Liquid-Phase Direct Oxidation of Methane to Methanol over Copper-Modified Mesoporous Catalysts: Effect of the Pore Size

Mehdi Hassan Milu[1], Luis A. Gallego-Villada[1], Päivi Mäki-Arvela[1], Pasi Virtanen[1],
Narendra Kumar[1], Dmitry Yu. Murzin[1]*

[1]Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, Turku, Finland

**Corresponding author: dmitry.murzin@abo.fi*

Highlights

- Mesoporous catalysts improve diffusion but show limited methane activation
- The balance between Brønsted and Lewis acid sites influences catalytic behavior
- Pore size affects mass transport and product distribution.
- Mesoporosity alone is insufficient for high methanol selectivity

1. Introduction

The direct oxidation of methane to methanol (DOMTM) is an attractive route for methane valorization; however, it remains highly challenging due to the strong C-H bond in methane and the high reactivity of methanol (CH_3OH), which often leads to over-oxidation into undesired products such as carbon dioxide. Conventional catalysts such as Cu-ZSM-5 have demonstrated promising activity due to their intrinsic acidity and active sites [1]. However, their microporous structure limits mass transfer and promotes over-oxidation due to restricted diffusion of intermediates and products. In contrast, mesoporous materials such as SBA-15 and MCM-41 provide larger pore sizes, which can improve diffusion and accessibility of reactants and products [2]. However, these materials typically exhibit lower acidity compared to zeolites, which may limit their ability to activate methane. Therefore, understanding the combined effect of pore size and the balance between Brønsted and Lewis acid sites is essential. In this study, we investigate how pore structure and acidity influence methane oxidation performance in copper-modified mesoporous catalysts.

2. Methods

Mesoporous supports SBA-15 and MCM-41 were synthesized using templated methods to obtain well-defined pore structures [3]. Aluminium was incorporated during synthesis using aluminium isopropoxide and aluminium nitrate as aluminium sources to introduce Brønsted acidity, resulting in Al-SBA-15 and Al-MCM-41 materials [4]. Copper was subsequently introduced via incipient wetness impregnation using copper (II) nitrate as the precursor, with a loading of 0.5-1 wt%. The catalysts were calcined at 400 °C to generate active copper species anchored to the silica framework.

The physicochemical properties of the catalysts were characterized using nitrogen physisorption to determine surface area and pore size distribution, pyridine-adsorbed FTIR to quantify Brønsted and Lewis acid sites, and X-ray diffraction (XRD) and transmission electron microscopy (TEM) to analyze structural properties. Catalytic performance was evaluated in a stirred high-pressure autoclave reactor at 50 °C and 30 bar CH_4 using hydrogen peroxide (H_2O_2) as the oxidant. Reaction products were analyzed using high-performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR) spectroscopy.

3. Results and discussion

The textural properties of the catalysts were analyzed using nitrogen adsorption-desorption isotherms, as shown in Fig. 1(a). All SBA-15 and MCM-41-based materials exhibit Type IV isotherms, confirming their mesoporous structure, with average pore diameters of 6.5 nm for SBA-15 and 2.3 nm for MCM-41. SBA-15 shows a more stated hysteresis loop, indicating larger pore size and pore volume, while MCM-41 exhibits smaller and more uniform mesopores. Also, aluminium incorporation does not significantly alter the mesostructure, confirming the stability of the mesoporous framework.

The catalytic performance, expressed as methanol productivity, is shown in Fig. 1(b). All mesoporous catalysts exhibit very low productivity (<125 µmol/gcat), with only slight increases over time, whereas Cu-ZSM-5 reaches 800-1000 µmol/gcat, demonstrating significantly higher activity. This indicates that improved diffusion alone does not lead to enhanced catalytic performance. The reaction proceeds via a stepwise oxidation pathway, where methane is converted into intermediate species such as methyl hydroperoxide and methanol, which can further oxidize into undesired products. The very low productivity suggests that methane activation is the rate-limiting step, which can be attributed to differences in acidity. Cu-ZSM-5 exhibits an optimal BAS/LAS ratio of 1-1.7, whereas mesoporous materials show lower acidity (<100-200 µmolg^{-1}) and a less favourable BAS/LAS ratio (0.4). Therefore, although larger pores enhance diffusion, the insufficient acidity and unfavourable acid site balance explain the very low methanol productivity observed in Fig. 1(b). These results demonstrate that pore size alone is not sufficient, and that acidity is the key factor controlling catalytic performance.

