

An efficient catalyst for selective methane oxidation under ambient conditions

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Abstract: A quasi-heterogeneous catalyst capable of selective methane (CH₄) oxidation under ambient conditions has been developed. The catalyst consists of a tricopper cluster complex immobilized in mesoporous silica nanoparticles. We will describe how this catalytic system functions, its performance, as well as its robustness and reuseability. The catalyst is activated by O₂ and catalytic turnover is sustained with a molecule of H₂O₂ for each CH₄ molecule oxidized. The catalytic efficiency is unprecedented. Progress toward developing this catalytic system to accomplish the conversion of the light alkanes in natural gas into their condensed oxidation products will be demonstrated.

Keywords: heterogeneous catalysis, methane oxidation, tricopper cluster complex.

1. Introduction

The conversion of methane (CH₄) into methanol (CH₃OH) is challenging chemistry. First, the C–H bonds of CH₄ are extremely inert because of their high bond dissociation energies (104 kcal mol⁻¹). In addition, the product CH₃OH is prone to further oxidation to other products (HCHO and HCOOH). To accomplish this chemistry selectively, we therefore need to develop a catalyst that is specific for the direct oxidation of CH₄ to CH₃OH without over-oxidation.¹

Based on our understanding of the active site in the particulate methane monooxygenase (pMMO), a multi-copper enzyme that mediates efficient selective oxidation of CH₄ to CH₃OH in methanotrophic bacteria, we have recently developed a biomimetic catalyst capable of oxidizing CH₄ to CH₃OH without over-oxidation.¹⁻³ This catalyst consists of a Cu^ICu^ICu^I tricopper cluster complex, which can be activated by O₂ to harness a hot “oxene” that is rapidly inserted into the C–H bond of CH₄ in the transition state to yield the product CH₃OH when a molecule of CH₄ is bound to the hydrophobic pocket of the tricopper complex (Figure 1). To accomplish multiple turnovers, the “spent” catalyst is reduced by a molecule of H₂O₂ to regenerate the catalyst; thus for each catalytic turnover, one molecule of CH₃OH is produced for each molecule of H₂O₂ consumed. However, when the CH₄ is not readily available, the “oxene” is rapidly deactivated by H₂O₂. Even so, the active catalyst is regenerated by reduction of the “spent” catalyst by another molecule of H₂O₂ just as in the productive cycle. This abortive cycling of the catalyst limits the efficiency of the catalytic turnover, as significantly greater amounts of H₂O₂ are then required to drive the catalytic turnover for the production of CH₃OH.³ To circumvent this problem, we have recently immobilized the tricopper cluster complex in the nanochannels of mesoporous nanoparticles to exploit the “over-solubility” of nonpolar gases such as CH₄ and O₂ in the solvent that is trapped within the mesopores of the nanoparticles.⁴ The performance of the tricopper catalyst is improved significantly and the overall catalytic efficiency can reach to 80-90%.

2. Experimental

The synthesis of **7-N-Etppz**, the organic ligand 3,3'-(1,4-diazepane-1,4-diyl)bis(1-(4-ethylpiperazin-1-yl) propan-2-ol), and the preparation and characterization of the tricopper cluster complex **Cu^{II}Cu^{II}Cu^{II}(7-N-Etppz)⁴⁺** have been described in our earlier publications.²⁻⁴ Mesoporous silica nanoparticles are functionalized by the anionic 3-(trihydroxysilyl)-propylmethyl-phosphonate (TP) to generate a negatively charged surface within the MSN channels⁴ for encapsulation of the positively charged **Cu^{II}Cu^{II}Cu^{II}(7-N-Etppz)⁴⁺**. Typically, 2.28 μmole (1 equiv.) of the tricopper

complex is immobilized in the MSN-TP to yield 20 mg of the **CuEtp@MSN-TP** catalyst. Prior to adding a slight excess of sodium ascorbate to reduce the tricopper complex to the active **Cu^ICu^ICu^I(7-*N*-Etpyz)¹⁺**, 10 ml of O₂ (*ca.* 180 equiv., based on the amount of catalyst) and 100 ml (at STP) of alkane gas (*ca.* 1800 equiv.) were added to the reaction mixture. An aliquot of different amounts of H₂O₂ solution (50, 100, 200, and 500 equiv., based on the amount of catalyst) is then added to drive the catalytic turnover mediated by the **Cu₃(7-*N*-Etpyz)** complex. The reaction mixture is stirred continuously for 3 h at room temperature and analyzed periodically at various intervals over this 3-h period by using GC–MS to monitor the formation of products.

