

Functional role of B-site substitution on the reactivity of CaMFeO_3 ($\text{M} = \text{Cu}, \text{Mo}, \text{Co}$) perovskite catalysts in heterogeneous Fenton-like degradation of organic pollutant

Rasyidah Alrozi^{a,b}, Nor Aida Zubir^{a,b,c,*}, Noor Fitrah Abu Bakar^d, Bradley P. Ladewig^e, Julius Motuzas^f, Noor Hana Hanif Abu Bakar^g, David K. Wang^h, João C. Diniz da Costa^{f,i,j}

^a Centre for Chemical Engineering Studies, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia

^b Hybrid Nanomaterials, Interfaces & Simulation (HYMFAST), Centre for Chemical Engineering Studies, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia

^c Water Research and Environmental Sustainability Growth (WAREG), Universiti Malaysia Perlis (UniMAP), 02600 Arau, Perlis, Malaysia

^d School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA Shah Alam, 40450 Shah Alam, Selangor, Malaysia

^e Karlsruhe Institute of Technology, Institute for Micro Process Engineering, 76344 Eggenstein-Leopoldshafen, Germany

^f The University of Queensland, FIM² Lab—Functional Interfacial Materials and Membranes Laboratory, School of Chemical Engineering, Brisbane, Qld 4072, Australia

^g Nanoscience Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

^h School of Chemical and Biomolecular Engineering, The University of Sydney, New South Wales 2006, Australia

ⁱ LAQV-REQUIMTE, (Bio)Chemical Process Engineering, Department of Chemistry, Faculty of Science and Technology, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

^j iBET – Instituto de Biologia Experimental e Tecnológica, 2781-901 Oeiras, Portugal

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Background: Substitution of different types of B-site metal cations in the perovskite structure led to a significant change in the catalytic reactivity of the resulting catalysts. In this work, the functional role of B-site substitution on the catalytic reactivity of mixed oxides containing B-site substituted CaMFeO_3 ($\text{M} = \text{Cu}, \text{Mo}$ and Co) perovskite catalysts is investigated.

Methods: The catalysts were synthesized via a modified EDTA-citric acid complexation method and tested for the heterogeneous Fenton-like reaction for oxidative degradation of acid orange II (AOII) dye in the presence of H_2O_2 .

Significant findings: CaCuFeO_3 exhibited the highest AOII degradation (97%) followed by CaMoFeO_3 (90%), CaFeO_3 (64%) and CaCoFeO_3 (40%) within 60 min of reaction, and the reaction followed a pseudo-second-order kinetics model. Interestingly, the partial substitution of Cu in the B-site of CaFeO_3 enhanced the reaction rate constant achieving a k value of $1.9 \times 10^{-2} \text{ L mg}^{-1} \text{ min}^{-1}$, approximately twenty-one times higher than that of the blank catalyst CaFeO_3 . The enhanced catalytic reactivity of CaCuFeO_3 is associated with the high reducibility of copper/iron ions within the B-site structure in the presence of oxidant which facilitated fast redox cycling of the active sites during catalysis. The fast redox cycling is attributed to the decent electron mobility due to low electron transfer resistance between the active sites.

1. Introduction

Synthetic dyes are a prominent source of industrial pollution and water contamination [1,2]. The residual dyes are not readily biodegradable and can be found in wastewater effluents originated from textile, paper, leather, cosmetics and other industries. The most common

type of synthetic dye used in the textile industry is azo dyes, accounting for half of all the commercial dyes [3]. These dyes are characterized by the existence of one or more azo ($-\text{N}=\text{N}-$) bonds. Despite its versatile use and chemical stability, azo dyes have been reported to be carcinogenic and mutagenic contaminants with poor environmental biodegradability [4]. In fact, the dissolution of azo dyes in water can caused discoloration

* Corresponding author at: School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh, Pulau Pinang 13500, Malaysia.

E-mail address: noraida709@uitm.edu.my (N.A. Zubir).

of the surface water, which hinders light penetration. As a result, the photosynthesis activities of marine flora will be affected and thus negatively impacting the aquatic marine organism's food source. Hence, untreated dyes pose a significant threat to human health and marine ecosystems. Various physical, biological and chemical treatment methods [5,6] have been developed and applied to overcome this issue. The physical treatments such as adsorption, membrane filtration and coagulation-flocculation typically require additional treatment as they are seriously affected by secondary pollution whilst the complete degradation of dye pollutant remain unsolved [7]. On the other hand, biological treatments have several drawbacks, including the need for longer retention time [8], and wastewater treatment plants with large footprint.

Advanced oxidation processes (AOPs) have been broadly used as water/wastewater treatment methods due to the generation of hydroxyl radicals ($\cdot\text{OH}$), which can rapidly and non-selectively degrade a wide range of organic pollutants. Fenton's reagent [9,10] and ultraviolet/hydrogen peroxide (UV/ H_2O_2) [11,12] are the most common type of AOPs. In principle, the $\cdot\text{OH}$ is generated when H_2O_2 is activated by iron ions or UV during catalysis. For instance, the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ process degraded >98% of AO7 dye solution within 1 h [13], while UV/ H_2O_2 exhibited complete degradation of AO7 after 30 min of reaction [14]. However, homogeneous oxidation processes have several disadvantages, including a narrow pH range of catalytic oxidation, catalyst deactivation, the need for catalyst regeneration, and the removal of iron compounds from the treated water [15]. Moreover, irradiation of UV light during reaction requires high energy consumption [16,17] and photocatalytic reactivity depends on UV light source availability and intensity [18]. Hence, there is a great benefit to develop heterogeneous catalysts that can initiate oxidation reactions without the need for illumination.

Modification of compounds containing iron oxides have been studied for the degradation of dyes, using graphene oxide [19,20], metal-organic frameworks (MOF) [21,22] and mixed oxides such as perovskites [23–25], whereas the latter is generally considered desirable for heterogeneous catalytic applications. Perovskites are crystalline ceramics that belong to the class of mixed oxides with a general formula of ABO_3 . A-site cation is commonly occupied by alkali metals, alkaline-earth metals or rare-earth metals. The B-site cation could be filled by transition metals. Perovskite can be formulated into binary (ABO), ternary ($\text{AA}'\text{BO}$ or $\text{ABB}'\text{O}$) or quaternary ($\text{AA}'\text{BB}'\text{O}$) compounds. Interestingly, the perovskite's catalytic reactivity can be modulated by substituting different A and/or B cation types within the structure to control the overall physicochemical properties of the perovskites. In addition, it was reported that the catalytic reactivity of the perovskite is affected by the partial substitution of the B-site with different transition metal cations [26]. For instance, the partially substituted Cu in LaCoO_3 in the B-site formed a tertiary LaCoCuO_3 perovskite for the degradation of phenol that boosted the catalytic performance of by approximately 99% within 12 min [27]. Quaternary perovskites also proved to be efficient heterogeneous catalyst for organic dye degradation. For example, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Ni}_x\text{Cu}_{1-x}\text{O}_{3-\delta}$ degraded 95% of AOII within 2 h, which was attributed to the effective redox cycles between $\equiv\text{Ni}^{2+}/\equiv\text{Cu}^{1+}$ and $\equiv\text{Ni}^{3+}/\equiv\text{Cu}^{2+}$ for the generation of reactive radical species during catalysis [28]. The synergistic interaction between Ni and Fe was also positive for $\text{CaNi}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ perovskites showing over 50% degradation of Reactive Red 141 and AOII after 5 min reaction time [29].

