflect the evolution of the oxidation state of supported Cu<sub>4</sub> clusters under *in-situ* reaction conditions, as displayed in Figure S1(a). By comparing the absorption edge of the reference spectra (Cu foil, Cu<sub>2</sub>O and CuO bulk standards in Figure S1(b)), a gradual reduction of Cu<sub>4</sub> clusters under reaction conditions (CO<sub>2</sub>/H<sub>2</sub> gas feed) can be identified upon heating to 425°C. To show the trend in the evolution of the average valence state of copper clusters, a quantitative linear combination fit (LCF) is performed using Cu (Cu<sup>0</sup>), Cu<sub>2</sub>O (Cu<sup>+</sup>) and CuO (Cu<sup>2+</sup>) bulk standards. Figure 1 presents the LCF results as well as the average valence state of Cu<sub>4</sub> clusters with increasing reaction temperature. At room temperature, Cu<sub>4</sub> clusters can be described as primarily composed of oxidized Cu<sup>2+</sup> (~60%) and Cu<sup>+</sup> (~40%), with an average valence state of 1.60. At 75°C a partial reduction takes place, yielding an average copper valence of 1.05. Starting at 125°C, the Cu<sub>4</sub> clusters are practically fully reduced as indicated by the ~0.1 average valence state (Figure 1). The observed non-zero value can be ascribed to some charge transfer to a fully reduced (i.e., Cu<sup>0</sup>) cluster from either the alumina support or adjacent acidic hydroxyls on the surface.<sup>23,24</sup>

The turn-over rate (TOR) of methanol formation from CO<sub>2</sub> hydrogenation over supported Cu<sub>4</sub> clusters is shown in Figure 2. Here, the TOR is defined as the yield of methanol formed per copper atom per second. As discussed earlier, under the reaction conditions, the catalyst becomes Cu<sup>0</sup> when 125°C is reached. This is also the temperature at which CH<sub>3</sub>OH starts to be produced, suggesting that the reduction of CO<sub>2</sub> to CH<sub>3</sub>OH is mainly catalyzed by the fully reduced state of the Cu<sub>4</sub> clusters. As displayed in Figure 2, the maximal TOR of ~4 × 10<sup>-4</sup> molecule·s<sup>-1</sup>·atom<sup>-1</sup> was obtained at 225°C and the rate of methanol production drops above 325°C, which falls into the thermodynamic-control regime.<sup>25</sup> The

observed TOR for methanol synthesis is fairly high in comparison to the numbers in the literature.<sup>25,26</sup> Table 1 lists the TOR's of CO<sub>2</sub> reduction to CH<sub>3</sub>OH for the present catalyst (Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> clusters), recently developed low-pressure catalyst (Ni<sub>5</sub>Ga<sub>3</sub>/SiO<sub>2</sub>), as well as bulk Cu materials (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and polycrystalline Cu foil). It is clear that all the materials reached the maximum activity of CH<sub>3</sub>OH in a similar temperature range, 200–240°C. Compared to Ni<sub>5</sub>Ga<sub>3</sub>/SiO<sub>2</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at the ambient pressure, our catalyst demonstrated much higher activity (one order of magnitude higher) at a slightly higher total pressure (1.25 atm), but with much lower partial pressures (down by up to two orders of magnitude) of the reaction gases (H<sub>2</sub> and CO<sub>2</sub>), although this activity of the supported Cu<sub>4</sub> clusters is lower than that of the polycrystalline Cu surface under a 6 times higher pressure (Table 1). It clearly shows an outstanding activity of the supported Cu<sub>4</sub> clusters for CO<sub>2</sub> reduction to CH<sub>3</sub>OH at a low pressure.

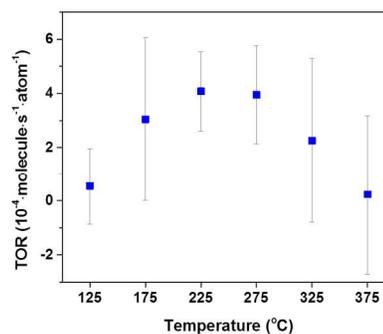


Figure 2. Turn-over rate (TOR) of CO<sub>2</sub> reduction to CH<sub>3</sub>OH over Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> clusters. The data plot is converted from Fig. S2(b) (See SI), by averaging 100 data points at each temperature.

