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<td>Chen, Sheng-Yu; University of Connecticut, Department of Chemistry Tang, Wenxiang; Institute of Materials Science, University of Connecticut He, Junkai; University of Connecticut, Institute of Materials Science Miao, Ran; University of Connecticut, Department of Chemistry Lin, Hui-Jan; Institute of Materials Science, Department of Materials Science and Engineering Song, Wenqiao; University of Connecticut, Department of Chemistry Wang, Sibo; University of Connecticut, Institute of Materials Science Gao, Pu-Xian; University of Connecticut, Suib, Steven; University of Connecticut, U-60, Department of Chemistry</td>
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</table>
Copper Manganese Oxide Enhanced Nanoarray-Based Monolithic Catalysts for Hydrocarbon Oxidation

Sheng-Yu Chen, a Wenxiang Tang, b Junkai He, b Ran Miao, a Hui-Jan Lin, a Wenqiao Song, a Sibo Wang, b Pu-Xian Gao, a,b and Steven L. Suib a,b

Copper manganese oxide (CuMn₂O₄) was introduced into the nanoarray-based monolithic catalysts system for advanced exhaust after-treatment. Through scalable and cost-effective hydrothermal reactions, nanosheet layers of copper manganese oxide were uniformly coated onto the manganese oxide nanoarrays (HM-PCR), which were grown on the cordierite honeycomb monoliths. The core nanoarray support, HM-PCR, a well-defined array architecture for active material deposition, contributed to an increase of open surface area and thus enhanced catalytic oxidation performance. The CuMn₂O₄ coated nanoarray-based catalyst, NA-CuMn₂O₄, shows efficient 90% propane (C₃H₈) conversion at around 400 °C, which is 50 °C and 75 °C lower than CuMn₂O₄ wash-coated catalyst (WC-CuMn₂O₄) and Pd loaded catalyst (WC-Pd), respectively. Compared to monolithic catalysts with a traditional alumina support, the benefit of nanoarray morphology was demonstrated by correlating the variation of surface area to the reactivity. The incorporation of cobalt ions was found to increase the specific surface area and thus enhance C₃H₈ conversion of CuMn₂O₄. The CuMn₂O₄/MnO₂ nanoarray-based monoliths are promising types of emission control devices.

1. Introduction

Air pollution is a long-term issue that has constantly deteriorated the global atmospheric quality and human health in the past.¹ The rapidly decayed air quality urges ever-tightened regulations by global legislatures for emissions control.² This also challenges the automotive industry to develop more efficient catalysts for after-treatment of various emissions, such as carbon monoxide (CO), nitrogen oxides (NOₓ), sulfur oxides (SOₓ), and hydrocarbons (HCs).³ Meanwhile, state-of-the-art platinum-group metal (PGM)-based (e.g. Pd, Pt, Rh) catalytic converters face challenges for a balance between catalytic efficiency and material cost.⁴-⁷ Introducing transition metal oxides (e.g. Co₃O₄, MnO₂, CuO, and CeO₂) is a cost-effective strategy to improve catalytic converters with enhanced surface area, porosity, reactivity, and thermal stability.⁸-¹¹ Perovskite materials also showed some outstanding catalytic performance with positive synergy with noble metals.¹²-¹⁴

Recently, nanoarray-based monolithic catalysts have attracted great interest in gas phase catalysis and detection.¹⁵-¹⁹ A new type of monolithic catalysts with hierarchical nanoarray structures was invented by Gao and co-workers. Different from conventional wash-coated catalytic converters, transition metal oxide nanoarrays (e.g. ZnO, Co₃O₄, and TiO₂) were in situ grown on bare ceramic cordierite (2MgO-2Al₂O₃-5SiO₂) honeycomb monoliths.²⁰-²⁴ Compared to the wash-coating method, this new configuration exhibited unique characteristics as a result of the nanoarray architectures. Firstly, the usually vertically-aligned nanoarrays on honeycomb channel surfaces provide open surfaces for more efficient molecular diffusion and improve heterogeneous interactions.²⁵ Secondly, micron-thick nanoarrays replace tens to hundred-micron thick porous alumina powder layer as supports, significantly reducing material usage and weight of monolithic converters.²⁰ Thirdly, uniform nanoarray coatings with thin thickness (1-10 µm) inside honeycomb channels further reduced the pressure-drop (Fig. S1).²⁵ Finally, the well-bound nanostructures with well-defined surfaces on the substrate surface not only improve the catalytic performance, but also prevent or mitigate the agglomeration of nanoparticles.²⁶ These beneficial characteristics have enabled these transition metal oxide nanoarray integrated monolithic catalysts as a promising class of new catalytic converters superior to the currently wash-coated commercial ones.

Previously, manganese oxide (MnO₂) based nanoarrays have been fabricated on honeycomb monoliths by a hydrothermal synthesis method.²⁷ Compared to other transition metal oxides such as ZnO and Co₃O₄, MnO₂ nanoarray-based monolithic catalysts feature various merits such as high robustness, low cost, good acidic tolerance, low toxicity, and no need of pre-seeding, demonstrating their good
potential for heterogeneous catalysis. However, the catalytic activity of MnO$_2$ is usually lowered when well-crystallized nanoarrays are formed. Therefore, combing additional highly active material to enhance the activity of MnO$_2$ nanoarrays is a major challenge.

