The effect of cerium incorporation on the catalytic performance of cobalt and manganese containing layer double oxides for acetone oxidation

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Abstract

BACKGROUND: Acetone is a volatile organic compound (VOC) that is often associated with poor air quality. Acetone has chronic toxicity towards humans and has significant impact to the overall atmospheric air quality. In this study, several layer double oxides (with $M^{2+} = \text{Mg, Ni, Co or Mn}$ and $M^{3+} = \text{Al or Ce}$) were tested as catalyst in acetone oxidation.

RESULTS: MnAl-LDO was found to be the most efficient catalyst. 50% acetone conversion was achieved at 170 °C ($T_{50\%}$) and 90% conversion at 200 °C ($T_{90\%}$). The incorporation of Ce on MnCeAl-LDO did not improve its catalytic properties over MnAl-LDO (the $T_{50\%}$ for MnCeAl-LDO was 12 °C higher than for MnAl-LDO). The good performance on MnAl-LDO was due to the presence of Mn^{3+} . MnAl-LDO was not affected when water was introduced into the catalytic reaction setup. Less than 5 % fluctuation in the acetone conversion rate at 170 and 200 °C was detected in the presence of 5.5% water. The incorporation of Ce on CoCeAl-LDO improved its catalytic performance over CoAl-LDO ($T_{50\%}$ of CoCeAl-LDO was 15 °C lower than CoAl-LDO). Our results showed that the good catalytic performance of CoCeAl-LDO was ascribed to the increased $\text{Co}^{2+}/\text{Co}^{3+}$ ratio and the abundance of lattice oxygen (O_{latt}).

CONCLUSION: MnAl-LDO has good catalytic properties for acetone oxidation, even under humid conditions. The LDO catalysts tested here can be developed into efficient catalysts for acetone oxidation and serve as functional materials for the

reduction in acetone or VOC emission.

Keywords: Hydrotalcite-derived oxides; Acetone; Catalytic oxidation; Active oxygen species; Low-temperature reduction

Introduction

Volatile organic compounds (VOCs) are a group of compounds that are often associated with air pollution. Various industrial processes and the use of fossil fuels contribute towards the release of a large amount of VOCs into the atmosphere. VOCs can crack into active free radicals, leading to the accumulation of photochemically active compounds. These photochemically active compounds pose significant environmental and health risks ^{1, 2} and their levels need to be kept low. Acetone (IUPAC preferred name: propan-2-one) is an example of a VOC that is extensively emitted. Acetone is emitted from the combustion of fossil fuels (e.g. transport and energy generation) and the incineration of household wastes. It is also a common organic solvent used in our everyday lives (in nail polish, paint thinner, adhesives etc). Acetone has chronic toxicity towards humans and has significant impact to the overall atmospheric air quality.

Various technological processes (such as adsorption, thermal processing and catalytic oxidation) have been developed to reduce the levels of acetone and other VOCs in the atmosphere³⁻⁶. Catalytic oxidation is generally regarded as an effective method for VOCs removal due to the high efficiency, low operation temperature, low energy consumption and the low abundance of harmful by-products^{7, 8}. Catalytic

oxidation of VOCs typically proceeds via the Mars-Van Krevelen (MVK) process^{9, 10}, in which VOC molecules are adsorbed onto the surface of the catalyst, it is then oxidized and desorbed. The catalyst is subsequently regenerated by oxidation with the oxygen in the air. The choice of the catalyst is important, as it will have a big impact on the overall efficiency of the process.

Several different types of materials have been considered as catalyst for VOC oxidation. Supported noble metal catalysts have shown good catalytic properties for the oxidation of VOCs, but their industrial application has so far been limited due to the high costs and low availability of the catalyst itself¹¹⁻¹³. Transition metals (including Fe, Cr, Cu, Ni, Co and Mn) are promising catalysts with variable valences and are able to facilitate fast electron transfer^{14, 15}. The cost of transition metals is low and they have high resistance towards sulfur and chlorine^{8, 16-18}. Mixed oxides (MnCuO, MnCeO, CoCeO and CoMnO) have demonstrated good catalytic performance¹⁹⁻²². Cerium oxide has also been reported to be effective catalyst for the oxidation of VOCs²³⁻²⁷. Konsolakis et al.²⁸ Chen et al.²⁹ and Carabineiro et al.³⁰ studied cerium containing mixed oxides (together with Co, Cu, Ni or La) and found that these oxides are good catalysis for oxidation of toluene or ethyl acetate. Unfortunately, heat treatment of some of these oxide catalysts (generally > 400 °C) can cause sintering and aggregation of the metal particles. Aggregation or sintering can rapidly diminish the catalytic functionalities of metal oxides^{23, 31}.

