Development of lead-free halide perovskite photocatalysts on porous support materials for oxidation of toluene under visible light

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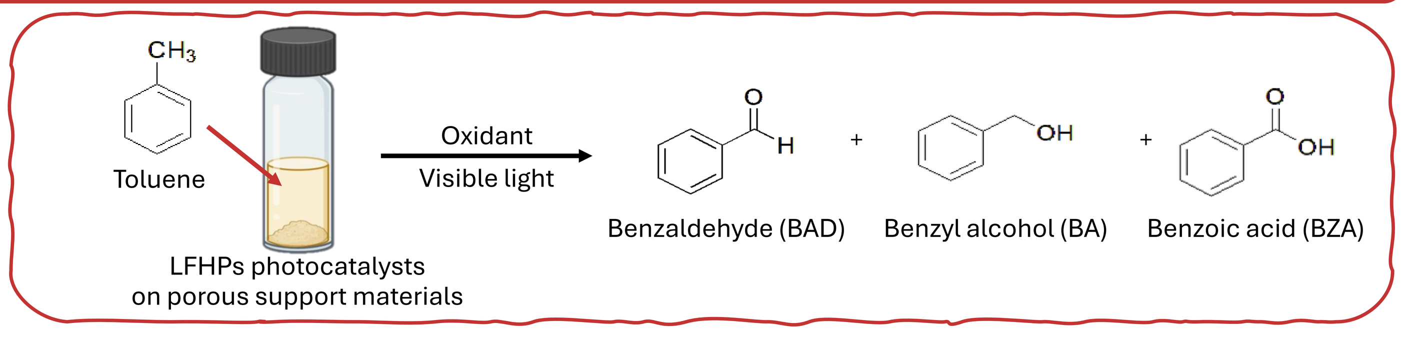
ABSTRACT

Lead-free halide perovskite photocatalysts (LFHPs) on porous support materials were prepared to address the catalyst filtration issue encountered when using catalyst powder. Photocatalytic activity of the obtained samples were evaluated through toluene oxidation under visible light. To compare the LFHPs loading efficiency, silica gel beads (SG) and MCM-41 modified SG (MSG) supports were employed as photocatalyst supports. Herein, two LFHPs, specifically cesium bismuth bromide ($Cs_3Bi_2Br_9$, CBB) and cesium antimony bromide ($Cs_3Sb_2Br_9$, CSB), were coated on both SG and MSG via anti-solvent precipitation method. Results showed that CSB/MSG (ca. 180 μmol g^{-1} h^{-1}) offered higher toluene oxidation than CBB/MSG (ca. 26 μmol g^{-1} h^{-1}) due to narrower band gap energy and lower charge recombination efficiency as supported by UV-vis diffuse reflectance and steady-state photoluminescence studies. The CSB/MSG gave better activity than CSB/SG probably due to higher CSB coating amount on the support, which needs to be further confirmed by ICP method. The spent CSB/MSG, though was easily recycled, showed a decrease photocatalytic performance, and thus need further investigation on the cause of catalyst deactivation.



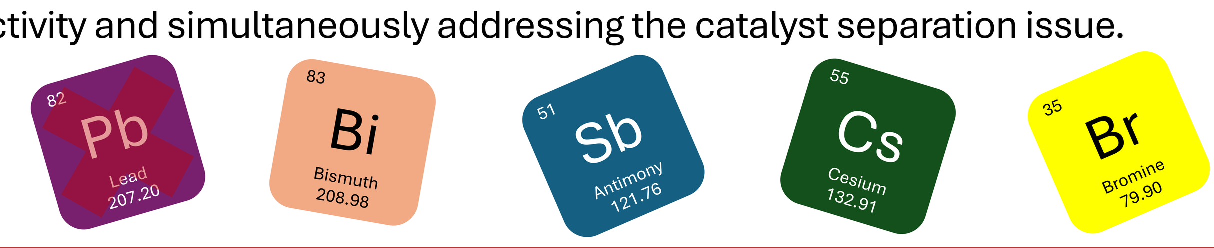
OBJECTIVES

I. To synthesize LFHPs photocatalysts on porous support materials, i.e. SG and MSG
II. To evaluate the performance of the obtained photocatalysts in toluene oxidation under visible light

