Photocatalytic versus Thermal Reaction Pathways of CO_2 Methanation over Single Ru–Ni/ZrO_2 Catalyst Proved by DFT Calculations

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Photocatalytic CO_2 reduction into fuels and/or valuable chemicals creates new C neutral cycle. Major problem to apply this technique in sustainable society is slow formation rates of fuels and/or value-added chemicals that are governed by photon number of the light reaching the earth [1].

In this report, the formation rates were increased both by increasing irradiated photons and by effective additive to photocatalyst. The effect of irradiated UV–visible light intensity on photocatalysis was evaluated. We previously reported one of the best photocatalytic CO_2 methanation activity using Ni/ZrO_2 photocatalyst: 0.98 mmol h^{-1} g_{cat}^{-1} irradiated by UV–visible light @186 mW cm^{-2} [2]. Therefore, the effect of single Ru doped onto Ni/ZrO_2 photocatalyst on CH_4 formation rate was also evaluated.

In the evaluation, reaction pathway including the activation energy was important based on density functional theory calculations using Vienna Ab Initio Simulation Package code version 6.4.1. The supercomputer of ISSP was ultimately essential for the searches of reaction pathway for each step from CO_2 to CH_4 over the composite surface of the best photocatalyst using climbing-image nudged elastic band method mostly owing to the CPU comprising more than 128 cores at ISSP.

When the UV–visible light intensity was increased from 186 mW cm^{-2} [2] to 713 mW cm^{-2}, the CO_2 methanation rate increased from 0.98 to 2.9 mmol h^{-1} g_{cat}^{-1} using Ni/ZrO_2 photocatalyst. Furthermore, by doping single Ru (1.0 wt %) to Ni/ZrO_2, the CO_2 methanation rate even increased to 8.9 mmol h^{-1} g_{cat}^{-1} @713 mW cm^{-2}.

DFT calculation results were summarized in Schemes 1 and 2 using single Ru–Ni/ZrO_2 photocatalyst (Panels A and B) in comparison to Ni/ZrO_2 photocatalyst (Panel B′). Scheme 1 corresponded to photocatalytic CO_2 methanation irradiated at 186 mW cm^{-2} or photocatalyst cooled in water bath irradiated at 568 mW cm^{-2}. The activation energy was the highest: 1.17 eV from adsorbed CO_2 to OCOH species at O vacancy site at ZrO_2 surface [3] using both single Ru–Ni/ZrO_2 and Ni/ZrO_2 (Scheme 1B and B′). In fact, under these photocatalytic reaction conditions, photocatalytic CO_2 methanation rates were essentially equivalent either using single Ru–Ni/ZrO_2 or Ni/ZrO_2.

Scheme 2 corresponded to photocatalytic CO_2 methanation irradiated by UV–visible light at 713 mW cm^{-2}, without water cooling. Under the reaction conditions, the catalyst was heated by light energy and the charge separation and resulting red-ox reactions over ZrO_2 surface became negligible compared to thermal steps over Ru and/or Ni (Scheme 2A). Under such reaction conditions, single Ru atom on Ni nanocluster lattice adsorbed CO_2 (Scheme 2B(b) and (b′)) and facilitated the dissociation to CO and O (species c), whereas over Ni cluster surface free from Ru, the weakly-adsorbed CO_2 was much more difficult to dissociate (Scheme 2B′(b) and (c)). This accounted for the rate difference of 2.9 mmol h^{-1} g_{cat}^{-1} using Ni/ZrO_2 versus 8.9 mmol h^{-1} g_{cat}^{-1} using single Ru–Ni/ZrO_2 @713 mW cm^{-2}. The reaction pathway illustrated in Scheme 2A and B was also supported by predominantly adsorbed CO species over single Ru–Ni/ZrO_2 under UV–visible light (Scheme 2A(c–e)) observed by FTIR.

References

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[2] H. Zhang, T. Itoi, T. Konishi, and Y. Izumi, *Angew. Chem. Int. Ed.* **60**, 9045–9054 (2021).

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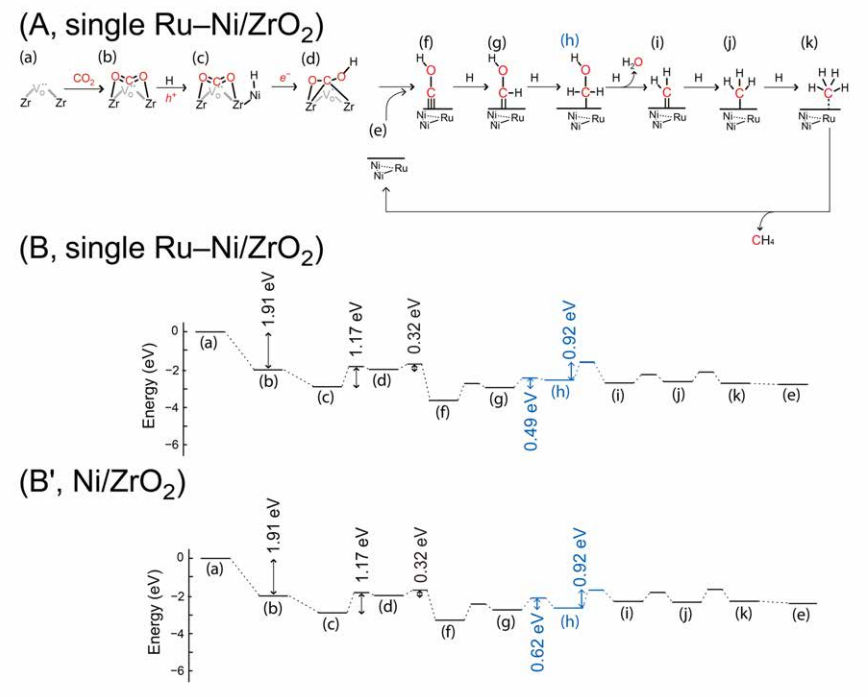
Scheme 1. Proposed photocatalytic reaction pathway and corresponding free energy calculations of CO_2 photoreduction to proceed over (A, B) single Ru–Ni/ZrO_2 and (B') Ni/ZrO_2.



Scheme 2. (A) Proposed thermal reaction pathway and corresponding free energy calculations of CO_2 reduction using (B) Ni/ZrO_2 and (B') single Ru–Ni/ZrO_2.