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Ni-substituted LaMnO<sub>3</sub> perovskites for ethanol oxidation<sup>+</sup>

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The B-site substitution of LaMnO<sub>3</sub> perovskites by Ni was investigated under the oxidation of ethanol. Proper characterization techniques, including BET surface area measurement, XRD, FTIR, XPS, TPR, O<sub>2</sub>-TPD, and FE-SEM experiments were performed to survey the physicochemical properties of perovskites. The results reveal that up to 25% of Mn can be replaced by Ni; beyond this limit, segregated NiO<sub>x</sub> can be synthesized. Inserting Ni into the solid solution of perovskite yields unique bridging lattice oxygen sites (Ni–O–Mn) in Ni-doped LaMnO<sub>3</sub>. Based on catalytic performance in ethanol oxidation, the Ni–O–Mn sites are likely to promote ethanol conversion and the oxidation of acetaldehyde to CO<sub>2</sub> at low reaction temperatures. The abatement of intermediates over Ni–O–Mn sites is hypothesized and a plausible reaction pathway is proposed. Moreover, the time on-stream testing revealed that the interaction between Ni and Mn is likely to enhance perovskite's thermal stability in ethanol oxidation.

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### Introduction

Ethanol can be derived from renewable energy crops and lignocellulosic biomass. Using ethanol as a fuel additive is a potential way to alleviate our fossil-fuel addiction. For example, 10% and 85% ethanol–gasoline blended fuels, *i.e.*, E10 and E85, are commercially available for drivers in the US. As demand for energy continues to increase, the market growth for ethanol fuel is inevitable.<sup>1</sup> However, burning ethanol-containing fuels yields different vehicle exhaust compounds from those produced by burning fossil fuels.<sup>2</sup> More volatile organic compounds (VOCs) are generated using 10% and 15% ethanol–diesel blends in existing engines when compared to certified diesel fuel.<sup>3</sup> Unburned ethanol and its derivatives, such as acetaldehyde, a carcinogen in humans,<sup>4</sup> are harmful pollutants. Hence, the development of suitable catalysts for the abatement of ethanol and ethanol derivatives is urgently required.

Perovskite (ABO<sub>3</sub>) is an effective catalyst for the removal of CO, NO<sub>x</sub>, VOCs, and hydrocarbons.<sup>5,6</sup> In some cases, perovskites perform comparably to, or even better than, conventional (precious metal-based) three-way catalysts, such as strontium-containing perovskites in NO<sub>x</sub> abatement.<sup>7</sup> Daihatsu Motors has

successfully implemented trace platinum group metal (pgm)doped perovskites in their exhaust converter systems.<sup>8-11</sup> The self-regeneration behavior of pgm-promoted perovskites under oxidative and reductive conditions makes them more active and durable than platinum-based catalysts. Our group has recently reported on the effectiveness of similar perovskites in methanol partial oxidation<sup>12,13</sup> and combustion.<sup>14</sup> The unique lattice structure and oxygen nonstoichiometry of perovskite are believed to be important in oxidation reactions.<sup>5</sup>

Surprisingly, only a few studies of ethanol combustion using perovskites are available. The pioneering study by the Hitachi research group<sup>15</sup> tested  $LnBO_3$  (Ln = La, Pr, Sm, and Gd; B = Fe, Co and Ni) as ethanol sensors in ethanol oxidation. The short response time at low ethanol concentration makes perovskite a promising candidate in ethanol conversion. This inspires follow-up studies to utilize various compositions and elements at the A- or B-site position.<sup>16-22</sup> Wang et al.<sup>17</sup> and Najjar and Batis<sup>21</sup> reported relatively high reactivities (low  $T_{50}$  and  $T_{95}$ , where the former denotes the temperature for 50% ethanol conversion, and the latter is the temperature for 95% ethanol conversion) of their catalysts in ethanol oxidation. Wang et al.17 used Ag-supported La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> in both methanol and ethanol oxidations, and reported that anchored Ag<sup>+</sup> on the surface of perovskite not only acts as a catalytic promoter, but also increases the surface adsorbed oxygen-to-lattice oxygen  $(O_2^{-2}/O^{-})$  ratio; both factors are essential in the conversion of alcohols. Najjar and Batis<sup>21</sup> investigated gelling agents (glycine and citric acid) for LaMnO3 synthesis using a combustion method, and discovered that LaMnO<sub>3</sub> made by using glycine as the gelling agent had a high thermal stability and activity in ethanol combustion. This is attributed to the decrease of surface La/Mn ratio and the increase of the adsorbed oxygen species on the perovskite's surface.

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<sup>†</sup> Electronic supplementary information (ESI) available: The reduction properties, C 1s core level spectra, and post-TPR XRD patterns of LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub>, TPR profiles of physically mixed LaMnO<sub>3</sub> and LaNiO<sub>3</sub> particles, ethanol conversion and product selectivity as functions of temperature of physically mixed LaMnO<sub>3</sub> and LaNiO<sub>3</sub> particles, the summary of XPS-derived Ni loading, amounts of α- and β-oxygen, and T<sub>50</sub> and T<sub>95</sub> of tested LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub>, the SEM images of as-synthesized and used samples. See DOI: 10.1039/c3ra46323k

This study investigates the use of Ni-incorporated LaMnO<sub>3</sub> in ethanol oxidation. LaMnO<sub>3</sub> is known to have a wide range of oxidative (excess oxygen) and reductive (oxygen vacancy) nonstoichiometries.23 The non-stoichiometric oxygen content markedly affects various oxidation reactions, such as methane<sup>24</sup> and propane<sup>23</sup> oxidations. This can be ascribed to the oxygen adsorption-activation step on catalyst surface and the enhancement of oxygen mobility.17 Partial substitution of Mn with cations with a valence less than three (such as Cu) is another way to improve the oxidation chemistry either in the bulk or on the surface of LaMnO<sub>3</sub>-based perovskites.<sup>23</sup> In this work, Ni is chosen as the B-site dopant because of its bivalence and reactivity in oxidative environments.25-27 Incorporating Ni in LaMnO<sub>3</sub> may have a synergistic effect on the conversion of ethanol and its derivatives in oxidative environments. This study attempts to explore the effect of Ni-substituted LaMnO<sub>3</sub> perovskite in ethanol combustion. Physicochemical properties of catalysts were examined, and the relationship between the Ni content and the catalytic behaviors of LaMnO3-based perovskites was elucidated.

