# Catalysis Science & Technology

# PAPER

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Cite this: DOI: 10.1039/c8cy02248h

# Design and synthesis of a highly efficient heterogeneous MnCo<sub>2</sub>O<sub>4</sub> oxide catalyst for alcohol oxidation: DFT insight into the synergistic effect between oxygen deficiencies and bimetal species<sup>†</sup><sup>‡</sup>

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The synergistic effect in multi-active site catalysts is difficult to monitor, and the effect of their intrinsic mecha-

nism on their catalytic performance is important but very difficult to understand owing to the large quantities of active species. Based on the results of density functional theory, herein we report the design and synthesis of

an oxygen vacancy-abundant spinel-structured MnCo2O4 oxide as a highly efficient catalyst for alcohol oxida-

tion, which highlights the importance of the synergistic effect between oxygen deficiencies and bimetal species.

Received 30th October 2018, Accepted 8th December 2018

DOI: 10.1039/c8cy02248h

rsc.li/catalysis

# 1. Introduction

Selective oxidations of alcohols to aldehydes/ketones are important reactions in organic transformations.<sup>1</sup> Aldehydes and ketones, which are traditionally obtained by selective oxidation of alcohols in the presence of stoichiometric amounts of explosive oxidizing agents and strong mineral acids, are essential building blocks in organic synthesis.<sup>2</sup> To meet the requirements of green chemistry, homogeneous catalysts based on noble metals, including palladium,<sup>1e,3</sup> gold<sup>4</sup> and platinum,<sup>5</sup> have recently been developed for alcohol-oxidation catalytic systems that are free of mineral acids and/or explosive oxidizing agents. Because of the high costs and limited reserves of noble metals, non-noble metals, such as cobalt, manganese and copper, are preferable, and have also been investigated in this oxidation reaction.<sup>6</sup> The corresponding heterogeneous catalysts have attracted extensive attention due to the salient advantages of ease of separation and reuse.

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However, in most cases, additives such as (2,2,6,6tetramethylpiperidin-1-yl)oxyl (TEMPO) and/or explosive oxidizing agents are essential for improving the activity and selectivity of this oxidation reaction. Simultaneous enhancement of the catalytic activity and selectivity in the oxidation of alcohols, using recyclable earth-abundant metal catalysts without additives, is therefore desirable.

Earth-abundant metal-based oxides, such as Co3O4 and MnO<sub>2</sub>, have been widely used as catalysts in alcohol oxidations due to their recyclable nature. Compared with simple metal oxides, bimetal oxides may exhibit higher activity due to the synergistic effect between the different metal active species.7 For example, Huang and co-workers7b reported MnCo<sub>2</sub>O<sub>4</sub> catalysts as active catalytic components in the condensation of benzyl alcohol and aniline to synthesize imine. They found that redox couples with similar Mn(III)/Mn(II) and Co(III)/Co(II) ratios had the highest activity, probably because they gave the best synergistic effect.

In addition to the synergistic effect between the metal active species, defects are always mentioned in the literature when the metal oxides are doped with heteroatoms. Recently, oxygen vacancies (OVs) produced over bi-metal oxides as typical important defects were often mentioned in the oxygen evolution reaction<sup>8</sup> but rarely reported in organic transformations. It is well known that adsorption on a heterogeneous catalyst surface is commonly an essential step for obtaining catalytic activity. In this case, using MnCo<sub>2</sub>O<sub>4</sub> as a bi-metal oxide example, we performed DFT calculations to elucidate the effect of OVs on the adsorption process of benzyl alcohol molecules (Fig. 1). It is found that the adsorption on the  $MnCo_2O_4$  surface (1.13 eV, Fig. 1b) is energetically about 0.34



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<sup>†</sup> Q. Ke was supported by the Anhui Provincial Science Fund for Excellent Young Scholars (gxyqZD2018034). This work was supported by the National Science Foundation of China (grant numbers 21476001, 21776002, 21306142). The authors acknowledge Shenzhen HUASUAN Technology Co., Ltd for providing theory computation support.

