Copper Phthalocyanines as Precursors for Direct Oxidation of Methane to Methanol in Liquid Phase

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Highlights

- Copper phthalocyanines are promising precursors for selective methanol formation.
- Optimal activity occurs at BAS/LAS ratios between 0.9 and 1.5.
- Isolated Cu^{2+} species improve the catalytic activity toward methanol.
- A suitable balance of Brønsted and Lewis acid sites is needed for the reaction.

1. Introduction

Methane, a key component of natural gas, is widely used for power generation but is also a major greenhouse gas. Traditional methanol production involves energy-intensive methane steam reforming followed by high-temperature synthesis. Direct oxidation of methane to methanol (DOMTM) in the liquid phase offers a milder alternative but is challenged by the strong C-H bond in methane and the overoxidation of methanol to other products [1]. Cu-ZSM-5 catalysts with H_2O_2 as oxidant have shown high activity under mild conditions [2], yet metallo-phthalocyanines remain underexplored despite their ability to mimic enzymes that enable highly selective methanol production [3]. In this work, α-substituted tetrakis[3,5-(di-tert-butyl)phenyl] Cu-phthalocyanine (CuPc) supported on ZSM-5 with tailored properties was prepared and evaluated for DOMTM under mild conditions.

2. Methods

Commercial NH_4-ZSM-5 zeolites (R = SiO_2/Al_2O_3 = 23 and 30) were desilicated through sequential alkaline (0.5 M NaOH, 10 mL g^{-1}, 70 ºC,1 h) and acid (0.5 M HCl, 100 mL g^{-1}, 65 ºC, 5 h) treatments, followed by three ion-exchange steps using 1 M NH_4NO_3 (10 mL g^{-1}) at 70 ºC for 2 h, to restore the ammonium form and subsequent calcination at 350 ºC for 4 h and 550 ºC for 4 h to obtain desilicated ZSM-5-23-DS and ZSM-5-30-DS. CuPc was synthesized by a previously reported two-step procedure [4]. For catalyst preparation, a specific amount of CuPc was dissolved in 20 mL of $CHCl_3$ and added to 1 g of support. The mixture was stirred at 45 ºC for 5 h to promote diffusion of CuPc into the zeolite pores. The solvent was then removed by rotary evaporation at 60 ºC, and the resulting solids (xCuPc-ZSM-5-R-DS, where x is the nominal Cu loading) were dried and, when required, calcined using the same stepwise program to remove the organic complex. Catalytic tests were performed using 150 mg of catalyst in 70 mL of 0.5 mol L^{-1} H_2O_2 solution under 30 bar CH_4 at 50 ºC with stirring at 1000 rpm.

3. Results and discussion

The incorporation of Cu-phthalocyanines (CuPc) into microporous supports is severely constrained by their large molecular dimensions. Consequently, accommodation within the micropores of conventional zeolites (ca. 0.55-0.6 nm) is not feasible. To overcome this limitation, the microporous solids were desilicated to generate mesoporosity, resulting in increased mesopore volume and, consequently, higher total pore volume, which enables anchoring of CuPc onto the desilicated supports. The successful incorporation of CuPc into the supports was confirmed by XRD, SEM, and TEM, as no structural collapse was observed. Textural properties, measured by N_2 physisorption, were determined for all the supports and CuPc-incorporated materials, exhibiting a hybrid contribution of type I(a) and IV(a) isotherms. The acidity properties, quantified by pyridine-FTIR, show that the Brønsted to Lewis acid site ratio (BAS/LAS) tends to decrease after CuPc incorporation, which is mainly driven by a stronger reduction in Brønsted acidity than the concurrent increase in the Lewis acidity. After calcination of the materials, the Lewis acidity significantly increases, leading to the lowest BAS/LAS of 1.5 and 0.9 for 0.5 wt.% and 1 wt.% Cu, respectively.

The catalytic performance was evaluated through the CH_3OH productivity at 1 h (Figure 1a) and the selectivity to CH_3OH at an isoconversion level (0.1%), as shown in Figure 1b. Figure 1a exhibits a clear inverse relationship between CH_3OH productivity and BAS/LAS. At low BAS/LAS ratios (0.9-1.5), the calcined materials show the highest productivity, with values of 553 and 513 μmol g_{cat}^{-1} h^{-1}. As BAS/LAS increases above 10, productivity decreases sharply, dropping below 25 μmol g_{cat}^{-1} h^{-1}. This trend indicates that a high relative abundance of Brønsted acid sites is unfavorable for methanol formation. Fig. 12b shows that the methanol selectivity follows a trend closely mirroring productivity, reaching the highest selectivities of about 42-46%, whereas the CuPc-ZSM-5 catalysts show intermediate selectivities of around 20-30%. The desilicated supports exhibit very low selectivity, typically below 10%. The high activity of the calcined catalysts was attributed to isolated Cu^{2+} species identified by complementary techniques such as XAS, UV-Vis-DRS, and H_2-TPR.

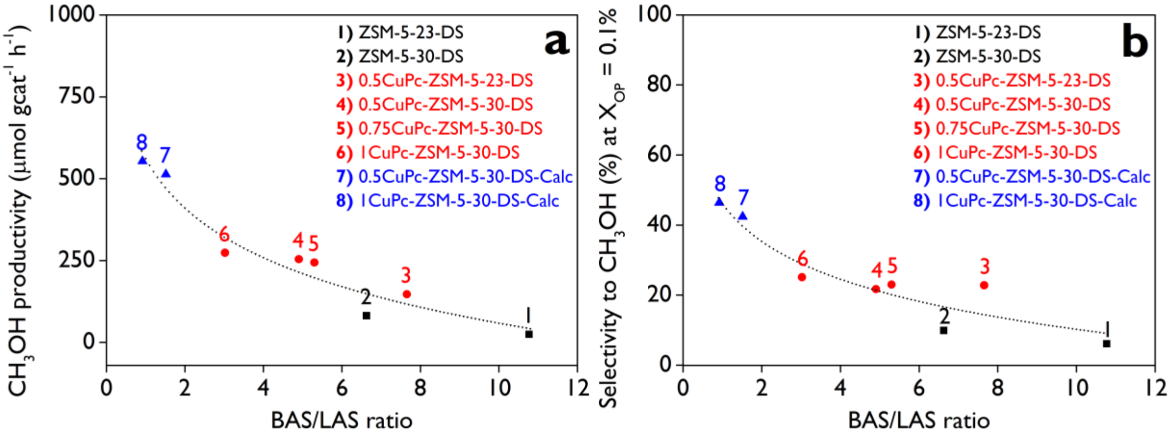

Figure 1. (a) CH_3OH productivity at 1 h and **(b)** selectivity to CH_3OH at CH_4 conversion of 0.1% as a function of the Brønsted to Lewis acid site ratio (BAS/LAS). Dashed lines are included only to indicate the trend.

4. Conclusions

Cu-phthalocyanine supported on desilicated ZSM-5 exhibited high performance for liquid-phase direct oxidation of methane to methanol. Desilication created mesoporosity for CuPc incorporation while preserving the MFI structure. Catalytic activity strongly depended on the Si/Al ratio and the copper speciation, with the best results achieved for 1 wt.% CuPc on $SiO_2/Al_2O_3 = 30$ after calcination, reaching methanol productivity of 553 μmol g_{cat}^{-1} h^{-1}. This work demonstrates Cu-phthalocyanine/ZSM-5 as a promising catalyst, achieving well-dispersed Cu^{2+} active sites and benchmarking favorably against other metallo-phthalocyanines.

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Keywords

Methane; Methanol; Cu-phthalocyanine; ZSM-5.