B-site Substitution Effects on The Catalytic Activity of Perovskites Compounds towards Oxidative Degradation of Orange II Solutions

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Abstract. Perovskite is known as potential decent ceramic metal oxides catalyst for wastewater treatment particularly in catalytic oxidation process. Perovskites can be uniquely and chemically tailored due to its simple structure which able to accommodate wide range of A and/or B-site cations. In this work, detailed investigations on the substitution effect of different B-site cations into the main structure of perovskite compounds towards catalytic oxidation of orange II solution were performed. Four (4) different types of B-site metal cations (Cu, Ni, Mo and Co) were substituted into perovskites structure via a combined EDTA-citric acid complexation method. The reactivity of resultant perovskites was found to be in sequence of Na₀.₂₇Ca₀.₄₈Cu₀.₂₅O₃ > Na₀.₂₅Ca₀.₄₈Ni₀.₂₇O₃ /g167 Na₀.₀₉Ca₀.₂₉Mo₀.₆₂O₃ > Na₀.₀₂Ca₀.₃₃Co₀.₃₉O₃ in the absence of stimulant or oxidant during 2 hours heterogeneous reaction. Interestingly, Na₀.₀₉Ca₀.₂₉Mo₀.₆₂O₃ perovskites catalyst exhibited superior catalytic activity by having complete Orange II removal (>99%) in the presence of oxidant (0.022M H₂O₂) within 15 min of reaction. The reactivity of B-site perovskites catalysts changed significantly in presence of oxidant during heterogeneous reaction that can be represented as Na₀.₀₉Ca₀.₂₉Mo₀.₆₂O₃ > Na₀.₂₇Ca₀.₄₈Cu₀.₂₅O₃ > Na₀.₀₂Ca₀.₃₃Co₀.₃₉O₃ > Na₀.₂₅Ca₀.₄₈Ni₀.₂₇O₃, respectively. Such findings confer tunable and unique catalytic properties of B-site perovskites catalysts in enhancing the oxidative degradation of recalcitrant dye contaminated wastewater effluents.

1. Introduction
Rapid widespread of urbanization as well as industrialization has led to susceptible water scarcity of nearly 80% global population due to water pollution [1] Dye contaminated wastewater effluents originated from various industries have been seen as one of main contributors that contributes persistence organic pollutants (dyes and various processing chemicals) into main water bodies [2]. For instance, dyes have been used extensively by various industries in leather tanning, food processing,
plastics, cosmetics as well as textile dyeing processes [3]. It is estimated that approximately 280 000 tons of dye contaminated wastewater have been discharged annually from those industries [4]. Such discharge of effluents are often toxic which can imposed on adverse impacts to aquatic ecosystem and human lifes [4-5].

Various physicochemical and biological treatment methods have been used to remove dyes from wastewater such as adsorption [6], coagulation-flocculation [7], chemical oxidation [8], electrochemical process [9], Fenton [10] and ozonation [11]. However, advanced oxidation process (AOPs) are considered as promising treatment to degrade dye and/ or recalcitrant organic pollutants in water. AOPs have been used extensively in oxidation process of huge range of organic contaminants in wastewater [9], [12-15]. AOPs implied in-situ generation of hydroxyl radicals (•OH) which can degrade recalcitrant organic pollutants effectively and non-selectively [12]. Some AOPs utilize perovskite compounds as heterogeneous catalyst in generating hydroxyl radicals (•OH) during catalysis.

Perovskites is known as ceramic-type materials with general formula of ABX3, where the A and B represent type of cations and X is an anion that bonds to both, respectively. Typically, the rare or alkali earth metals accommodate the A-site cation whilst transition metals accommodate the B-site cation. Meanwhile, oxygen and/or other ions such as halides, sulfides and nitrides [16-17] accommodate the X-site. Interestingly, several perovskites compounds have been used to initiate strong oxidative process while achieving modest mineralization capability in recent years [16-20]. Such enhancement of catalytic performance was attribute to the high generation of active radical species (•OH radicals) during catalysis. For instance, SrFeO3-δ was able to degrade 98% acid orange 8 within 10 min [21], Ca0.5Sr0.5NiO degraded 97% orange II within 5 min [22] and BaFeO3-x catalyst enable to degrade 80% methyl orange within 30 h [23]. Most of the past research works [21-23] were only focused on the influence of A-site cations rather than B-site cations; eventhough both sites serve importance role in modulating the overall catalytic performance of the perovskite compounds.

On contrary, detailed investigations on perovskites’ catalytic activity in presence of different types of B-site cation as an active phase during heterogeneous catalysis are yet to be addressed. Therefore, this work investigates on the substitution effect of different B-site cations (copper, nickel, molybdenum and cobalt) into the main structure of perovskite compounds in modulating catalytic activity of resultant AxByO3 perovskite catalyst towards oxidative degradation of orange II solution.