Layered double hydroxides (LDHs) have a characteristic lamellar structure and are known to intercalate various anions. LDHs, also referred to as hydrotalcite-like

compounds (HTLcs), have a general chemical formula of $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]_x(A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ ³², where M^{2+} and M^{3+} are divalent and trivalent metal cations that form a laminate with positive charges. The positive charges of LDHs layers are balanced by anions (A^{n-}) located between the layers. The anions are exchangeable, with the most typical anion being CO_3^{2-} . HTLcs with other anions (e.g. SO_4^{2-} , NO_3^- , Cl^- , OH^- , etc) have been synthesized by other researchers^{33, 34}. The cation compositions can also be varied by adjusting the ratio between M^{2+} and M^{3+} ($M^{2+} = \text{Ni}^{2+}$, Zn^{2+} , Cu^{2+} etc; $M^{3+} = \text{Fe}^{3+}$, Cr^{3+} , Al^{3+} etc), with M^{3+} ranging from 17 to 33 atomic % of the total number of cations³⁵⁻³⁷. LDHs are interesting because they have a large number of highly dispersed metal sites both on the external and internal surfaces^{38, 39}. The anions of LDHs can be removed by calcination at high temperatures (>400 °C) at which LDHs transform to layered double oxides (LDO), according to the reaction: $M_{1-x}^{2+}M_x^{3+}(\text{OH})_2(\text{CO}_3^{2-})_{x/2} \cdot m\text{H}_2\text{O} \rightarrow M_{1-x}^{2+}M_x^{3+}\text{O}_{1+x/2} + x/2\text{CO}_2 + (m+1)\text{H}_2\text{O}$ ⁴⁰ (Fig. 1).

Fig. 1 Schematic representation of decomposition of LDHs

LDOs have properties that make them interesting for catalysis. The cation composition of LDOs can be controlled by altering the synthesis procedures of LDHs^{15, 41}. The highly dispersed arrangement of the metal cations is preserved during the calcination LDHs to form LDOs, as the transformation proceeds via topochemical

transformation. Furthermore, as the metals ions are dispersed within the structure of LDO, it has the ability to inhibit the agglomeration of metal ions, which can prolong the life of the catalyst¹⁵. Other properties of LDOs, such as the high specific surface area and high thermal stability, make LDOs interesting candidate catalysts for VOCs removal.

The flexibility of LDOs means that metals such as Co and Mn can be included in the LDO structure. Co and Mn oxides have been found to be capable of mobilizing electrons and provide an electron mobile environment that favors catalytic processes. Thus, Co and Mn containing LDOs can be promising catalysts for VOCs oxidation. Aguilera et al.⁴² tested Cu-Mn and Co-CuLDOs for catalytic oxidation of VOCs (toluene, ethanol and butanol). These mixed oxides, however, were less efficient and required a higher reaction temperature when compared with other reported noble metal catalysts. Pérez et al.⁴³ found that the addition of Ce to Cu/CoMgAl-LDOs improved its catalytic performance due to the enhanced oxygen storage capacity.

In this work we synthesized and tested a series of LDOs as catalyst for acetone oxidation. We employed a wide range of analysis techniques in order to understand the catalytic properties of the LDOs. The effect of Ce addition onto LDOs was also investigated.

Materials and methods

Preparation of M/Al and MCeAl LDH

M/Al and M/CeAl (M= Mg^{2+} , Ni^{2+} , Co^{2+}) HTLc-like LDH materials were prepared by co-precipitation at low super-saturation⁴⁴. The molar ratio of $\text{M}^{2+}/\text{M}^{3+}$

was kept at 3:1, and the molar ratio of $\text{Al}^{3+}/\text{Ce}^{3+}$ was kept at 1:1. An example of the synthesis of Mg/Al LDH is presented here. Two solutions were prepared. The first solution (solution 1) was prepared in a beaker by dissolving the 0.36 mol of $\text{Mg}(\text{NO}_3)_2$ and 0.12 mol of $\text{Al}(\text{NO}_3)_3$ in 250 mL of ultrapure water. The second solution (solution 2) was prepared in a beaker by adding 0.24 mol of NaOH and 0.06 mol of Na_2CO_3 to 250 mL of ultrapure water. Both solution 1 and 2 were then added dropwise to a third beaker that contained 500 mL of ultrapure water under mechanical stirring and was kept at 40 °C (room temperature for MnAl and MnCeAl LDHs). The mixture in the third beaker was kept at pH 10 ± 0.2 by adjusting the addition rates of solutions 1 and 2. When both solutions were completely transferred to the third beaker, the obtained slurry was stirred for an additional 35 min and then aged at 70 °C (room temperature for MnAl and MnCeAl LDHs) in a temperature controlled water bath for 12 h. After aging, the precipitate was collected by filtration and washed with ultrapure water until the pH of the filtrate was neutral. The obtained solid product was dried at 70 °C in a vacuum oven for 16 h to obtain dried LDHs powder.