In terms of methane formation (CO<sub>2</sub> + 4H<sub>2</sub> → CH<sub>4</sub> + 2H<sub>2</sub>O), no CH<sub>4</sub> (m/z 15) was obtained as a product below 325°C, see Figure S2. This indicates that methanation is not favorable in this temperature range. Nevertheless, we obtain an increasing CH<sub>4</sub> signal at 375°C accompanied by a rise of m/z 18 signal of water, which likely implies the preference of methanation over methanol synthesis at higher temperatures. However, above 375°C, we also observed the background desorption of hydrocarbon traces (m/z 43 and 56). We note that the fragmentation pattern of these hydrocarbons may also contribute to the CH<sub>4</sub> (m/z 15) signal in the mass spectrometer. Thus, to draw an affirmative conclusion on the high-temperature selectivity of CH<sub>4</sub>, further experiments, e.g., with higher sample loading/purified gas feed, are needed, which is beyond the scope of this paper.

Copper may also catalyze a reverse water-gas shift reaction (rWGS, CO<sub>2</sub> + H<sub>2</sub> → CO + H<sub>2</sub>O)<sup>26,27</sup> at high temperatures. A clear assignment of CO (m/z =28) with mass spectrometry is not feasible in our experiments due to its overlap with fragment ions of CO<sub>2</sub> in the feedstock. However, we observe an increasing water signal m/z 18) above 375°C when the TOR of methanol synthesis declines (see SI). This is a strong indication of other reaction pathways for CO<sub>2</sub> conversion at elevated temperatures, e.g., rWGS or methanation.

DFT calculations were carried out to help understand the

Table 1. Comparison of turn-over rates (TOR)/turn-over frequencies (TOF) of the present work and previous studies

Catalyst	Temperature	Total Pressure	Partial Pressure of H <sub>2</sub>	Partial Pressure of CO <sub>2</sub>	Maximum TOR/TOF of CH <sub>3</sub> OH (molecule·s <sup>-1</sup> ·atom <sup>-1</sup> )	Reference
Cu <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	225°C	1.25 atm	0.038 atm	0.013 atm	4.0×10 <sup>-4</sup> (TOR)	This work
Ni <sub>5</sub> Ga <sub>3</sub> /SiO <sub>2</sub>	200 - 220°C	1 atm	0.75 atm	0.25 atm	6.7×10 <sup>-5</sup> (TOF)*	<sup>25</sup>
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	200 - 220°C	1 atm	0.75 atm	0.25 atm	6.7×10 <sup>-5</sup> (TOF)*	<sup>25</sup>
Polycrystalline Cu foil	237°C	5 atm	4.6 atm	0.4 atm	1.2×10 <sup>-3</sup> (TOR)	<sup>26</sup>

\*These values were converted from the graphs in ref <sup>25</sup>.