#### Experimental

#### **Catalyst synthesis**

Substituted LaMn<sub>1-v</sub>Ni<sub>v</sub>O<sub>3</sub> (y = 0.1, 0.25, and 0.4) and plain LaMnO3 and LaNiO3 were synthesized by the Pechini method.<sup>28,29</sup> Metal nitrates precursors (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Merck, 99%), Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Merck, 99%), and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck, 99%)) were used during the synthesis of the respective perovskites. These precursors were dissolved in water in the desired stoichiometric ratios. The obtained solution was then added dropwise to a 1 M citric acid solution, which contained approximately four times as many citric acid ions in relation to the metal ions of the precursors. The mixture was stirred and heated to 80 °C in a water bath. After stirring for an hour, an equivalent molar ratio of ethylene glycol (Alfa Aesar, 99%) using citric acid as the reference was poured into the solution. The resulting solution was then stirred at 90 °C for more than four hours until a gel was formed. The gel was transferred to a furnace, and dried at 80 °C for 24 h. The remaining paste was then calcined in air from 80 to 400  $^{\circ}$ C at a heating rate of 1  $^{\circ}$ C min<sup>-1</sup>, and kept isotherm for two hours. Finally, the precursors were calcined from 400 to 900 °C (3 °C min<sup>-1</sup>) for four hours.

#### Characterization

Powder X-ray diffraction patterns were obtained using a Shimadzu Labx XRD-6000 with Cu Ka radiation (0.15418 nm). The scan rate was set to  $4^{\circ}$  min<sup>-1</sup> and the  $2\theta$  range was 20–80°. The Scherrer relation was employed to estimate the crystallite size of each sample, based on the strongest peak from the  $(1\ 1\ 0)$  plane of perovskite.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded in the 400-4000 cm<sup>-1</sup> region with a Perkin-Elmer Spectrum 100 Optica using the KBr pellet method. The catalyst powder was diluted to about 1 wt% within KBr. The mixture was then pulverized and pelletized. Prior to the test, the pellet was

#### Activity evaluation

Catalytic performances were examined in a continuous fixed-bed system.30 Ethanol was injected into the system by a HPLC pump (Jasco PU-2080) at a feeding rate of  $3 \times 10^{-3}$  mL min<sup>-1</sup>. Oxygen and nitrogen were regulated using mass flow controllers (Brooks 5850E). The molar composition of the feed was  $C_2H_5OH/O_2/N_2 =$ 1.7/18.1/80.2 and the gas hourly space velocity (GHSV) was 10 446  $h^{-1}$ . About 10 mg of catalyst with a 40–80 mesh size was used in each trial. To maintain an isothermal condition, the catalyst was diluted with 150 mg SiO2 (40-80 mesh). SiO2 was inert in each trial. Internal and external mass transfer limitations were examined prior to the tests. The former was probed by measuring the catalytic performances using two different catalyst particle sizes (20-40 mesh and 40-80 mesh); the latter was tested by comparing two catalyst bed loadings, 10 mg catalyst mixed with 150 mg SiO2 and 15 mg catalyst mixed with 220 mg SiO<sub>2</sub>, with different flow rates but the same contact time (GHSV = 10 446 h<sup>-1</sup>). Both internal and external mass transfer resistances could be ignored because the differences of ethanol conversions in these trials were trivial (less than 3%).

dehydrated at 130 °C for 30 min in a N<sub>2</sub> stream (25 mL min<sup>-1</sup>).

All the spectra were obtained with an average of 16 scans and 4

a Thermo Scientific K-Alpha system equipped with a 180°

hemispherical sector analyzer and an Al monochromator (Al Ka

X-ray sources, 1486.6 eV). The diameter of the X-ray spot was

400 µm. The C 1s signal (284.5 eV) of adventitious carbon was

programmed reduction (TPR), and O<sub>2</sub>-temperature-pro-

grammed desorption (O2-TPD) were carried out using a

Micromeritics apparatus model Autochem II 2920 with a

thermal conductivity detector (TCD). Approximately 100 mg of

sample was consumed per trial. Prior to each test, the sample was dehydrated at 150 °C under an N<sub>2</sub> stream (30 mL min<sup>-1</sup>) for

30 min. In the BET test, a 30% N<sub>2</sub>/He stream was used for N<sub>2</sub>

physisorption at -196 °C. The specific surface area of each

sample was estimated from the desorbed N<sub>2</sub> area using the

single-point BET equation. In TPR analysis, a 10% H<sub>2</sub>/Ar (30 mL min<sup>-1</sup>) stream was passed through the sample and the temperature was raised from 50 to 900 °C with a ramp of 5 °C

 $min^{-1}$ . For O<sub>2</sub>-TPD, the sample was treated in a He stream

 $(30 \text{ mL min}^{-1})$  from 50 to 1000 °C at 5 °C min<sup>-1</sup> followed by an

samples were determined using a field-emission scanning

electron microscope (FE-SEM, JEOL JSM-6701F). The acquisi-

tion time per location was 10 min. The SEM accelerating voltage

was 10 kV. The scanned area was  $\sim$ 4  $\mu$ m  $\times$  3  $\mu$ m. Both as-

The surface morphologies of as-synthesized and used

Single-point BET surface area measurement, temperature-

X-ray photoelectron spectroscopy (XPS) was performed using

cm<sup>-1</sup> resolution at room temperature.

used to correct the energy shift.

isotherm at 1000 °C for half an hour.

synthesized and used catalysts were examined.