INTRODUCTION

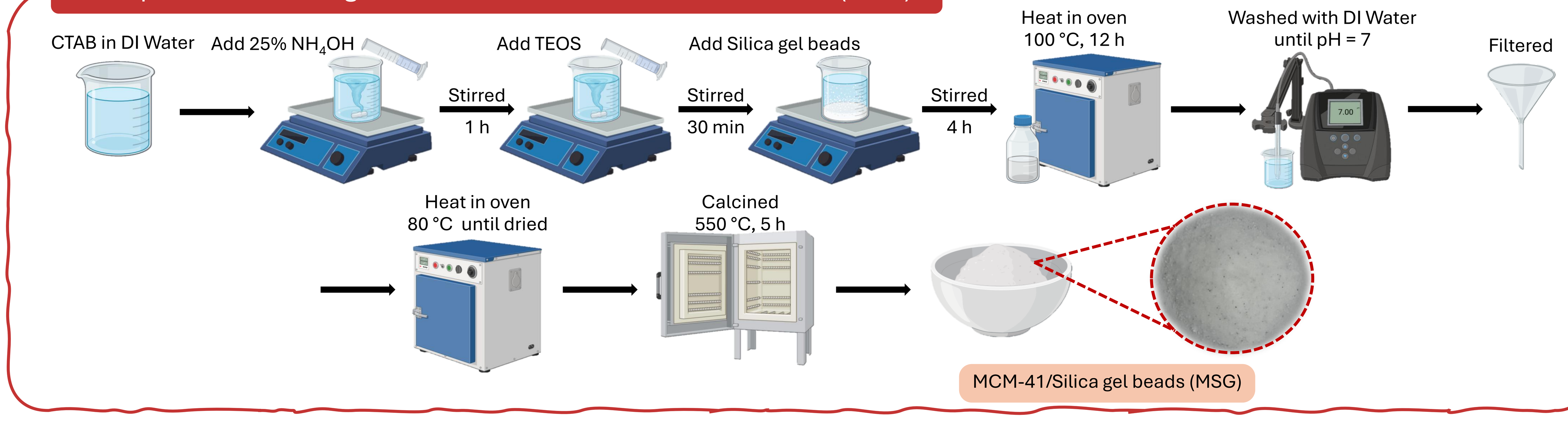
The urgent need for sustainable and environmentally friendly materials has driven extensive research into advanced photocatalysts for pollution control and energy applications. Lead-free halide perovskites (LFHPs) have emerged as promising candidates due to their strong light absorption, high carrier mobility, tunable bandgaps and environmentally friendly materials. LFHPs such as $Cs_3Sb_2Br_9$ and $Cs_3Bi_2Br_9$ have shown potential as a heterogeneous photocatalyst for toluene oxidation [1,3]. However, the use of catalyst powder often presents a challenge with catalyst separation, requiring filtration or centrifugation. Immobilizing the catalyst on support provides viable solutions to this issue. Porous support materials are considered effective platforms to enhance photocatalyst performance by increasing surface area, improving catalyst distribution, and addressing the catalyst separation problem.

Herein, the LFPHs were loaded onto silica gel bead (SG) and MCM-41 modified silica gel bead (MSG). Modifying the SG with MCM-41 provides additional anchoring sites for LFHPs catalysts, thereby enhancing catalytic activity and simultaneously addressing the catalyst separation issue.

