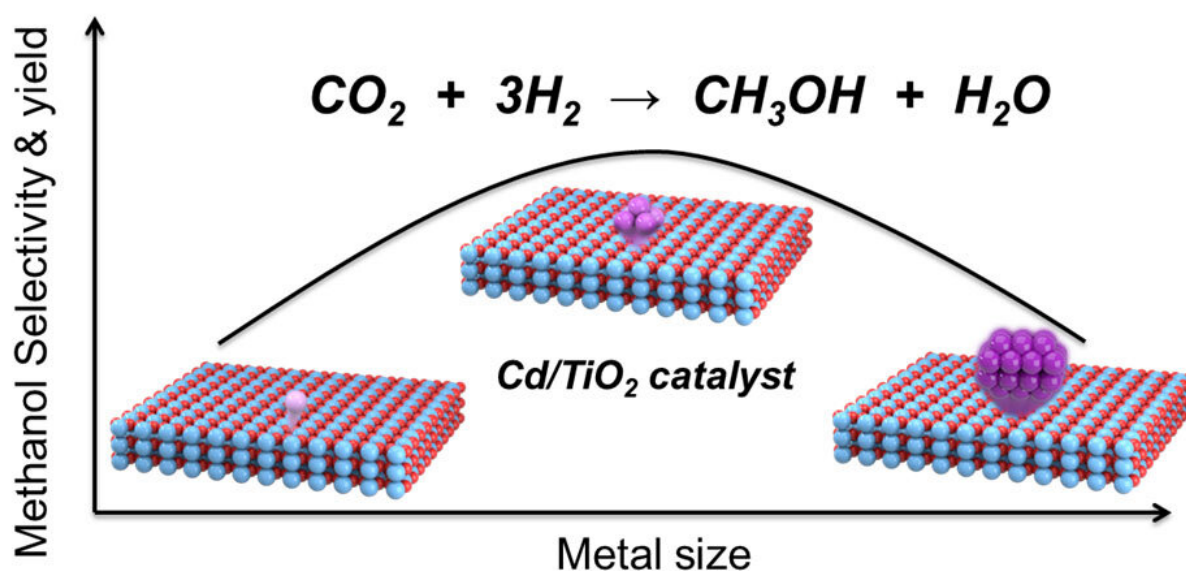


Discovery of a new catalyst for highly active and selective carbon dioxide hydrogenation to methanol

March 11 2022



Credit: *Chinese Journal of Catalysis*

A new catalyst of Cd/TiO₂, enabling 81% methanol selectivity at 15.8% CO₂ conversion with the CH₄ selectivity below 0.7% was discovered. The combination of experimental and computational studies show that the unique electronic properties of Cd cluster supported on TiO₂ are responsible for the high selectivity for CO₂ hydrogenation to methanol via a HCOO* pathway realized at the interface catalytic sites.

Carbon dioxide capture and utilization (CCU) using [renewable energy](#) is an effective way to achieve carbon neutrality, thus drawing increasing attention from industry and academia worldwide. A promising route for CO₂ utilization is [methanol](#) production ($\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$) since methanol can be used as an easily transportable fuel, an H₂-storage molecule, or a precursor for the production of olefins and aromatics. Heterogeneous catalysts are commonly available for CO₂ [hydrogenation](#) to methanol by using a fixed bed reactor, which is capable for scale-up industrial applications. Until now, CuZnO catalysts have been widely investigated for CO₂ hydrogenation to methanol. However, the methanol selectivity reported so far hardly exceeds 60% under the optimal operation conditions because of the competing side reactions, such as reverse water-gas shift reaction (RWGS). Besides, Cu-based catalysts usually suffer from deactivation caused by sintering. Thus, non-Cu catalysts have drawn increasing attentions in recent years.

Recently, a research team led by Prof. Can Li from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China discovered a Cd cluster based Cd/TiO₂ catalyst, which shows 81% methanol selectivity at CO₂ conversion of 15.8%, while enabling to keep the CH₄ under 0.7% at 5 MPa. The results were published in *Chinese Journal of Catalysis*.

Cd/TiO₂ catalysts were prepared by wet impregnation using TiO₂ support. Both the activity and selectivity increase with the increase of Cd loading and reach the maximum at 3.5% Cd. Further increasing the Cd loading from 3.5% to 7% just results in a slight decrease of both activity and selectivity. 3.5% Cd/TiO₂ catalyst exhibits 81% methanol selectivity and 15.8% CO₂ conversion under 5 MPa, and exhibits a methanol yield of 6.7% ($X(\text{CO}_2)=9.4\%$, $S(\text{CH}_3\text{OH})=71\%$), which is approaching the thermodynamic equilibrium under the conditions of 2 MPa, 290 °C.

The structure characterizations show that Cd species of 0.35% Cd/TiO₂

catalyst are atomically dispersed with isolated Cd sites on TiO₂. For 3.5%Cd/TiO₂ [catalyst](#), a lot of sub-nanometer Cd clusters emerge besides isolated Cd sites. When the Cd loading further increases to 7%, nanometer-size Cd particles are observed in addition to Cd clusters and isolated Cd sites. During the reaction, the Cd species are in the +2 [oxidation state](#) for 0.35%Cd/TiO₂ and 3.5% Cd/TiO₂, Cd species are reduced to metal state for 7%Cd/TiO₂.

The mechanism investigations show that the HCOO* pathway is a possible pathway for CO₂ hydrogenation to methanol. DFT calculations show that the key reaction intermediates of HCOO*, HCOOH*, and CH₂O*_H₂O* on the surface of CdTiO₃ (Cd₁ structure) are much more stable compared to the respective states on the Cd₄/TiO₂ interface. Accordingly, the evolution of these intermediates along with the catalytic reaction coordinate proceeds with much higher barriers, evidencing a much higher catalytic CO₂ hydrogenation activity of the Cd₄/TiO₂ over the bulk CdTiO₃ mixed oxide phase.

More information: Jijie Wang et al, Highly dispersed Cd cluster supported on TiO₂ as an efficient catalyst for CO₂ hydrogenation to methanol, *Chinese Journal of Catalysis* (2022). [DOI: 10.1016/S1872-2067\(21\)63907-4](#)

Provided by Chinese Academy of Sciences

Citation: Discovery of a new catalyst for highly active and selective carbon dioxide hydrogenation to methanol (2022, March 11) retrieved 19 April 2024 from <https://phys.org/news/2022-03-discovery-catalyst-highly-carbon-dioxide.html>

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