In the case of B-site perovskite catalyst containing Cu/Fe and Co/Fe, the typical type of A-site substitutions are based mainly on La [30,31], Bi [32], Sr [33,34] and Ba/Sr [35]. A number of mixed oxides containing Ca in the A-site perovskites such as $\text{Ca}_x\text{Sr}_{1-x}\text{CuO}_{3-\delta}$ [36], $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Ni}_x\text{Cu}_{1-x}\text{O}_{3-\delta}$ [28], $\text{CaNi}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ [29] and $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{NiO}$ [37] were also effective in the degradation of AOII dyes. Ca is particularly effective in the A-site of some of these catalysts, but limited work has been reported for compounds containing Fe oxides in the B-site. Herein,

we investigate the functional role of B-site substitution on the calcium-iron-based mixed oxide perovskite catalysts; CaMFeO_3 ($\text{M} = \text{Mo}, \text{Cu}, \text{Co}$) for H_2O_2 activation in heterogeneous Fenton-like reaction. AOII was chosen as model pollutants as it represents 15% of worldwide dye production [38] and the most discharged dye from the textile industry [36,39]. In this study, CaMFeO_3 ($\text{M} = \text{Mo}, \text{Cu}, \text{Co}$) mixed oxides containing perovskite synthesized via EDTA citric acid complexation method were prepared and their catalytic activities were investigated in the absence and presence of H_2O_2 . The functional role of transition metals on substituted CaMFeO_3 towards AOII degradation rate was evaluated using reaction kinetics models and mechanistic understanding was correlated to their resultant physicochemical properties.

2. Materials and methods

2.1. Synthesis and characterization

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; $\geq 99\%$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; 99%), ammonium molybdate ($(\text{NH}_4)_2\text{MoO}_4$; 99%), cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; 98%), copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; $\geq 99\%$), ethylenediaminetetraacetic acid (EDTA), ammonium hydroxide (NH_4OH) solution, hydrogen peroxide (H_2O_2 ; 30% (w/w)) and acid orange II (AOII) were supplied by Sigma Aldrich. Citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$; $\geq 99\%$) was purchased from QReC (Asia). All chemicals were of analytical grade and used as received without further purification.

The EDTA-citric acid complexation method was used to synthesize a series of B-site-substituted CaMFeO_3 ($\text{M} = \text{Mo}, \text{Co}, \text{Cu}$) perovskites in this study. Each A/B-site cation molar concentration was fixed at 0.05 M. A set of molar ratios of A-site precursor: B'-site precursor: B-site precursor: ethylenediamine tetra-acetic acid (EDTA): citric acid: ammonium hydroxide was kept constant at 1:1:1:1.2:10. For instance, in the synthesis of CaMoFeO_3 catalyst, 0.05 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.05 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.05 M $(\text{NH}_4)_2\text{MoO}_4$ and 0.1 M $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ solutions was mixed and stirred for 15 min at the beginning. Then, a solution mixture containing 0.05 M NH_4OH and 0.055 M EDTA was added to the former mixture and stirred for 15 min at room temperature until well mixed.

Subsequently, the resultant homogeneous mixture was heated at 100°C under stirring to evaporate water to form a viscous solution. Further gelation of the viscous solution was carried out in the oven at 90°C for 24 h. The dried gel samples then underwent a two-stage sintering process in a muffle furnace: first stage at 450°C for 8 h and second stage at 800°C for 4 h at a ramping rate of 5°C min^{-1} in air. The resultant CaMoFeO_3 perovskite was ground and stored prior to further use. Similar procedures were repeated for other substituted B-site perovskite catalysts using copper and cobalt precursors to synthesize CaCuFeO_3 and CaCoFeO_3 , respectively. In addition, CaFeO_3 was also synthesized as a blank catalyst for comparison purposes.

The phase identification of the materials was performed by X-ray powder diffraction (XRD, D8 Advance, Bruker, USA) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA by step scanning in the range of $10^\circ \leq 2\theta \leq 100^\circ$. The surface morphology was analyzed using a field emission scanning electron microscope (FE-SEM), equipped with energy-dispersive X-ray spectroscopy (EDS) for elemental analysis. Nitrogen adsorption analysis was carried out at 77 K using a Micromeritics ASAP 2020 to determine the BET surface area of samples that were degassed overnight at 200°C under vacuum.

Oxygen-temperature-programmed desorption (O_2 -TPD) analysis was performed using AutoChem II 2920 (Micromeritics). Each sample (100 mg) was pretreated in helium (carrier gas, 50 mL min^{-1}) from room temperature to 350°C for 30 min at a rate of $10^\circ\text{C min}^{-1}$. After cooled down to 50°C , the sample was saturated by pure oxygen gas (50 mL min^{-1}) for 1 h then purged with helium (50 mL min^{-1}). After acquiring a stable baseline, the catalyst was heated to 800°C at 5°C min^{-1} ramping rate, and the O_2 -TPD profile was recorded. For hydrogen-temperature-

programmed reduction (H_2 -TPR), the analysis was conducted using the same instrument as in the O_2 -TPD procedure. Initially, 100 mg of each sample was pretreated in helium to 350°C (at $10^\circ\text{C min}^{-1}$) for 1 h. After cooling to 50°C , the helium was switched to hydrogen flow (10 vol% H_2 in Ar, 50 mL min^{-1}). Once stable baseline acquired, the H_2 -TPR profile of the catalyst was recorded while heating to 800°C at a rate of 5°C min^{-1} . Details analysis on the determination of pH zero-point charge (pH_{zpc}), ions metal leaching and the electrical impedance spectroscopy analysis are summarized in Supplementary Information (Text S1).

2.2. Catalytic reactivity and kinetics evaluation

The catalytic reactivity of the B-site-substituted CaFeO_3 catalysts was evaluated in oxidative degradation of AOII (35 mg L^{-1}) by dispersing 0.1 g catalyst in 100 mL of AOII solution and 22 mM of H_2O_2 at room temperature stirred at 200 rpm for 90 min. At regular interval, 5 mL of reaction suspension was withdrawn and filtered through a $0.2\text{ }\mu\text{m}$ filter syringe. UV-vis spectrophotometer (Perkin Elmer, Lambda 25) was used to determine the concentration of AOII solution at λ_{max} of 486 nm. Further, 2-propanol (Merck, 10 M) mixed in an AOII solution was used as hydroxyl radical ($\cdot\text{OH}$) scavenger. The results are reproducible with duplicate experiments conducted. The data show average value with experimental errors of less than 5%. Details analysis on the identification of AOII's intermediate compounds are provided in Supplementary Information (Text S2).

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 displays the XRD patterns of resultant CaFeO_3 and B-site-substituted CaMFeO_3 samples. The XRD pattern of CaFeO_3 sample exhibited four major peaks at 2θ of 33.56° , 35.48° , 37.82° and 49.84° corresponding to perovskite CaFeO_3 (COD 96-152-6749), whilst peaks at 2θ of 32.74° and 33.26° are related to perovskite-like structure (COD 96-152-0830) [40]. Impurity phases consist of calcium ferrite CaFe_2O_7 (COD 96-901-3961) is observed at 2θ of 34.04° , 34.78° , 36.16° and 40.16° , maghemite $\gamma\text{-Fe}_2\text{O}_3$ (COD 96-901-2692) at 2θ of 32.22° and 44.72° ; and calcium oxide (COD 96-900-6746) at 2θ of 30.88° , 35.72° and 51.36° .