<sup>‡</sup> Electronic supplementary information (ESI) available: Experimental section, and NMR. See DOI: 10.1039/c8cy02248h

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Fig. 1 Side view of benzyl alcohol molecules adsorbed on  $Co_3O_4$  (a),  $MnCo_2O_4$  (b) and defective  $MnCo_2O_4$  surfaces (c). Colour code: white is hydrogen, grey is carbon, red is oxygen, blue is cobalt, ice blue (yellow dotted frame) is manganese and transparent purple (yellow dotted frame) is oxygen vacancy.

eV more stable than that on the  $Co_3O_4$  surface (0.77 eV, Fig. 1a), which indicated the presence of the synergistic effect between the Co and Mn species. On the MnCo<sub>2</sub>O<sub>4</sub> surface, when OVs are present, the adsorption (2.96 eV, Fig. 1c) of the benzyl alcohol molecules is further enhanced. This result should be due to the fact that the octahedrally coordinated  $Co^{3+}$  center is more active towards the adsorption of the –OH group near an OV on the MnCo<sub>2</sub>O<sub>4</sub> surface, to achieve a coordination number of six, than on the MnCo<sub>2</sub>O<sub>4</sub> surface without an OV, highlighting the importance of the OV.

Herein,  $MnCo_2O_4$  spinel-structured catalysts are first put forward as ideal materials for investigating the synergistic effect between oxygen deficiencies and bimetal species in alcohol oxidations. The DFT calculations indicate that the oxygen deficiencies in  $MnCo_2O_4$  are of great importance in improving the adsorption stability and lowering the reaction energy.  $MnCo_2O_4$  catalysts with a high density of oxygen vacancies exhibit excellent aldehyde selectivity (selectivities greater than 99.9% for all examples including aromatic, substituted aromatic and heterocyclic) and good to excellent yields under mild conditions (60 °C, air). In addition, the mechanism for alcohol oxidation over  $MnCo_2O_4$  with different oxygen deficien-



Fig. 2 XRD (a) patterns of various bi-metal oxides, O 1s XPS spectra (b and c), SEM (d) and TEM (e and f) images of the  $MnCo_2O_4$  sample. The EDS mapping images (e–j) of the  $MnCo_2O_4$  sample shown in different colors: blue-Co-K, green-Mn-K and red-O-K.

cies was also studied by control experiments and DFT calculations.

### 2. Experimental

#### 2.1. Materials synthesis

Bimetal oxides were prepared by a hydrothermal method using urea as a precipitant. As a typical example for the preparation of pineapple-like spinel  $MnCo_2O_4$  nanorods (Co/Mn = 2:1), a homogeneous mixture was prepared by vigorously stirring cobalt(II) nitrate hexahydrate (20.0 mmol), manganese(II) acetate tetrahydrate (20.0 mmol) and ethylene glycol (80.0 mL) at room temperature for 20 min, then urea (80 mmol) was added into the mixture under vigorous stirring to form MnCo2O4 precursors. The precursors were stirred for 30 min at room temperature and transferred into a stainless steel autoclave for another 5 h at 150 °C. After filtration, a pink powder was dried at 80 °C for 10 h. Then, the final black catalysts of  $\sim 2$  g were obtained by calcination under an air atmosphere at 350 °C. As a comparison, the final black catalyst obtained by calcination under an oxygen atmosphere at 350 °C was denoted as T-MnCo2O4. Before calcining, the sample was treated in an oxygen atmosphere for 30 min with a flux of 30 mL  $min^{-1}$ . Metal oxides (Co<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub>) were prepared by the same method without adding the second metal salts.

#### 2.2. Catalytic activity test

A typical procedure for oxidation of alcohols was as follows. A mixture of 4-methylbenzyl alcohol (1 mmol), catalyst (150



Fig. 3  $O_2$ -TPD profiles of the synthesized  $Co_3O_4$ ,  $Mn_3O_4$ ,  $MnCo_2O_4$ , and T-MnCo\_2O\_4.