Calcination of LDHs

Calcination of the synthesized LDHs was carried out in air using a tube furnace at 400 °C for 5 h. The calcination of MgAl-LDH and MgCeAl-LDH was carried out in air at 600 °C for 4 h. After calcination, all catalysts were kept in a vacuum desiccator in order to minimize rehydration and transformation back to LDH. Calcination was performed to transform the LDHs to their respective LDO form.

Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku (Tokyo, Japan) powder X-ray diffractometer with Cu-K α radiation ($\lambda=0.154056$ nm) operated at 40 kV and 200mA for a 2θ range of 5-70° at a scan rate of 3°/min. The Joint Committee on Powder Diffraction Standards (JCPDS) database was used to identify the observed crystalline phases.

Nitrogen sorption/desorption experiments were performed on a Micromeritics (Norcross, USA) Tristar II 3020 surface area and porosity analyzer. Prior to the analysis, LDOs were degassed at 200 °C for 5 h under vacuum. Specific surface area was determined by using the Brunauer-Emmett-Teller (BET) equation. The total pore volume was determined by N₂ uptake at $p/p_0 = 0.97$. Pore size distributions were evaluated by the Barrett-Joyner-Halenda (BJH)–desorption method.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos (Manchester, UK) XSAM-800 spectrometer with Al- K α radiation under ultra-high vacuum; the C1s peak (284.8 eV) was used for calibration of the binding energies.

Temperature programmed reduction (TPR) experiments were carried out using a Micromeritics (Norcross, USA) TPD-TPR Autochem 2910 analyzer equipped with a thermal conductivity detector (TCD). The samples (44-48mg) were treated with a 50 mL/min flow of N₂:H₂ (90:10vol) gas at a heating rate of 20 °C/min from room temperature to 800 °C. High resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL (Tokyo, Japan) JEM-2100F transmission electron microscope.

Catalysts evaluation

Catalytic oxidation experiments were carried out in a fixed-bed quartz tube (8 mm i.d. × 200 mm length) under atmospheric pressure. LDO catalysts of 0.38-0.83 mm diameter were obtained by pelletizing, crushing and sieving. All LDO catalysts (0.15g) were activated at 100 °C in air for 60 min prior to the acetone oxidation reaction. After activation, a gas mixture containing 1000 ppm of acetone in 20 vol.% of O₂ and balanced by N₂ was introduced into the quartz tube at 82 mL/min. This setup gave a gas hourly space velocity (GHSV) of approximately 33,000 mL (g/h). The catalytic performance of the synthesized LDO catalysts was tested from 150 °C to 300 °C in 15 °C steps. The temperature was kept constant for 60 min at each measurement point. The temperature of the setup was monitored by a K-thermocouple located near the catalyst bed inside the quartz tube. The concentrations of the reactants and products were monitored on-line using a FuLi (Zhejiang, China) GC-9790 II gas chromatograph equipped with a flame ionization detector (FID). The presence of carbon dioxide (CO₂) was determined with a Ni catalyst converter placed in front of the FID. The converter was used to convert CO₂ into CH₄ in the presence of hydrogen. The VOC conversion rate was calculated as follows:

$$X_{\text{VOCs}} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

Where C_{in} and C_{out} are the inlet and outlet VOCs concentration at different temperatures, respectively.

The acetone oxidation efficiency was also evaluated by CO₂ generation as follows:

$$Y_{\text{VOCs}} = \frac{C_{\text{CO}_2}}{C_{\text{CO}_2}^*} \times 100\%$$

Where $C_{\text{CO}_2}^*$ is the outlet concentration of CO_2 when acetone is oxidized completely; C_{CO_2} is the outlet concentration of CO_2 at different temperatures.

Acetone oxidation was also carried out at 5.5% relative humidity (RH) to test the ability for the MnAl-LDO to withstand water. Water vapor was introduced into the gas mixture by saturation at the given temperature in order to obtain a relative volume of 5.5% water vapor.

Results and discussion

In this section we first present a general characterization (XRD and N_2 sorption) of all of the LDHs and LDOs synthesized by us. We also show the catalytic performance of the LDOs. Based on their catalytic properties, we then selected the most interesting LDOs (MnAl-, MnCeAl-, CoAl- and CoCeAl-LDOs) and performed further characterizations (TPR and XPS) on these LDOs in order to fully understand their catalytic properties.