The system outlet was connected to a gas chromatograph (GC, SRI 8610) equipped with a TCD, a methanizer, and a flame ionization detector (FID). Two packed columns, 5 Å molecular sieve and Porapak Q, were used to separate reactants and products. The detected compounds were ethanol, acetaldehyde,  $CO_2$ , CO,  $CH_4$ ,  $O_2$ , and  $N_2$ .

Nitrogen also served as the internal standard. All products were measured relative to GC calibration standards. Catalytic results were reported with carbon atom mass balances less than 10% errors. Three to four runs were made for each data point, providing 95% confidence intervals (error bars) for conversion and selectivity. Ethanol conversion was calculated as moles of ethanol reacted divided by moles of ethanol injected. Selectivity of carbon-containing product was defined as  $100 \times$  (moles of ethanol converted to product *Xi*)/(moles of ethanol converted). The data of conversion or selectivity was interpolated with a B-spline function to allow a better comparison.

#### Results and discussion

Table 1 lists the surface areas of the LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub> catalysts. All catalysts displayed similar surface areas, ranging from 7.6 to 10.5 m<sup>2</sup> g<sup>-1</sup>. Fig. 1 shows the XRD patterns of LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub>. Those of LaMnO<sub>3</sub> ([JCPDS: 35-1353]) and LaNiO<sub>3</sub> ([JCPDS: 33-0711]) were included for reference. All samples yielded the characteristic peaks of ABO<sub>3</sub>-type perovskite phase. The main diffraction peak of NiO ([JCPDS: 89-5881]) at  $2\theta = 43.3^{\circ}$  was observed on LaNiO<sub>3</sub>. It reveals the segregation of NiO particles from perovskite solid solution. However, NiO was not identified on Ni-substituted catalysts, possibly because no segregated NiO was present or the NiO clusters were too small to be detected. The crystallite size decreased from 15.1 to 13.0 nm with increasing *y* values, suggesting the formation of disorder or deformation in LaMnO<sub>3</sub> perovskite by adding Ni.

A close inspection of the XRD patterns showed that the  $2\theta$  angle of each peak increased slightly with increasing Ni amount. This correlation is attributed to the decrease of interplanar distance by Ni substitution: the more Ni incorporated, the more Mn<sup>3+</sup> (low-spin 0.58 Å, high-spin 0.65 Å) could be replaced by Ni<sup>3+</sup> (low-spin 0.56 Å, high-spin 0.60 Å) ions, resulting in a decrease of the unit cell volume.<sup>31</sup> Blasco *et al.*<sup>32</sup> have also observed a similar tendency regarding unit cell volume with increasing Ni content in LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub> perovskites.

Fig. 2 shows (1 1 0), (1 1 1), (2 0 0), and (2 1 1) diffraction shifts as functions of Ni content. The shift gradually increased with Ni content from y = 0 to y = 0.25 then leveled off. Provendier *et al.*<sup>26</sup> and Pecchi *et al.*<sup>31</sup> have observed the same trend of XRD peak shift in the LaFe<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub> system. The shift has been ascribed to the degree of Ni substitution, and a certain



Fig. 1 XRD patterns of LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub> perovskites. The diffraction of (1 1 0) plane is zoomed in to show the  $2\theta$  angle shift with increasing Ni loading.

proportion of segregation has been noted in the high substitution region with the maximum shift value. LaMnO<sub>3</sub> has an orthorhombic unit cell. Substituting Mn with smaller Ni ions destabilizes the MnO<sub>6</sub> octahedra and enhances the rhombohedral distortion (due to the Jahn–Teller effect).<sup>33</sup> This structural phase transition of LaMn<sub>1–y</sub>Ni<sub>y</sub>O<sub>3</sub> may lead to the coexistence of multiple phases (*e.g.*, La<sub>2</sub>NiMnO<sub>6</sub> and LaNiO<sub>3</sub>) at a high Ni-loading.<sup>32,33</sup> Therefore, the complete insertion of Ni in perovskite structure should occur at y < 0.25; NiO<sub>x</sub> phases should segregate at y = 0.25 and above.<sup>31</sup>

Fig. 3 shows the FTIR spectra of the LaMn<sub>1- $\nu$ </sub>Ni<sub> $\nu$ </sub>O<sub>3</sub> catalysts. Besides LaNiO<sub>3</sub>, all perovskites displayed an adsorption band at approximately 600 cm<sup>-1</sup>. This band is related to Mn–O stretching in octahedral site.34 The band of Mn-O stretching was shifted from 610 to 601  $\text{cm}^{-1}$  (red shift) with an increase of Ni loading. The red shift may be explained by the photon response theory<sup>35</sup> since Ni is heavier than Mn in the solid solution. Therefore, the downward-shifted wavenumber suggested the presence of Ni-O-Mn bonding in Ni-containing LaMnO<sub>3</sub>. Moreover, at y = 0.25 and 0.4, a band at 411 cm<sup>-1</sup> and a shoulder at 638 cm<sup>-1</sup> were observed. The former is the stretching vibration of Ni-O bond;<sup>36,37</sup> the latter, Ni-OH bending.<sup>38</sup> This is consistent with the XRD diffraction shifts:  $NiO_x$  could be formed on the surface at y = 0.25 and above. The IR spectrum of LaNiO<sub>3</sub> was not well resolved; a close inspection within 400-600 cm<sup>-1</sup> was inserted in Fig. 3. The unclear vibrational modes of LaNiO<sub>3</sub> may be related to its low electrical resistivity  $(10^{-1} \Omega \text{ cm})$ .<sup>39</sup> At such a low resistivity, the residence time  $(10^{-12} \text{ s})$  of charge carriers at a site can be comparable to

Table 1	Surface area.	mean crystallite	size, and XPS-	derived surface	composition of	LaMn₁	Ni.O
Tuble 1	Surface area,	mean crystattice s		actived surface	composition of		y = 3

