UNIVERSITI TEKNOLOGI MARA

SYNTHESIS OF SUBSTITUTED $CaFe0_3$ PEROVSKITE CATALYSTS WITH SERIES B-SITE ACTIVE PHASES FOR CAFFEINE MICROPOLLUTANTS' OXIDATIVE DEGRADATION

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Thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy
(Chemical Engineering)

College of Engineering

February 2025

ABSTRACT

In recent years, substituted perovskite with a general formula of ABB'Cb is considered as promising type of ceramic metal oxide heterogeneous catalyst for oxidative degradation of emerging micropollutants. The variation of B-site metal cation substitution in the perovskite structure led to a significant change in the overall catalytic performance of the resulting catalysts. However, the substitution of molybdenum (Mo), copper (Cu) and cobalt (Co) as an active phase for the B-site of CaFeCb for micropollutants' oxidative degradation in non-irradiation-assisted AOP remain unexplored. Hence, this research work aims to investigate the functional role of partially substituted B-site cations (Mo, Cu, Co) as an alternative type for B-site active phase towards modulation of resultant catalytic reactivity of substituted CaMFeCb (M = Mo, Cu, Co) perovskite catalyst. The partially substituted CaMFeCb (M = Mo, Cu, Co) perovskite catalyst was synthesized via modified EDTA citric acid complexation method. Then, a series of the selected high-performance substituted CaM_xFei-_x03 were synthesized by varying the B-site composition loading (x = 0, 0.2, 0.4, 0.6, 0.8). The catalytic performance of resultant catalysts was evaluated in oxidative degradation using caffeine solution as a model micropollutant. The perovskite catalysts were characterized using x-ray diffraction, field emission scanning electron microscopy, energy dispersive x-ray spectroscopy, nitrogen sorption analysis, oxygen temperature-programmed desorption, hydrogen temperature-programmed reduction, x-ray photoelectron spectroscopy, and electrochemical impedance spectroscopy. The reusability test and mineralization efficiency in the presence of optimum B-site composition loading (CaMxFei-xCb) was carried out at optimum operational conditions for caffeine degradation. The mechanism and degradation pathways of caffeine in the presence of optimum substituted CaM_xFei-_x03 were elucidated. The substituted CaCuFeCb exhibited the highest caffeine degradation (38%) within 4 hr of reaction compared to other partially substituted active phases. The high reducibility of copper/iron ions and decent electron mobility within the structure of substituted CaCuFeCb catalyst in the presence of H2O2 enables fast redox cycling of the active sites during catalysis. The optimum B-site composition loading of the perovskite was found at CaCuo.2Feo.8O3, which exhibited 66% caffeine degradation. Interestingly, the low amount of oxygen vacancies presence within the CaCuo.2Feo.8O3 perovskite structure led to a faster rate of electron transfer, thereby enhancing the redox cycling between $=Fe^{2+}/=Fe^{3+}$ and $=Cu^{+}/=Cu^{2+}$. This behaviour effectively promotes the activation of H2O2 in generating reactive »OH radicals during heterogeneous catalysis. The optimum operational conditions were proposed at 10 mg $L"^{1}$ caffeine, 0.1 g $L"^{1}$ catalyst, pH 3, 22 mM H2O2 and T = 27°C, with the highest caffeine degradation at 100% within 4 hr of reaction. It is noteworthy that the degradation efficiency of caffeine decreased slightly in the second cycle and then remained at -98% within five cycles of reactions. Nevertheless, caffeine was mineralized by the average of -30% within 4 hr in every cycle, despite the significant caffeine degradation performance. The proposed mechanism for caffeine degradation revealed that the oxygen vacancies facilitate facile Fe/Cu redox cycle by regenerating the active sites ($=Fe^{2+}$ and $=Cu^{+}$) within the CaCuo.2Feo.8O3 catalyst's structure. Detailed plausible caffeine degradation pathways were proposed based on the presence of intermediates compounds (N-N'-Dimethyl urea, methylparabanic acid and 1,7-Dimenthylxanthin) that were detected during catalysis prior to complete mineralization.

ACKNOWLEDGEMENT

Alhamdulillah, all praises to Allah s.w.t for his blessing, grace and guidance in this life.