Characterization and LDHs and LDOs

The powder XRD pattern of MgAl-, NiAl-, CoAl- and MnAl-LDHs synthesized in this study are shown in Fig.2A. The characteristic diffraction peaks of LDHs were observed at $2\theta = 10.9^\circ$, 22.2° , 34.2° , 38.6° , 44.8° , 60.1° , and 61.2° . These peaks corresponded to the (003), (006), (012), (015), (018), (110) and (113) crystal planes, respectively^{45, 46}. These characteristic peaks confirmed the successful synthesis of LDH compounds. For MnAl-LDH, there was a secondary phase with XRD peaks at $2\theta = 18.1^\circ$, 28.9° , 31.0° , 50.9° and 64.7° , which corresponded to Mn_3O_4 (JCPDS

75-1560).

Apart from the LDHs discussed above, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added to the synthesis (with $\text{Ce}:\text{Al} = 1:1$) of LDHs in order to investigate the effect of Ce. These LDHs are referred to as MgCeAl-, NiCeAl-, CoCeAl- and MnCeAl-LDHs. Their XRD patterns also showed characteristic XRD peaks of LDHs (Fig. 2B). However, the Ce containing LDHs had lower overall crystallinity when compared with MgAl-, NiAl-, CoAl- and MnAl-LDHs. Furthermore, a minor secondary phase at $2\theta = 28.5^\circ$ which was ascribed to the (101) crystal plane of $\text{Ce}(\text{OH})_4$ (JCPDS 19-0284). It is important to note that the formation of a minor secondary phase meant that a small amount of Ce was not incorporated into the LDH structure.

Fig.2 XRD patterns of samples before calcination (A) with various metal cations and (B) with Ce cation (● Mn_3O_4 and □ $\text{Ce}(\text{OH})_4$)

LDO catalysts were successfully obtained by calcination of the synthesized LDHs. Calcination was carried out at 400 °C in air for 5h for NiAl-, CoAl- and MnAl-LDHs, but 600 °C was required for MgAl-LDH. Fig. 3 showed that in all cases, the characteristic XRD peaks of LDHs were no longer observable. After calcination, diffraction peaks corresponding to the (111), (200) and (220) crystal planes of MgO were observed on the diffraction pattern of MnAl-LDO (Fig 3A insert). Diffraction peaks corresponding to the (101), (012) and (110) crystal planes (JCPDS 45-0946) of NiO (JCPDS 75-0197) were observed on the diffraction pattern of NiAl-LDO (Fig. 3A, blue). Diffraction peaks corresponding to the (111), (220), (311), (400), (422), (511) and (440) crystal planes were observed on the diffraction pattern of CoAl-LDO (Fig. 3A red). For MnAl-LDO, diffraction peaks corresponding to the (101), (112), (103), (211), (004), (220), (105), (312) and (224) crystal planes of Mn_3O_4 (JCPDS 24-0734), the (101), (212), (312) and (020) crystal planes of MnO_2 (JCPDS 43-1455), and the (222) and (523) crystal plane of Mn_2O_3 (JCPDS 65-7467) were observed after calcination (Fig. 3 black). The XRD patterns of the Ce incorporated LDHs after calcination (Fig. 3B) showed additional diffraction peaks at around $2\theta = 28.4^\circ$, 32.9° , 47.3° and 56.2° , these peaks corresponded to the (111), (200), (220) and (311) crystal planes of CeO_2 (JCPDS 81-0792). HRTEM images of these LDOs can be found in the supporting information.

Fig. 3 XRD patterns of LDH samples after calcination at 400 °C in air for 5 h (A) with various metal cations and (B) with Ce cation (■ HTLcs, Δ MgO, ∇ NiO, $\circ$ Co_3O_4 , $\star$ Mn_3O_4 , $\diamond$ CeO_2 , $\bullet$ MnO_2 , $\blacklozenge$ Mn_2O_3)

One typical property of LDOs is their high porosity and high specific surface area. N_2 adsorption was used to further characterize the LDOs. All LDOs in this study showed noticeable mesoporosity with high surface area and pore volume (Table 1). NiAl-LDO had the highest BET surface area of over $180 \text{ m}^2/\text{g}$ and the other LDOs all had BET surface area over $100 \text{ m}^2/\text{g}$. The total pore volume varied between 0.19 and $0.44 \text{ cm}^3/\text{g}$. The presence of Ce generally decreased the BET surface area of LDO.

Table 1 Catalytic activities, pore and surface properties of all catalysts.