When Cu was partially substituted into the B-site of CaFeO_3 , additional new peaks are observed at 2θ of 17.20° , 34.80° and 42.80° which corresponds well to perovskite $\text{CaCu}_{2.79}\text{Fe}_{4.21}\text{O}_{12}$ (COD 96-434-4870). Meanwhile, peaks at 2θ of 35.50° and 38.70° are assigned to copper oxide phase (COD 96-721-2242). Partial substitution of Co into the

CaFeO_3 resulted in peaks at 2θ of 33.44° that are ascribed to perovskite $\text{Ca}_2\text{FeCoO}_5$ (COD 96-400-0920). Cobalt (II) oxide (COD 96-153-1762) is also noticeable at 2θ of 16.00° . In the case of partial substitution of Mo, perovskite phases appeared at 2θ of 32.68° that corresponds to $\text{Ca}_2\text{FeMoO}_6$ (COD 96-400-2219). Peaks at 2θ of 24.60° , 27.72° , 29.92° and 34.84° are assigned to $\text{Fe}_2(\text{MoO}_4)_3$ (COD 96-152-4203). Moreover, the peaks at 2θ of 21.02° , 28.16° and 44.66° are attributed to orthorhombic $\text{Mo}_{15.39}\text{O}_{47}$ phase (COD 96-154-0782); whilst peaks at 2θ of 29.10° and 54.58° are related to CaMoO_4 (COD 96-900-9634). Hence, these findings confirm that the resultant CaFeO_3 and B-site-substituted CaMFeO_3 samples contained mixtures of perovskites and mixed oxides phases.

The surface morphology of the samples was analyzed by FE-SEM as depicted in Fig. 2. All substituted perovskite catalysts exhibited heterogeneous surfaces which consists of irregular shape and sizes. CaFeO_3 mixed oxides shows the formation of rugged features consisting of larger particles and smaller particles showing lamellar structures that agglomerated during sintering. Changes in particle size can be clearly observed when transition metals of Cu, Mo and Co were partially substituted as demonstrated by the inset histograms. For instance, evolution of particle size can be observed in the sequence of $\text{CaCuFeO}_3 < \text{CaFeO}_3 < \text{CaMoFeO}_3 < \text{CaCoFeO}_3$. CaCuFeO_3 resulted in a narrow particle size distribution of small irregular particles ($1\text{--}2\text{ }\mu\text{m}$) and the most homogeneous sample. Contrary to this, the other mixed oxides consisted of a broader size distribution ranging from connected smaller particles ($< 1\text{ }\mu\text{m}$) forming rugged particles to larger particles ($2\text{--}7\text{ }\mu\text{m}$). This is clearly observed in $\text{CaFeO}_3 < \text{CaMoFeO}_3 < \text{CaCoFeO}_3$ samples, giving an indication that different phases were formed as evidenced in the XRD patterns (Fig. 1).

The elemental mapping (Fig. 3a-o) reveals that Ca, Fe, Mo, Cu, Co and O elements were evenly distributed throughout the surface of the catalysts. Further analysis indicates that the distribution of Cu and Co occurred as discrete particles at the surface of the catalysts whilst Mo distribution was relatively uniform. Table 1 presents the detailed composition of all catalysts. The composition of substituted Cu, Mo and Co into the perovskite and metal oxide structures were found to be 12.3, 12.2 and 14.5 wt%, respectively. The composition of Fe decreased from 31.6 wt% from the blank catalyst (CaFeO_3) to an average value of 25 wt% for the B-site-substituted CaMFeO_3 . These results indicate the successful partial substitution of transition metals (Mo, Cu and Co) into the CaFeO_3 catalyst structures.

Fig. 4 illustrates the representative sorption isotherm of the resultant catalysts. All catalysts produced low N_2 sorption volumes, a clear indication of the formation of non-porous materials. Although the isotherms are of type III with a hysteresis loop at $p/p_0 > 0.45$, this is not associated with mesopores but attributed to the spacing within the rugged small particles. This is clearly seen in the SEM images for CaFeO_3 , CaMoFeO_3 and CaCoFeO_3 samples. The CaCuFeO_3 sample consisted mainly of smaller particle with a narrow distribution (Fig. 2) and the hysteresis is ascribed to the smaller interparticle spacing. For the increase in the sorption volume at $p/p_0 > 0.9$, this is generally related to the larger interparticle spacing. The blank sample CaFeO_3 resulted in the highest surface area, attributed to the rugged surfaced in the FE-SEM image (Fig. 2). The BET surface areas were $12.8\text{ m}^2\text{ g}^{-1}$ (CaFeO_3), $6.0\text{ m}^2\text{ g}^{-1}$ (CaCuFeO_3), $3.5\text{ m}^2\text{ g}^{-1}$ (CaCoFeO_3) and $2.0\text{ m}^2\text{ g}^{-1}$ (CaMoFeO_3).

The profiles of O_2 -TPD analysis are shown in Fig. 5a. It can be observed that all catalysts exhibit dominant peaks between 561°C to 590°C . The O_2 uptake decreased from 1.02 mmol g^{-1} (CaFeO_3) to 0.50 mmol g^{-1} (CaCuFeO_3), 0.42 mmol g^{-1} (CaMoFeO_3) and 0.18 mmol g^{-1} (CaCoFeO_3). Therefore, partially substituting the B-site with metals (Cu, Co and Mo) reduced the overall O_2 uptake. Further, these results confirm that all catalysts tested in this work have oxygen related sites with potential active sites for H_2O_2 activation during catalysis. The H_2 -TPR profile of all catalysts in Fig. 5b exhibits well-defined reduction peak at a temperature range between 638 and 651°C . This temperature range corresponds to the partial reduction of Fe^{3+} to Fe^{2+} [41]. Interestingly,

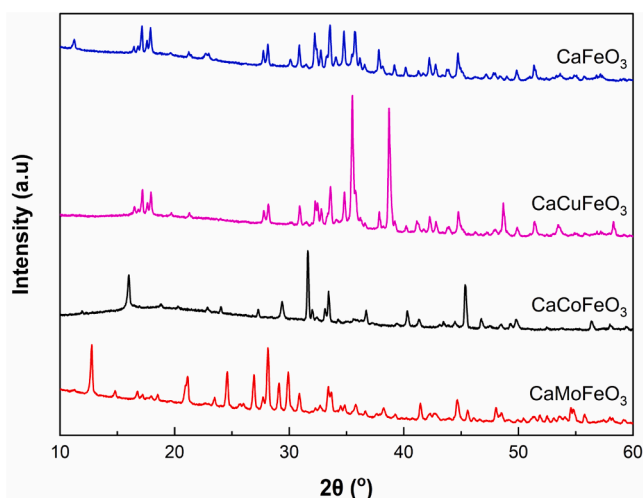


Fig. 1. XRD patterns of B-site substituted perovskite catalysts.