First and foremost, I would like to extend my heartfelt appreciation to my main supervisor, Dr. Nor Aida Zubir, for her invaluable guidance, support, advice, and motivation throughout every stage of my PhD journey. Her expertise, patience, and constructive comments played a crucial role in shaping the direction of my PhD research study. I would also like to extend my sincere thanks to my co-supervisors: Assoc. Prof. Dr. Noor Fitrah Abu Bakar, Assoc. Prof. Dr. Noor Hana Hanif Abu Bakar and Dr. Julius Motuzas for their invaluable contributions to this research work. Special thanks to Dr. Fadlul Wafi Badrudin for his guidance and expertise in simulation analysis.

My appreciation also goes to lab assistants of Chemical Engineering Studies, UiTMCPP: Pn. Khaironiswah, Cik Siti Maznah, En. Saiful, Pn. Faiza and Pn. Salmiah for their kind help and support during the execution of experimental work for this thesis. Also, special thanks to all my friends: Dr. Hawaiah, Dr. Siti Aminah, Ir. Dr. Norhaslinda, Nadhratul Nur Ain, Riza Lydia Liyana and other friends for their kindness, concern, motivation, and support.

Most importantly, I really appreciate the unconditional love, understanding and support of my beloved husband, Assoc. Prof. Ts. Dr. Mohamad Anuar Kamaruddin and beautiful daughters, Afia Raisya, Aira Raihanah and Amna Radhiyah. They are my strength throughout this journey. Also, special thanks to my father, Haji Sukandar bin Simun, father-in-law, Haji Kamaruddin bin Harun and siblings, Rahimi binti Alrozi and Amir Ridzuan bin Alrozi for their doas and unwavering supports.

I would like to dedicate this thesis to the loving memory of my very dear late father, Allahyarham Haji Alrozi bin Shamsuddin and my late mother, for the vision and determination to educate me. Both my mother and mother-in-law passed away during my PhD journey. Their doas, unwavering love, support, and encouragement were constant sources of strength for me, and their absence is deeply felt as I reach this significant milestone. May Allah s.w.t. place them among the pious and faithful and raise their status in the sight of Allah s.w.t.

Allahumma Aminn Ya Mujib.

Finally, I would like to express my gratitude to everyone who indirectly contributed to this research.

Alhamdulillah.

Rasyidah Alrozi

February 2025

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INTRODUCTION

1.1 Research Background

The presence of pharmaceutical^ active compounds (PhACs) micropollutants, a form of emerging contaminant in the environment, has become a growing concern due to their potential risks to the water bodies and human health [1]. The term "micropollutant" typically refers to the emerging harmful contaminants, which are characterized by nanoscale molecular size that usually detected at low concentration levels (ranging from nanograms per liter to micrograms per liter) in aquatic environments [2-4]. The sources of PhACs varies from drugs and pharmaceuticals (e.g caffeine, carbamazepine diclofenac, sulfadiazine, ibuprofen [5-8]) plasticizers (e.g bisphenol A, diethyl phthalate [9-12]), pesticides (e.g atrazine, 2,4-dichlorophenoxyacetic acid [13-15]), and disinfectants (e.g triclosan, 2-phenylphenol, chlorophene [16]) that are produced by both industrial and human activities.

Among these PhACs micropollutants, caffeine is commonly known as the most frequently detected PhACs in the water bodies [17]. Caffeine (1,3,7-trimethylxanthine), a natural alkaloid belonging to the methylxanthine family, is being used as a central nervous system stimulant in a variety of pharmaceutical products (including drugs, analgesics, and cold medicines) as well as foods and caffeinated beverages [18,19]. Caffeine is also regarded as the most prevalent psychoactive drugs used globally, with an estimated consumption of around 120,000 tonnes/year [20,21].

In recent studies, Wilkinson et al. [22] reported that caffeine was found in more than 50% of the 1052 sampling locations spread across 104 nations on several continents, making it one of the main PhACs micropollutants with the highest concentrations in river surface water. Li et. al [23] also reported the presence of caffeine residues in water bodies in over 70% of 132 reports analysed globally, primarily in Asian and European nations. It was found that the wastewater in Singapore comprised an unexpectedly high concentration of caffeine, reaching up to 3600 ug L^{-1} [24]. Meanwhile, in Malaysia, the concentration of caffeine in sewage treatment plant influent and effluent and hospital effluent were found to be approximately 8.7, 1.19 and 2.86 ug L^{-1}, respectively [25]. Moreover, caffeine is also found in surface water of