3. Results and discussion

Figure 2 summarizes the turnover numbers (TONs) obtained for the oxidation of CH₄, ethane (C₂H₆), and propane (C₃H₈) mediated by the **CuEtp@MSN-TP** catalyst at room temperature when the catalytic turnover is initiated with 200 equiv. of H₂O₂. Interestingly, the TONs are the same for all three alkane gases. This is the expected outcome, as the rate-limiting step in the catalytic turnover is the reduction of the “spent” catalyst by H₂O₂ to regenerate the active **Cu^ICu^ICu^I(7-*N*-Etpyz)¹⁺** catalyst. The alkane oxidation step is significantly more facile. The turnover frequency (TOF) of the catalyst is 1.68 min⁻¹ at the start of the catalytic run, when the [H₂O₂] is 200 equiv. From the limiting TONs observed at the end of the 3-h catalytic run, we obtain catalytic efficiencies of ~80%, which is remarkable given that the oxidation of these light alkane gases are performed at room temperature.

Information on the facile “oxene” transfer step is obtained when we carry out the oxidation with a 1:1:1 mixture of CH₄, C₂H₆, and C₃H₈ (total (C1+C2+C3) = 500 equiv.(1.14 mmole)). In Figure 3, we show the TONs obtained when the catalytic turnover is initiated in this alkane mixture by 200 equiv. of H₂O₂ at room temperature. Here, we observe kinetic competition of the catalyst for the three light alkane gases. From the kinetic fractionation of the oxidized products, we deduce the following selectivity for the alkane oxidation: C1:C2:C3 = 1:22:30.

4. Conclusions

We have demonstrated in this work that the **Cu₃(7-*N*-Etpyz)** complex is a highly efficient catalyst for the selection oxidation of CH₄, C₂H₆ and C₃H₈ at room temperature when formulated as a quasi-heterogeneous catalyst in MSN-TP.

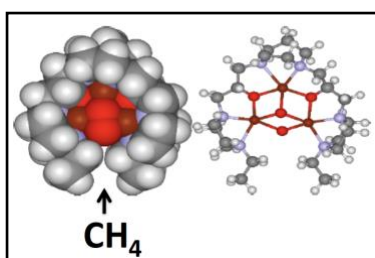


Figure 1. CPK and ball-and-stick models of the O₂-activated **Cu^ICu^ICu^I(7-*N*-Etpyz)¹⁺** complex.

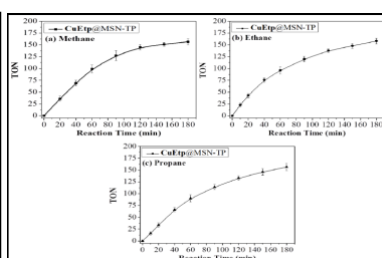


Figure 2. Time course of the product TONs in the oxidation of CH₄, C₂H₆, and C₃H₈ mediated by the **CuEtp@MSN-TP** catalyst.

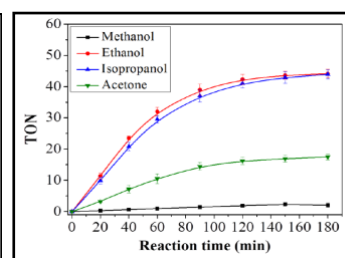


Figure 3. Time course of the product TONs in the oxidation of a 1:1:1 mixture of CH₄, C₂H₆, and C₃H₈ mediated by the **CuEtp@MSN-TP** catalyst.

References

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