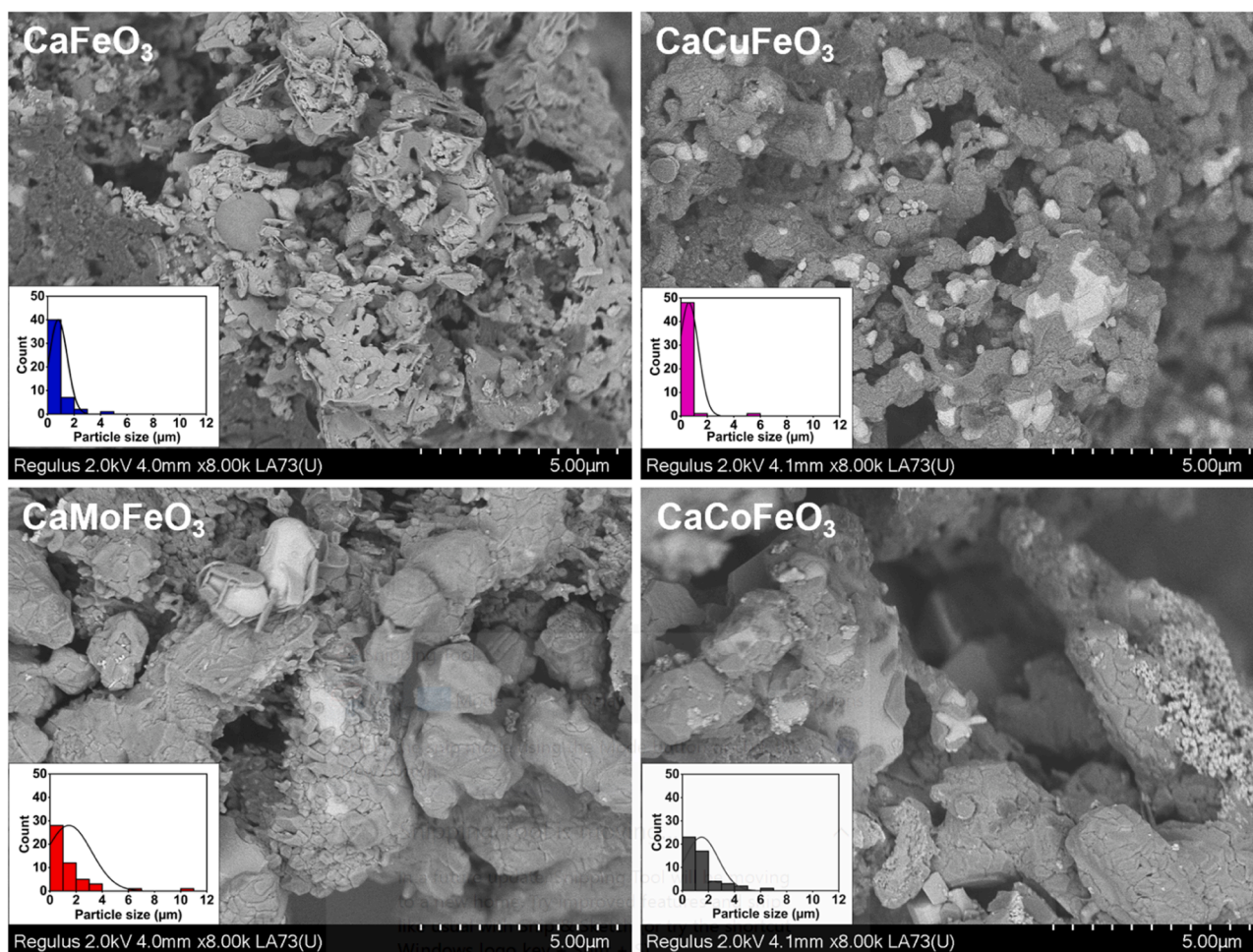


Fig. 2. FE-SEM images and corresponding inset histogram of particle size distributions of the B-site substituted perovskite catalysts.

two reduction peaks observed at 225 and 271°C was observed for the CaCuFeO_3 . These peaks can be attributed to the reduction of Cu^{2+} to Cu^+ and Cu^+ to Cu [42]. The hydrogen consumption of CaCuFeO_3 started at a much lower temperature compared to other catalysts, suggesting the high-valence-state copper/iron ions in CaCuFeO_3 are more easily reduced to a lower oxidation state than those in CaFeO_3 , CaCoFeO_3 and CaMoFeO_3 in this work. In other words, copper/iron ions in CaCuFeO_3 are better electron acceptors, which can efficiently accelerate the redox cycle during catalysis.

3.2. Catalytic performance

The performance of the catalysts for AOII oxidation in the absence and presence of H_2O_2 are presented in Fig. 6. In the absence of H_2O_2 , the adsorption capacities CaFeO_3 , CaCuFeO_3 , CaMoFeO_3 and CaCoFeO_3 for AOII removal were 25%, 28%, 14% and 12% within 60 min, respectively. The low AOII adsorption is due to strong repulsion between the negative-charged of perovskite catalyst (Fig. S1) and anionic AOII behavior. Heterogeneous Fenton-like degradation of AOII in the presence of H_2O_2 was used as a model reaction to evaluate the catalytic reactivity of the catalysts quantitatively. Fig. 6 shows that no AOII removal was observed in the presence of H_2O_2 alone. In the presence of the catalysts and H_2O_2 , the AOII removal was enhanced significantly. The overall catalytic performance improvement within 60 min of reaction were as follows: CaCuFeO_3 (97%) > CaMoFeO_3 (90%) > CaFeO_3 (64%) > CaCoFeO_3 (40%). This result reveals that mixed metal oxides and B-site substituted perovskite catalysts activated H_2O_2 to accelerate the generation of $\cdot\text{OH}$ radicals, resulting in a much higher rate of AOII

removal. The decomposition of AOII occurs mainly at the solid-liquid interfaces of the catalysts; where the activation of H_2O_2 took place.

It is interesting to observe that the CaFeO_3 had the highest surface area of $12.8 \text{ m}^2 \text{ g}^{-1}$ and highest O_2 uptake of 1.02 mmol g^{-1} , parameters of which significantly contribute to reaction performance. Contrary to this, AOII degradation by CaFeO_3 was relatively lower at 64%. This lack of performance is attributed to the lower reactivity of CaFeO_3 mixed oxides. Further, these results suggest that the smaller particles in the rugged surface as observed in the SEM image of CaFeO_3 (Fig. 2) which contribute to high surface area are related to a low performance of the CaFeO_3 mixed oxides phase. The CaCuFeO_3 catalyst resulted in the highest reaction performance of 97% though with a surface area and O_2 uptake around 50% that of the CaFeO_3 catalyst. In principle, the SEM image shows that CaCuFeO_3 catalyst constituted mainly of small particles with a narrow distribution and in overall terms more homogenous than the other catalysts tested in this work. Further, the high catalytic performance of CaCuFeO_3 was aided by the decent copper/iron redox coupling to activate H_2O_2 into $\cdot\text{OH}$ radicals during catalysis.