Catalysts	T _{50%} of acetone oxidation (°C)	T _{90%} of acetone oxidation (°C)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
MgAl	320	355	121	0.41	10.7
MgCeAl	252	290	106	0.44	10.5
NiAl	244	275	189	0.26	7.1
NiCeAl	222	263	149	0.24	6.0
CoAl	198	220	127	0.19	4.8
CoCeAl	183	205	103	0.19	6.4
MnAl	170	200	144	0.27	10.3
MnCeAl	182	215	136	0.35	3.1

Catalytic activity of LDOs

The performance of the LDOs as catalysts for acetone oxidation was tested. Fig. 4A compares the performance of MgAl-, NiAl-, CoAl- and MnAl-LDO as catalysts in acetone oxidation. MnAl-LDO had the highest catalytic activity, with the 50% acetone conversion temperature (T_{50%}) at 170 °C, and 90% acetone conversion temperature (T_{90%}) at 200 °C. MnAl-LDO appeared to be a more effective catalyst than the ferrites and perovskites catalysts reported by Rezlescu et al.⁴⁷. CoAl-LDO had noticeable catalytic activity, with T_{50%} = 198 °C and T_{90%} = 220 °C. NiAl-LDO and MgAl-LDO also showed good catalytic activity with T_{50%} = 244 °C and T_{90%} =

275 °C for NiAl-LDO, and $T_{50\%} = 320$ °C and $T_{90\%} = 355$ °C for MgAl-LDO. The CO_2 generation of these LDOs adopted a similar trend as their catalytic activity as shown in Fig. 4B. It was clear that the presence of Mn and Co in the LDOs was favorable for acetone oxidation.

Fig.4 (A) Acetone oxidation light-off curves on MgAl, NiAl, CoAl, MnAl; (B) CO_2 generation light-off curves on MgAl, NiAl, CoAl, MnAl

The Ce incorporated LDOs were also tested for their catalytic performance in acetone oxidation (Fig. 5). The CoCeAl-, NiCeAl- and MgCeAl-LDOs showed an increase in catalytic activity over CoAl-, NiAl- and MgAl-LDO. The effect of Ce was most profound on MgAl-LDO, as the addition of Ce decreased the $T_{50\%}$ from 320 °C

for MgAl-LDO to 252 °C for MgCeAl-LDO. Unfortunately, MgCeAl-LDO was still less efficient than all of the other tested LDOs. The addition of Ce had an effect on NiAl- and CoAl-LDO as well. The $T_{50\%}$ of NiCeAl-LDO was 22 °C lower than for NiAl-LDO. The $T_{50\%}$ of CoCeAl-LDO was 15 °C lower than for CoAl-LDO. In contrast, Ce did not enhance the catalytic activity of MnAl-LDO. The $T_{50\%}$ for MnCeAl-LDO was 12 °C higher than for MnAl-LDO (an increase of 15 °C was observed for $T_{90\%}$). On a separate note, the catalytic performance of the tested LDO did not correlate with the amount of surface area and porosity available on the LDOs (see table 1 for comparison).

According to the acetone conversion temperatures ($T_{50\%}$ and $T_{100\%}$), MnAl-LDO and CoCeAl-LDO were the most effective catalysts in this study. In particular, MnAl-LDO showed the highest catalytic activity of all the tested LDOs.

Fig.5 (A) Acetone oxidation light-off curves on MgCeAl, NiCeAl, CoCeAl, MnCeAl; (B) CO₂ generation light-off curves on MgCeAl, NiCeAl, CoCeAl, MnCeAl.

Catalytic performance of MnAl-LDO under humid conditions

We further tested the best performing MnAl-LDO for acetone oxidation under humid conditions. In many industrial applications water vapor is present and can often deactivate the catalyst even at a low temperature⁴⁸. Fig. 6 shows the catalytic performance of MnAl-LDO when 5.5 vol.% H₂O was introduced to the stream at the 170 and at 200 °C ($T_{50\%}$ and $T_{90\%}$ of MnAl-LDO in dry conditions, respectively), the catalytic performance of MnAl-LDO was not noticeably affected. There was a slight fluctuation (less than 5 %) in the conversion rate at both temperatures when water was introduced into the system. We could conclude that the presence of water did not

affect the catalytic performance of MnAl-LDO in acetone oxidation. Furthermore, once water vapor was removed from the system, the acetone conversion rate rapidly restored to the original (dry) level at both temperatures. The slight fluctuation in the acetone conversion efficiency upon the introduction of water was believed to be related to the physisorption of water, which could be reversed when water vapor was removed from the system. Nevertheless, these results showed that the MnAl-LDO was not sensitive to water under these test conditions.

