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Promotion effect of Ga-Co spinel derived from layered double hydroxides for toluene oxidation

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Considering the radius similarity of Al^{3+} (0.50 Å) and Ga^{3+} (0.62 Å), Al-Co and Ga-Co layered double hydroxides (LDH) was prepared as precursor to improve the synergetic interaction of the transition metals. The Al-Co and Ga-Co spinel catalysts were obtained by the following calcination for the toluene oxidation. The Ga-Co ($E_a = 79.5 \text{ kJ mol}^{-1}$) showed higher activity than the Al-Co ($E_a = 95.4 \text{ kJ mol}^{-1}$), and it exhibited excellent stability and resistance to carbon deposition during a 50 h reaction period at 300 °C. Characterization results indicated that the improved activity of Ga-Co spinel could be attributed to the higher reducibility (H_2 -TPR), more surface Co^{3+} and adsorbed oxygen in quantity (XPS) and adsorbed toluene (Toluene-TPD) than Al-Co spinel. Compared with traditional Ga-Co binary catalyst, the spinel structure possessed more B-sites cations outermost of the surface and surface oxygen vacancies for the toluene adsorption and ring-open reaction.

Volatile organic compounds (VOCs), derived from the prevailing energy and transport technologies, became a serious problem due to its short- and long-term health risks.^[1] Catalytic oxidation is one of the most effective technologies for the VOCs removal at low temperature.^[2] The reported catalysts for the VOCs oxidation can be classified into two categories.^[3] (1) Supported noble metal catalysts usually exhibit high catalytic activity. However, the disadvantages of these catalysts, such as limited resources, easy poisoning and sintering, hinder their widely industrial applications.^[4] (2) Transition metal oxides usually possessed high thermal stability, good resistant to poisoning and low cost.^[5] Co-based catalyst exhibited good catalytic activity for toluene oxidation due to its multivalent nature and nonstoichiometric composition. These properties favor the adsorption and activation of VOCs and O_2 , even though it shows less effective as compared to the noble metal.^[6] Our previous work reported the Al-Co spinel catalysts, derived from layered double hydroxides (LDH), possessed excellent activity and thermally stable for the VOCs oxidation.^[7]

LDH, a large family of two-dimensional materials, can serve as a precursor and improve the dispersion of active components on catalyst support. The general formula is $[\text{M}_1^{2+}\text{M}_2^{3+}(\text{OH})_2]^{x+}[\text{A}_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are metal cations, respectively. A^{n-} is a counter anion and $x = 0.17\text{--}0.33$

defined by $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ ratio.^[8] LDH precursors can generate a variety of spinel oxides through controlled thermal decomposition. Transformation of the LDH precursors into spinel oxides is a topotactic process because the layers comprise ordered and uniformly distributed metal cations.^[9] The obtained spinel oxides usually possess a higher surface area and metal cations with a better dispersion capacity and good thermal stability.^[10] In this work, The BET surface areas are summarized in Table 1, the specific surface area of Al-Co spinel and Ga-Co spinel are 120.9 and 84.5 $\text{m}^2 \text{g}^{-1}$, respectively.

In Al-Co LDH, Co is the active element and Al is typically an inert component. It would be interesting to study the effects of replacing the inert component Al^{3+} with a trivalent metal (M^{3+}), which has catalytic activity. Considering the limitations of LDH formations, such as those related to the valence of metal cations and the sizes of the M^{2+} and M^{3+} radii, the candidate should maintain a valence state that is trivalent and has a cationic radius that is similar to Al^{3+} (0.50 Å). Thus, a good candidate is suggested to be Ga in Group 13 in the periodic table.^[11] A Ga-based catalyst was also found to exhibit better catalytic performance with respect to the destruction of volatile aromatic pollutants in photocatalysts.^[12] Alternatively, Ga-Co spinel is a highly efficient electrochemical catalyst because of the existence of oxygen vacancies.^[13] Recently, the mixed spinel oxides that containing Co, Ni and Ga, have different Co/Ni ratios, and implement Ga as the trivalent metal cations derived from LDH, demonstrate higher capacitance during the oxygen evolution reaction.^[14] In addition, the structures and properties of the obtained spinel oxides can be modified by altering the composition of the LDH precursors.^[10] Therefore, combining Co and Ga may be a promising strategy to improve the VOCs oxidation.

