

Understanding Methanation Inhibition Using Cs-promoted Defective Carbon Supports for Ru Catalysts in Ammonia Production

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Significance and Relevance

Our study investigates the role of Cs promoters and vacancy of carbon support in ammonia production, focusing on hydrogen spillover leading to methanation issues. Using density functional theory (DFT), we explored the role of the Ru-carbon interface, carbon vacancies, and Cs promoters. Our findings reveal that the vacancies of carbon supports and CsOH promoters are crucial in reducing methanation. This insight highlights the importance of support material properties and promoter effects in enhancing catalyst stability and activity, offering strategies for catalysts design in hydrogen-related reactions.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis, Multiscale modeling and advanced simulation aspects Preferred presentation: Poster

Introduction and Motivations

Ru-based catalysts, produced using the Kellogg Advanced Ammonia Process (KAAP) and supported on graphite, are widely used in industrial ammonia synthesis. However, methanation through hydrogen spillover on these carbon-supported Ru catalysts poses a significant problem, reducing both catalyst stability and activity. Experimental results have shown that adding a Cs promoter and altering the graphitization degree of carbon supports can reduce methanation.¹ However, the mechanism behind this reduction remains unclear. To address this, we used density functional theory (DFT) to investigate the role of the Ru-carbon interface, carbon vacancies, and promoters in carbon support methanation. Our results indicate that the synergistic effect of the graphitization degree of carbon supports and the promoter is crucial for reducing methanation.

Materials and Methods

Spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP). The Ru and Cs promoted Ru cluster were bound to a 7 × 7 supercell of the vacancy graphene (VG) with dimensions a = 17.27 Å, b = 17.27 Å, and c = 20 Å. Adsorption energy per hydrogen atom was using the equation $E_{ads} = (E_{nH/cat} - E_{cat} - n \times 0.5 \times E_{H2})/n$ to calculate, where $E_{nH/cat}$ represents the total energy of hydrogen adsorption on the VG supported Ru or Cs promoted Ru catalyst models, E_{cat} denotes the total energy of the bare catalyst models, n symbolizes the number of H atom adsorbed, and E_{H2} is the total energy of the H₂ molecules.

Results and Discussion

In our previous study, we used a single Ru atom on graphene to understand the role of Cs promoters. CsOH acts as a spillover site for hydrogen, lowering the activation barrier for hydrogen spillover.¹ To further investigate the hydrogen spillover pathway and the effect of vacancies on the carbon support, we built a model with Ru₈ cluster on graphene with two vacancies (Ru₈/VG), as shown in Figure 1(a). The Ru₈ cluster is the smallest size to model the B₅ active site. Of the two vacancies on graphene, one anchors the Ru₈ cluster, and the other facilitates hydrogen spillover. In the previous study, the Cs



promoter was found between the Ru and carbon support interface.² Therefore, we placed CsOH near the Ru₈ model (CsOH–Ru₈/VG, Figure 1(b)) to discuss the mechanism with and without CsOH.

Our results show that as more hydrogen atoms are adsorbed on Ru₈/VG, the $E_{ads/H}$ values become more positive, indicating weaker hydrogen adsorption strength with increased coverage. When a hydrogen atom spills over to the top site of graphene, the $E_{ads/H}$ values of the spillover structure are always more positive than those of non-spillover structures. Conversely, when hydrogen atoms spill over to a vacancy on graphene, the $E_{ads/H}$ values of the spillover structure are always more negative than those of non-spillover structures (Figure 1(c)). These findings indicate that high graphitization degree (graphene without defects) in carbon supports prevent hydrogen spillover to the support, leading to methanation. In contrast, carbon materials with vacancies facilitate hydrogen spillover, resulting in methanation on carbon supports.

For the CsOH–Ru₈/VG system, when hydrogen spills over to graphene, the $E_{ads/H}$ values indicate that the preferred site for spillover is the vacancy, similar to the result for Ru₈/VG. However, in the absence of a vacancy, hydrogen will spill over to the OH group of CsOH at high hydrogen coverage. This result demonstrates that the Cs promoter and the vacancy of carbon materials play crucial roles in reducing hydrogen poisoning and methanation. A higher graphitization degree of carbon materials reduces carbon support methanation, while CsOH provides an additional spillover site to mitigate hydrogen poisoning.



Figure 1 (a) Optimized structure of Ru_8/VG . (b) Optimized structure of CsOH- Ru_8/VG . (c) Adsorption energy per hydrogen ($E_{ads/H}$) of non-spillover and spillover with different numbers of H atoms on Ru_8/VG . Atom color: grey: Ru atoms, dark grey: Ru atoms of B_5 site, brown: carbon atoms, blue dash line: vacancy, pink: hydrogen atoms, green: Cs atom, and red: O atom.

References

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- 2. Z. Kowalczyk, M. Krukowski, W. Raróg-Pilecka, D. Szmigiel and J. Zielinski, *Applied Catalysis A: General*, 2003, **248**, 67–73.

Acknowledgements

Acknowledge National Science and Technology Council, NSTC (111-2221-E-007-087-MY3, 111-2112-M-007-028-MY3) and National Tsing Hua University (113QI021E1, 113Q2773E1) in Taiwan for their financial support. The computational resources were supported by TAIWANIA at the National Center for High-Performance Computing of National Applied Research Laboratories in Taiwan.