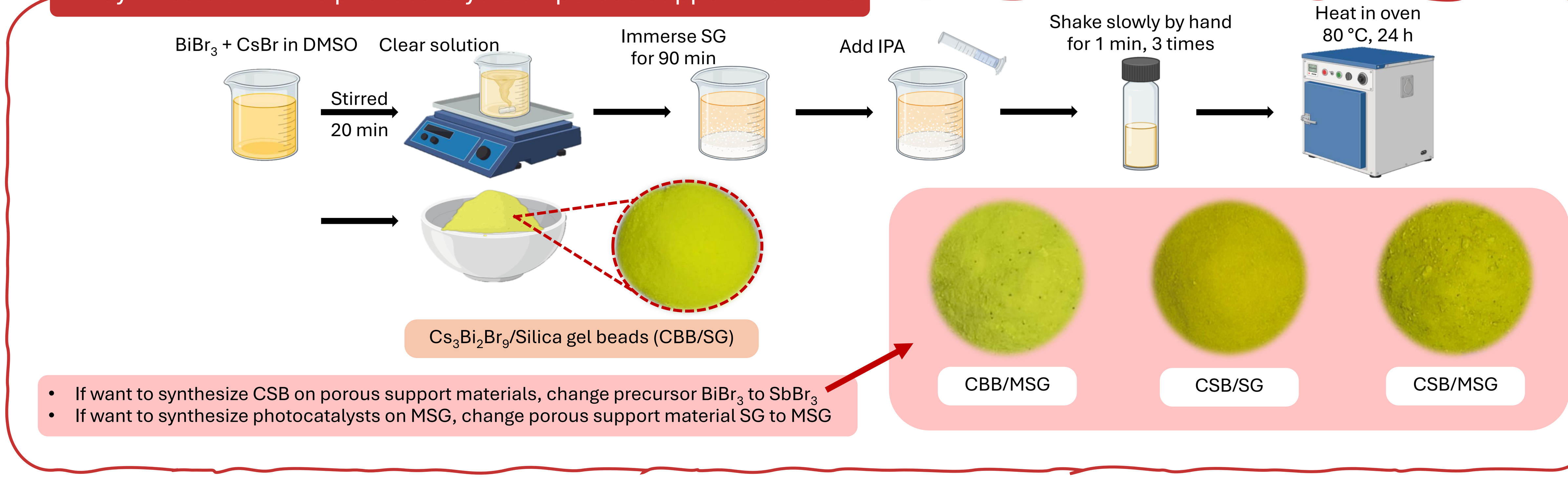


METHODOLOGY

I. Preparation of silica gel beads modified surface with MCM-41 (MSG)



II. Synthesis of LFHPs photocatalysts on porous support materials



RESULTS & DISCUSSION

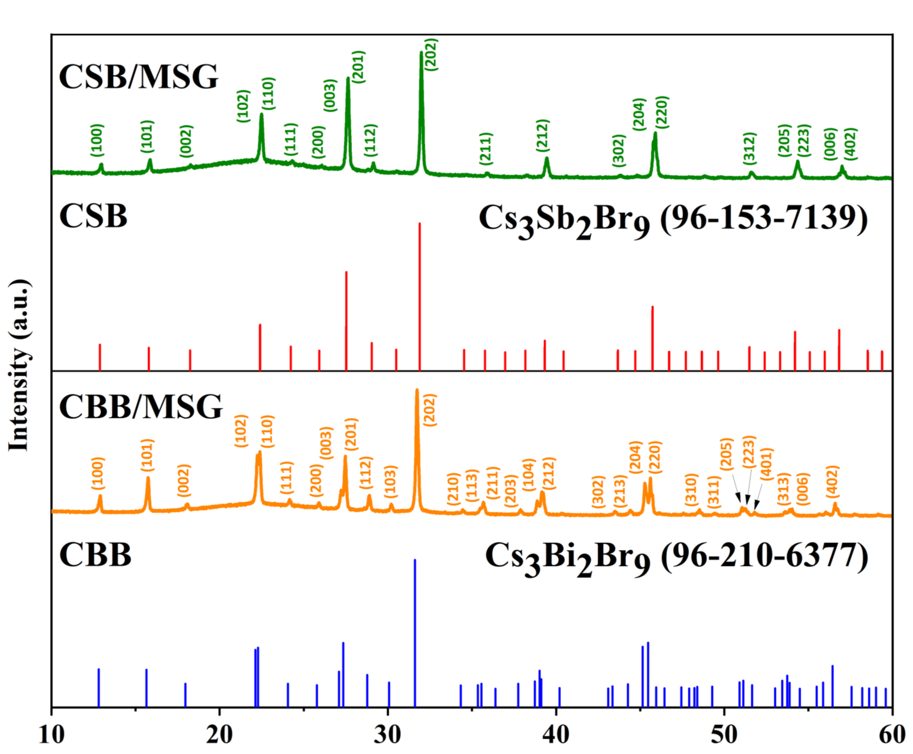


Fig. 1. XRD patterns of CBB, CSB, CBB/MSG, and CSB/MSG together with COD patterns

The XRD results of CBB/MSG and CSB/MSG in **Fig. 1,** reveal that CBB and CSB on MSG support were highly crystalline and were in good agreement with reference patterns (hexagonal $Cs_3Bi_2Br_9$ (ICSD no. 96-210-6377) and $Cs_3Sb_2Br_9$ (ICSD no. 96-153-7139)). No other impurity peaks detected suggesting a successful synthesis of CBB/MSG and CSB/MSG.