LaMn <sub>1-y</sub> Ni <sub>y</sub> O <sub>3</sub>	SAA $(m^2 g^{-1})$	$d_{\rm XRD} \left( nm \right)$	Mn/La	Ni/La	Ni/Mn	La/(Mn + Ni)	Ni/(Mn + Ni)	$(Mn^{4+}/Mn^{3+})$	$O_x/O_{latt}$
v = 0	8.7	15.1	0.83	_	0	1.21	0	1.03	0.63
y = 0.1	9.3	14.8	1.21	0.16	0.13	0.73	0.12	1.10	0.66
y = 0.25	10.5	14.5	1.08	0.28	0.26	0.74	0.21	1.21	0.70
y = 0.4	8.2	13.2	0.79	0.37	0.47	0.86	0.32	1.06	0.64
y = 1	7.6	13.0	_	0.67		1.49	1	_	2.00



Fig. 2 High angle shifts of the diffraction peaks as functions of Ni substitution content.



the lattice vibrational period  $(10^{-13} \text{ s})$ , at which a localized vibrational mode may not be specified.<sup>40</sup> Two tiny bands at 428 cm<sup>-1</sup> and 502 cm<sup>-1</sup> were identified, in accord with an earlier work.<sup>41</sup> However, the assignment of these two responses is unclear.

Fig. 4 displays the XPS spectra of  $LaMn_{1-\nu}Ni_{\nu}O_{3}$  perovskites. The La 3d spectra included two doublet peaks at 830 eV to 840 eV and 850 eV to 860 eV, corresponding to La 3d<sub>5/2</sub> and La  $3d_{3/2}$  signals, respectively. Notably, the responses of La  $3d_{3/2}$ and Ni 2p<sub>3/2</sub> overlap each other, and are difficult to be differentiated. A small hump at approximately 870 eV, which is associated with Ni  $2p_{1/2}$ , was identified in the spectrum of LaNiO<sub>3</sub> (y = 1). Multiple states of Ni (Ni<sup>3+</sup>/Ni<sup>2+</sup>) have been noted in LaNiO<sub>3</sub>-based perovskites.<sup>42</sup> The spin-orbit splitting of the La 3d level for each sample was close to 16.8 eV;  $^{\rm 42}$  moreover, the La 3d<sub>5/2</sub> and La 3d<sub>3/2</sub> responses were close to the index peaks of pure La<sub>2</sub>O<sub>3</sub>,<sup>43</sup> indicating that La ions are in a trivalent state. Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> signals were located at approximately 641.7 eV and 653.3 eV, respectively. Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup> could coexist in the Mn 2p3/2 region;44 however, the lack of a satellite peak of Mn<sup>2+</sup> (648.8 eV)<sup>45</sup> eliminates the possibility of the



Fig. 4 La 3d, Ni 2p, Mn 2p, and O 1s core level spectra of  $LaMn_{1-y}Ni_yO_3$  perovskites.

presence of  $Mn^{2+}$  ions. The responses of  $Mn 2p_{3/2}$  and  $Mn 2p_{1/2}$  can be deconvoluted into four peaks. The responses at 641.5 eV and 653.0 eV were assigned to  $Mn^{3+}$  cations, while the peaks at 642.9 eV and 654.5 eV were attributed to  $Mn^{4+}$  ions.<sup>42</sup> To provide quantitative analysis, the surface atomic ratios (see Table 1) were estimated from the intensities of La  $3d_{5/2}$ , Ni  $2p_{1/2}$ , and Mn  $2p_{3/2}$  peaks using the atomic sensitivity factors provided by Wagner *et al.*<sup>46</sup> The  $Mn^{4+}/Mn^{3+}$  molar ratio was reported in Table 1 as well.

The surface enrichment of La can be speculated for plain LaMnO<sub>3</sub> and LaNiO<sub>3</sub> because the Mn/La and Ni/La ratios at y = 0 and 1 were all less than unity. However, this is not the case for the y = 0.1 to 0.4 samples: the La/(Mn + Ni) ratios were all less than unity. This suggests the surface of Ni-containing LaMnO<sub>3</sub> was enriched by Ni and Mn cations. To provide a clear view of the distribution of La, Mn, and Ni on the surface of perovskite, Fig. 5 displays measured surface atomic ratios as functions of nominal surface atomic ratios of Mn/La, Ni/La, Ni/ Mn, and Ni/(Mn + Ni). Apparently, the surface became Mnenriched for Ni-containing LaMnO3 because their experimental Mn/La values were all greater than nominal ones. The measured Ni/La, Ni/Mn, and Ni/(Mn + Ni) all displayed a descending trend with growing y value. Segregation of NiO<sub>x</sub> on perovskite's surface at y = 0.25 and above is a possible explanation. This is because segregated NiOx particles contained Ni cations in the bulk that cannot be detected by XPS, thereby lowering the surface atomic ratio for Ni with respect to La or Mn. The y = 0.1sample had all its experimental Ni/La, Ni/Mn, and Ni/(Mn + Ni)



Fig. 5 Experimental Mn/La, Ni/La, Ni/Mn, and Ni/(Mn + Ni) atomic ratios versus nominal ones.

ratios greater than nominal ones, indicating the presence of highly dispersed Ni on its surface. The  $Mn^{4+}/Mn^{3+}$  molar ratios were close to 1, decreased followed the order as: y = 0.25 (1.21) > y = 0.1 (1.10) > y = 0.4 (1.06) > y = 0 (1.03). This is in accordance with Zhang *et al.*,<sup>42</sup> who have reported similar values of LaMnO<sub>3</sub> at 0.975 and LaMn<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> at 1.216. Apparently, Ni substitution in the B-site position can increase the composition of Mn<sup>4+</sup> in LaMnO<sub>3</sub> perovskites.