Fig. 6 Effect of water vapor on acetone conversion over the MnAl catalyst at 170, and 200 °C

TPR of MnAl-, MnCeAl-, CoAl- and CoCeAl-LDOs

As discussed in the previous sections, MnAl-LDO had the best overall catalytic properties for acetone oxidation. On the other hand, CoCeAl-LDO performed very comparably. In order to understand the role of Mn, Co and Ce in acetone oxidation, further characterization of the MnAl-, MnCeAl-, CoAl- and CoCeAl-LDOs were carried out. The TPR profiles of the MnAl- and, MnCeAl-LDOs are shown in Fig. 7A.

MnAl-LDO showed two main broad reduction peaks. The first broad peak was located between ~150 to 400 °C and corresponded to the reduction of MnO_2 (Mn^{4+}) and Mn_2O_3 (Mn^{3+}) to Mn_3O_4 (Mn^{3+} and Mn^{2+})⁴⁹. The second broad peak was located at ~ 400 to 500 °C, which corresponded to the reduction of Mn_3O_4 to MnO (Mn^{2+}). The addition of Ce in the MnAl-LDO had some effect on the overall TPR profile of the MnAl-LDO. The TPR profile of MnCeAl-LDO showed that the high temperature peak related to the reduction of Mn_3O_4 to MnO shifted to a lower temperature when compared with MnAl-LDO. The peak related to the reduction of MnO_2 and Mn_2O_3 to Mn_3O_4 remained relatively unchanged. This indicated that the reduction of Mn^{3+} to Mn^{2+} occurred more easily on MnCeAl-LDO than on MnAl-LDO, but there were no noticeable differences in the reduction of Mn^{4+} . An extra peak might related to the reduction of Ce^{4+} to Ce^{3+} was detected between around 310 and 370 °C. The TPR profile of CoAl-LDOs is displayed in Fig. 7B and it showed two reduction peaks. The first peak, between around 200 and 350 °C, was related to the reduction of Co^{3+} to Co^{2+} . The second peak was located at a much higher temperature (~700 °C) and was related to the reduction of Co^{2+} to Co^0 . The addition of Ce in CoAl-LDO shifted the peak related to the reduction of Co^{3+} to Co^{2+} to a lower temperature when compared with CoAl-LDO. This indicated that reduction of the Co^{3+} in CoCeAl-LDO occurred more easily than in CoAl-LDO. Furthermore, the peak related to the reduction of Co^{2+} to Co^0 also shifted to a lower temperature (to ~680 °C). The extra peak related to the reduction of Ce^{4+} to Ce^{3+} was not clearly observed and could be related to an overlap with the Co^{3+} to Co^{2+} reduction peak.

Fig. 7 Hydrogen TPR profiles for (A) Mn-catalysts (MnAl and MnCeAl) and (B) Co-catalysts (CoAl and CoCeAl)

H₂ consumption of LDOs and the relationship to their catalytic performance

In order to evaluate the reducibility of the LDOs, the H₂ consumption level was calculated from the first peak of the TPR profile. The H₂ consumption level increased in the following order: MnAl < CoAl < MnCeAl < CoCeAl. CoCeAl-LDO consumed the most H₂ of all LDOs tested, suggesting that it had the largest reduction capacity. Additionally, Ce also increased the H₂ consumption of Co containing LDOs.

The first TPR peak of MnAl- and MnCeAl-LDOs was located at a lower temperature than that on CoAl and CoCeAl-LDOs, which indicated that Mn containing LDOs was

more easily reduced than Co containing LDOs. An easily reduced catalyst would catalyze acetone oxidation more readily. This corresponded well with the catalytic performance of the various LDOs shown in Fig. 4 and 5, which showed that MnAl-LDO was the best performing catalyst with the lowest $T_{50\%}$ and $T_{90\%}$. The addition of Ce did not decrease the $T_{50\%}$ and $T_{90\%}$ of the Mn containing LDO. No enhancement on the catalytic performance due to Ce was observed.

The Ce in CoCeAl-LDOs decreased the reduction temperature of Co^{3+} , meaning that low oxidation state Co^{2+} could form more easily on CoCeAl-LDO than CoAl-LDO. This could also be the reason for the improved catalytic performance of CoCeAl-LDO. According to the TPR profile, the reduction temperature of CoCeAl-LDO was still higher than MnAl-LDO, but the H_2 consumption level of CoCeAl-LDO was also higher. This observation suggested that there were more sites or oxidative species available on CoCeAl-LDO than on CoAl-LDO. The combination of the relatively low reduction temperature and the high availability oxidative species are the reasons for the high catalytic activity of CoCeAl-LDO.