2. Experimental

2.1. Material
All chemicals are used as received such as ethylenediamine tetra-acetic acid disodium salt dehydrate solution (EDTA-2Na, ≥99%), ammonium hydroxide (NH4OH, 25%), calcium nitrate tetrahydrate (Ca(NO3)2.4H2O, ≥99%), citric acid monohydrate (C6H8O7.H2O, ≥99%), ammonium molybdate ((NH4)2MoO4, 99.98%), copper (II) nitrate trihydrate (Cu(NO3)2.2.5H2O, ≥99%), nickel (II) nitrate hexahydrate (Ni(NO3)2.6H2O, 99.99%), cobalt (II) chloride hexahydrate (CoCl2.6H2O, 98%), hydrogen peroxide (H2O2,30% wt/wt) and orange II sodium salt (C16H11N2NaO4S, ≥98%).

2.2. Synthesis of Perovskites Catalyst
A series of AxByO3 perovskite catalyst at different B-site cations’ substitution were synthesized via a combined EDTA-citric acid complexation method [4], [22] at fixed precursor molar concentration of 0.05 M. A set of molar ratio of total metal ions:ethylenediamine tetra-acetic acid disodium salt dehydrate (EDTA-2Na):citric acid:ammonium hydroxide was kept constantly at 1:1.1:2.10 [4], [22]. For instance, in the synthesis of Ca0.5Mo0.5O3 catalyst; 0.05 M of Ca(NO3)2.4H2O, 0.05 M (NH4)2MoO4 and 0.1 M citric acid solutions were initially mixed and stirred for 15 min. After that, a mixture containing 0.05 M NH4OH and 0.055 M EDTA-2Na solution was added into the former mixture and stirred for 15 minutes at room temperature until homogeneous mixtures were attained. The homogeneous mixture was then heated at 100°C while stirring to evaporate most water until a viscous
solution formed. Further evaporation of viscous solution was carried out in oven at 90°C for 24 hours. The resultant gel samples were then pre-sintered in a muffle furnace up to 450°C for 8 hours in atmospheric air at heating and cooling rates of 5°C min^-1. A second sintering process was applied up to 800°C for 4 hours using similar ramping rates. The resultant Ca_{x}Mo_{3}O_{9} perovskites were milled and stored prior to further use. Similar procedures were repeated for other B-site cations using copper, nickel and cobalt precursors for the synthesis of Ca_{x}Cu_{2}O_{5}, Ca_{x}Ni_{2}O_{3} and Ca_{x}Cu_{9}O_{3} perovskites catalysts, respectively.

2.3. Catalytic Performance and Physico-chemical Properties Characterization

The catalytic activity of perovskites catalysts at different B-site cation’s substitution were evaluated in oxidative degradation of orange II solution (35 mg/L) as the model pollutant. The reaction is carried out by dispersing 0.1 g catalyst in 100 mL orange II solution at room temperature without having any external reagents or energy input. The solution was continuously stirred under constant stirring at 200 rpm for 2 hours. At specific time intervals, 5mL aliquots were taken out and filtered through 0.2 μm syringe filter. The concentration of orange II aliquots were monitored by measuring the absorption intensity at maximum wavelength of orange II dye at 486nm using UV-Vis spectrophotometer (Perkin Elmer, Lambda 25). Analogous procedures of catalytic performance test were repeated by adding 22 mM oxidant (H_{2}O_{2}) whilst dispersing catalyst into the reaction solution. The decolorization of orange II was calculated by following equation (1):

\[
\text{Decolorization percentage (\%) = } \left( \frac{(C_0 - C_t)}{C_0} \right) \times 100
\]

where \(C_0\) is the initial concentration of orange II and \(C_t\) is the final concentration at specific reaction time.

The morphology and elemental composition of resultant A_{x}B_{y}O_{3} perovskite catalysts were which equipped with energy dispersive X-ray (EDX) detector. The zeta potential and average particle size of perovskite catalysts were measured using Zetasizer Nano (Malvern Instruments, Nano-ZS).

3. Results and Discussions

3.1. Catalytic Performance of A_{x}B_{y}O_{3} perovskite catalyst

Figure 1 shows degradation of orange II solutions using four different types of B-site perovskite catalysts. The catalytic performances were performed within 120 minutes of heterogeneous reaction without pH adjustment. The Ca_{x}Cu_{2}O_{5} catalyst exhibited the highest decolorization of 39% removal which subsequently followed by Ca_{x}Ni_{2}O_{3} (27%), Ca_{x}Mo_{3}O_{9} (27%) and Ca_{x}Co_{2}O_{4} (15%), respectively. Such results show that Ca_{x}Cu_{2}O_{5} is more reactive compared to other catalysts in the absence of oxidant (self catalysis). Similar findings were also reported by Chen et. al [4], whom observed CaCuO as the most reactive catalyst amongst calcium strontium copper perovskites which shown 86% orange II degradation within 120 min of reaction at initial dye concentration of 20 ppm.