Combined signals were obtained from the O 1s state, suggesting the presence of different oxygen species on the surface layer. Lattice oxygen (e.g., La-O-Mn at 529.1 eV),<sup>13</sup> (O<sub>2</sub>)<sup>-</sup> species or low coordinated oxygen ions located at special site or domains of the surface (531.0 eV),47 and hydroxyl/carbonate groups (532.3 eV)<sup>31</sup> are believed to coexist on the surface of perovskite. Therefore, the O 1s spectra were deconvoluted based on these three responses. As the Ni content increased, the BE of lattice oxygen shifted from 529.2 eV to 528.1 eV. Tabata et al.45 observed a similar O 1s chemical shift in LaMn<sub>1-v</sub>Cu<sub>v</sub>O<sub>3</sub> (y = 0, 0.1, 0.2, 0.3, and 0.4). They proposed that more defects and oxygen vacancies could be generated as the substitution of Cu ions at the B-site increased. This effect alters the bond strength of the surface lattice oxygen. Similarly, replacing Ni in LaMnO<sub>3</sub> generates defects and/or segregated NiO particles, which weakening the lattice oxygen bonds in perovskite. Therefore, the BEs of lattice oxygen declined as the Ni content increased. The molar ratio of  $(O_2)^-$  species or low coordinated oxygen ions to lattice oxygen  $(O_x/O_{latt})$  was presented in Table 1. The  $O_x/O_{latt}$ ratio showed a same trend as that of  $(Mn^{4+}/Mn^{3+})$ , declined as: y = 0.25 (0.70) > y = 0.1 (0.66) > y = 0.4 (0.64) > y = 0 (0.63).Accordingly, the more  $Mn^{4+}$  on the surface, the more  $(O_2)^$ species or low coordinated oxygen ions could exist.42 Plain LaNiO<sub>3</sub> displayed higher O<sub>x</sub>/O<sub>latt</sub> value (2.00) than the other samples because La-Ni oxides are prone to form oxygen-deficient perovskites, which can be described as a superstructure with a formula  $La_n Ni_n O_{3n-1}$ .<sup>48</sup> Hence, less lattice oxygens were available on LaNiO<sub>3</sub> than other perovskites.

The C 1s spectra were presented in Fig. S1 (ESI<sup>†</sup>). The C 1s signals of all perovskites showed responses of adventitious

carbon (284.5 eV),<sup>49</sup> lanthanum carbonate ( $\sim$ 286.2 eV),<sup>50</sup> and carbonyl group ( $\sim$ 288.6 eV).<sup>49,51</sup> This is in agreement with the literature that lanthanum-based perovskites are often contaminated by carbonate species.

Fig. 6 presents the TPR profiles of tested perovskites and Table S1 (ESI<sup>†</sup>) lists the amounts of H<sub>2</sub> consumed by them. The TPR patterns of pure LaMnO<sub>3</sub> and LaNiO<sub>3</sub> included multiple peaks. The reduction of LaMnO<sub>3</sub> is complicated: Mn<sup>4+</sup> and Mn<sup>3+</sup> can coexist at the outset of TPR, and a full reduction of Mn ions to metallic Mn is not possible.52,53 Therefore, the low-temperature responses (<400  $^{\circ}$ C) are attributed to the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup>; the high-temperature signals (>400 °C) are referred to the reduction of Mn<sup>3+</sup> to Mn<sup>2+</sup>. Some reduction of Mn<sup>3+</sup> to Mn<sup>2+</sup> at low temperatures cannot be ruled out.54 The reduction of LaNiO<sub>3</sub> was similar to that in an earlier study:55 the reduction of  $Ni^{3+}$  to  $Ni^{2+}$  (*i.e.*,  $La_2Ni_2O_5$ ) at 347 °C was followed by that of  $Ni^{2+}$ to metallic Ni at 469 °C. The XRD patterns of post-TPR LaMnO<sub>3</sub> and LaNiO<sub>3</sub> (see Fig. S2 of ESI<sup>†</sup>) further support the aforementioned assertions: the index peaks of La2O3 and MnO were with the reduction of LaMnO<sub>3</sub>; those of La<sub>2</sub>O<sub>3</sub> and Ni were associated with the reduction of LaNiO<sub>3</sub>.

The first reduction of  $LaMn_{1-y}Ni_yO_3$  occurred in the range of 250 °C to 500 °C, in which the  $LaMnO_3$  and  $LaNiO_3$  phases were reduced. Hence, Mn and Ni ions were reduced concurrently in this range of temperatures. The second reduction of  $LaMn_{1-y}Ni_yO_3$  may be related to Mn and Ni ions since the amount of H<sub>2</sub> consumed in the high temperature range does not increase in proportional to the extent of Ni replacement (see Table S1†).

To provide a comparison, Fig. S3 (ESI<sup>†</sup>) presents the TPR results for physical mixtures of LaNiO<sub>3</sub> and LaMnO<sub>3</sub> with LaNiO<sub>3</sub>-to-LaMnO<sub>3</sub> ratios of 0.1, 0.25, and 0.4. In Fig. 6, Niincorporated LaMnO<sub>3</sub> exhibited two TPR responses at 200 °C to 500 °C and 650 °C to 850 °C. The high-temperature responses of LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub> shifted to higher temperatures than those of plain LaMnO<sub>3</sub> and LaNiO<sub>3</sub>, especially for the y = 0.1 sample. Tailing of reduction response at 800 °C and above could be



Fig. 6 TPR profiles of  $LaMn_{1-v}Ni_vO_3$  perovskites.

observed for the y = 0.1 and 0.25 samples. This suggests an existence of Ni–O–Mn interaction, which retards the reduction process. The TPR profiles of physically mixed LaNiO<sub>3</sub> and LaMnO<sub>3</sub> further support the above-mentioned hypothesis: three distinct peaks at 331, 466, and 731 °C appear to be the merged responses of LaNiO<sub>3</sub> and LaMnO<sub>3</sub>. Notably, LaMn<sub>0.9</sub>N<sub>0.1</sub>O<sub>3</sub> exhibited the highest reduction signal at 783 °C, indicating that the interaction within the solid solution of LaMn<sub>0.9</sub>N<sub>0.1</sub>O<sub>3</sub> is the strongest among all samples. Conversely, the weakest interaction between Ni and Mn was found in LaMn<sub>0.6</sub>N<sub>0.4</sub>O<sub>3</sub> since it had the lowest high-temperature reduction response at 736 °C.