In industry, copper-manganese mixed oxides have been widely projected as promising heterogeneous catalysts with remarkable reactivity for CO, NO$_x$, and hydrocarbons (HCs) at low temperature and cheap cost for several decades, but the detailed mechanism of catalysis still needs more future investigations. The reactivity of copper manganese oxide varies with several factors such as elemental composition, crystal structure, calcination temperature, surface area, and aging. Among the various copper manganese oxides, amorphous copper-manganese oxide is commonly considered as the most active one. Veprek et al. showed Cu$^{2+}$ and Mn$^{4+}$ as dominant active sites in both active and plasma reoxidized catalysts, which might contribute to the catalytic activity. During the catalytic process, thermal effects usually cause conversion of amorphous copper-manganese oxides into Hopcalite (CuMn$_4$O$_8$), a spinel structure with a general formula of AB$_2$O$_4$, with partial activity loss. According to the resonance system proposed by Fortunato et al. and Cocke et al., Cu$^{2+}$ + Mn$^{4+}$ $\leftrightarrow$ Cu$^{4+}$ + Mn$^{2+}$, the co-existence of Cu and Mn species retain some activity of hopcalite catalysts. Specifically, Cu$^{2+}$/Mn$^{4+}$ and Cu$^{4+}$/Mn$^{2+}$ promote the adsorption of CO and O$_2$, respectively. In addition, partial replacement of the tetrahedral sites in spinel AB$_2$O$_4$ by other transition metals (e.g., Co, Ni, Fe, and Au) might promote the catalytic performance by enhancing surface lattice oxygen mobility.

In this study, copper manganese oxide (CuMn$_2$O$_4$) and nanoarray architectures were combined to form CuMn$_n$O$_x$/nanoarray-based monolithic catalysts for propane (C$_3$H$_8$) oxidation. It is noted that, although co-alloyed MnO-based nanoparticles have shown a promising 90% conversion for total propane oxidation at ~200 - 300 °C while adopting the high pressure-drop fixed bed reactor configuration, the respective nanoarray-based monolithic catalysts display so far a 90% conversion temperature at a higher range of 300 - 400 °C. Here we utilize the previously reported manganese oxide nanoarray, HM-PCR, as the core, and precipitate on top the CuMn$_2$O$_4$ and Co-doped CuMn$_n$O$_x$ nanocoating by mild hydrothermal reactions, denoted as NA-CuMn$_2$O$_4$, NA-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$, and NA-Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ based on the composition revealed by inductively coupled plasma-mass spectrometry (ICP-MS). All three catalysts possess CuMn$_2$O$_4$ based compositions with low crystallinity and high conversion of hydrocarbon oxidations. Incorporation of trace cobalt ions led to partial Cu replacement by Co, which was found to enhance reactivity at low temperature, with increased surface area but compromised thermal stability. To understand the catalytic contribution from nanoarray architectures, monolithic catalysts loaded with similar amounts of CuMn$_2$O$_4$ and Co$_x$Cu$_{1-x}$Mn$_2$O$_4$ materials were prepared by a wash-coating method using alumina powder (α-Al$_2$O$_3$) as the support. An additional Pd-loaded catalyst was used as a reference to compare the high reactivity of our CuMn$_2$O$_4$ catalysts. Further studies of nitrogen isothermal adsorption, X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H$_2$-TPR), and oxygen temperature-programmed desorption (O$_2$-TPD) show how the increased surface area and lattice oxygen mobility correlate closely with catalytic performance of Co-doped CuMn$_2$O$_4$ catalysts.

2. Experimental section and synthesis

2.1 Synthesis of Catalysts

All chemicals in this study were purchased from chemical vendors without further purification. The cordierite honeycomb monolith substrates were obtained from Corning Corp. The cordierite substrate was sonicated in ethanol and water for 30 min and dried at 90 °C for 12 h before reaction.

The synthesis of core MnO$_2$ nanoarray, HM-PCR, followed previous work. 15.2 g manganese sulfate monohydrate (MnSO$_4$·H$_2$O, 90 mmol) and 19.4 g potassium chlorate (KClO$_3$, 158 mmol) were dissolved in 300 mL Deionized (DI) water with 5 mL sulfuric acid. Then the solution was transferred into a 400 mL capped glass bottle with the cordierite substrate located on the bottom and heated at 90 °C in an oil bath with a mechanical stirrer from the top for 12 h (Fig. S2). The reactor was cooled down at room temperature for 2 h after the reaction was complete. Rinsing with water and drying in air were applied alternatively to remove the residual reagent inside the monolith channels. The monolithic catalysts were sonicated in water for 2 h to remove loose manganese oxide powder, then dried in a vacuum oven at 60 °C for overnight.

A layer of copper manganese oxide (CuMn$_2$O$_4$) was applied onto the core nanoarrays, HM-PCR, by a secondary hydrothermal reaction. 3.79 g potassium permanganate (Kmno$_4$, 24 mmol) and 2.89 g copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, 12 mmol) were dissolved in 60 mL DI water. The mixed solution was transferred to a 150 mL glass bottle within a nanoarray (HM-PCR) coated honeycomb monolithic substrates and heated at 90 °C in a water bath for 16 h. After the reaction, similar workup as the synthesis of HM-PCR was applied following the order, rinsing, sonication, and vacuum drying. For Co-doped catalysts, NA-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ and NA-Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ 1% and 2% mole ratios with respect to the total reagent of cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) were added into the solution, respectively. All CuMn$_2$O$_4$ series of monolithic catalysts were calcined at 300 °C for 2 h under ambient condition.

CuMn$_2$O$_4$ and Co-doped CuMn$_2$O$_4$ powder collected from each hydrothermal reaction were loaded on cordierite substrates using wash-coating methods for comparison with nanoarray-based monolithic catalysts. Mixtures of 0.2 g CuMn$_2$O$_4$, 0.8 g α-Al$_2$O$_3$, and 5 mL DI water were stirred for 2 h to form a slurry with 20% active materials. For each wash-coating cycle, the cordierite substrate was dipped into the slurry for 30 min and blown by nitrogen flow to remove extra slurry. The wet cordierite substrate was dried at 150 °C for 1 h in an oven. The same procedure was repeated for 4 to 5 times.
to obtain similar loading amounts of CuMn₂O₄ materials to nanoarray-based catalysts. Each wash-coated substrate was also calcined at 300 °C for 2 h before catalytic tests.

Following the same procedure given above, a commercial solution of 1% Pd/Al₂O₃ was used to prepare Pd wash-coated monolithic catalysts. The calculated Pd loading amount on cordierite substrates was 1 g/L. The Pd loaded monolithic catalysts were calcined at 500 °C for 2 h before the catalytic tests.