To the best of our knowledge, there are very few reports on the Co-Ga based catalysts for VOCs oxidation. Here, we report on the synthesis of a Co-Ga spinel that uses LDH as a catalyst precursor, and the catalytic oxidation of toluene in terms of catalyst performance.

XRD patterns of the as-prepared precursors of Ga-Co LDH and Al-Co LDH are presented in Figure S1(Supporting Information). The corresponding patterns of the LDH with the characteristic reflections at 2θ values of 11.8°, 23.7° and 34.6° corresponding to (003), (006) and (012) planes of crystalline Al-Co LDH, respectively. Furthermore, no detectable impurity phases can be observed. Compared with the peaks of Al-Co LDH, a slight peak down shift was observed for Ga-Co LDH. It can be due to the radius difference between Ga^{3+} (0.62 Å) and Al^{3+} (0.50 Å), resulting in a perturbation within the hydroxalite lattice.^[15]

Figure 1 illustrates the XRD patterns of Al-Co spinel, Ga-Co spinel and Ga-Co sol-gel calcined at 500 °C. For Al-Co spinel, all the peaks for Al-Co spinel between the standard peaks of AlCo_2O_4 , Al_2CoO_4 and Co_3O_4 ,

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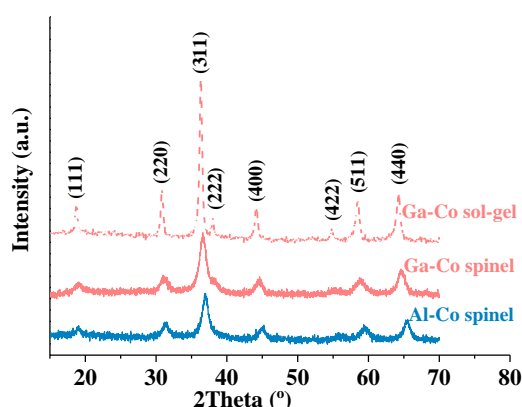


Figure 1. XRD spectra Al-Co spinel, Ga-Co spinel and Ga-Co sol-gel.

these peaks can be indexed to the spinel oxide phases (Co_2AlO_4 , JCPDS 38-0814; CoAl_2O_4 , JCPDS 44-0160; Co_3O_4 , JCPDS 74-2120).^[7b, 7c] All the peaks for Ga-Co spinel and Ga-Co sol-gel are between the standard peaks of Ga_2CoO_4 and Co_3O_4 , which were attributed to the mixed spinel oxide phases (CoGa_2O_4 , JCPDS 11-0698; Co_3O_4 , JCPDS 74-2120).^[14] But we cannot assign these peaks to the specific phases of spinel, because several spinel phases (AlCo_2O_4 , Al_2CoO_4 , CoGa_2O_4 and Co_3O_4) have the relatively close XRD peak positions. Therefore, we preferred to assign the XRD patterns to the combination or mixture of these spinel species. The similar results were also reported in previous works.^[7b, 7c, 14] Meanwhile, the average crystallite sizes of all samples were calculated by X-ray diffraction with the Scherrer equation. The average crystallite sizes of Al-Co and Ga-Co spinels are 7.8 and 8.4 nm, respectively; however, for the Ga-Co sol-gel that does not use LDH as the catalyst precursor, the size is 34.7 nm. Thus, it can be seen that implementing LDH as the catalyst precursor is conducive to the formation of smaller catalytic nanoparticles, which is essential to the improvement of the catalytic activity and stability.