Fig. 7 shows the O<sub>2</sub>-TPD profiles. For clarity, the signal of LaNiO<sub>3</sub> was multiplied by a factor of 0.1. O<sub>2</sub>-TPD can be used to estimate the lability of oxygen in tested perovskites. The outset of desorption signal increased in the order of y = 0 (82 °C) <  $y = 0.1 (114 \ ^{\circ}C) < y = 0.25 (132 \ ^{\circ}C) < y = 0.4 (211 \ ^{\circ}C) < y = 1$ (677 °C), suggesting that more substituted Ni at B-site resulted in lower oxygen lability in  $LaMn_{1-\nu}Ni_{\nu}O_3$ . Desorbed oxygen is frequently categorized as  $\alpha$ - and  $\beta$ -oxygen, using 500 °C as the demarcation.  $\alpha$ -oxygen is adsorbed and near-surface oxygen, while β-oxygen is lattice oxygen in the perovskite framework.<sup>56</sup> Negligible  $\alpha$ -oxygen desorption was detected in LaNiO<sub>3</sub>. Table 2 summarizes the amounts of desorbed oxygen and the temperatures of peak desorption of tested perovskites. The desorption temperatures of  $\alpha$ - and  $\beta$ -oxygen increased with Ni content for LaMn<sub>1-v</sub>Ni<sub>v</sub>O<sub>3</sub>. Plain LaNiO<sub>3</sub> exhibited a distinct peak at 948 °C. Ni-containing LaMnO<sub>3</sub> perovskites had higher α-oxygen-to-βoxygen ratios than pure LaMnO<sub>3</sub> and LaNiO<sub>3</sub>. The α-oxygen-toβ-oxygen ratio followed the sequence of y = 0.25 (0.47) > y = 0.1(0.39) > y = 0.4 (0.32) > y = 0 (0.30), in consistent with the trend of the Ox/Olatt ratio observed by XPS. Among all catalysts, LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> released the most  $\alpha$ -oxygen (72.2  $\mu$ mol/g cat.); LaNiO<sub>3</sub> contained the highest  $\beta$ -oxygen (695.9  $\mu$ mol/g cat.).

Ni substitution negatively affects oxygen lability/oxygen availability in LaMnO<sub>3</sub>-based perovskites. This can be explained by estimating the oxygen content from the charge balance. According to the XPS results, trivalent and tetravalent Mn ions could coexist in LaMnO<sub>3</sub>; therefore, its chemical formula is



Fig. 7  $O_2$ -TPD profiles of LaMn<sub>1-y</sub>Ni<sub>y</sub>O<sub>3</sub> perovskites.

Table 2 Oxygen desorption characterization of  $LaMn_{1-\textit{y}}Ni_\textit{y}O_3$  catalysts

		O <sub>2</sub> -TPD					
Catalyst		$\alpha$ -O <sub>2</sub> <sup><i>a</i></sup>	$\beta$ - $O_2^{b}$	$\alpha$ -O <sub>2</sub> / $\beta$ -O <sub>2</sub>			
y = 0	T (°C) μmol/g cat.	131	686				
		69.8 (23.0%)	233.2 (77.0%)	0.30			
y = 0.1	$T$ (°C) $\mu$ mol/g cat.	136	697				
		72.2 (28.1%)	184.5 (71.9%)	0.39			
y = 0.25	$T$ (°C) $\mu$ mol/g cat.	205	928				
		68.1 (32.1%)	144.0 (67.9%)	0.47			
y = 0.4	$T$ (°C) $\mu$ mol/g cat.	255	1000				
-		24.8 (24.1%)	78.0 (75.9%)	0.32			
y = 1	$T$ (°C) $\mu$ mol/g cat.		948				
-		—	695.9 (100%)	0			

 $^a$  Maximum temperature of oxygen desorption peak below 500  $^\circ {\rm C.}$   $^b$  Maximum temperature of oxygen desorption peak above 500  $^\circ {\rm C.}$ 

LaMn<sup>3+</sup><sub>*a*</sub>Mn<sup>4+</sup><sub>1-a</sub>O<sub>3+ $\delta$ </sub> ( $\delta = (1 - a)/2$ ). Divalent and trivalent Ni ions were present in LaNiO<sub>3</sub>, yielding the formula LaNi<sup>2+</sup><sub>*b*</sub>Nt<sup>3+</sup><sub>1-b</sub>O<sub>3+ $\lambda$ </sub> ( $\lambda = -(1 - b)/2$ ). Since  $\delta$  is positive and  $\lambda$  is negative, LaMnO<sub>3</sub> should host excess oxygen while oxygen vacancies are formed in LaNiO<sub>3</sub>. Substituting Ni in LaMnO<sub>3</sub> should satisfy the charge balance condition, yielding an oxygen content between  $\delta$  and  $\lambda$ . The only exception is LaNiO<sub>3</sub>, which released the most oxygen in O<sub>2</sub>-TPD. This finding is consistent with the XPS results concerning the inhomogeneity of the surface and unstable Ni<sup>3+</sup> in perovskite, which yields weak lattice oxygen bonding in LaNiO<sub>3</sub>. Still, doping Ni has a positive effect on  $\alpha$ -oxygen content, which is optimal at y = 0.1.