2.2 Materials Characterization

The powder X-ray diffraction (PXRD) analyses were conducted using a Rigaku Ultimate IV diffractometer (Cu Kα radiation, λ = 1.5406 Å) with an operating beam voltage of 40.0 KV and a beam current of 44 mA. The diffraction patterns were collected between a 2 θ range of 5 - 75°. The surface morphologies of all monolithic and powder samples were determined with a field emission scanning electron microscope (FE-SEM) FEI Nova NanoSEM 450 at an accelerating voltage of 2 kV. The surface elemental analysis of catalysts was conducted with X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM spectrometer with multi-probes and Al-K α radiation source (λ = 1486.6 eV). For correction of surface charging, the binding energies in XPS spectra were calibrated using the signal from adventitious carbon (C 1s, 284.6 eV). The elemental analysis of transition metals in catalysts was tested by an Agilent 7900 ICP-MS.

The surface areas of monolithic and powder-form samples were measured with nitrogen adsorption-desorption experiments using a Quantachrome Autosorb-1-1C automated adsorption system and calculated with the Brunauer–Emmett–Teller (BET) method. Both nanoarray-based and wash-coated monolithic catalysts were degassed at 150 °C for 6 h to remove moisture and other physically adsorbed species. The experiments of N₂ isothermal adsorption were measured at relative pressures (P/P₀) from 0.005 to 0.995 then followed by desorption from 0.995 to 0.12.

Both hydrogen temperature programmed reduction (H₂-TPR) and oxygen temperature programmed desorption (O₂-TPD) tests were performed using a Micromeritics ChemiSorb 2720 flow gas analyzer coupled with a thermal conductivity detector (TCD). Each piece of monolithic samples with 7 × 7 channels in cross section (7 mm × 7 mm × 10 mm, W x H x L) was packed in a quartz tube and located in the attached programmable furnace. All monolithic samples were pretreated with a nitrogen flow (N₂, 20 SCCM) at 200 °C for 1 h to remove surface adsorbed moisture and impurities. 1% hydrogen (H₂) balanced by nitrogen (N₂) with 50 SCCM flow rate was used in the H₂-TPR experiments. For O₂-TPD experiments, pure oxygen was purged through samples with a 25 SCCM flow rate at 250 °C for 1 h to stabilize lattice oxygen populations of active materials. All temperature-programmed measurements were performed from room temperature to 600 °C with a ramping rate of 10°C/min.

The catalytic performances of all copper manganese oxide coated monolithic catalysts were evaluated by carbon monoxide (CO) and propane (C₃H₈) oxidations using a BenchCAT reactor (Altamira Instruments). A Dycor Dymaxion
mass spectrometer and an Agilent MicroGC were used for the analysis and quantification of gas species. For each catalytic test, one piece of the monolithic catalyst with 5 × 5 channels in cross section (5 mm × 5 mm × 10 mm, W × H × L) was packed in quartz tubing. The feed gas was 0.3% \( \text{C}_2\text{H}_6 \), 10% \( \text{O}_2 \) and balanced by \( \text{N}_2 \) with a 100 SCCM flow rate and 24,000 h\(^{-1}\) space velocity. A pretreatment under nitrogen was applied at 200 °C for 1 h before the catalytic tests to remove surface adsorbed moisture and impurities from the active materials.

3. Results

3.1 Structural and morphology, and surface area characterization

Fig. 1 shows the SEM images of core manganese oxide nanoarrays (HM-PCR) and copper manganese oxide coated nanoarrays fabricated on the cordierite honeycomb monoliths. As shown in the first column [(a), (e), and (i)], the HM-PCR nanoarrays have average lengths of ~ 5 µm and small diameters of ~ 50 nm. Through hydrothermal reactions, transition metal oxide layers of CuMn\(_2\)O\(_4\) and Co-doped CuMn\(_2\)O\(_4\) \((\text{Co}_{0.36}\text{Cu}_{0.64}\text{Mn}_2\text{O}_4\) and \(\text{Co}_{0.53}\text{Cu}_{0.47}\text{Mn}_2\text{O}_4\)) were coated uniformly on the HM-PCR nanoarrays while maintaining the array architectures, as revealed in Figs. 1(b)-(d) and Figs. 1(f)-(h). The cross-section SEM images shown in Figs. 1(j)-(l) reveal that the homogeneous CuMn\(_2\)O\(_4\) coatings occur along each nanorod of HM-PCR nanoarrays from top to bottom. Figs. 1(m) and 1(n) present that the CuMn\(_2\)O\(_4\) based nanoarrays were smoothly fabricated on the cordierite substrate even inside the channels of honeycomb monoliths, especially no coating aggregation around corner areas. The thickness of all coating layers is controllable by adjusting reaction conditions of hydrothermal synthesis, i.e. temperature, time, concentration, and Co amount. In general, the average thickness of CuMn\(_2\)O\(_4\) coating can reach 100 nm with 16 h hydrothermal reaction, but only 4 h with addition of 1% Co and 1 h with 2% Co, respectively. Both core nanoarrays and CuMn\(_2\)O\(_4\) coatings were stable on cordierite substrates without obvious detachment after 2 h of sonication in water.

X-ray diffraction (XRD) was conducted on the powders collected from each hydrothermal reaction to identify their crystal structures [Fig. 2(a)], because the intensities of the diffraction patterns from the cordierite substrate were much stronger than the diffraction patterns from the manganese oxide arrays, HM-PCR, and coating material, CuMn\(_2\)O\(_4\). XRD patterns Fig. 2(a) revealed that the core nanoarrays grown on the cordierite substrates were indexed to the cryptomelane manganese oxide \((K_2\text{Mn}_2\text{O}_4\) tetragonal, \(a = b = 9.82 \) Å and \(c = 2.85 \) Å, JCPDS: 29-1020). In Fig. 2(a), The XRD patterns of coated copper manganese oxide materials displayed very low crystallinity and it was hard to identify the crystal structure, even after calcination at 400 °C.\(^{39, 13}\) The XRD patterns of each catalyst calcined at temperatures from 300 to 500 °C are shown in Figs. 2(b)-(d). Fig. 2(b) shows that the pure CuMn\(_2\)O\(_4\) coating layer was converted to the hopcalite structure (JCPDS: 74-2422) after calcination at 500 °C.\(^{43}\) In Figs. 2(c) and 2(d), diffraction peaks around 13° and 29° can be observed and indexed to the (110) and (310) planes of \(\alpha\)-Mn\(_2\)O\(_4\) (JCPDS: 44-0141), respectively, which indicates an additional phase segregation happened in the two Co-doped catalysts after high temperature calcination.

