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Dissertation Defense

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Mechanism and Kinetics of Photocatalytic Partial Oxidation of Methane on Single MO_x Reaction Centers

ABSTRACT:

Single-site transition-metal doped photocatalysts are a class of materials in which small transition-metal oxide clusters are embedded onto the surface of zeolites, graphene, and bulk semiconductors. Experimental findings demonstrate that VO_4 , CrO_4 , NbO_4 , and WO_4 clusters embedded on an MCM-41 mesoporous amorphous SiO_2 are effective photocatalysts for oxidative reactions. The selective direct partial oxidation of methane (POM) to form methanol is an important reaction for the efficient utilization of natural gas.¹⁻⁴ Photocatalytic methane oxidation has advantages over traditional thermal catalysis as it can be deployed at small-scale facilities to potentially reduce methane release into the atmosphere due to flaring. Our work has aimed to examine the nature of the V, Cr, Nb, and W transition-metal oxide doped MCM-41 amorphous SiO_2 ($\text{MO}_x/\text{MCM-41}$) materials for their viability in the POM reaction towards the formation of methanol.⁵⁻⁸

Photoexcited state manifolds are examined to determine the nature of electronic excitation in these $\text{MO}_x/\text{MCM-41}$ materials. To examine if the excited state electronic structures are localized to MO_x species and to examine if the low-lying excited states possess electronic structures that can facilitate the POM methanol producing reaction. We then elucidate the POM reaction mechanisms using computational studies involving density functional theory (DFT).⁹ We examine the role of terminal versus bridging oxygens at the photocatalytic center in enhancing photocatalytic efficiency. We calculate the energetics of the POM reaction on the various $\text{MO}_x/\text{MCM-41}$ materials across reaction maps showing multiple possible photocatalytic reaction pathways. The calculated energetics are then analyzed through microkinetic modeling (MKM) in order to locate rate determining intermediates and the reaction time scale of the POM cycle to find which photocatalytic $\text{MO}_x/\text{MCM-41}$ material would most efficiently facilitate the selective formation of methanol.¹⁰⁻¹⁵

REFERENCES:

1. Hu, Y.; Anpo, M.; and Wei, C. *J. Photochem. Photobiol. A*, **2013**, *264*, 48–55.
2. Hall, T.; Hargreaves, J.; Hutchings, G.; Joyner, R.; Taylor, S. *Fuel Process. Technol.*, **1995**, *42*, 151–178.
3. Lunsford, J. *Catal. Today*, **2000**, *63*, 165–174.
4. Nguyen, L.; Loridant, S.; Launay, H.; Pigamo, A.; Dubois, J.; Millet, J. *J. Catal.*, **2006**, *237*, 38–48.
5. Zakaria, Z.; Kamarudin, S. *Renewable Sustainable Energy Rev.*, **2016**, *65*, 250–261.
6. Ozkan, U.; Watson, R. *Catalysis Today*, **2005**, *100*, 101–114, 100th Anniversary Issue.
7. Gao, X.; Wachs, I.; Wong, M.; Ying, J. *Journal of Catalysis*, **2001**, *203*, 18–24.
8. Gomes, H. *et al. Microporous and Mesoporous Mater.*, **2005**, *86*, 287–294.
9. Liang, W.; Bell, A.; Head-Gordon, M.; Chakraborty, A. *J. Phys. Chem. B*, **2004**, *108*, 4362–4368.
10. Motagamwala, A.; Dumesic, J. *Chem. Rev.*, **2021**, *121*, 1049–1076.
11. Park, J.; Kim, H.; Lee, W.; Park, M. *Catalysts*, **2020**, *10*, 655.
12. Cui, C. *et al. J. Catal.*, **2016**, *343*, 257–265.
13. Thompson, L.; Jarrold, C.; Hratchian, H. *J. Chem. Phys.*, **2017**, *146*, 104301.
14. Evrard, C.; Mahler, A.; Thompson, L. *ACS Symposium Series*, **2019**, *1331*, 327–341.
15. Wang, Y.; Hu, P.; Yang, J.; Zhu, Y.; Chen, D. *Chem. Soc. Rev.*, **2021**, *50*, 4299–4358.