XPS analysis of MnAl-, MnCeAl-, CoAl- and CoCeAl-LDOs

The exact role of Ce in the tested LDOs was further investigated by XPS. Fig. 8A shows the XPS spectra of Mn 2p on MnAl- and MnCeAl-LDO. Table 2 lists the molar ratio of the different metal species in MnAl-, MnCeAl-, CoAl- and CoCeAl-LDOs. The asymmetrical Mn 2p_{3/2} spectra could be separated into three components, at BE = 640.6-640.9 eV, 641.2-642.1 eV and 643.5-644.0 eV. These peaks were attributed to surface Mn^{2+} , Mn^{3+} and Mn^{4+} species⁵⁰. Table 2 shows that

the $\text{Mn}^{4+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$ ratio was essentially the same for MnAl- and MnCeAl-LDO. The addition of Ce did not affect the Mn^{4+} content. The $\text{Mn}^{3+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$ ratio was 0.47 on MnAl-LDO, but reduced to 0.34 on MnCeAl-LDO. The decreased presence of Mn^{3+} on MnCeAl-LDO was coupled with the increase in the $\text{Mn}^{2+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$ ratio, which went from 0.09 on MnAl-LDO to 0.21 on MnCeAl-LDO. TPR profile also revealed that Mn^{3+} reduction to Mn^{2+} occurred at a lower temperature on MnCeAl-LDO than on MnAl-LDO (Fig. 6A). We, therefore, could concluded that the presence of Ce in MnCeAl-LDO promoted the presences of Mn^{2+} , possibly by the reduction of Mn^{3+} or by Ce occupation of the M^{3+} sites.

Fig. 8 XPS spectra of CoAl, CoCeAl, MnAl and MnCeAl: (A)fitted Mn 2p photoelectron, (B)fitted Co 2p photoelectron, (C)fitted Ce 3d photoelectron and (D1-D4) fitted O 1s photoelectron

Table 2. XPS analysis of the CoAl, CoCeAl, MnAl and MnCeAl catalysts.

Samples	$\text{Co}^{2+}/\text{Co}^{3+}$	$\text{Mn}^{3+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$	$\text{Mn}^{4+}/(\text{Mn}^{2+}+\text{Mn}^{3+}+\text{Mn}^{4+})$	$\text{Ce}^{3+}/\text{Ce}^{4+}$	$\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$
CoAl	1.89	--	--	--	2.78
CoCeAl	2.70	--	--	0.24	3.57
MnAl	--	0.47	0.44	--	1.41
MnCeAl	--	0.34	0.45	0.21	1.33

The difference in catalytic activity between MnAl- and MnCeAl-LDO may be linked to the changes in the oxidation states of Mn upon the addition of Ce. As the Mn^{4+} content were the same in both MnAl- and MnCeAl-LDO (Table 2), we could conclude that the Mn^{4+} content was not responsible for the differences in the catalytic activity between the two LDOs. On the other hand, the difference in the Mn^{3+} and Mn^{2+} content between MnAl-LDO and MnCeAl-LDO affected catalytic performance of these catalysts. The decrease presence on Mn^{3+} (or the increased presence of Mn^{2+}) appeared to have lowered the performance of MnCeAl-LDO ($T_{90\%} = 215\text{ }^{\circ}\text{C}$) when compared with MnAl-LDO ($T_{90\%} = 200\text{ }^{\circ}\text{C}$). The results here showed that the Mn^{3+} content was related to catalytic performance of MnAl- and MnCeAl-LDO in acetone oxidation. Other researchers reported that oxidation state of Mn affected the performance of manganese oxide catalysts for VOC oxidation significantly, and that the active oxygen species also played an important role (discussed later)⁵¹⁻⁵⁴.

The Co 2p XPS spectra of CoAl- and CoCeAl-LDO are shown in Fig. 8B and the data are summarized in Table 2. According to the report by Gautier et al.⁵⁵, the Co 2p peak shown in Fig. 8B was split into a spin-orbit doublets (A1 and A2) and three satellite peaks (B1, B2 and B3): A1 with a binding energy (BE) of 779.8-780.7 eV (a $2p_{3/2}$ - $2p_{1/2}$ splitting of 14.9 eV) corresponded to surface Co^{3+} species; and A2 with BE of 781.2-782.4 eV (a $2p_{3/2}$ - $2p_{1/2}$ splitting of 15.1 eV) corresponded to surface Co^{2+} ^{56, 57}. The surface $\text{Co}^{2+}/\text{Co}^{3+}$ molar ratio of CoCeAl-LDO (2.70) was higher than CoAl-LDO (1.89). One possible reason was that Co^{3+} was more easily reduced to Co^{2+} upon the Ce incorporation, as revealed by TPR (Fig. 7B). It was also possible that

M^{3+} sites became occupied by Ce^{3+} ⁵⁸. The increased Co^{2+}/Co^{3+} ratio was likely to have a role in the improved catalytic activity observed for CoCeAl-LDO over CoAl-LDO.