Compared with **Figure S1**, the peaks corresponding to LDH disappeared, replaced by the peaks of mixed spinel oxide, indicating that the LDH structure was completely transformed into the mixed spinel oxide after calcination. The main reason is that the gallium (aluminum) and cobalt ions are uniformly distributed at the atomic level in the layers of LDH, which is beneficial for forming the spinel structure.^[9] The mixed metal oxide spinel is our target catalysts, and it was found to exhibit higher activity and thermal stability as compared to monophasic metal oxides, this is

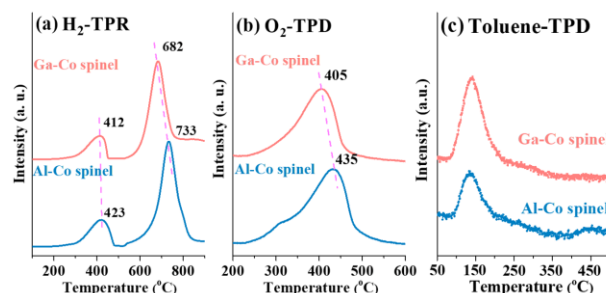


Figure 2. H_2 -TPR spectra (a), O_2 -TPD spectra (b) and Toluene-TPD spectra (c) of Ga-Co spinel and Al-Co spinel.

because it had a larger surface area and increased spinel geometry, which thus significantly affected the monomer yield via increased catalytic activity.^[16]

The redox ability of the as-obtained Ga-Co spinel and Al-Co spinel were studied using the H_2 -TPR and O_2 -TPD techniques, as presented in **Figure 2a-b**, respectively. There were two peaks in the H_2 -TPR profile of each sample. The reduction peaks at 412 °C and 682 °C are attributed to the reduction of Co^{3+} to Co^{2+} and then Co^{2+} to metallic cobalt, respectively.^[17] Comparing the peaks of Al-Co spinel revealed that all peaks of the Ga-Co spinel tended toward lower temperatures, indicating that the Ga in the Ga-Co spinel can promote the reduction of Co^{3+} . The similar results were also reported by He et al.^[18] who studied the $\text{CoGa-ZnAl-LDO}/\gamma\text{-Al}_2\text{O}_3$ catalyst for higher alcohol synthesis from syngas. Thus, the Ga-Co spinel exhibited better low-temperature reducibility than the Al-Co spinel. The O_2 -TPD results can further confirm this viewpoint, as it can be seen that the O_2 desorption temperature of the Ga-Co spinel (405 °C) is lower than that of the Al-Co spinel (435 °C); this suggests that Ga promotes low-temperature oxygen species adsorption in the Ga-Co spinel. Note that better low-temperature reducibility is beneficial to improving toluene oxidation. Quantitative analysis of the O_2 -TPD profiles and the oxygen amount were respectively performed and calculated by using the normalization method described in **Table 1**. It can be seen that the oxygen amount per unit area of Ga-Co spinel ($7.5 \mu\text{mol m}^{-2}$) is higher than that of Al-Co spinel ($5.7 \mu\text{mol m}^{-2}$).

The toluene-TPD experiment was performed to further investigate the difference of toluene adsorption capacity of Ga-Co and Al-Co spinel, as presented in **Figure 2c**. Only one toluene desorption peak at 150 °C was found for both samples. Additionally, Ga-Co spinel exhibited a higher toluene adsorption amount ($0.043 \mu\text{mol m}^{-2}$) than Al-Co spinel ($0.021 \mu\text{mol m}^{-2}$), suggesting that the Ga-Co spinel adsorbs more toluene species than the Al-Co spinel. As known, the first step of the toluene

Table 1. BET surface areas, surface element compositions, oxygen amount (O_2 -TPD), toluene adsorption amount (Toluene-TPD), toluene conversion and apparent activation energy (E_a) of Ga-Co spinel and Al-Co spinel.

Catalysts	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Surface element molar ratio (XPS)		Oxygen amount ($\mu\text{mol m}^{-2}$)	Toluene adsorption amount ($\mu\text{mol m}^{-2}$)	Toluene conversion (°C) and apparent activation energy (kJ mol^{-1})		
		$\text{Co}^{3+}/\text{Co}^{2+}$	$\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$			T_{50}	T_{90}	E_a
Al-Co spinel	120.9	0.90	0.59	5.7	0.021	305	320	95.4
Ga-Co spinel	84.5	1.47(1.45) ^a	0.73(0.68) ^a	7.5	0.043	275	288	79.5

^a the surface element molar ratio (XPS) of Ga-Co spinel after 50 h stability at 300 °C.