Interestingly, Ca_{x}Mo_{3}O_{9} surpassed the overall catalytic performance of Ca_{x}Cu_{2}O_{5} in the presence of oxidant (H_{2}O_{2}). In fact, Ca_{x}Mo_{3}O_{9} exhibited complete orange II removal (\approx 99%) within 15 min of reaction which lead to enhancement of overall catalytic performance (\approx 100%) of five time higher than its’ self catalysis (27%). The overall catalytic activity of B-site perovskites catalysts changed significantly that can be represented as Ca_{x}Mo_{3}O_{9} > Ca_{x}Cu_{2}O_{5} > Ca_{x}Co_{2}O_{4} > Ca_{x}Ni_{2}O_{3}. Enhancement in decolorization of orange II were plausible to effective decomposition of H_{2}O_{2} in producing more reactive -OH radicals during catalysis. These findings are in tandem with Atalay et al. [16], which found that few substituted transition metals in perovskite compounds were able to activating peroxymonosulfate oxidant to form reactive radicals during oxidative reaction.
3.2. Physico-Chemical Properties Characterization

The surface morphologies of B-site perovskites catalysts were examined at different magnification as shown in figure 2. Back-scattering imaging were used to distinguish each elemental boundary presence within the structure of B-site perovskites catalysts. Such approach is crucial in understanding the actual composition as well as elemental distribution throughout the catalysts. Figure 2a,c,e,g represent the surface morphology at magnification of 6k, whereas fFigure 2,d,f,g illustrate magnified image of selected surface at 12k magnification.

Ca$_x$Cu$_y$O$_3$ (figure 1a,b) presents corrugated surface which consists of small grains that randomly distributed within the whole surfaces. The size of these small grains were found to be within 2-10μm. Similar observations were also observed in Ca$_x$Ni$_y$O$_3$ (figure 1c,d) catalysts as well. On contrary, relatively big clump of particles agglomeration was observed on the surface of Ca$_x$Mo$_y$O$_3$ (figure 1e,f) and Ca$_x$Co$_y$O$_3$ catalysts (figure 1g,h). Such differences in surface morphology can be plausibly explained due to heterogeneity formation of different surface energy between the calcium oxide and molybdenum/cobalt oxides phases during sintering process. Hence, such observations can be deduced that different type of transition metal cations’ substitution may lead to different surface morphology of resultant B-site perovskites catalysts.
Further EDX analysis were performed to analysis the actual elemental compositions of resultant B-site perovskite catalysts. Details compositions of B-site perovskite catalysts \( \text{Ca}_x\text{Cu}_y\text{O}_3 \), \( \text{Ca}_x\text{Ni}_y\text{O}_3 \), \( \text{Ca}_x\text{Mo}_y\text{O}_3 \) and \( \text{Ca}_x\text{Co}_y\text{O}_3 \) are summarized in table 1. Table 1 presents that the main element of Ca, Cu, Ni, Mo and Co present within the full spectrum, small grains and surface background, respectively. The overall actual composition of \( \text{Ca}_x\text{Cu}_y\text{O}_3 \), \( \text{Ca}_x\text{Ni}_y\text{O}_3 \), \( \text{Ca}_x\text{Mo}_y\text{O}_3 \) and \( \text{Ca}_x\text{Co}_y\text{O}_3 \) were represented by \( \text{Na}_{0.27}\text{Ca}_{0.48}\text{Cu}_{0.25}\text{O}_3 \), \( \text{Na}_{0.25}\text{Ca}_{0.48}\text{Ni}_{0.27}\text{O}_3 \), \( \text{Na}_{0.09}\text{Ca}_{0.29}\text{Mo}_{0.62}\text{O}_3 \) and \( \text{Na}_{0.02}\text{Ca}_{0.33}\text{Co}_{0.65}\text{O}_3 \) accordingly.