Fig. 8 plots ethanol conversions of  $LaMn_{1-y}Ni_yO_3$  as functions of temperature. Each catalyst yields an S-shaped curve besides  $LaNiO_3$ , which displays an abrupt increase of ethanol conversion at 250 °C. At temperatures below 200 °C, all catalysts converted less than 20% ethanol, except for  $LaMn_{0.9}Ni_{0.1}O_3$ , which achieved 21% conversion at 200 °C. The  $T_{50}$  increased in



Fig. 8 Conversion of ethanol as a function of temperature over  $LaMn_{1-\nu}Ni_{\nu}O_3$  perovskites.

the order of LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> (226 °C) < LaMn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>3</sub> (243 °C) < LaMnO<sub>3</sub> (249 °C) < LaMn<sub>0.6</sub>Ni<sub>0.4</sub>O<sub>3</sub> (255 °C) < LaNiO<sub>3</sub> (266 °C); the T<sub>95</sub>, LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> (252 °C) < LaMn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>3</sub> (269 °C) < LaMnO<sub>3</sub> (288 °C) < LaMn<sub>0.6</sub>Ni<sub>0.4</sub>O<sub>3</sub> (309 °C) < LaNiO<sub>3</sub> (314 °C). This indicates that LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> is the most active catalyst in ethanol combustion while LaNiO<sub>3</sub> is the least active. Ling *et al.*<sup>57</sup> have observed a sudden increase of conversion at 250 °C for LaNiO<sub>3</sub> in ethanol oxidation. By a conductivity test, surface reaction of chemisorbed ethanol and oxygen species was discovered to be promoted at 250 °C. This leads to an increase of LaNiO<sub>3</sub> conductivity due to oxygen consumption, and ethanol conversion can be greatly improved on partially reduced surface. They also pointed out that the maximum conductivity change of LaNiO<sub>3</sub> occurs in the range of 250 to 350 °C, in accordance with our conversion trend.

Fig. 9 shows acetaldehyde and carbon dioxide selectivities as functions of temperature. Negligible amounts of CO and CH<sub>4</sub>, both less than 1%, were detected in each catalyst, and are ignored for clarity. At temperatures below 225 °C, the selectivity of acetaldehyde exceeded 80% while that of CO<sub>2</sub> was less than 20%. With increasing temperature, the selectivity of acetaldehyde declined and that of CO<sub>2</sub> increased. At 235 °C, LaMn<sub>0.9</sub>. Ni<sub>0.1</sub>O<sub>3</sub> generated about 38% acetaldehyde and 62% CO<sub>2</sub>. The other catalysts produced more than 80% acetaldehyde and less than 20% CO<sub>2</sub> at this temperature. At 250 °C, LaMn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>3</sub> yielded equal amounts of acetaldehyde (30%) and CO<sub>2</sub> (70%) to those of LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub>. The remaining catalysts at 260 °C and above yielded less than 40% acetaldehyde and over 60% CO<sub>2</sub>. LaNiO<sub>3</sub> seems to be the least effective in acetaldehyde



Fig. 9 Acetaldehyde and carbon dioxide selectivities as functions of temperature over  $LaMn_{1-y}Ni_yO_3$  perovskites.

abatement because more than 40% acetal dehyde selectivity was detected at 275  $^{\circ}\mathrm{C}.$ 

The oxidation activity and chemistry of alkane and alcohol are known to be strongly associated with the transport and storage of oxygen.<sup>23,58</sup> The above catalytic outcomes indicate that adsorbed and near-surface oxygen ( $\alpha$ -oxygen) are more effective than lattice oxygen ( $\beta$ -oxygen) in ethanol oxidation. Hence, the  $\alpha$ -oxygen-lean LaNiO<sub>3</sub> was the least active catalyst whereas the activities of α-oxygen-rich LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> and LaMn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>3</sub> were enhanced. The high onset temperature of O2-TPD and low concentration of α-oxygen of LaMn0.6Ni0.4O3 reflected low reactivity, implying the critical role of  $\alpha$ -oxygen in ethanol oxidation.  $\alpha$ -oxygen is known to act as an activated oxygen species, which initiates the oxidation of chemisorbed intermediates into carbon oxides and water.59 The role of  $\alpha$ -oxygen in ethanol oxidation is as proposed elsewhere.<sup>17,21</sup> To provide a better comparison, Fig. S4 (ESI<sup>†</sup>) displays the variations of XPS-derived Ni loading, amounts of α- and β-oxygen, and  $T_{50}$  and  $T_{95}$  of tested LaMn<sub>1-v</sub>Ni<sub>v</sub>O<sub>3</sub>.

LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> possesses the highest activity among all catalysts, even greater than that of LaMn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>3</sub>, which has the highest  $O_x/O_{latt}$  ratio. This implies that besides  $\alpha$ -oxygen effect, other factors should be considered for catalyst's efficacy in ethanol oxidation. Presumably, at a lower Ni loading, Ni can be distributed more evenly in perovskite, generating more Ni-O-Mn linkages on the surface. Increasing the Ni loading in LaMnO<sub>3</sub> produces segregated NiO<sub>x</sub> clusters on the surface of perovskite, reducing the amounts of Ni-O-Mn bonds. The bridging oxygen of Ni-O-Mn should possess an unique interaction, which is effective in promoting ethanol oxidation and intermediate conversion to carbon dioxide. Similar bridging sites have been noted on different perovskites (*e.g.*, Ni<sup>2+</sup>–O–Ni<sup>3+</sup> species of  $La_{2-x}Sr_xNiO_4$ ,<sup>60</sup>  $Mn^{3+}-O-Mn^{4+}$ bonds  $LaMn_{1-\nu}Cu_{\nu}O_{3}$ ,<sup>52</sup> and Fe<sup>3+</sup>-O-Fe<sup>5+</sup> pairs of SrFeO<sub>3</sub><sup>61</sup>). These sites have been proposed to be effective in promoting charge transfer and oxygen mobility of the catalysts in N2O decomposition60 and CH4 combustion.52,61

Fig. 10 displays the proposed reaction pathway of ethanol conversion over LaMn<sub>1-v</sub>Ni<sub>v</sub>O<sub>3</sub>. The strongly basic O-La-O sites are known to be active in ethanol activation;<sup>21</sup> however, the pathway for the possibility of ethanol chemisorption on La is excluded when considering only the effect of B-site substitution on LaMnO<sub>3</sub>. At the outset of the reaction, ethanol chemisorbs on the surface, and forms an ethoxide at the metal site (Mn or Ni) and a hydroxyl at the neighboring lattice oxygen site. Subsequent dehydration yields an acetaldehyde-derived intermediate and an oxygen vacancy. At low temperatures, the reduced surface is re-oxidized, and acetaldehyde is desorbed. At high temperatures, the acetaldehyde intermediate may associate with the surface bridging oxygen (Mn-O-Mn, Ni-O-Mn, or Ni–O–Ni) to form an acetyl, which is then converted to carbon oxides, water, and methane.62 Ethanol dehydrogenation to acetaldehyde was excluded in Fig. 10 because negligible conversion (less than 5%) of ethanol was identified without feeding  $O_2$  in our system.