Table 1. Elemental components of CuMn2O4 based coating layers (%)

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<th>Element</th>
<th>Mn</th>
<th>Cu</th>
<th>Co</th>
<th>Total</th>
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<tr>
<td>NA-CuMn(_2)O(_4)</td>
<td>64.9</td>
<td>35.1</td>
<td>-</td>
<td>100.0</td>
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<tr>
<td>NA-Co(<em>0.36)Cu(</em>{0.64})Mn(_2)O(_4)</td>
<td>65.7</td>
<td>22.1</td>
<td>12.3</td>
<td>100.0</td>
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<tr>
<td>NA-Co(<em>0.53)Cu(</em>{0.47})Mn(_2)O(_4)</td>
<td>64.0</td>
<td>16.9</td>
<td>19.2</td>
<td>100.0</td>
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</tbody>
</table>

The - entries signify not applicable or measured.
The transmission electron microscopy (TEM) images in Figs. 3(d) - 3(f) reveal the material morphologies affected by the doping of Co ions into the CuMnO\textsubscript{4} coatings. Obviously, the average size of the CuMnO\textsubscript{4} nanosheets increases with the higher concentration of Co (Fig. S3). The inset of selected area diffraction patterns (SAED) showing dim amorphous ring patterns confirmed the low crystallinity of all three CuMnO\textsubscript{4} coatings, which correlate with the low intensities of XRD patterns in Fig. 2(a). Elemental mapping conducted by energy-dispersive X-ray spectroscopy (EDS) shows well-dispersed Mn, Cu, and Co on the three CuMnO\textsubscript{4} and Co-doped CuMnO\textsubscript{4} coatings (Fig. S4).

ICP-MS tests were conducted to analyze the elemental ratios between Cu and Mn of copper manganese oxides, which are listed in Table 1. The Cu to Mn ratio of undoped copper manganese oxide (NA-CuMnO\textsubscript{4}) was closed to 1:2, which identifies its chemical formula as CuMn\textsubscript{2}O\textsubscript{4}. For the two Co-doped CuMnO\textsubscript{4} materials, the percentage of Cu decreased dramatically with increasing Co ion concentration, but with slight Mn change. The detected Co ion concentration in NA-Co\textsubscript{0.36}Cu\textsubscript{0.64}Mn\textsubscript{2}O\textsubscript{4} and NA-Co\textsubscript{0.53}Cu\textsubscript{0.47}Mn\textsubscript{2}O\textsubscript{4} is almost ten times the designed doping ratios, showing that the Co-O-Mn was preferred to be formed during the hydrothermal reaction rather than Cu-O-Mn. These observations are in consistence with earlier reports that Co\textsuperscript{3+} would replace Cu\textsuperscript{2+} in tetrahedral sites and Co\textsuperscript{4+} substituting Mn\textsuperscript{3+} in octahedral sites of the CuMnO\textsubscript{4} lattice.\textsuperscript{24}

Table 2 summarizes the weight loading percentages and surface areas (SA) of both nanoarray-based and wash-coated monolithic catalysts. The nanoarray-based monolithic catalysts have relatively higher surface areas (35-43 m\textsuperscript{2}/g) than the wash-coated monolithic catalysts (12-17 m\textsuperscript{2}/g). Overall, all CuMnO\textsubscript{4} based monolithic catalysts show a trend of increasing surface area with increasing Co doping. Furthermore, both nanoarray-based and wash-coated monolithic catalysts have partial surface area contributed by their supporting materials, MnO\textsubscript{2} nanoarrays (HM-PCR) core, and α-Al\textsubscript{2}O\textsubscript{3}, respectively. The main substrate, cordierite honeycomb monoliths, is partially etched by acid during the hydrothermal synthesis of HM-PCR fabrication.\textsuperscript{27} Therefore, the surface areas of the nanoarray-based and wash-coated monolithic catalysts were subtracted from the surface area of core supports and uncoated substrates (cordierite) using Equations 1 and 2 correspondingly, to obtain the recalculated surface area of CuMnO\textsubscript{4} coatings and powders.

\[
S_{\text{CMO}} = \frac{S_{\text{M}} \times W_{\text{M}} - S_{\text{BC}} \times W_{\text{BC}} - S_{\text{PCR}} \times W_{\text{PCR}}}{W_{\text{CMO}}} \quad (1)
\]

\[
S_{\text{WC}} = \frac{S_{\text{M}} \times W_{\text{M}} - S_{\text{BC}} \times W_{\text{BC}} - S_{\text{AID}} \times W_{\text{AID}}}{W_{\text{WC}}} \quad (2)
\]

In Equations 1 and 2, \(S_{\text{CMO}}\) and \(W_{\text{CMO}}\) are the surface areas and weights of CuMnO\textsubscript{4} material coatings on the HM-PCR core nanoarrays, respectively; \(S_{\text{WC}}\) and \(W_{\text{WC}}\) are used for the wash-coated monolithic catalysts; \(S_{\text{M}}\) and \(W_{\text{M}}\) are used for the whole monolithic catalysts; \(S_{\text{BC}}\) and \(W_{\text{BC}}\) refer to the uncoated cordierite substrate; \(S_{\text{PCR}}\) and \(W_{\text{PCR}}\) refer to the core nanoarrays, HM-PCR; \(S_{\text{AID}}\) and \(W_{\text{AID}}\) refer to the α-Al\textsubscript{2}O\textsubscript{3} support powder.