The UV-vis spectra in Fig. 7a shows the evolution of AOII degradation by CaCuFeO_3 in the presence of H_2O_2 . Several absorption peaks are present in the AOII solution prior to reaction at $t = 0$ min. For instance, two main peaks at 430 and 486 nm are attributed to the transition of the azo and hydrazone forms [43], while the other two peaks at 230 and 310 nm are assigned to the benzene and naphthalene rings [44] of AOII molecules. Noticeably, all peaks decreased as reaction time increased except for the peak at 254 nm. These results clearly indicate the destruction of azo bonds (at $\lambda = 430$ and 486 nm) and the opening of benzene and naphthalene rings (at $\lambda = 230$ and 310 nm) [29]. The

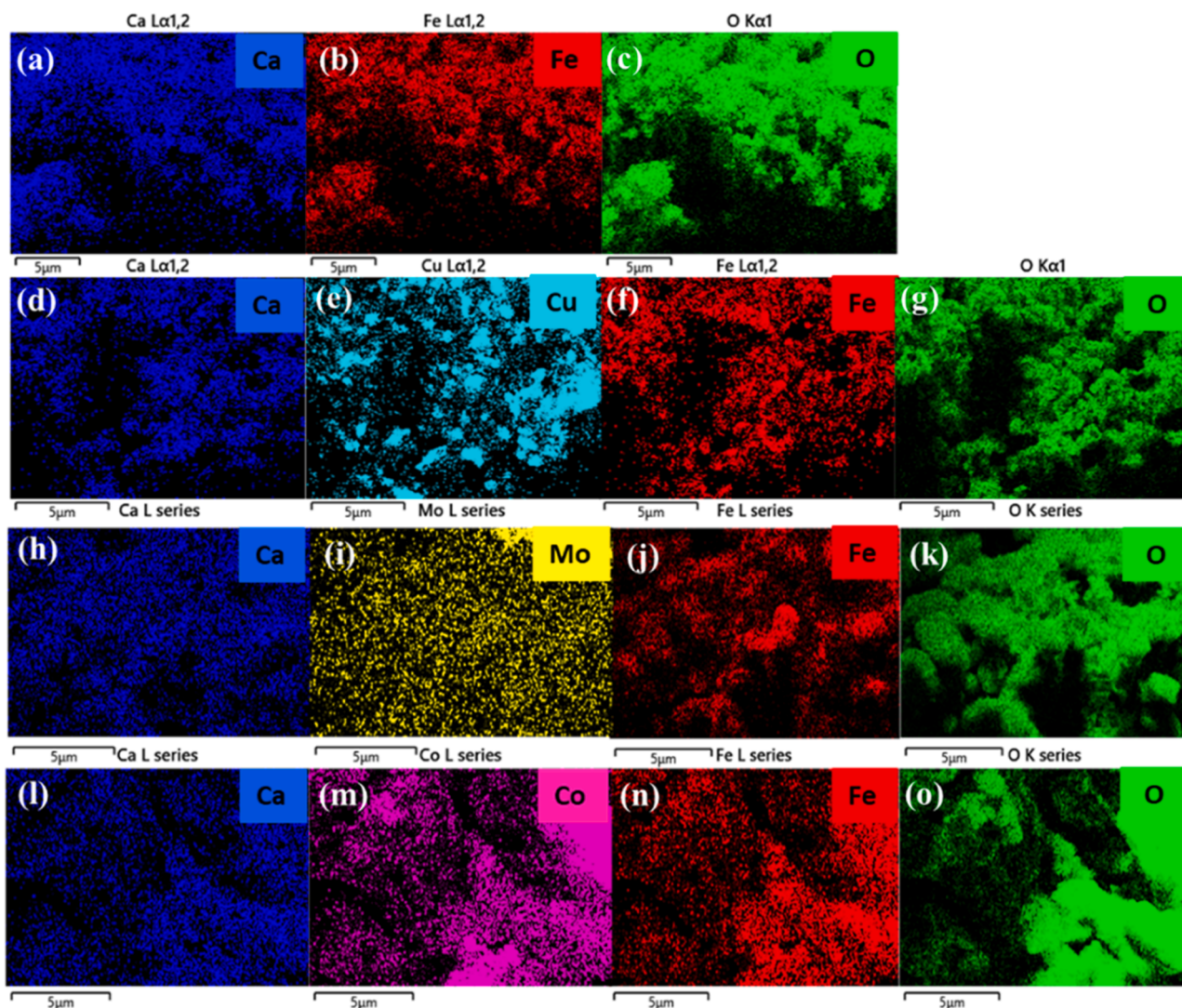


Fig. 3. Elemental mapping of (a-c) CaFeO_3 , (d-g) CaCuFeO_3 , (h-k) CaMoFeO_3 and (l-o) CaCoFeO_3 catalysts.

Table 1

Chemical composition of CaFeO_3 , CaCuFeO_3 , CaMoFeO_3 and CaCoFeO_3 by EDS analysis.

Samples	Chemical compositions (%)					
	Ca	Fe	O	Cu	Mo	Co
CaCuFeO_3	18.05	26.88	42.77	12.30	–	–
CaMoFeO_3	16.14	20.96	50.67	–	12.23	–
CaCoFeO_3	18.41	27.95	39.15	–	–	14.49
CaFeO_3	23.88	31.63	44.49	–	–	–

UV-vis spectra profiling of AOII by CaFeO_3 , CaMoFeO_3 and CaCoFeO_3 catalysts (Fig. S2) indicate a lower efficiency of AOII degradation by these catalysts compared to CaCuFeO_3 .

Further analysis on the intermediate peak profiling at $\lambda = 310$ nm and 254 nm are displayed in Figs. 7b and 7c for all catalysts. The peak intensity at 310 nm decreased significantly for the CaCuFeO_3 within 30 min with $C_t/C_0 = 0.2$, followed by CaFeO_3 ($C_t/C_0 = 0.6$), CaCoFeO_3 ($C_t/C_0 = 0.7$) and CaMoFeO_3 ($C_t/C_0 = 1.0$). These results indicate higher decomposition of naphthalene rings in the presence of CaCuFeO_3 compared to other catalysts. Nevertheless, the C_t/C_0 intensity at $\lambda = 254$ nm increased over time due to the formation of benzene intermediate. From Fig. 7c, the C_t/C_0 intensity doubled for CaMoFeO_3 and started to be levelled off after 30 min. Similar trend was observed for CaFeO_3 ,

CaCuFeO_3 and CaCoFeO_3 , which implied that the benzene intermediates were not degraded during this period. The presence of intermediate compounds was identified by GCMS analysis. Detailed chromatogram and proposed chemical structure of the intermediates (1,3-benzenediol, 2-acetyl; 2,6-dihydroxybenzoic acid; 3-hydroxy-benzoic acid; 2-heptanol,6-amino-2-methyl; 3-hydroxy-3-methyl-benzoic acid; 4-(1,2-dihydroxyethyl) 1,2-benzenediol) were summarized in Fig. S3 and Table S1, respectively. Hence, the oxidative degradation mechanism of AOII is proposed as presented in Fig. 8.