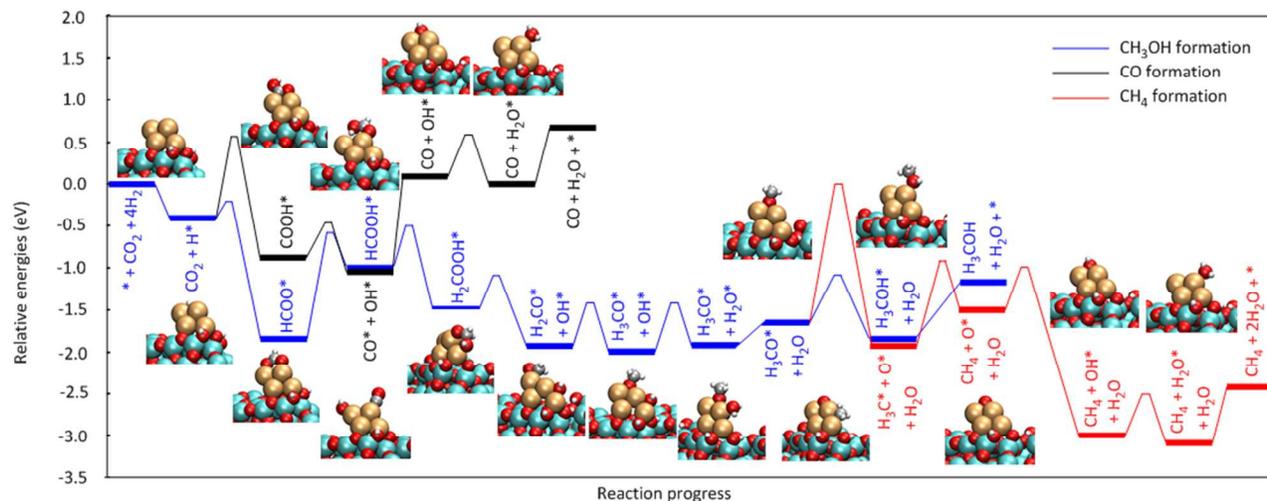


Figure 3. Calculated reaction pathways of CO<sub>2</sub> reduction to CH<sub>3</sub>OH, CO and CH<sub>4</sub> on Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> clusters. The catalyst surface site is labeled as “\*”. To improve legibility, “H<sub>2</sub>” was omitted from the labels after the initial state.

reaction mechanism of the catalytic reduction of CO<sub>2</sub>. The Al<sub>2</sub>O<sub>3</sub> supported Cu<sub>4</sub> cluster (Cu<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>) was constructed by binding the Cu<sub>4</sub> cluster onto a hydroxylated amorphous Al<sub>2</sub>O<sub>3</sub> surface model obtained from a molecular dynamics (MD) simulation<sup>28</sup>. A GGA\_PBE functional<sup>29</sup> with a plane wave basis set was used for geometry optimization and energy calculations. (see SI). The average charge on the supported Cu<sub>4</sub> cluster is found to be +0.16 |e|/atom using Bader charge analysis<sup>30</sup>. In the cluster, the two Cu atoms that are bound to the surface oxygens/hydroxyls have slightly positive charges while the other two Cu atoms carry no charge (see SI). This agrees well with the experimental measurements that the catalyst is mainly fully reduced Cu (Figure 1). The slightly positive charges on the bound Cu atoms are due to the partial oxidation of Cu by the bridging O atoms and the hydroxyl groups on the support. The calculated reaction pathways for the CO<sub>2</sub> reduction to CH<sub>3</sub>OH, CO and CH<sub>4</sub> on Cu<sub>4</sub> are shown in Figure 3. In general, the calculated reaction mechanism of CH<sub>3</sub>OH formation on a supported Cu<sub>4</sub> cluster is similar to that on bulk Cu materials as reported in previous investigations<sup>3,8,31</sup>. The initial step of CH<sub>3</sub>OH formation is the formation of the HCOO\* species (“\*” represents an adsorbed species). The hydrogenation of the HCOO\* species produces HCOOH\*, which is further hydrogenated to H<sub>2</sub>COOH\*. Cleavage of the C-OH bond of H<sub>2</sub>COOH\* leads to its dissociation into H<sub>2</sub>CO\* and OH\*, followed by further hydrogenation of H<sub>2</sub>CO\* to H<sub>3</sub>CO\* and OH\* to H<sub>2</sub>O\*. The hydrogenation of H<sub>3</sub>CO\* generates the final product, CH<sub>3</sub>OH. The rate-limiting step of the CH<sub>3</sub>OH pathway on Cu<sub>4</sub> is found to be the hydrogenation of the HCOO\* species with a predicted

barrier of 1.18 eV. This barrier for the Cu<sub>4</sub> cluster is lower than the predicted rate-limiting barriers for the Cu (111) surface (1.60 eV) and the Cu<sub>20</sub> cluster (1.41 eV), both of which were calculated using a GGA\_PW functional by Yang *et al.*<sup>8</sup> It is also notable that the reaction pathway of the Cu<sub>4</sub> cluster is energetically lower-lying than that of the Cu<sub>20</sub> cluster, which is lower than that of the Cu(111) surface.<sup>8</sup> This indicates that the Cu<sub>4</sub> cluster could be more active for CH<sub>3</sub>OH formation compared to bulk Cu surfaces and larger Cu nanoparticles.

The low reaction barrier for Cu<sub>4</sub> can be explained by the adsorption strength of the adsorbate species to the catalyst. Under-coordinated Cu sites in Cu<sub>4</sub> clusters lead to strong adsorption energies of the adsorbates as found in previous studies of subnanometer clusters,<sup>14</sup> resulting in an energetically lower lying reaction pathway and a lower barrier. Previous work<sup>3-5</sup> has illustrated that high CO<sub>2</sub> and H<sub>2</sub> pressure increase adsorption energies and make the formation of methanol energetically more favorable. This is why high pressures are needed for CO<sub>2</sub> reduction on Cu surfaces.<sup>3-5</sup> It is further consistent with how the strong adsorption of the adsorbates on the under-coordinated Cu<sub>4</sub> clusters leads to high activity at a low CO<sub>2</sub> and H<sub>2</sub> pressures.