The small grains were found to be dominant in B-site cation for Cu (81 wt%), Ni (39 wt%), Mo (73 wt%) and Co (67 wt%), respectively. Meanwhile, the dominant elements on the surface background were found to be Ca, Na and Ni for \( \text{Na}_{0.27}\text{Ca}_{0.48}\text{Cu}_{0.25}\text{O}_3 \) and \( \text{Na}_{0.25}\text{Ca}_{0.48}\text{Ni}_{0.27}\text{O}_3 \) but not in the \( \text{Na}_{0.09}\text{Ca}_{0.29}\text{Mo}_{0.62}\text{O}_3 \) and \( \text{Na}_{0.02}\text{Ca}_{0.33}\text{Co}_{0.65}\text{O}_3 \) catalysts. Cu and Ni are prone to be phase separated by its dominancy of element phase between the grains and its background surfaces. Interestingly, both \( \text{Na}_{0.09}\text{Ca}_{0.29}\text{Mo}_{0.62}\text{O}_3 \) and \( \text{Na}_{0.02}\text{Ca}_{0.33}\text{Co}_{0.65}\text{O}_3 \) perovskites catalysts shown relatively uniform distribution of Mo and Co within the structure of perovskites compounds due to negligible change of elemental composition between the small grains and surface background analysis. Uniform distribution of B-site cations within the surface of perovskites provides good pollutants’ accessibility towards catalysts’ active sites during heterogeneous catalysis.

Further investigations on average particle size as well as its dispersion stability of resultant B-site perovskites catalysts in aqueous solution were performed using zeta potential and zeta sizer analysis. Bimodal particle size’s pattern of was observed for all B-site perovskites catalyst at specific average diameter. The average diameter for small particle of \( \text{Na}_{0.27}\text{Ca}_{0.48}\text{Cu}_{0.25}\text{O}_3 \), \( \text{Na}_{0.25}\text{Ca}_{0.48}\text{Ni}_{0.27}\text{O}_3 \), \( \text{Na}_{0.09}\text{Ca}_{0.29}\text{Mo}_{0.62}\text{O}_3 \) and \( \text{Na}_{0.02}\text{Ca}_{0.33}\text{Co}_{0.65}\text{O}_3 \) were 0.69 μm, 0.42μm, 1.65μm and 1.64 μm, respectively. Meanwhile average for bigger particle size distribution for were 4.99 μm, 4.98 μm, 3.43 μm and 3.30 μm. Zeta potential of \( \text{Na}_{0.27}\text{Ca}_{0.48}\text{Cu}_{0.25}\text{O}_3 \), \( \text{Na}_{0.25}\text{Ca}_{0.48}\text{Ni}_{0.27}\text{O}_3 \), \( \text{Na}_{0.09}\text{Ca}_{0.29}\text{Mo}_{0.62}\text{O}_3 \) and \( \text{Na}_{0.02}\text{Ca}_{0.33}\text{Co}_{0.65}\text{O}_3 \) were at -23.53mV, -35 mV, -19.80 mV and -22.39 mV. Intriguingly, despite its poor dispersion [24] in an aqueous solution, \( \text{Na}_{0.09}\text{Ca}_{0.29}\text{Mo}_{0.62}\text{O}_3 \) catalysts had shown decent catalytic activity in oxidative degradation of orange II solution as been discussed previously.
Table 1. Chemical composition of synthesized B-site perovskites catalysts

| Types of B-site perovskites | Elemental composition (FESEM-EDX analysis) |
|-----------------------------|------------------------------------------|
| CaxCuyO3                    | Na0.27Ca0.48Cu0.25O3                      |
| CaxNiO3                     | Na0.25Ca0.48Ni0.27O3                      |
| CaxMoO3                     | Na0.09Ca0.29Mo0.62O3                      |
| CaxCoO3                     | Na0.02Ca0.33Co0.65O3                      |

4. Conclusions
Four types of B-site perovskites catalysts (Na0.27Ca0.48Cu0.25O3, Na0.25Ca0.48Ni0.27O3, Na0.09Ca0.29Mo0.62O3 and Na0.02Ca0.33Co0.65O3) have been synthesized via a combined EDTA-citric acid complexation method. The catalytic performance of resultant B-site perovskite catalyst were evaluated in oxidative degradation orange II solution in the absence as well as presence of oxidant. Na0.09Ca0.29Mo0.62O3 displayed almost complete orange II removal (>99%) within 15 min of reaction which subsequently conferred towards overall catalytic performance enhancement of five time higher than its pristine self catalysis. The overall catalytic activity of B-sites perovskite can be represented in the sequence of Na0.09Ca0.29Mo0.62O3 > Na0.27Ca0.48Cu0.25O3 > Na0.02Ca0.33Co0.65O3 > Na0.25Ca0.48Ni0.27O3 respectively. Therefore, it can be concluded that different types of B-site cations’ substitution into the main structure of perovskite compounds led to different catalytic activity because of its resultant unique physico-chemical properties. These findings provide some beneficial insights in preliminary understanding of B-site perovskite catalysts performances as well as its properties towards oxidative degradation of dye contaminated wastewater.

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