The oxidative degradation of AOII by all catalysts fits a pseudo-second-order reaction kinetics model ($R^2 > 0.93$) as shown in Fig. 9a following Eq. (1) and its integrated form Eq. (2):

$$\frac{dC_t}{dt} = k(C_t)^2 \quad (1)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + kt \quad (2)$$

where k ($\text{L mg}^{-1} \text{min}^{-1}$) is an apparent kinetics rate constant of second-order, t is reaction time, and C_t is AOII concentration at a given time t . The reaction rate constants are given in Fig. 9b. It is observed that CaCuFeO_3 ($k = 1.9 \times 10^{-2} \text{ L mg}^{-1} \text{min}^{-1}$) was the highest value followed by CaMoFeO_3 ($k = 4.5 \times 10^{-3} \text{ L mg}^{-1} \text{min}^{-1}$). These reaction rate constants were higher by factors of twenty-one and five times than that

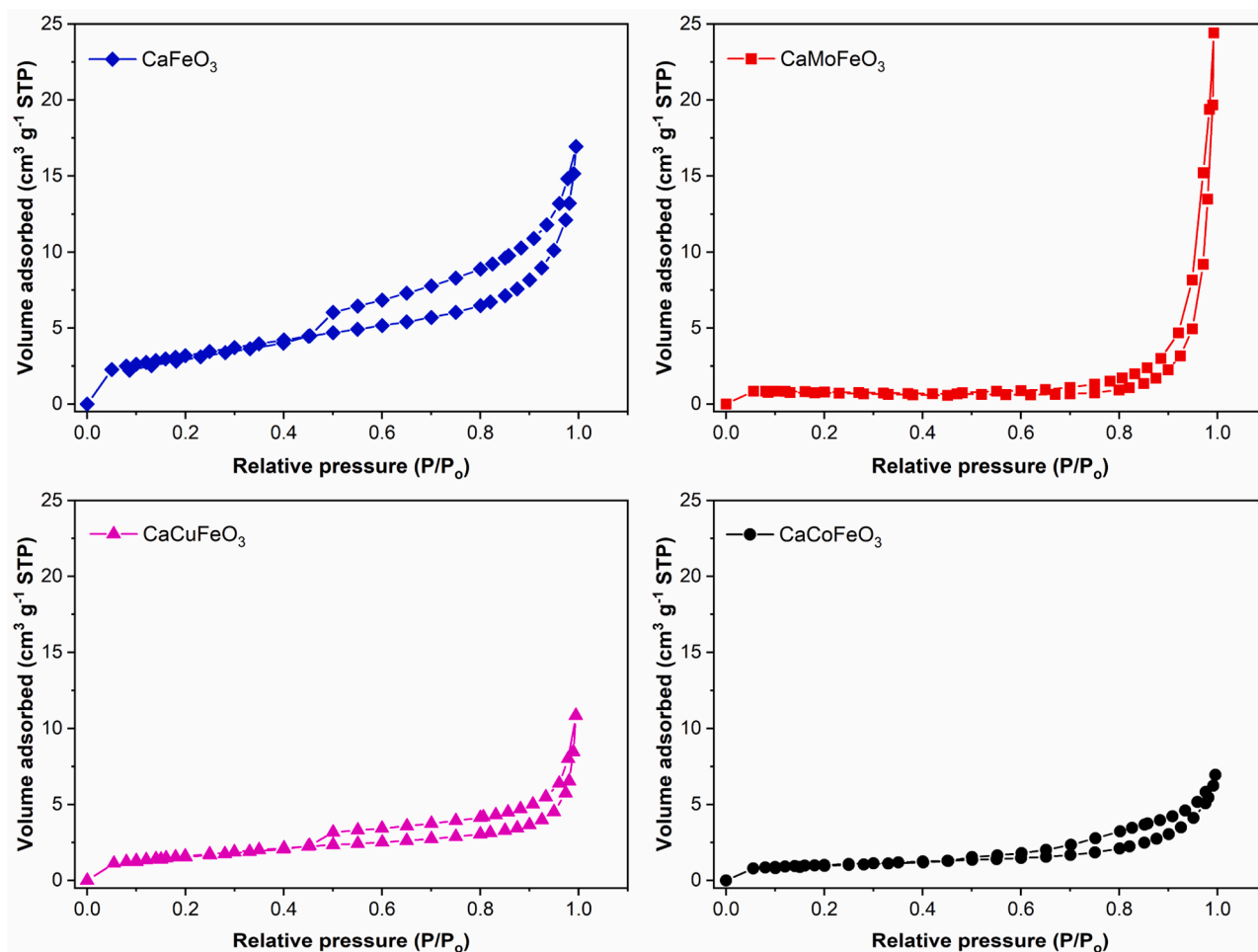


Fig. 4. Nitrogen adsorption/desorption isotherms of the catalysts.

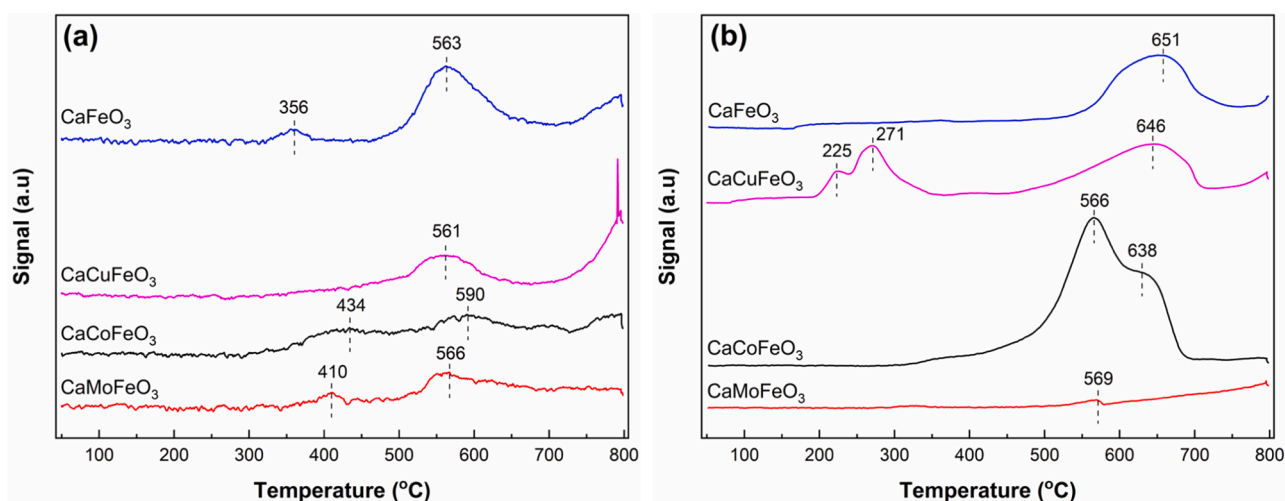


Fig. 5. (a) O₂-TPD and (b) H₂-TPR of the catalysts.

of CaFeO₃ ($k = 0.9 \times 10^3 \text{ L mg}^{-1} \text{ min}^{-1}$), respectively. CaCoFeO₃ yielded the lowest reaction rate constant of ($k = 0.3 \times 10^3 \text{ L mg}^{-1} \text{ min}^{-1}$). The kinetic behavior of all the catalysts can be well supported by the magnitude of electron transfer rate. Interestingly, CaCuFeO₃ exhibited the lowest electron transfer resistance as indicated by the smallest arc diameter compared to others CaMFeO₃ (M = Mo, Co) which are presented in Fig. 9c. The low resistance implies a faster electron

transfer mobility and a higher surface reaction rate [45–47]. Faster electron transfer is beneficial to facilitate fast redox cycling of active sites during catalysis. The evolution of electron transfer rate and surface reaction rate can be observed in the order of CaCuFeO₃ > CaMoFeO₃ > CaFeO₃ > CaCoFeO₃. For comparison purposes, Fig. 9d displays the performance of CaCuFeO₃ against various catalysts containing La, Ca and CaSr in the A-site, and Co, Cu, Fe, Ni, NiFe and NiCu in the B-site.