After subtraction of core supports and cordierite substrates, the recalculated surface area of the CuMnO\textsubscript{4} coatings showed the same trend as monolithic catalysts, NA-Co\textsubscript{0.36}Cu\textsubscript{0.64}Mn\textsubscript{2}O\textsubscript{4} > NA-Co\textsubscript{0.53}Cu\textsubscript{0.47}Mn\textsubscript{2}O\textsubscript{4} > NA-CuMnO\textsubscript{4}, but the surface areas of the CuMnO\textsubscript{4} coating on nanoarray-based monolithic catalysts are much higher than the CuMnO\textsubscript{4} powders used for the wash-coated monolithic catalysts, i.e. NA-Co\textsubscript{0.36}Cu\textsubscript{0.64}Mn\textsubscript{2}O\textsubscript{4} (218 m\textsuperscript{2}/g) > WC-Co\textsubscript{0.53}Cu\textsubscript{0.47}Mn\textsubscript{2}O\textsubscript{4} (113 m\textsuperscript{2}/g). Correlating the surface areas to their morphologies in Fig. 3 reveals that the CuMnO\textsubscript{4} coatings on nanoarray architectures can maintain high surface area [Figs. 3(d)-(f)] and avoid/mitigate aggregation.

**Table 2.** Average Weight (W, g/L), loading percentages (%) of active materials, and Brunauer–Emmett–Teller (BET) surface areas (SA, m\textsuperscript{2}/g)

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<thead>
<tr>
<th>Sample ID</th>
<th>Support type</th>
<th>Average W of monolith catalysts (g/L)</th>
<th>W% of materials loading on monolithic substrates (%)</th>
<th>SA of monolith catalysts (m\textsuperscript{2}/g)</th>
<th>SA of MO removed substrates (m\textsuperscript{2}/g)</th>
<th>Calculated SA of active materials (m\textsuperscript{2}/g)</th>
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<td>Cordierite substrate\textsuperscript{a}</td>
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<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
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<tr>
<td>HM-PCR core</td>
<td>NA-CuMnO\textsubscript{4}</td>
<td>492</td>
<td>-</td>
<td>15</td>
<td>36</td>
<td>10</td>
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<tr>
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<td>NA-PCR</td>
<td>596</td>
<td>12</td>
<td>15</td>
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<td>63</td>
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<tr>
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<td>NA-PCR</td>
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<td>9</td>
<td>13</td>
<td>32</td>
<td>126</td>
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<tr>
<td>NA-Co\textsubscript{0.53}Cu\textsubscript{0.47}Mn\textsubscript{2}O\textsubscript{4}</td>
<td>NA-PCR</td>
<td>564</td>
<td>9</td>
<td>9</td>
<td>43</td>
<td>27</td>
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<tr>
<td>α-Al\textsubscript{2}O\textsubscript{3} powder\textsuperscript{b}</td>
<td>α-Al\textsubscript{2}O\textsubscript{3}</td>
<td>808</td>
<td>8</td>
<td>31</td>
<td>12</td>
<td>46</td>
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<td>WC-CuMnO\textsubscript{4}</td>
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<td>852</td>
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<td>WC-Co\textsubscript{0.53}Cu\textsubscript{0.47}Mn\textsubscript{2}O\textsubscript{4}</td>
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<td>806</td>
<td>8</td>
<td>31</td>
<td>17</td>
<td>113</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All MnO\textsubscript{2} and CuMnO\textsubscript{4} materials were removed by aqueous oxalic acid solution.

\textsuperscript{b} The - entries signify not applicable or measured.

\textsuperscript{c} Commercial products.
3.2 Catalytic propane oxidation behavior

The catalytic performance of the CuMn$_2$O$_4$ coated nano-array based and wash-coated monolithic catalysts was studied using oxidation of propane (C$_3$H$_8$) as shown in Fig. 4(a) in comparison with a Pd/α-Al$_2$O$_3$ wash-coated monolithic catalyst. In general, catalytic performance varied with the feed gas rate. Fig. S5 shows both the light-off temperature (T$_{90}$) and the 90% conversion temperature (T$_{90}$) of NA-CuMn$_2$O$_4$ are directly proportional to the feed gas rate. Then, we simply used 100 SCCM gas rate and space velocity of 24,000 h$^{-1}$ for each C$_3$H$_8$ oxidation test. Overall, the nanoarray-based monolithic catalysts showed better catalytic performance than both Pd and wash-coated CuMn$_2$O$_4$ monolithic catalysts. All the three nanoarray-based monolithic catalysts, NA-CuMn$_2$O$_4$, NA-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$, and NA-Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ possessed good reactivity with light-off temperature (T$_{90}$) around 300°C, 25°C lower than the wash-coated catalysts, WC-Cu$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ (325°C) and 50°C lower than WC-CuMn$_2$O$_4$ and the Pd loaded catalyst, WC-Pd (350°C). Among the three nanoarray-based monolithic catalysts, the NA-CuMn$_2$O$_4$ presented the higher reactivity to C$_3$H$_8$ oxidation and T$_{90}$ at 400°C, which was 50°C lower than the Co-doped catalysts. The NA-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ and NA-Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ showed better performance than the NA-CuMn$_2$O$_4$ below 350°C.

For the series of wash-coated monolithic catalysts, the CuMn$_2$O$_4$ powders loaded catalyst also revealed higher activity than the Pd loaded catalyst. WC-CuMn$_2$O$_4$ has similar T$_{90}$ (360°C) but lower T$_{90}$ (450°C) as compared to WC-Pd (T$_{90}$ ~ 360°C, T$_{90}$ ~ 500°C). Similar to the nano-array based catalysts, Co doping also increases the reactivity of wash-coated CuMn$_2$O$_4$ catalysts in the lower temperature region and reach 50% conversion at 325°C. Comprehensively, the nanoarray-based catalysts have better catalytic performance and lower T$_{90}$ at around 400°C than the wash-coated catalysts, WC-CuMn$_2$O$_4$ (450°C), WC-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ (475°C), and WC-Pd (475°C).