Cat. $Cat.$									
Entry	Catalyst	Temp./time	Conv. (%)	Sel (1a) (%)	Yield (%)	TON <sup>c</sup>			
1	_	60 °C/6 h	0	0	0	0			
2	FeCo <sub>2</sub> O <sub>4</sub>	60 °C/6 h	1.2	>99.9	1.2	0.01			
3	MoCo <sub>2</sub> O <sub>4</sub>	60 °C/6 h	0.5	>99.9	0.5	0.01			
4	CuCo <sub>2</sub> O <sub>4</sub>	60 °C/6 h	16.1	>99.9	16.1	0.18			
5	MnCo <sub>2</sub> O <sub>4</sub>	60 °C/4 h	93.7	>99.9	93.7	1.56			
6	MnCo <sub>2</sub> O <sub>4</sub>	60 °C/6 h	>99.9	>99.9	>99.9	1.11			
$7^a$	T-MnCo <sub>2</sub> O <sub>4</sub>	60 °C/6 h	79.4	>99.9	79.4	0.88			
8	CoO	60 °C/6 h	3.6	>99.9	3.6	0.04			
9	MnO	60 °C/6 h	0.2	>99.9	0.2	$\sim 0$			
10	$Co_3O_4$	60 °C/6 h	6.9	>99.9	6.9	0.08			
11	$Mn_3O_4$	60 °C/6 h	25.6	>99.9	25.6	0.28			
12	MnO <sub>2</sub>	60 °C/6 h	1.96	>99.9	1.96	0.02			
13	$Co(NO_3)_2$	60 °C/6 h	0.21	>99.9	0.21	$\sim 0$			
14	$Mn(OAc)_2$	60 °C/6 h	0.08	>99.9	0.08	$\sim 0$			
15	PdO	60 °C/6 h	0.85	>99.9	0.85	0.01			
16	CeO <sub>2</sub>	60 °C/6 h	0.20	>99.9	0.20	$\sim 0$			
17	$\tilde{Co_2Mn_3O_8}$	130 °C/18 h	_	_	76.0 (ref. 11)	0.42			
18	Co-NG-750	130 °C/5 h	94.8	97.5	92.4 (ref. 12)	1.85			
$19^b$	CoAl(OH) <i>x</i> /graphite oxide	120 °C/4 h	79.4	96.5	76.6 (ref. 13)	1.92			

Reaction conditions: catalyst (0.15 g), reactant (4-methyl benzyl alcohol, 1 mmol, 123  $\mu$ L), toluene (2 mL), open to air. <sup>*a*</sup> Catalyst was prepared by calcination under an oxygen atmosphere. <sup>*b*</sup> The reaction performed under 1 bar oxygen atmosphere, with DMF (5 mL) as the solvent. <sup>*c*</sup> Turnover number given in mol<sub>alcohol</sub> g<sub>Catal</sub><sup>-1</sup> is based on the conversion at 4–18 h.



Fig. 4 Co 2p (a-c) and Mn 2p (d-f) XPS spectra of the  $MnCo_2O_4$  sample, where a and d refer to the raw  $MnCo_2O_4$  sample; b and e refer to the used  $MnCo_2O_4$  sample under an air atmosphere; c and f refer to the used  $MnCo_2O_4$  sample under a nitrogen atmosphere.

mg), and toluene (2 mL) was added into a Schlenk flask. The mixture was stirred at 60 °C for 6 h under an air atmosphere. After reaction, the product was taken out of the mixture and analyzed using a gas chromatograph (GC, Agilent 7890B, USA) equipped with a flame ionization detector and an HP-5 column (30 m × 0.25 mm). The product yields are reported using both GC yields. The products were then characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.¶

#### 2.3. Catalyst reusability test

The procedure for oxidation of 4-methylbenzyl alcohol (1 mmol) is the same as that in section 2.2. The  $MnCo_2O_4$  catalyst (200 mg) was selected to evaluate the recyclability of the CMO-*n* catalysts. The used catalyst was separated from the

<sup>¶ 4-</sup>Methylbenzaldehyde, white oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.88 (s, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  191.97 (s), 145.54 (s), 134.20 (s), 129.77 (d, J = 12.0 Hz), 21.83 (s).



Fig. 5 Reaction energy profile for the two-step dehydrogenation process of benzyl alcohol; the red line is on the intact  $MnCo_2O_4$  surface and the black line on the defective  $MnCo_2O_4$  surface. Colour code follows Fig. 1.



Fig. 6 A plausible mechanism for alcohol oxidation over the  $MnCo_2O_4$  catalyst.

Table 2	Oxidation	of	alcohols	to	aldehy	/de



Fig. 7 Recyclability test of the MnCo<sub>2</sub>O<sub>4</sub> catalyst for oxidation of 4-methyl benzyl alcohol to 4-methyl benzyl aldehyde (a). O<sub>2</sub>-TPD spectra of MnCo<sub>2</sub>O<sub>4</sub> and used MnCo<sub>2</sub>O<sub>4</sub> catalysts (b).

reaction mixture by filtration, then the sample was washed with a certain quantity of ethanol, dried at 100  $^{\circ}$ C for 6 h and calcined at 500  $^{\circ}$ C for 4 h.