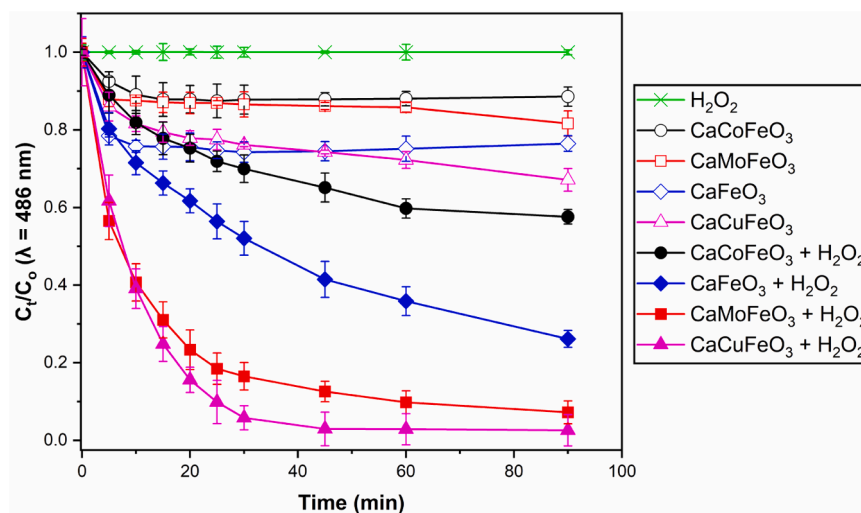


Fig. 6. Removal profile of AOII solution by $CaFeO_3$, $CaCuFeO_3$, $CaMoFeO_3$ and $CaCoFeO_3$ in the absence and presence of H_2O_2 . Experimental conditions: AOII 35 mg L^{-1} , H_2O_2 22 mM, 1.0 g L^{-1} catalyst and unadjusted pH solution.

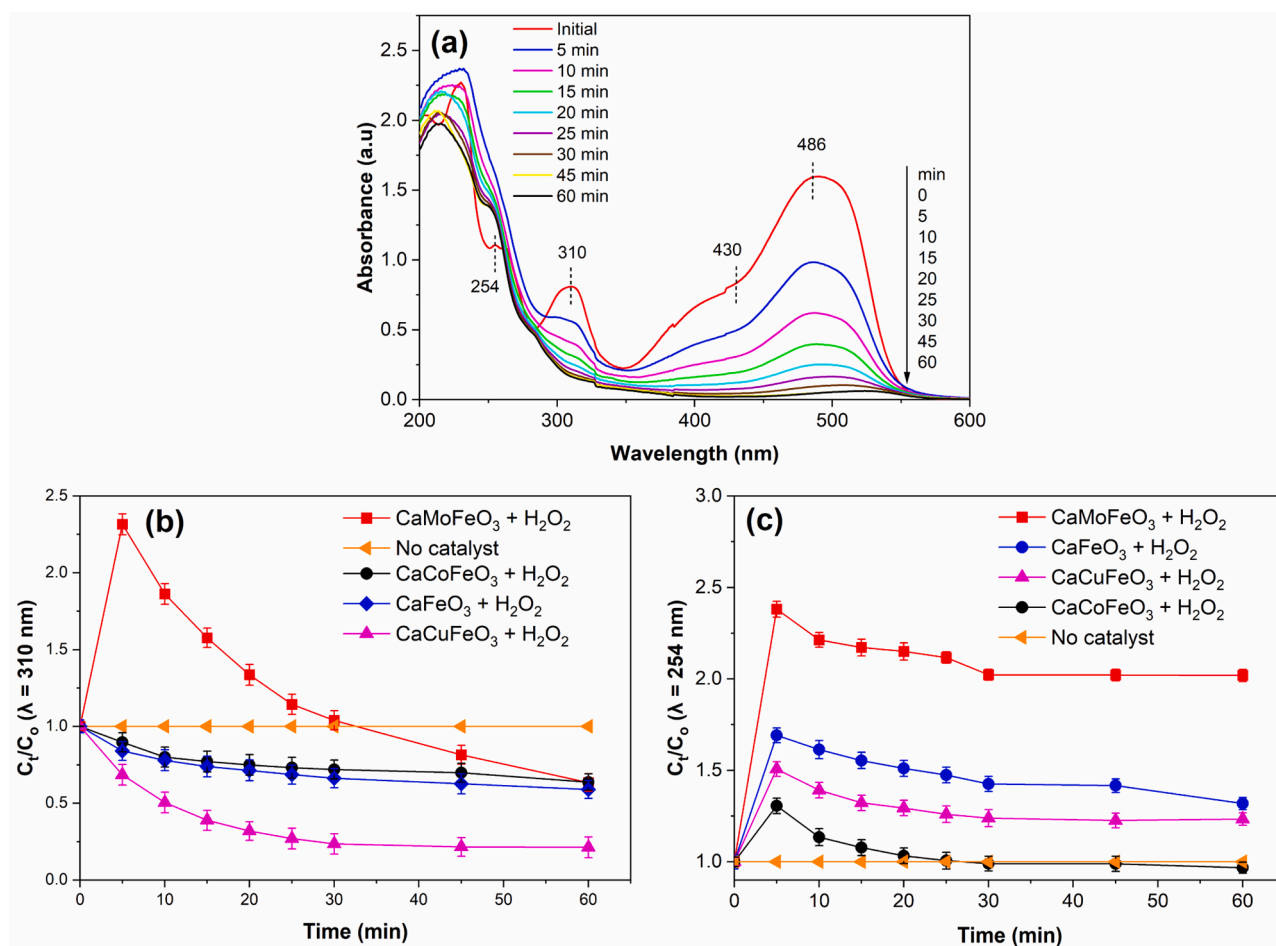


Fig. 7. UV-vis spectra of AOII degradation as a function of time by (a) $CaCuFeO_3$ and the normalized peak intensity at (b) 310 nm and (c) 254 nm by $CaFeO_3$, $CaCuFeO_3$, $CaMoFeO_3$ and $CaCoFeO_3$ in the presence of H_2O_2 . Experimental conditions: AOII 35 mg L^{-1} , H_2O_2 22 mM, 1.0 g L^{-1} catalyst and unadjusted pH solution.

$CaCuFeO_3$ outperformed all catalysts for the degradation of AOII and other dyes, with the exception of $LaCoO_3$. Further additional comparison on others relevant aspects is also provided in Table S2.