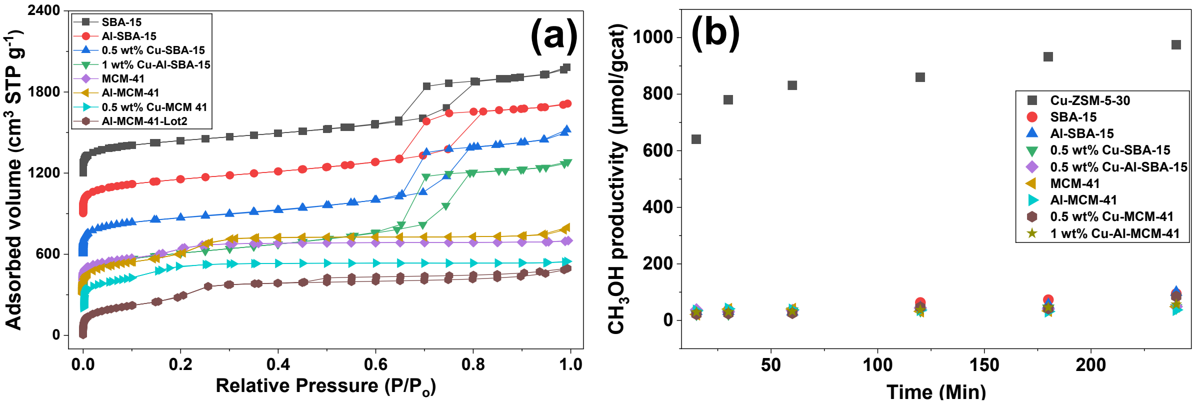

Fig.1: N_2 adsorption-desorption isotherms (a) and methanol productivity vs. time (b) for Cu-modified SBA-15 and MCM-41 catalysts.

4. Conclusions

Mesoporous catalysts such as SBA-15 and MCM-41 provide improved diffusion properties due to their larger pore structures; however, they exhibit limited performance in methane oxidation to methanol under the studied conditions. The results indicate that pore size alone is not sufficient to achieve high catalytic performance, and that surface acidity, particularly the balance between Brønsted and Lewis acid sites (BAS/LAS), plays a critical role in methane activation. These findings highlight the importance of combining appropriate pore structure and acidity when designing catalysts for methane valorization.

The authors acknowledge funding from the Research Council of Finland (Project No. 361444).

References

[1] X. Tang *et al.*, "Direct oxidation of methane to oxygenates on supported single Cu atom catalyst," *Appl. Catal. B Environ.*, vol. 285, no. December 2020, p. 119827, 2021, doi: 10.1016/j.apcatb.2020.119827.

[2] M. Fedyna, M. Śliwa, K. Jaroszewska, L. Kępiński, and J. Trawczyński, "Procedure for the synthesis of AlSBA-15 with high aluminium content: Characterization and catalytic activity," *Microporous Mesoporous Mater.*, vol. 292, no. June 2019, 2020, doi: 10.1016/j.micromeso.2019.109701.

[3] L. A. Gallego-Villada, E. A. Alarcón, F. Bustamante, and A. L. Villa, "One-Pot tandem catalysis: Green synthesis of β-pinene derivatives with MgO and mesoporous catalysts," *J. Catal.*, vol. 438, no. July, 2024, doi: 10.1016/j.jcat.2024.115698.

[4] Z. Wu *et al.*, "Fabrication of mesoporous Al-SBA-15 as a methylene blue capturer via a spontaneous infiltration route," *New J. Chem.*, vol. 39, no. 2, pp. 985–993, 2015, doi: 10.1039/c4nj01473a.

Keywords

Methane oxidation; Methanol synthesis; Mesoporous catalysts; Effect of Pore Size.