#### 2.4. Characterization

Unless mentioned otherwise, all manipulations were performed in an open environment. The products were characterized by using <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (101 MHz) spectroscopy using CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard. Mass spectra (MS) were measured on a Shimadzu GCMS-QP2010 Plus spectrometer (Shimadzu, Kyoto, Japan). The conversion of the reactant and the selectivity to the product were obtained using an Agilent 7890B chromatograph (Agilent, USA). The mesopore volumes and Brunauer-Emmett-Teller (BET) surface areas were determined by using a surface area and porosity analyzer (ASAP 2020, Micromeritics Inc., USA). SEM images were obtained with a field emission scanning electron microscope (NanoSEM 430, FEI, USA) operated at 15 kV. All the samples were coated with a thin layer of Au to prevent charging before scanning. Transmission electron microscopy (TEM) images of

$R^{1}_{-} OH \xrightarrow{Cat.} R^{1}_{-} OH \xrightarrow{Cat.} + Others$					
Entry	Product	Selectivity (%)	Yield (%)		
1		>99.9	81.7		
2		>99.9	>99.9		
3		>99.9	54.6		
4	o <sub>zN</sub> · · · ·	>99.9	77.5		
5		>99.9	96.5		

Reaction conditions: MnCo<sub>2</sub>O<sub>4</sub> (0.15 g), reactant (1 mmol), toluene (2 mL), open to air, 6 h.

the samples were taken on a JEM-2100 microscope, and the electron beam accelerating voltage was 200 kV (JEOL LTD., Japan). X-ray photoelectron spectroscopy (XPS) spectra were measured with a PHI-5000C ESCA system (Perkin-Elmer, USA) with Al K $\alpha$  radiation (hv = 1486.6 eV) for the X-ray source; the binding energies were calibrated using C 1s as a reference set at 284.6 eV. Temperature programmed oxidation (O<sub>2</sub>-TPD) was carried out on an automated chemisorption analyzer (Quantachrome Instruments, USA).

# 3. Results and discussion

#### 3.1. Structural and morphological characterization

A series of bimetal oxide catalysts were synthesized using urea as a precipitant. To shed light on the role that OVs play in alcohol oxidation, we prepared bi-metal oxides such as MnCo<sub>2</sub>O<sub>4</sub>, rich or poor in OVs, by calcining the corresponding precipitant in an air or oxygen atmosphere, respectively. The powder XRD patterns in Fig. 2a show that the synthesized Co-based bimetal oxide catalysts are spinel-type oxides; the corresponding heteroatom oxides are not observed for all Co-based spinel oxides. In the O 1s XPS spectra, the three peaks at 529.9, 530.6 and 531.6 eV were fitted according to previous research.9 For MnCo<sub>2</sub>O<sub>4</sub>, the sample rich in OVs (MnCo<sub>2</sub>O<sub>4</sub>, cal.O<sub>vac</sub>/cal.O<sub>Latt</sub> = 1.75) was obtained through calcination in an air atmosphere (Fig. 2b), while that poor in OVs (T-MnCo<sub>2</sub>O<sub>4</sub>, cal.O<sub>vac</sub>/cal.O<sub>Latt</sub> = 1.43) was achieved by calcination in an oxygen atmosphere (Fig. 2c), according to the O 1s XPS data. The SEM images show that the as-prepared MnCo<sub>2</sub>O<sub>4</sub> possesses pineapple-like morphologies (Fig. 2d). The TEM images show that  $MnCo_2O_4$  possesses abundant mesoporous structures (Fig. 2e) and its spinel type structure is also confirmed by TEM (Fig. 2f) based on the determined fringe separations. Different colors are clearly observed in the EDS mapping images: blue-Co-K, green-Mn-K and red-O-K.

The as-prepared  $MnCo_2O_4$ , rich or poor in OVs, was also confirmed by  $O_2$ -TPD experiments (Fig. 3). The  $O_2$ -TPD experiments were carried out to investigate the oxygen species over the synthesized Co and Mn oxides. Three oxygen desorption peaks were identified<sup>10</sup> at temperatures of 80–120 °C, 120– 450 °C and above 450 °C, which are assigned to molecular oxygen species adsorbed on oxygen vacancies (OVs), surface lattice oxygen or surface adsorbed oxygen ions,<sup>10</sup> and surface and bulk phase lattice oxygen. As shown in Fig. 3, the OV decomposition of the  $MnCo_2O_4$  sample was larger and broader (in the range of 80–120 °C) than those of  $Mn_3O_4$  and T-MnCo<sub>2</sub>O<sub>4</sub> samples.