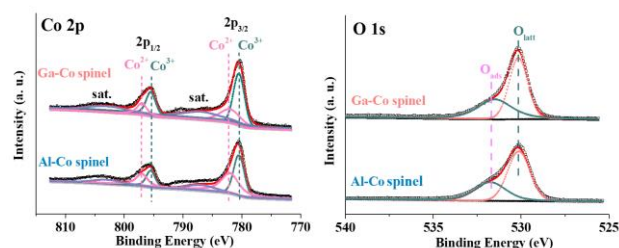


Figure 3. XPS spectra of Ga-Co spinel and Al-Co spinel.

oxidation is its adsorption on catalyst surface.^[19] Thus, it can be deduced that the Ga-Co spinel provides more adsorbed toluene species for reaction, thereby increasing the reaction rate.

XPS is an effective surface analysis technique to study the surface metal oxidation states and the adsorbed species over the surface of a sample. **Figure 3** shows the XPS spectra of Co 2p and O 1s for Ga-Co spinel and Al-Co spinel. The Co 2p_{3/2} and Co 2p_{1/2} peaks were located at ~780 and 795 eV. The Co 2p spectra were decomposed into Co²⁺ and Co³⁺ signals with additional satellites. The peaks at ~780 and 795 eV were assigned to Co²⁺, while the peaks at 782 and 797 eV were assigned to Co³⁺.^[20] The fitted O 1s spectra displayed two major oxygen contributions centered at ~530 and 532 eV. These bands can be attributed to the surface lattice oxygen (O_{latt}) species and surface adsorbed oxygen (O_{ads}) species.^[21]

According to the quantitative analysis of the XPS spectra, the surface Co³⁺/Co²⁺ and O_{ads}/O_{latt} atomic ratios were calculated as summarized in **Table 1**. The surface Co³⁺/Co²⁺ ratio of the Ga-Co spinel (1.47) is higher than that of the Al-Co spinel (0.90), and the surface O_{ads}/O_{latt} molar ratio of the Ga-Co spinel (0.73) is higher than that of the Al-Co spinel (0.59); this proves that the Ga-Co spinel is more abundant in surface Co³⁺ and O_{ads} species than the Al-Co spinel. According to the conclusions of Ye et al.^[6d] and Li et al.^[7a], the samples with a higher proportion of Co³⁺ and O_{ads} species showed higher catalytic performance because the adsorbed oxygen species could attack an organic molecule and thus facilitate the degradation of carbon skeletons as toluene is fully oxidized.^[22]

The XPS spectra for Ga 3d (Ga-Co spinel) and Al 2p (Al-Co spinel) are presented in **Figure S2**. The Ga 3d spectra were resolved into two individual component peaks (19.6 eV and 22.4 eV); this phenomenon is attributed to the fact that Ga is in the form of a Ga-Co spinel rather than the pure Ga₂O₃ (20.5 eV).^[23] In addition, the binding energy (BE) of Al 2p are shown to be located at 73.8 eV for Al-Co spinel; this is in agreement with the BE results of Al that have been observed in the spinel of Co-Al.^[24] These results are also consistent with the XRD results, which show that no other monophasic impurities (Ga₂O₃ or Al₂O₃ phase) were formed in the Ga-Co or Al-Co spinel.

Toluene oxidation over Ga-Co spinel, Al-Co spinel and Ga-Co sol-gel catalysts were measured in the range of 250–360 °C. Evaluation of the catalytic performance of all samples is presented in **Figure 4a**. No carbon-containing products other