Due to different precipitation rates and the loading ratio of CuMn$_2$O$_4$ from hydrothermal synthesis and wash-coating process, the comparison of reactivity among monolithic catalysts was normalized by loading weight as shown in Fig. 4(b). After normalization using the exact coating weight, the wash-coated Pd catalyst, WC-Pd, exhibits better activity than all CuMn$_2$O$_4$-coated monolithic catalysts. For the nanoarray-based catalysts, the order of normalized activity is NA-Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ > NA-Cu$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ > NA-CuMn$_2$O$_4$. Each CuMn$_2$O$_4$ coated nanoarray-based catalyst still possessed higher activity than their wash-coated counterparts, which proved that the nanoarray structure benefit to the catalytic performance of C$_3$H$_8$ oxidations.

For further comparison among the CuMn$_2$O$_4$ and Co-doped CuMn$_2$O$_4$ materials, their activities were normalized simultaneously with both surface area and active material loading weight as shown in Fig. 4(c). A reversed order of the normalized activities, NA-CuMn$_2$O$_4$ > NA-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ > NA-Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ indicates the significance of surface area contributing to the oxidation reactivity. The slight Co doping efficiently increases the surface area of CuMn$_2$O$_4$ materials and promotes their catalytic performance in this study.

Fig. 4(d) presents the calculated activation energies of the three nanoarray-based monolithic catalysts in the Arrhenius plot with the order, NA-Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ (62.1 KJ/mol) < NA-
CoO.53CuO.47Mn2O4 (87.1 KJ/mol) < NA-CuMn2O4 (98.2 KJ/mol). CuMn2O4 possesses lower activation energies with the incorporation of cobalt ions. The 1% Co-doped catalyst shows the lowest activation energy among all catalysts, which agreed with its lowest light-off temperature (~300°C) as shown in Fig. 4(a).

3.3 Temperature programmed reduction and desorption characteristics

Hydrogen temperature programmed reduction (H2-TPR) was conducted to study the effect of cobalt ion doping on the reducibility of CuMn2O4 based catalysts. In Fig. 5(a), the H2-TPR profile of NA-CuMn2O4 shows two typical consecutive peaks at around 260 °C and 350 °C that are consistent with the results of Jones et al. and Cai et al. which can be attributed to the reduction of Cu2+ → Cu+ and Mn3+ → Mn2+, respectively.44, 45 The broadened reduction peaks compared to those results are due to the open channel configuration of monolithic samples. In the TPR profiles of both two Co-doped catalysts, the reduction of cobalt ions (Co3+ → Co2+) slightly changed the profile shape of CuMn2O4 and led to the diminished troughs around 300 °C and small humps around 350 °C. With Co doping, NA-Co0.36Cu0.64Mn2O4 and NA-Co0.53Cu0.47Mn2O4 showed relatively lower starting temperatures in H2-TPR tests, which followed the same tendency as their activation energies, NA-Co0.36Cu0.64Mn2O4 < NA-Co0.53Cu0.47Mn2O4 < NA-CuMn2O4.

The nature of oxygen species in coated CuMn2O4 materials was investigated using oxygen temperature programmed desorption (O2-TPD) experiments. Overall, the three catalysts had similar starting temperatures of oxygen evolution around 350 °C. Between 350-750 °C, each O2-TPD profile can be separated into three regions: (i) 350-540 °C, (ii) 540-660 °C, and (iii) 660-750 °C, according to the major desorption peaks. In Fig. 5(b), the TPD profile of CuMn2O4 only shows two oxygen desorption peaks in regions I and II, which belong to the bulk lattice oxygen evolution from metal-oxygen bonding, Cu-O, and Mn-O. But the TPD profiles of the two Co-doped CuMn2O4 catalysts show clear desorption peaks in region III indicating oxygen evolution from Co-O bonding. The relative intensities of desorption peaks in region I and region III also varied with the change of Cu and Co ratio in the catalysts NA-Co0.36Cu0.64Mn2O4 and NA-Co0.53Cu0.47Mn2O4. For example, from the ICP test, the elemental component of NA-Co0.53Cu0.47Mn2O4 catalyst possesses less copper but more cobalt compared to the NA-Co0.36Cu0.64Mn2O4 catalyst, and the O2-TPD profile simultaneously shows a lower intensity peak in region I and a higher peak in region III. This phenomenon agrees with the study of Morales et al., which presented an analogous result of the varied ratio between Cu and Mn in Mn3Cu4 mixed oxides.46 These results also demonstrate that the three regions of lattice oxygen evolution in our O2-TPD profiles can be distinguished as follows, (i) region I (350-540 °C): Cu-O, (ii) region I (540-660 °C): Mn-O, and (iii) region I (660-750 °C): Co-O.

3.4 Thermal analysis and stability of catalysts

Thermogravimetric analysis (TGA) of the powder-form CuMn2O4 materials collected from respective hydrothermal synthesis are shown in Fig. 5(c) with sample weight percentages as a function of temperature. The TGA profiles show a 6~8% weight loss before 100 °C by the release of physisorbed water molecules. As shown in the O2-TPD study [Fig. 5(b)], the evolution of lattice oxygen starts with heating up to 350 °C. An obvious decay around 450 °C should be due to the crystal phase formation of hopcalite CuMn2O4 and phase segregation of MnO2 according to the XRD patterns at high temperature as shown in Figs. 2(b)-(d). Co0.36Cu0.64Mn2O4 shows more weight loss as compared to CuMn2O4 and Co0.53Cu0.47Mn2O4 indicating the lower thermal stability among the three materials.