#### 3.2. Catalytic performance

Next, we examined the catalytic performance of the asprepared bi-metal oxides for the oxidation of 4-methyl benzyl alcohol as a model substrate (Table 1). The reaction does not proceed without loading any catalyst. The desired product (1a) was observed over almost all the as-prepared bi-metal oxides (Table 1, entries 2–6). Among them,  $MnCo_2O_4$  was found to be the best choice for alcohol oxidation catalysis, and produced excellent yield (>99.9%) of the desired product (1a) in toluene at 60 °C under an open atmosphere for 6 h (Table 1, entry 6). Notably, the  $MnCo_2O_4$  catalyst gave the best catalytic performance; it was better than those reported for  $Co_2Mn_3O_8$ ,<sup>11</sup> Co-NG-750 (ref. 12) and Co/C-N700 (ref. 13) catalysts (Table 1, entries 17–19) under additive-free conditions. Meanwhile, the catalytic performance of  $MnCo_2O_4$  for this reaction is much better than the corresponding metal oxides and metal salts (Table 1, entries 8–14), confirming the existence of the synergistic effect between Co and Mn species for promoting alcohol oxidation.

It should be noted that there was a significant difference in the catalytic performance of  $MnCo_2O_4$  rich and poor in OVs; the desired yield of 99.9% over  $MnCo_2O_4$  (Table 1, entry 6), rich in OVs, is obviously higher than that of 79.4% over T-MnCo<sub>2</sub>O<sub>4</sub> poor in OVs (Table 1, entry 7). This result highlights the important role of OVs in spinel  $MnCo_2O_4$  oxide in alcohol oxidation catalysis.

#### 3.3. Role of Co and Mn species

A significant difference in the desired product yields over MnCo<sub>2</sub>O<sub>4</sub> was obtained when the reaction was performed under air (yield >99.9%) or nitrogen (yield = 36.3%). We used XPS to probe the oxidation states of Co, Mn and O of the MnCo<sub>2</sub>O<sub>4</sub> catalysts before and after reaction under an air or nitrogen atmosphere (Fig. 4). The oxidation state of Co was estimated as a ratio of  $Co^{3+}/Co^{2+} = 1.7$  in both the raw (Fig. 4a) and used MnCo<sub>2</sub>O<sub>4</sub> (air or nitrogen, Fig. 4b or c). Therefore, the Co species in the MnCo<sub>2</sub>O<sub>4</sub> catalyst should act as reactant adsorbents but not as active sites. Meanwhile, the oxidation state of Mn persisted at a ratio of  $Mn^{4+}/Mn^{3+} = 2.3$ (Fig. 4d and e). In contrast, the reduction of Mn  $(Mn^{4+}/Mn^{3+})$ = 1.8, Fig. 4f) was observed when  $MnCo_2O_4$  was subjected to reaction under a nitrogen atmosphere. There was an increase in the concentration of  $Mn^{3+}$  due to the reduction of  $Mn^{4+}$  to Mn<sup>3+</sup> by oxidation of alcohol to aldehyde, although this catalytic cycle was not completed owing to the absence of oxygen (the catalytic cycle will be provided in Fig. 6). Oxygen from air played an important role in the composite oxides<sup>14</sup> and also the MnCo2O4 catalyst to promote alcohol oxidation, which should be adsorbed onto Mn species before reaction and left as a water molecule after reacting with hydrogen from alcohol. The results based on the DFT calculations (Fig. 1), catalytic activity tests (Table 1) and the above discussion clearly stated the synergistic effect of Co and Mn species for promoting alcohol oxidation.

#### 3.4. Proposed mechanism

DFT calculations were firstly employed to investigate the role of OVs in alcohol oxidation. Fig. 5 shows the reaction energy profile for benzyl alcohol oxidation on the intact MnCo<sub>2</sub>O<sub>4</sub> surface (CMO) and defective MnCo<sub>2</sub>O<sub>4</sub> surface (D-CMO). As shown in the energy profile, the alcohol is easily adsorbed on D-CMO compared with CMO (II). Once the molecule is adsorbed on the surface, the hydrogen from -OH is bonded to oxygen defects by a hydrogen bond (III). Then, the first step dehydrogenation process initiates the whole reaction (IV): that is -OH is transferred to the neighboring O2c site. A previous study<sup>15</sup> showed that H on the O2c site can easily transfer to the neighboring site and expose an active site. The second hydrogen from the  $-CH_2$ - group is bonded to oxygen defects by a hydrogen bond (V). Then, the second step dehydrogenation process occurs from the  $-CH_2$ - group (VI). All of the adsorption and dehydrogenation processes are easily completed on O-CMO according to DFT calculations (Fig. 5), which indicates that the OV is of great importance in improving the adsorption stability and lowering the reaction energy.