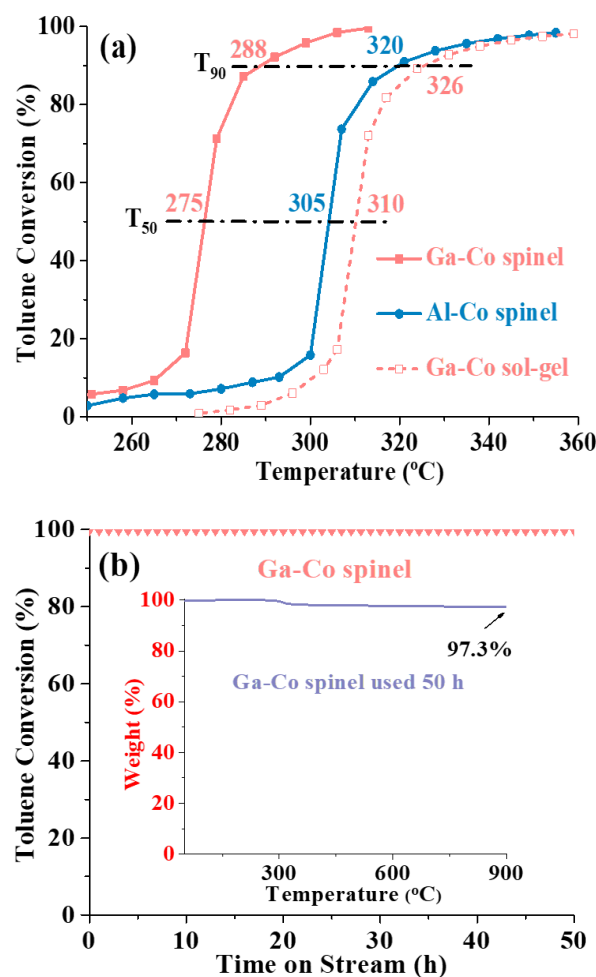


Figure 4. Toluene conversion over Ga-Co spinel, Al-Co spinel and Ga-Co sol-gel (a), long-term stability of Ga-Co spinel at 300 °C and TG curve (insert) for Ga-Co spinel after 50 h stability (b). Reaction conditions: 0.10 g catalyst, 1000 ppm toluene, 20% O₂, balance N₂, total flow rate = 100 mL min⁻¹, WHSV = 60000 mL g⁻¹ h⁻¹.

than CO₂ were detected in the catalytic system, which was confirmed by a carbon balance of 99.5% in each run. T₅₀ and T₉₀ (corresponding to toluene conversion = 50 and 90%) are summarized in **Table 1**.

These results suggest that the catalytic activity increased in the following order: Ga-Co spinel > Al-Co spinel > Ga-Co sol-gel. It is important to note that Ga-Co spinel (T₉₀ = 284 °C) is much more active than Ga-Co sol-gel (T₉₀ = 326 °C), meaning that implementing LDH as the catalyst precursor facilitates toluene conversion; this is primarily because the Ga-Co spinel nanoparticles derived from Ga-Co LDH are smaller than the Ga-Co catalysts employed in the citrate sol-gel method. It is well known that a smaller catalyst nanoparticle size corresponds to a higher number of active sites exposed on the catalyst surface, which thus increase the catalytic activity. Additionally, Ga-Co

spinel is also much more active than Al-Co spinel ($T_{90} = 320\text{ }^{\circ}\text{C}$) in toluene oxidation.

As compared to the Al-Co spinel, the Ga substitution for Al in Co-based spinel, the Al-Co spinel with three kinds spinel (Co_3O_4 , CoAl_2O_4 and Co_2AlO_4) transform to the Ga-Co spinel with two kinds spinel (Co_3O_4 and CoGa_2O_4), which can promote the Co^{3+} species reduction, due to the Co^{2+} and Co^{3+} ions in spinel phases can interact with neighboring groups through the Co-O bonds polarized by Al^{3+} (with the formation of CoAl_2O_4 or Co_2AlO_4 phases).^[25] Meanwhile, CoGa_2O_4 in Ga-Co spinel possessed abundant oxygen vacancies,^[13] which further providing adequate O species to take part in toluene oxidation. Therefore, the better low-temperature reducibility, the easier release of the adsorption oxygen, more abundant adsorbed toluene species and more surface Co^{3+} and O_{ads} species result in the superior low-temperature catalytic activity for Ga-Co spinel.

