CellPress

Chem Catalysis

Previews

Edge-confined under-coordinated Cu atoms on Ru nanosheets enable efficient CH_4 activation

Pawan Kumar,[1] Jinguang Hu,[1,*] and Md Golam Kibria[1,*]

In this issue of *Chem Catalysis*, Jinchang Fan et al. demonstrate that Cu atoms confined in ultrathin 2D metallic Ru nanosheets ($Ru_{11}Cu$ NSs) favor bi-coordinated adsorption of O* species to reduce the activation energy barrier for a facile C–H bond cleavage to C_1 oxygenates (CH_3OOH and CH_3OH) with 99% selectivity.

The one-step selective oxidation of methane to liquid oxygenates is a long-foreseen reaction that has the potential to substitute energy-hungry steam methane reforming (SMR) and Fischer-Tropsch (FT) processes. However, exorbitant stability, negligible electron affinity, and low polarizability ($2.84 \times 10^{-40}\ C^2\ m^2\ J^{-1}$) due to non-polar tetrahedral structure render a significantly high energy barrier for the dissociation of the $C(sp^3)-H$ bond (439 kJ mol^{-1}).[1] Initial progress using noble-metal- and transition-metal-based homogeneous and stoichiometric catalysts demands harsh conditions (high temperature, acids, and strong oxidants) with poor conversion and selectivity. Further, after the first C–H bond cleavage, thermodynamically favorable deep mineralization of generated oxygenates produces CO and CO_2, which compromise the carbon economy.

Ideally, CH_4 oxidation should be driven by molecular oxygen; however, the direct reaction of spin-prohibited singlet CH_4 and triplet O_2 ground states is highly unfavorable.[2] Methanotrophs armed with methane monooxygenase (MMO) enzymatic assemblies and cytochrome P450s (P450s) can activate molecular oxygen to direct the selective methane oxidation to oxygenates.[3] Bioinspired catalytic systems provide faster product delivery than metalloenzymes with the added advantage of resiliency and structural tunability. The avant-garde work of Hutching and co-workers on TiO_2-supported Au-Pd alloy nanoparticles for CH_4 oxidation using H_2O_2 has stimulated tremendous progress in designing supported nanoparticulate catalysts.[4] Sub-nanometric size reduction to a few atoms or single-atom states manifests better activity and selectivity as a result of maximized exposed sites, high surface energy, and metal-ligand-induced $CH_3^{\delta-}$-$H^{\delta+}$ electrostatic polarization of CH_4. Isolated mono-/bis(μ-oxo)metal species in metal-organic framework (MOF) nodes and metal (Cu, Fe)-exchanged zeolitic frameworks (ZSM-5, CHA, MOR, etc.) are among the high-potential candidates because of the formation of active hypervalent M=O species and stabilization of intermediate state by methoxy group migration, which prevent deep mineralization.[5,6] Despite significant advancements, the low space-time yield of oxygenates remains far below commercial applicability.

Recent research on single-atom catalysts and single-atom alloy catalysts demonstrated that under-coordinated metal centers implanted on a support provide coordination sites for CH_4 activation.[7] In contrast to bulk 3D crystals, 2D nanosheets bestow ample edge termination to pin under-coordinated metallic entities. Extensive research on Cu-ZSM-5 has demonstrated that Cu possesses a high affinity for methane oxidation and also prevents deep mineralization because of its innate ability to scavenge $^{\bullet}OH$ radicals.[8] Further, dimeric and trimeric Cu nanoclusters are reported to form bridged Cu(μ-oxo) species like in pMMO via oxygen/H_2O_2 activation followed by O* transfer to CH_4, facilitating cooperative catalysis.[9]