Based on the above analysis and previous references,<sup>11</sup> a plausible mechanism for alcohol oxidation over the MnCo<sub>2</sub>O<sub>4</sub> catalyst is proposed in Fig. 6. Firstly, oxygen from air is adsorbed and activated on Mn sites (Fig. 6, a). Then, alcohol is diffused on MnCo2O4 and its -OH group is adsorbed by Co<sup>3+</sup> sites (Fig. 6, b). The hydrogen of the -OH group is bonded to oxygen vacancies through the hydrogen bond effect. This hydrogen-bond effect could decrease the O-H bond activation barrier from 0.32 eV to 0.24 eV (Fig. 5, III), and the same effect over the Fe-FeO/Pt(111) interface and Ni<sub>7</sub>O<sub>6</sub>/ Au(111) was also obtained.<sup>16</sup> The first-step dehydrogenation occurs from the -OH group and transfers to the Mn-O group. This process leads to the abstraction of a proton and the formation of an unstable metal-alkoxide species. The metalalkoxide species undergoes the second-step dehydrogenation (Fig. 6, from b to c). Finally, benzaldehyde is obtained and desorbed from the MnCo<sub>2</sub>O<sub>4</sub> surface (Fig. 6, d), and the catalytic cycle is completed by desorption of the water molecule from the MnCo<sub>2</sub>O<sub>4</sub> catalyst (Fig. 6, e).

#### 3.5. General applicability of the MnCo<sub>2</sub>O<sub>4</sub> catalyst

Finally, sub-scopes and limitations were evaluated over the  $MnCo_2O_4$  catalyst. Functionalized alcohols underwent aerial oxidation to the corresponding aldehydes (Table 2). Good to excellent yields (54.6%  $\geq$  99.9%) were obtained for alcohols containing electron-donating (-CH<sub>3</sub>) and strong electron-withdrawing (-NO<sub>2</sub>) groups. Notably, good aldehyde yields (77.5%) were obtained from alcohol containing a sulfur-containing heterocycle (Table 2, entry 4) over the MnCo<sub>2</sub>O<sub>4</sub> catalyst. The formation of the corresponding products from alcohols with heterocyclic products was more difficult over the reported  $Co_2Mn_3O_8$  (ref. 11) and Co/C-N700 (ref. 12) catalysts, and even with palladium-based coordination complexes.<sup>17</sup>

In addition to giving good to excellent aldehyde yields, MnCo<sub>2</sub>O<sub>4</sub> catalyzed the selective oxidation of 4-(methylthio)benzyl alcohol (Table 2, entry 5) to the corresponding 4-(methylthio) benzaldehyde in excellent yield (96.5%), which is industrially used as a raw material to produce sulindac.

#### 3.6. Stability of the MnCo<sub>2</sub>O<sub>4</sub> catalyst

Further investigations on the recyclability of  $MnCo_2O_4$  verify that the  $MnCo_2O_4$  catalyst is recyclable in alcohol oxidation,

since the catalytic performance was maintained after eight cycles (Fig. 7a). Before and after the reaction, the OV in the  $MnCo_2O_4$  catalyst shows no obvious difference in  $O_2$ -TPD patterns (Fig. 7b).

### Conclusions

In summary, by taking  $MnCo_2O_4$  spinel oxides as an example, we have clearly identified the importance of oxygen vacancies in alcohol oxidation catalysts besides the synergistic effect between (Co(m)/Co(n) and Mn(m)/Mn(n); these were confirmed by theoretical and experimental studies. The  $MnCo_2O_4$ catalyst with abundant oxygen vacancies  $(cal.O_{vac}/cal.O_{Latt} =$ 1.75) was prepared by calcination in air and showed excellent aldehyde selectivity (>99.9%) and good-to-excellent yields for alcohol oxidation under mild conditions (60 °C, additive-free and air as an oxidant). Tuning the catalytic performance of  $MnCo_2O_4$  by oxygen deficiencies and bi-metal redox couples offers atomic-level insights into the surface oxygen-metal species interactions toward the rational design of highperformance spinel oxide catalysts.

# Conflicts of interest

There are no conflicts to declare.

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