3.5 Surface composition and oxidation state

X-ray photoelectron spectroscopy (XPS) was used to obtained detailed valence states of the major component in the surfaces of catalysts. The XPS spectra in Fig. 6 illustrate the surface elemental compositions of the powder collected from hydrothermal coating synthesis of NA-CuMn2O4. NA-Co0.36Cu0.64Mn2O4, and NA-Co0.53Cu0.47Mn2O4. All binding energies (BEs) and elemental ratios correspond to the peaks of Mn 2p, Cu 2p, Co 2p, and O 1s and are summarized in Table 3. In Fig. 6(a), the Mn 2p3/2 peaks at around 641 eV indicate the Mn4+ as the major Mn in each CuMn2O4 material.48 The Cu 2p spectra in Fig. 6(b) are characterized by the peaks of Cu 2p3/2 (932 eV) and Cu 2p1/2 (952 eV), and observable satellite peaks...
at around 940 eV and 962 eV, which correspond to Cu$^{2+}$; with no obvious peaks from Cu$^0$ and Cu$^{+}$ detected.\(^{47, 48}\) In Fig. 6(c), the respective Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks at around 780 eV and 795 eV are accompanied with satellite peaks at 786 eV and 806 eV due to the majority of Co$^{2+}$. Detectable shoulders at around 782 eV indicate the minor existence of Co$^{3+}$ in the catalysts. The Shirley function was not applied to correct the background of Mn LMM (945 eV) and Mn 2s peaks (772 eV), respectively. The O 1s spectra in Fig. 6(d) can be de-convoluted to two or three Gaussian peaks associated with lattice oxygen (O$_{L}$, 529.4 eV), surface-adsorbed oxygen species (O$_{ads}$, 531.4 eV, i.e. O$_{2-}$, O$_{2-}$, and O$^-$), and surface adsorbed OH groups and molecular water (O$_{OH}$, 532.5 eV, i.e. OH$^-$ and H$_2$O).\(^{39}\)

4. Discussion

4.1 Synthesis and morphologies

The cryptomelane MnO$_2$ nanoarray HM-PCR, synthesized using manganese sulfate (MnSO$_4$) and potassium chlorate (KClO$_3$), was chosen as the core support due to the high length-to-diameter ratio (average lengths of 5 µm and diameters of 50 nm). The appropriate interspaces between the rods provide enough room for the growth of CuMn$_2$O$_4$ layers without sacrificing active surface. Additional advantages, like the simple synthetic procedure, potential scalability, high robustness, and good stability in hydrothermal reactions ensure that nanoarray HM-PCR has no influence on the
secondary transitional metal oxide coatings during the synthesis.

The mild conditions of the hydrothermal CuMn$_2$O$_4$ coating, e.g. neutral solution, low temperature, and slow precipitation rate, contribute to the uniform and tunable thickness of CuMn$_2$O$_4$ layers from top to bottom along the whole HM-PCR nanoarrays. The introduction of cobalt ions accelerate the precipitation rate to obtain the same thickness of coating layers in a shorter reaction time. Correlating the elemental ratio between Co and Cu ions in NA-Cu$_{0.36}$Co$_{0.64}$Mn$_2$O$_4$ and NA-Cu$_{0.53}$Co$_{0.47}$Mn$_2$O$_4$ from ICP-MS tests (Table 1), Co ions replace the Cu ions in the CuMn$_2$O$_4$ system due to the more energetically favorable formation of Co-O bonds ($\Delta H_f = 368$ KJ/mol) than Cu-O bonds ($\Delta H_f = 343$ KJ/mol), which results in more Co in the materials than expected.

Comparing the supporting types and preparation methods, nanoarray-based catalysts have less average weight (~ 600 g/L) of unit monolithic size than wash-coated catalyst (~ 800 g/L). nanoarray-based catalysts also have less weight percentage of the core nanoarrays (9 – 15%) but higher surface area (35 – 43 m$^2$/g) compared to the wash-coated catalysts with alumina powder support (SA: 12 – 17 m$^2$/g; loading: 31 – 34%).

In addition, the calculated SA of NA-Cu$_{0.36}$Co$_{0.64}$Mn$_2$O$_4$ from the nanoarray-based catalyst (218 m$^2$/g) is almost double that of WA-Cu$_{0.53}$Co$_{0.47}$Mn$_2$O$_4$ (113 m$^2$/g). This result indicated that the core nanoarrays (HM-PCR) provide a useful support for CuMn$_2$O$_4$ coating layers preventing material aggregation and efficiently maintaining high surface area, and maximizing active sites.

4.2 Catalytic performance

Propane (C$_3$H$_8$) oxidations were conducted to evaluate the catalytic performance of all nanoarray-based and wash-coated monolithic catalysts as shown in Fig. 4. The Pd/Al$_2$O$_3$ wash-coated catalyst (WC-Pd) was used as a state-of-art monolithic catalyst to compare with our CuMn$_2$O$_4$ coated catalysts. In Fig. 4(a), all CuMn$_2$O$_4$ based monolithic catalysts exhibit lower light-off temperatures ($T_{50}$) and 90% conversion temperatures ($T_{90}$) than the Pd loaded catalyst, WC-Pd, indicating the high reactivity to hydrocarbons of the CuMn$_2$O$_4$ coatings.

In general, nanoarray-based monolithic catalysts possess open surfaces of nanoarray architectures with exposure to more sufficient active sites than traditional wash-coated monolithic catalysts. The promoted activities by the open surfaces of nanoarrays were examined by comparing the normalized activities of nanoarray-based and wash-coated catalysts shown in Fig. 4(b). All the three nanoarray-based catalysts reveal higher activities of C$_3$H$_8$ oxidation than each correlated wash-coated monolithic catalyst after normalization with loading weight. This result indicates that the CuMn$_2$O$_4$ nanosheet coatings on nanoarrays lead to better mass transfer during C$_3$H$_8$ oxidations than mixing with a-Al$_2$O$_3$ powder. Furthermore, the order of weight normalized activities for the three nanoarray-based catalysts (NA-Cu$_{0.36}$Co$_{0.64}$Mn$_2$O$_4$ > NA-Cu$_{0.53}$Co$_{0.47}$Mn$_2$O$_4$ > NA-CuMn$_2$O$_4$) became reversed after normalization with material surface area, which demonstrates the largely increased surface area of CuMn$_2$O$_4$ nanosheets by Co doping contributing to high catalytic activities. Among the nanoarray-based catalysts, the order of reactivity is NA-Cu$_{0.53}$Co$_{0.47}$Mn$_2$O$_4$ ~ NA-Cu$_{0.36}$Co$_{0.64}$Mn$_2$O$_4$ > NA-CuMn$_2$O$_4$ as the same tendency as the wash-coated catalysts. The two Co-doped catalysts present similar reactivity but are higher than the pure CuMn$_2$O$_4$ catalyst below 350 °C showing the enhanced reactivity by the incorporation of Co ions in the low-temperature region.