In this issue of *Chem Catalysis*, Fan et al.[10] rationally designed atomically dispersed metallic Cu sites on the surface of Ru nanosheets (Ru NSs) for selective room-temperature CH_4 oxidation to C_1 oxygenates. The Ru/Cu atomic-ratio optimization (3–13) reveals that $Ru_{11}Cu$ can afford a maximum CH_4 utilization yielding 1,533 mmol $g^{-1}{}_{Cu(surf.)}\ h^{-1}$ C_1 products (CH_3OOH and CH_3OH) with 99% selectivity by using H_2O_2 as an oxidant. The authors employed atomic force microscopy and high-angle annular dark-field scanning transmission electron microscopy coupled with fast Fourier transform, which demonstrated 2.6 ± 0.4-nm-thick Ru sheets with (101) exposed facets arranged in an ABAB pattern. X-ray photoelectron spectroscopy and Cu K-edge X-ray absorption near-edge structure analysis showed predominant metallic Cu^0 and Ru^0 entities with a slight binding energy shift due to a partial charge transfer from Cu to Ru, which stabilized the Cu species. The Fourier-transform extended X-ray absorption fine structure data fitting showed an increase in Cu-Ru coordination ($CN_{Cu\text{-}Ru}$)

---

[1] Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive NW, Calgary, AB T2N 1N4, Canada

*Correspondence:
jinguang.hu@ucalgary.ca (J.H.),
md.kibria@ucalgary.ca (M.G.K.)

https://doi.org/10.1016/j.checat.2022.08.007

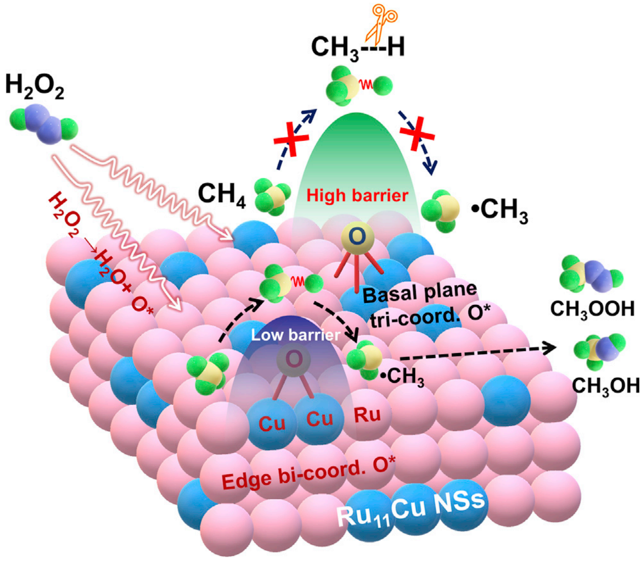

Figure 1. Schematic representation of CH_4 oxidation of $Ru_{11}Cu$ NSs

H_2O_2 dissociation followed by the formation of bi-coordinated O* species on the edge, which are more favorable (i.e., offer a lower activation energy barrier for $^{\bullet}CH_3$ radical generation) than tri-coordinated O* species on the basal plane.

from 4.3 to 5.5 and a decrease in $CN_{Cu\text{-}Cu}$ coordination from 2.5 to 1.6 when the Ru/Cu ratio was varied from 3 to 13, suggesting the existence of Cu in 1–3 atomic units. Fan et al. observed that the total Cu coordination number (∼7) was close to edge-confined Cu (4–8) and much lower than the surface (9) and bulk (12) Cu atoms, substantiating the presence of under-coordinated Cu on Ru NSs edges. The product trajectory of isotopically labeled $^{13}CH_4$ followed by ^{1}H NMR and ^{1}H-^{13}C heteronuclear multiple-quantum correlation afforded dominant CH_3OOH with small amounts of CH_3OH and $HOCH_2OOH$ and overruled any contamination.

Fan et al. also performed electron paramagnetic resonance analysis, which demonstrated a methyl radical ($^{\bullet}CH_3$) and hydroxyl radical ($^{\bullet}OH$) and the absence of any ^{18}O-labeled product by using $H_2{}^{18}O$, showing active participation of H_2O_2 in reactions. The mechanism determination using density functional theory showed the facile decomposition of H_2O_2 and spillover of active O* species over the Ru NS surface. The edge-confined bi-coordinated O* on Cu_{1-3} aggregates provided a lower activation energy barrier (0.79, 0.47, and 0.38 eV for Cu_1, Cu_2, and Cu_3 sites, respectively) for the CH_4-to-$^{\bullet}CH_3$ radical generation than did tri-coordinated O* species at the basal plane (Figure 1). Interestingly, pure Cu (111) edges imposed a high activation barrier (ΔG_{act} = 1.53 eV) for the transformation of O* from OH*, so reaction on pure Cu was not feasible. The improved activity was due to cooperative adsorption of O* on Cu-decorated Ru edges, which increase the O 2p state density near the Fermi level. The authors proposed a free-radical mechanism where CH_4 reacts with bi-coordinated O* sites to generate a $^{\bullet}CH_3$ radical, which then reacts with $^{\bullet}OOH$ radicals to produce CH_3OOH in high yield.