The influence of key operational reaction conditions (catalyst dosage, initial pH solution, initial H_2O_2 concentration, initial AOII

concentration and temperature) on the AOII degradation in the presence of $CaCuFeO_3$ catalyst is presented in Fig. S4. AOII degradation significantly enhanced from 16% to 99% as the catalyst dosage increased from 0.25 to 1.25 g/L within 60 min reaction time (Fig. S4a). The higher catalyst dosage led to the increased amount of active sites which are

A series of mixed oxide catalysts (CaMoFeO_3 , CaCuFeO_3 and CaCoFeO_3) were successfully synthesized via the combined EDTA-citric acid complexation, containing both mixed oxides and B-partially substituted perovskite phases. The AOII oxidative degradation in the presence of H_2O_2 fitted a pseudo-second-order kinetics model. The order of reaction rate constant was found to be in the sequence of CaCuFeO_3 ($k = 1.9 \times 10^{-2} \text{ L mg}^{-1} \text{ min}^{-1}$) $>$ CaMoFeO_3 ($k = 4.5 \times 10^{-3} \text{ L mg}^{-1} \text{ min}^{-1}$) $>$ CaFeO_3 ($k = 0.9 \times 10^{-3} \text{ L mg}^{-1} \text{ min}^{-1}$) $>$ CaCoFeO_3 ($k = 0.3 \times 10^{-3} \text{ L mg}^{-1} \text{ min}^{-1}$). The enhanced catalytic reactivity of CaCuFeO_3 was attributed to the fast redox cycling of active sites due to the high reducibility of copper/iron ions and the decent electron mobility within the structure of the catalyst that facilitates efficient generation of reactive radicals during catalysis. In fact, the CaCuFeO_3 catalyst has also shown decent catalytic performance over five cycles of reactions with significantly low metal leaching that are well below the permissible discharge limit.

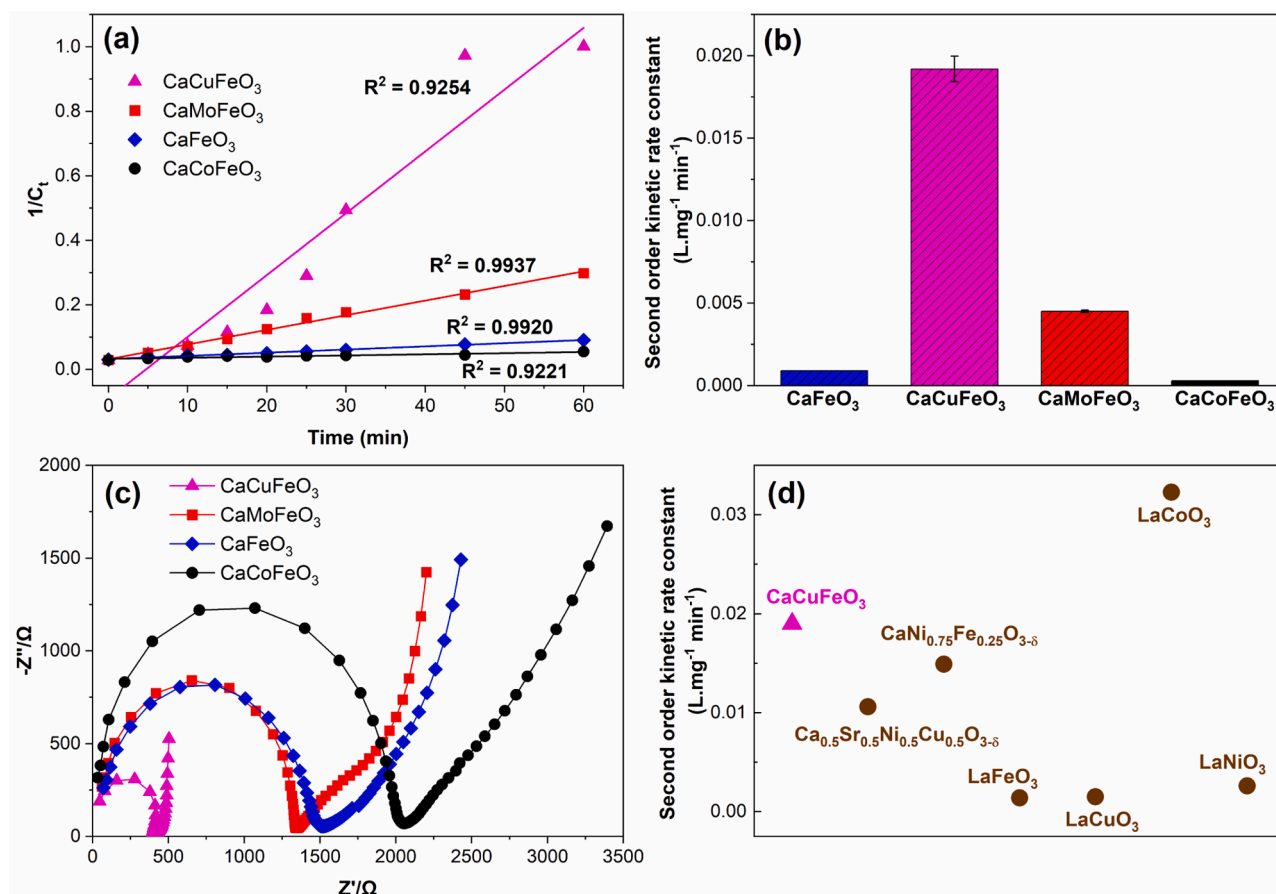


Fig. 9. (a) AOII removal in the presence of H_2O_2 using second-order reaction kinetics models, (b) rate constant of the perovskite catalysts, (c) Nyquist plot of the perovskite catalysts and (d) comparison of rate constant between CaCuFeO_3 (this work) and others reported B-site perovskite catalysts particularly to dye-contaminated remediation (LaFeO_3 , LaCuO_3 , LaNiO_3 and LaCoO_3 [48]; $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{3-\delta}$ [28]; $\text{CaNi}_{0.75}\text{Fe}_{0.25}\text{O}_{3-\delta}$ [29]). Experimental conditions: AOII 35 mg L^{-1} , H_2O_2 22 mM , 1.0 g L^{-1} catalyst and unadjusted pH solution.

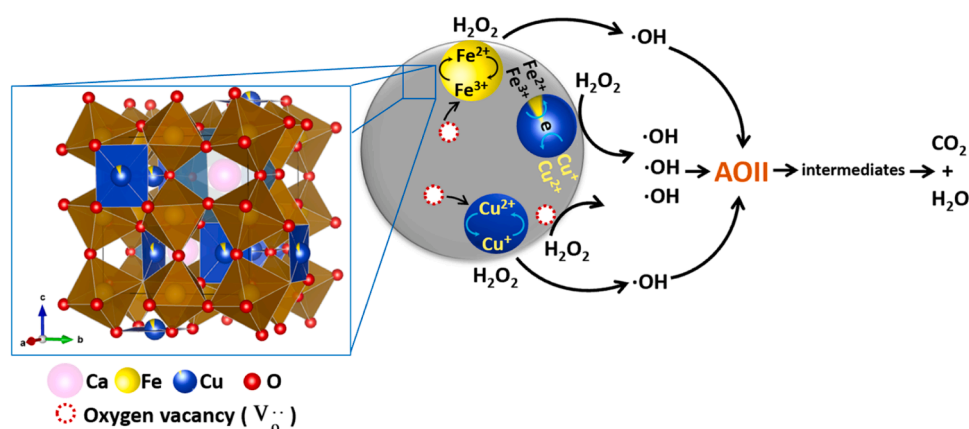


Fig. 10. Possible mechanism for AOII degradation by CaCuFeO_3 .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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