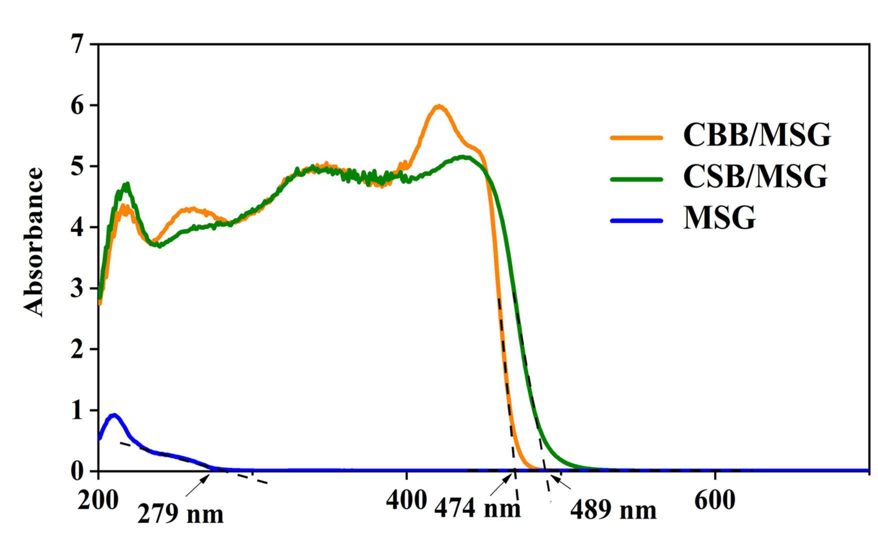


Fig. 2. UV-vis absorption spectra of MSG, CBB/MSG, and CSB/MSG

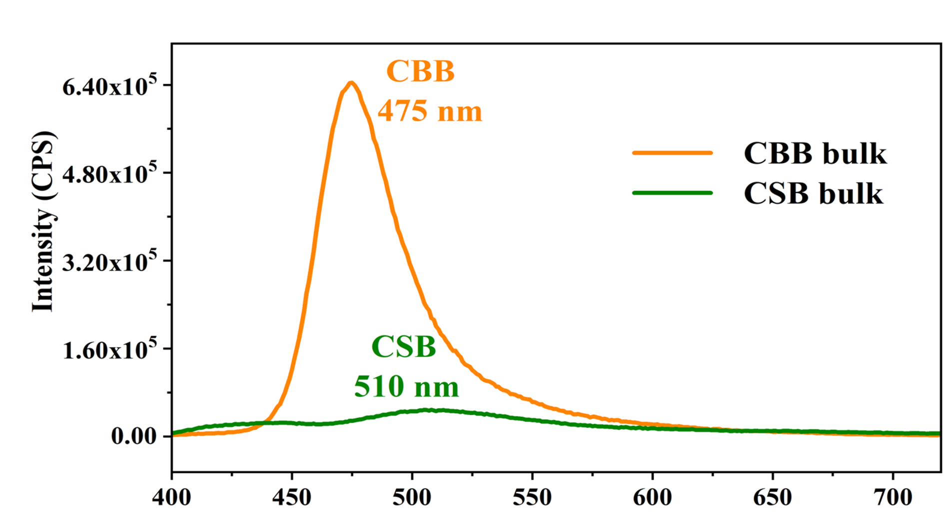


Fig. 3. Steady-state PL spectra of CBB and CSB bulk

The UV-vis absorption spectra shown in **Fig. 2,** indicate that the MSG support absorbed light only in the UV range, with an absorption edge at 279 nm (approximately 4.44 eV). In contrast, both the CBB/MSG and CSB/MSG composites displayed strong absorption in the visible light region, with absorption onsets at 474 nm (approximately 2.61 eV) and 489 nm (approximately 2.54 eV), respectively. The CSB/MSG, with a narrower band gap than the CBB/MSG, likely contributes to its enhanced photocatalytic activity.