Fan et al.'s study highlights an important aspect of molecular-level control of the coordination environment, which concomitantly governs the reactivity as a result of the generation of active O* species for CH_4 oxidation. The study also demonstrates that 2D sheets might serve as a support material for manipulating localized charge distribution over metal species to enhance CH_4 conversion. Although this study puts forth new understandings for transforming polluting CH_4 into valuable chemicals, the use of costly noble metals and stringent H_2O_2 oxidant is concerning; these should be replaced with cheap Earth-abundant transition metals and O_2 oxidants. Additionally, the rapid drop in oxygenate productivity and the emergence of CO_2 could indicate overoxidation of products during the course of the reaction. The probable mechanism for CH_3OH generation and strategies to prevent deep mineralization over the catalyst's surface remain unaddressed. Additionally, the CH_4 conversion rate and selectivity toward more desirable CH_3OH must be galvanized by methods that can populate the concentration of edge-confined species and ligate two or more metal species.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support provided by the Canada First Research Excellence Fund (CFREF) at the University of Calgary.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Li, Q., Ouyang, Y., Li, H., Wang, L., and Zeng, J. (2022). Photocatalytic conversion of methane: Recent advancements and prospects. Angew. Chem. Int. Ed. *61*, e202108069. https://doi.org/10.1002/anie.202108069.

2. Montemore, M.M., van Spronsen, M.A., Madix, R.J., and Friend, C.M. (2018). O_2 activation by metal surfaces: Implications for bonding and reactivity on heterogeneous catalysts. Chem. Rev. *118*, 2816–2862. https://doi.org/10.1021/acs.chemrev.7b00217.

3. Wang, V.C.-C., Maji, S., Chen, P.P.-Y., Lee, H.K., Yu, S.S.-F., and Chan, S.I. (2017). Alkane oxidation: Methane monooxygenases, related enzymes, and their biomimetics. Chem. Rev. *117*, 8574–8621. https://doi.org/10.1021/acs.chemrev.6b00624.

4. Ab Rahim, M.H., Forde, M.M., Jenkins, R.L., Hammond, C., He, Q., Dimitratos, N., Lopez-Sanchez, J.A., Carley, A.F., Taylor,

S.H., Willock, D.J., et al. (2013). Oxidation of methane to methanol with hydrogen peroxide using supported gold–palladium alloy nanoparticles. Angew. Chem. Int. Ed. *52*, 1280–1284. https://doi.org/10.1002/anie.201207717.