The calculated activation energies ($E_a$) are listed in Fig. 4(d) with the increasing order NA-Cu$_{0.36}$Co$_{0.64}$Mn$_2$O$_4$ (62.1 KJ/mol) < NA-Cu$_{0.53}$Co$_{0.47}$Mn$_2$O$_4$ (87.1 KJ/mol) < NA-CuMn$_2$O$_4$ (98.2 KJ/mol). This result shows the same tendency with the study of Salker et al. in 2000 that Co$_x$Cu$_{1-x}$Mn$_2$O$_4$ catalysts were tested with varied Co/Cu ratios (x = 0.0, 0.3, 0.5, 0.7, and 1.0). And the catalytic performance of CO oxidations indicates the catalysts with x = 0.3 and 0.7 show a relatively higher reactivity than catalysts with x = 0.0, 0.5, and 1.0. Correlating the activation energies of nanoarray-based catalysts to our H$_2$-TPR and O$_2$-TPD results, the additional reduction peak of Co ions (Co$^{3+}$ → Co$^{2+}$) and lower evolusion temperature of lattice oxygen (Mn-O$_2$) respectively contribute to higher reducibility and oxygen mobility and lower $E_a$ of Co-incorporated catalysts.

4.3 Oxidation States

The XPS study reveals the oxidation states of metal elements near the surface, which usually play a significant role influencing the catalytic reactivity. The major oxidation states of Mn, Cu, and Co in the series of CuMn$_2$O$_4$ are determined as Mn$^{4+}$, Cu$^{2+}$, and Co$^{2+}$ according to their binding energies (BEs) and corresponding satellite peaks as shown in Figs. 6(a)-(c). The BEs of Mn, Cu, and O for all catalysts decrease with increasing contents of Co suggesting that the incorporation of Co might enhance the mobility of lattice oxygen.

For the two Co-doped catalysts, Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ and Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$, the existence of Mn LMM peaks (~944.1 eV) in Cu 2p spectra [(Fig. 6(b)] and Mn 2s peaks (~768.6 eV) in Co 2p spectra [(Fig. 6(c)] cause some difficulty to distinguish the major oxidation states of Mn, Cu, and Co from Co$_x$Cu$_{1-x}$Mn$_2$O$_4$. Correlating the intensity of Mn 2s signal observed from Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ is relatively higher than Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ indicating the higher surface concentration of Mn in Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$.

In Fig. 6(d), the O 1s peak of Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ can only be de-convoluted into two well-fitting Gaussian peaks for lattice oxygen and surface-adsorbed oxygen species rather than three peaks as shown in CuMn$_2$O$_4$ and Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$. This result suggests that the Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ material has trace surface adsorbed hydroxyl species (OH) and molecular water but a relatively higher percentage of surface-adsorbed oxygen species (Oads~ 45.4%), which are usually considered as better catalytic oxidation promoters, than the other two catalysts.

Correlating the $E_a$ of each catalyst to the XPS analysis, the order of $O_{ads}$ percentages in catalysts, Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ (45.4%) > Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ (32.1%) > CuMn$_2$O$_4$ (24.1%), reveals a reversed tendency of activation energies presented in Fig. 4(d). Co$_{0.36}$Cu$_{0.64}$Mn$_2$O$_4$ (62.1 KJ/mol) < Co$_{0.53}$Cu$_{0.47}$Mn$_2$O$_4$ (87.1 KJ/mol) < CuMn$_2$O$_4$ (98.2 KJ/mol).
Overall, the lower $E_a$ of Co-doped CuMn$_2$O$_4$ than the pure CuMn$_2$O$_4$ is due to the higher concentrations of Mn and O$_{ads}$ near the material surface. The highest amounts of Mn$^{4+}$, O$_{ads}$, and negligible O$_{001}$ lead to the lowest $E_a$ of Co$_{0.33}$Cu$_{0.67}$Mn$_2$O$_4$.

5. Conclusions

Advanced nanoarray-based monolithic catalysts were successfully fabricated by coating CuMn$_2$O$_4$ nanosheets onto the HM-PCR nanoarrays. The synthetic process exhibits good hydrothermal durability and loading capability of HM-PCR nanoarrays for additional transitional metal oxide layers. The composite monolithic catalysts combine the high reactivity of CuMn$_2$O$_4$ materials and open surface efficacy of nanoarray architecture to provide better catalytic performance for CH$_4$ oxidation. Compared to wash-coated catalysts, nanoarrays are able to replace alumina supports and efficiently reduce the integrated weight of monolithic catalysts. The incorporation of cobalt ions effectively increases the specific surface area from 63 m$^2$/g to 218 m$^2$/g, and lowers the apparent activation energy from 98.2 KJ/mol to 62.1 KJ/mol with compromised thermal stability. XPS studies show that the NA-Cu$_{0.33}$Cu$_{0.67}$Mn$_2$O$_4$ catalyst possesses a higher surface concentration of Mn and surface-adsorbed oxygen, which contribute to the highest catalytic performance observed in this study. Different from traditional hydrothermal syntheses, all procedures were conducted in an open system reactor at atmospheric pressure revealing the potential for scalability for industrial manufacturing processes.

Conflicts of interest

The authors declare no conflicts to declare.

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Notes and references

2. Adoption of the Paris Agreement, UNFCCC. Conference of the Parties (COP), 2015.