The Ce 3d XPS spectra of CoCeAl- and MnCeAl-LDO are shown in Fig. 8C with the u and v peaks labeled accordingly. There were two peaks at BE = 884.1-884.7 eV and 902.1-903.7 eV. These were ascribed to the characteristics peaks of the Ce^{3+} species, while the other six peaks proved the existence of Ce^{4+} species^{59, 60}. On both CoCeAl- and MnCeAl-LDO, Ce^{3+} existed at low Ce^{3+}/Ce^{4+} ratios. The detected Ce^{3+} is believed to occupy the M^{3+} sites on the LDO structure. The low Ce^{3+} content suggests that Ce incorporation onto the LDO was partial. The Ce^{4+} content may not be part of the LDO structure. Ce^{4+} (as $Ce(OH)_4$) was detected by XRD on all Ce containing LDHs (Fig. 2B).

Fig. 8D showed O 1s spectra of CoAl and CoCeAl. Two major types of oxygen atoms were detected by XPS; lattice oxygen (O_{latt}) and adsorbed oxygen (O_{ads}). The O 1S XPS spectra could be divided into three components: the peaks at 529.7-530.4 eV were assigned to O_{latt} ⁶¹, the peaks at 531.3-531.7 eV were allocated to O_{ads} ⁶²; and the peaks at BE=532.1-532.8 eV were assigned to surface oxygen from OH groups or molecular water species⁶³. The O_{latt}/O_{ads} molar ratio of CoAl-LDO was markedly higher than MnAl-LDO. The high abundance of O_{latt} on CoAl-LDO matched its high H_2 consumption rate when compared with the MnAl-LDO, as shown by the TPR data (Fig. 7). The addition of Ce further increased the O_{latt}/O_{ads} ratio on CoCeAl-LDO, but decreased the O_{latt}/O_{ads} ratio on MnCeAl-LDO. The high O_{latt}/O_{ads} ratio of

CoCeAl-LDO corresponded well with its enhanced catalytic activity over CoAl-LDO. In contrast, the decreased $O_{\text{latt}}/O_{\text{ads}}$ content on MnCeAl-LDO also corresponded to the reduced catalytic activity when compared with MnAl-LDO. These results suggested that O_{latt} played an important catalytic role in acetone oxidation. The participation of the O_{latt} from CoCeAl-LDO and MnAl-LDO catalysts in the acetone oxidation was reported by other researchers, even though O_{latt} species are typically released only at high temperatures. Liu. et al reported that O_{latt} could desorb at low temperatures and participate in the catalytic oxidation through a suprafacial mechanism ⁶⁴. Li. et al reported that O_{latt} benefited benzene oxidation on CuCo-based catalyst derived from LDHs ¹⁵. Their findings further supported our observations with regards to the importance of O_{latt} in catalytic oxidation of acetone. In summary, the oxidation state of the metal and the abundance of O_{latt} are both important factors for the overall performance of LDO catalysts in acetone oxidation. (Note that we were not able to analyze the effect of each factor separately based on our data)

Conclusion

A series of layered double oxides (LDOs) with $M^{2+} = \text{Mg, Ni, Co or Mn}$ and $M^{3+} = \text{Al or Al with Ce}$, were obtained by calcination of their respected layer double hydroxides (LDHs). These LDOs were found to be efficient catalysts in acetone oxidation. MnAl-LDO was the best performing LDO with $T_{50\%} = 170\text{ }^{\circ}\text{C}$ and $T_{90\%} = 200\text{ }^{\circ}\text{C}$. The surface area and porosity of the LDOs played no obvious role in the catalytic performance of the LDOs. The presence of Ce in MnCeAl-LDO increased the abundance of Mn^{2+} but lowered its catalytic performance when compared with

MnAl-LDO. TPR studies of the LDOs revealed that the good catalytic performance of MnAl-LDO was related to the low reduction temperature. The presence of Ce in CoCeAl-LDO improved its catalytic performance over CoAl-LDO. The presence of Ce also increased the relative content of Co^{2+} and increased the abundance of lattice oxygen (O_{latt}) species significantly, both of which enhanced the catalytic performance of CoCeAl-LDO. The catalytic performance of MnAl-LDO in acetone oxidation was not affected by the presence of water. In short, we showed here that MnAl-LDO as well as other LDOs can be promising catalysts for acetone oxidation. These LDOs can be developed into functional materials for the reduction of atmospheric VOC levels.

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