The steady-state photoluminescence (SSPL) spectra in **Fig. 3,** indicate that the CSB has lower recombination rate than CBB, which is beneficial for enhancing photocatalytic activity.

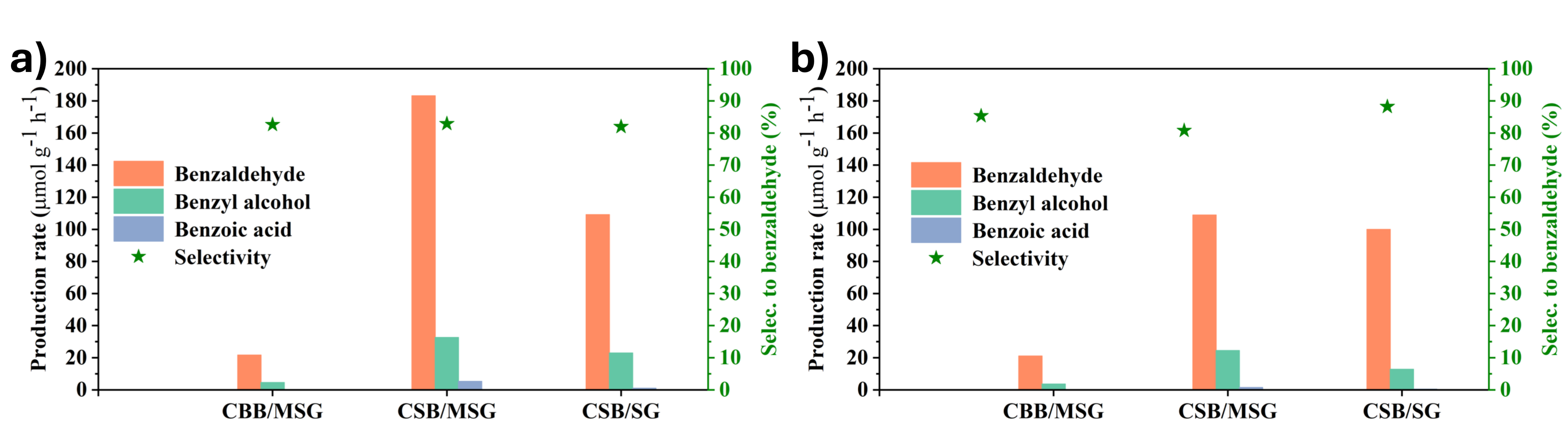


Fig. 4. Photocatalytic performance of toluene oxidation over CBB/MSG, CSB/MSG and CSB/SG in a) 1st cycle, and b) 2nd cycle

From **Fig. 4a**, all catalysts offered high selectivity to benzaldehyde (>82%). CSB/MSG showed the highest product formation rate (180 μmol g^{-1} h^{-1}) compared to CBB/MSG (26 μmol g^{-1} h^{-1}), and CSB/SG (133 μmol g^{-1} h^{-1}). From **Fig. 4b**, the activity of CSB/MSG decreased significantly in the 2nd cycle. Further investigations on catalyst deactivation cause such as ICP, FTIR, XRD , and XPS need to be conducted.

CONCLUSION

In summary, LFHPs on porous support materials for the oxidation of toluene under visible light irradiation were successfully synthesized by impregnation and anti-solvent precipitation methods as supported by XRD results. The best performing photocatalyst, CSB/MSG, achieved a toluene oxidation rate of ca. 180 μmol g^{-1} h^{-1}, with 83% selectivity toward benzaldehyde. This performance is nearly two times higher than CSB/SG and almost eight times higher than CBB/MSG. UV-vis and SSPL spectra revealed that CSB/MSG has a narrower band gap, and a lower charge recombination rate compared to CBB/MSG, which contribute to its superior photocatalytic activity. Although the catalyst easily precipitates, eliminating the need for a catalyst separation step, there is a significant decrease in catalytic activity during the second cycle. Therefore, further analysis using ICP, Raman, BET surface area measurements, and XPS techniques is recommended to confirm the photocatalysts' properties and the amount of catalyst on the MSG surface.

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