5. Ravi, M., Sushkevich, V.L., Knorpp, A.J., Newton, M.A., Palagin, D., Pinar, A.B., Ranocchiari, M., and van Bokhoven, J.A. (2019). Misconceptions and challenges in methane-to-methanol over transition-metal-exchanged zeolites. Nat. Catal. *2*, 485–494. https://doi.org/10.1038/s41929-019-0273-z.
6. Simons, M.C., Prinslow, S.D., Babucci, M., Hoffman, A.S., Hong, J., Vitillo, J.G., Bare, S.R., Gates, B.C., Lu, C.C., Gagliardi, L., and Bhan, A. (2021). Beyond radical rebound: Methane oxidation to methanol catalyzed by iron species in metal–organic framework nodes. J. Am. Chem. Soc. *143*, 12165–12174. https://doi.org/10.1021/jacs.1c04766.
7. Kumar, P., Al-Attas, T.A., Hu, J., and Kibria, M.G. (2022). Single atom catalysts for selective methane oxidation to oxygenates. ACS Nano *16*, 8557–8618. https://doi.org/10.1021/acsnano.2c02464.
8. Hammond, C., Forde, M.M., Ab Rahim, M.H., Thetford, A., He, Q., Jenkins, R.L., Dimitratos, N., Lopez-Sanchez, J.A., Dummer, N.F., Murphy, D.M., et al. (2012). Direct catalytic conversion of methane to methanol in an aqueous medium by using copper-promoted Fe-ZSM-5. Angew. Chem. Int. Ed. *124*, 5219–5223. https://doi.org/10.1002/anie.201108706.
9. Tsai, Y.-F., Natarajan, T., Lin, Z.-H., Tsai, I.-K., Janmanchi, D., Chan, S.I., and Yu, S.S.-F. (2022). Voltage-gated electrocatalysis of efficient and selective methane oxidation by tricopper clusters under ambient conditions. J. Am. Chem. Soc. *144*, 9695–9706. https://doi.org/10.1021/jacs.2c01169.
10. Fan, J.L., Zhu, S., Mao, K., Cui, J., Ma, X., Yu, C., Deng, L., and Dehui. (2022). Boosting room-temperature conversion of methane via confining Cu atoms into ultrathin Ru nanosheets. Chem Catal. *2*, 2253–2261. https://doi.org/10.1016/j.checat.2022.07.025.

Theoretical and experimental uncovering of Nb-TiO_2 single atoms for NRR electrocatalysts

Michele Melchionna[1] and Paolo Fornasiero[1,*]

In this issue of *Chem Catalysis*, Gao et al. have devised a single-atom catalyst (SAC) based on Nb-TiO_2 for the N_2 reduction (NRR) to NH_3 achieving a very competitive performance with those of the NRR benchmark catalysts. Notably, the employed approach is based on a rational design of the catalytic materials, where theory and experiment go hand in hand toward a sensible exploitation of all the features that play a critical role in the mechanism of reduction.

Single-atom catalysts (SACs) have projected a long shadow in the last decade that, in a way, is jeopardizing the popularity of conventional nanoparticle-based heterogeneous catalysts. Indeed, SACs are catching up with other longer-tradition catalysts and are today considered as the latest frontier in catalysis. There are a number of solid reasons for the buzzing interest in SACs, and two main levers concern the very fashionable concept of "atom economy" (with concomitant increase of the catalyst turnover frequencies) and the possibility to allow unique reaction pathways because of the isolated state of the catalytic active species, therefore meaning the absence of adjacent metal atoms. These powerful properties justify the versatility of SACs, which set new benchmark performances in an extended range of catalytic processes.[1]

Among the various types of catalysis, electrocatalysis represents one of the pillars of modern chemistry. It's renaissance is due to the fact that it embraces concepts of sustainability and new energy schemes whereby small molecules (e.g., CO_2, O_2, and N_2) can be converted into fuels and is generally relevant for green energy strategies.[2,3] The electrocatalytic reduction of N_2 (NRR) to ammonia is perhaps the most challenging reaction among the above-mentioned conversions. In the first place, the high stability of the N_2 molecule combined with its poor solubility in aqueous electrolytes (which are the most attractive in connection with sustainability) makes this transformation highly demanding, thermodynamically and kinetically. Still, the central role of the NH_3 molecule in industry motivates the extensive (and often frustrating) search for new electrocatalytic materials that are able to compete economically with the Haber-Bosch process, today the industrially most-used synthetic scheme for NH_3. In addition to the thermodynamic and kinetic constraints of the NRR, a significant number of other technical issues has continued to emerge over the years, which has raised many concerns within the electrocatalysis community. In particular, the proliferation of articles (encouraged by the hotness of the topic) is questioned based on doubtful data that are in reality affected by the enormous analytical hurdles associated with the rigorous NH_3 detection and quantification.[4] Efforts have therefore been channeled by some scientists

---

[1] Chemistry Department, INSTM and ICCOM-CNR Trieste Research Unit, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

*Correspondence: pfornasiero@units.it

https://doi.org/10.1016/j.checat.2022.07.010

© 2022 Elsevier Inc.