The catalytic results show that acetaldehyde selectivities are nearly identical (above 80%) at temperatures below 225 °C.





Acetaldehyde is known to be derived through a redox cycle in ethanol oxidation.<sup>21,63</sup> Therefore, the redox properties for LaMnO<sub>3</sub>, LaNiO<sub>3</sub>, and LaMn<sub>1-v</sub>Ni<sub>v</sub>O<sub>3</sub> perovskites should be similar. Carbon dioxide selectivities of these catalysts increase differently with increasing temperature, implying changing oxidation power in converting the chemisorbed intermediate (herein acetyl species). In the proposed pathway, acetyl oxidation proceeds on the bridging oxygen in Mn-O-Mn, Ni-O-Mn, or Ni-O-Ni. The amount of CO2 increased abruptly over LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> at the lowest temperature (235  $^{\circ}$ C) of any of the tested perovskites, suggesting that its bridging oxygen was the most strongly oxidizing. This is attributed to the unique Ni-O-Mn interaction of LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub>, as revealed by the TPR test. To ascertain whether the Ni-O-Mn interaction in perovskite is uniquely responsible for its reactivity and acetaldehyde oxidation, catalytic tests of physically mixed LaNiO3 and LaMnO3 in LaNiO<sub>3</sub>-to-LaMnO<sub>3</sub> ratios of 0.1, 0.25, and 0.4 were conducted (see Fig. S5 and S6 of ESI<sup>†</sup>). The T<sub>50</sub> values of the physically mixed samples were in the range of 245 °C to 254 °C - about 20 °C higher than that of LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> but close to those of LaMn<sub>0.75</sub>Ni<sub>0.25</sub>O<sub>3</sub> and LaMn<sub>0.6</sub>Ni<sub>0.4</sub>O<sub>3</sub>. However, the T<sub>95</sub> values of the physically mixed samples exceeded their respective counterparts, ranging from 300 to 321 °C. For all samples, below 250 °C, acetaldehyde selectivity exceeded 80% and CO<sub>2</sub> selectivity was less than 20%. These results demonstrate that the Ni-O-Mn interaction in Ni-doped LaMnO3 promotes the conversion of ethanol and the oxidation of acetaldehyde to CO<sub>2</sub>.

Fig. 11 illustrates the evolution of time on-stream ethanol conversion over a 36 h period at 300 °C. Initially, ethanol was fully converted over LaMnO<sub>3</sub>, LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub>, and LaMn<sub>0.75</sub>. Ni<sub>0.25</sub>O<sub>3</sub>, while 93.7% and 91.9% conversions were achieved by LaMn<sub>0.6</sub>Ni<sub>0.4</sub>O<sub>3</sub> and LaNiO<sub>3</sub>, respectively. All catalysts suffered of ageing but at different extents. Ethanol conversion decreased from 100% to 96.2% for LaMnO<sub>3</sub> (a decrease of ~2.8%), 100% to 98.0% for LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> (a decrease of ~2.5%), 93.7% to 89.7% for LaMn<sub>0.6</sub>Ni<sub>0.4</sub>O<sub>3</sub> (a decrease of ~4.4%), and 91.9% to 78.6% for LaNiO<sub>3</sub> (a decrease of ~14.5%). Moreover, LaMn<sub>0.9</sub>Ni<sub>0.1</sub>O<sub>3</sub> remained its activity for more than 25 h, whereas deactivation



Fig. 11 Conversion of ethanol as a function of time on-stream over  $LaMn_{1-\nu}Ni_{\nu}O_3$  perovskites at 300 °C.

could be observed within 20 h for other catalysts. Apparently,  $LaMn_{0.9}Ni_{0.1}O_3$  has the highest thermal stability while  $LaNiO_3$  has the least among tested catalysts. Since coking is less likely to occur under oxygen-rich environments, agglomeration of catalyst particle and/or deconstruction of perovskite structure should be responsible for catalyst deactivation.<sup>64</sup> The SEM micrographs of freshly prepared and used  $LaMn_{1-y}Ni_yO_3$  after on-stream testing (see Fig. S7 of ESI†) further supported this claim: some welding and particle agglomeration could be identified on used samples; however, no carbon deposition (*e.g.*, carbon nanotubes) was specified. The high thermal stability of  $LaMn_{0.9}Ni_{0.1}O_3$  may, again, ascribe to the unique interaction between Ni and Mn, thereby suppressing the destruction of its perovskite framework.

#### Conclusions

Doping Ni into LaMnO<sub>3</sub> perovskite can substantially alter its physicochemical properties, and thereby changing its catalytic performances. A limited amount of Ni (less than 25%) can be dispersed in LaMnO<sub>3</sub> framework; adding more Ni forms segregated NiO<sub>x</sub> clusters. Incorporating Ni generates Ni–O–Mn sites, which are associated with a unique interaction, is assumed to play a key role in enhancing catalytic activity, acetaldehyde abatement, and stability in ethanol oxidation. A plausible mechanism based on the surface bridging oxygen site was thereby proposed. Future study should seek to clarify the nature of the bridging oxygen site, possibly through computational chemistry such as density functional theory,<sup>65</sup> to provide a molecular-level understanding of perovskite catalyst design.

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