For comparison, the reaction pathways for the CO<sub>2</sub> reduction to CO (rWGS) and CH<sub>4</sub> were also investigated (Figure 3). In agreement with a previous DFT study,<sup>32</sup> our calculations showed that the formation of COOH\* on Cu<sub>4</sub>, which initiates rWGS, has much higher barrier (1.08 eV) than that of HCOO\* (0.18 eV), and the rWGS pathway is energetically higher-lying than the CH<sub>3</sub>OH pathway. This suggests that the CH<sub>3</sub>OH formation is likely to be predominant at lower

temperatures for Cu<sub>4</sub>. However, at higher temperatures rWGS could become significant due to a bigger reaction rate consistent with the decreasing signal of CH<sub>3</sub>OH above 325 °C (Figure 2). CH<sub>4</sub> formation, on the other hand, follows the same path as CH<sub>3</sub>OH formation to form the H<sub>3</sub>CO\* species. Then, the breaking of the C-O bond of H<sub>3</sub>CO\* leads to H<sub>3</sub>C\* and O\*, after which H<sub>3</sub>C\* is hydrogenated to CH<sub>4</sub> and O\* is finally hydrogenated to H<sub>2</sub>O. The rate-limiting step of the CH<sub>4</sub> pathway (H<sub>3</sub>CO\* → CH<sub>3</sub>\* + O\*) has a much higher barrier (1.69 eV) than that of the CH<sub>3</sub>OH pathway, suggesting that the CH<sub>4</sub> formation would require a much higher reaction temperature than CH<sub>3</sub>OH formation. This result supports our experimental observations that CH<sub>3</sub>OH was obtained as the main product at a lower temperature range (<375°C), and explains why Cu clusters favor the CH<sub>3</sub>OH formation by the gas-phase hydrogenation of CO<sub>2</sub> rather than the CH<sub>4</sub> formation, even though the net reaction of the latter is thermodynamically more favorable.

To conclude, to our best knowledge the Al<sub>2</sub>O<sub>3</sub> supported size-selected Cu<sub>4</sub> clusters exhibit the highest reported activity to date for CO<sub>2</sub> reduction to CH<sub>3</sub>OH at a low CO<sub>2</sub> partial pressure. The unique coordination environment of Cu atoms in size-selected subnanometer clusters results in the active sites that are superior to those of larger Cu particles. These results for size-selected Cu clusters demonstrate their great potential for the development of novel low-pressure catalysts for CH<sub>3</sub>OH synthesis from catalytic conversion of CO<sub>2</sub> using alternative feed streams with low CO<sub>2</sub> concentration.

## ASSOCIATED CONTENT

### Supporting Information

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## AUTHOR INFORMATION

### Corresponding Author

\*Corresponding authors: [zapol@anl.gov](mailto:zapol@anl.gov) (PZ), [vajda@anl.gov](mailto:vajda@anl.gov) (SV) and [curtiss@anl.gov](mailto:curtiss@anl.gov) (LAC).

### Author Contributions

‡These authors contributed equally.

### Notes

The authors declare no competing financial interests.

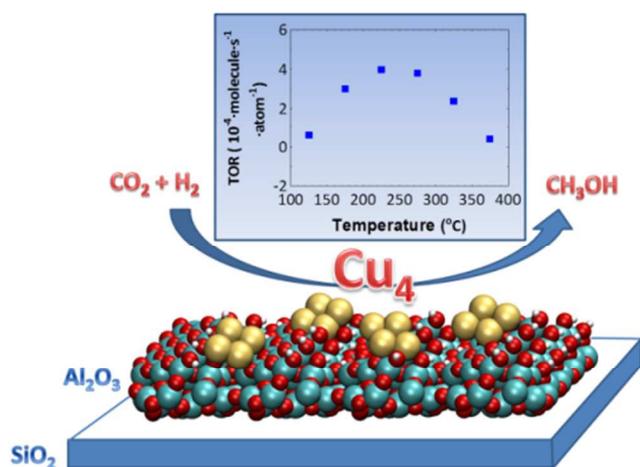
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