To illustrate the intrinsic catalytic difference of Ga-Co spinel and Al-Co spinel, the E_a value was calculated for a more detailed comparison. The Arrhenius plots for toluene conversion were shown in **Figure S3**. On the basis of the slope of the linear fit of the Arrhenius scatter plots, the E_a for toluene conversion over the Ga-Co spinel and Al-Co spinel were calculated and summarized in **Table 1**. The E_a value of the Ga-Co spinel (79.5 kJ mol^{-1}) was lower than that of the Al-Co spinel (95.4 kJ mol^{-1}). The surface oxygen species is most likely the cause of the difference in E_a . It is universally acknowledged that the oxidation of VOCs over transition metal oxide catalysts takes place as according to the Mars-van Krevelen type redox cycle, and that the nucleophilic attack of O_{latt} results in the occurrence of this reaction.^[26] Thus, the O_{latt} species play a vital role in the catalytic reaction. As compared to the Al-Co spinel, the Ga-Co spinel better facilitated O species release according to the O_2 -TPD, which enhanced the O_{latt} mobility on the catalyst and resulted in an improvement in the Mars-van Krevelen mechanism. The fact that the Ga-Co spinel had the lowest E_a value confirmed that the Ga-Co spinel exhibits the best catalytic activity for toluene combustion. These results suggest that the Ga-Co spinel better facilitated toluene oxidation than the Al-Co spinel.

To probe the stability of Ga-Co spinel catalyst, an on-stream reaction experiment was carried out over Ga-Co spinel for 50 h at $300\text{ }^{\circ}\text{C}$, as shown in **Figure 4b**. No decrease in the catalytic activity was observed during the stability test. To better illustrate the stability of Ga-Co spinel, it was characterized via TG, XRD and XPS after stability test. The amount of carbon deposited on the Ga-Co spinel after 50 h was analyzed via TG and the results are illustrated in **Figure 4b**. The weight loss of the catalyst was 2.7 wt.%, and according to the O_2 -TPD results, this includes the 2.02 wt.% weight loss of the O species. There was little weight reduction within the temperature range of $30\text{--}900\text{ }^{\circ}\text{C}$, indicating it showed excellent resistance to carbon deposition. This excellent resistance to carbon deposition may be partially attributed to the high oxygen vacancies in the Ga-Co spinel, which activate the oxygen species that consequently react with the deposited carbon.^[27] As is shown in **Figure S4**, the phase structure of the Ga-Co spinel was well retained after stability test, and no extra peaks were observed. The diffraction peaks intensities of the Ga-Co spinel are shown to have slightly increased following stability testing. The corresponding average crystallite size of Ga-Co spinel increased from 8.4 nm to 9.3 nm following stability

testing. The superior low-temperature catalytic activity of the Ga-Co spinel is associated with more surface Co^{3+} and O_{ads} species. Ga-Co spinel after 50 h at $300\text{ }^{\circ}\text{C}$ was further investigated by the XPS technology. Compared with the mole ratio of $\text{Co}^{3+}/\text{Co}^{2+}$ (1.47) and $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ (0.73) of the fresh Ga-Co spinel, $\text{Co}^{3+}/\text{Co}^{2+}$ (1.45) and $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ (0.68) for Ga-Co spinel after stability decreases slightly. Meanwhile, there is nearly no change can be obtained by comparing the XPS spectra (Co 2p, O 1s and Ga 3d) for Ga-Co spinel and Ga-Co spinel after 50 h stability in **Figure S5**. These results indicate that the Ga-Co spinel exhibited excellent catalytic stability including excellent resistance to sintering and carbon deposition.

Typical references about the related cobalt based oxide catalysts for toluene oxidation at comparable reaction condition are shown in **Table S1**. Among the various cobalt metal oxide catalysts (such as Co_2AlO_4 ,^[25] Co_3O_4 ,^[25] $\text{LaCoO}_3/\text{SBA-15}$ ^[28] and $\text{CoMn}_{0.5}$ ^[29]), the Co-Ga spinel showed better toluene oxidation performance. With further loading of noble metal, it can be compared to the state-of-the-art catalysts (Pd/CoAlO_3 ^[7c] and 1% $\text{Pt}/\text{Al}_2\text{O}_3$ ^[29]) for toluene oxidation. In this work, the Ga substitution for Al in Co-based spinel promote the reducibility of Co^{3+} and increase the ratio of surface Co^{3+} and O_{ads} . This strategy provides insight for the design of new catalysts for VOCs oxidation.

In conclusion, the Ga-Co spinel exhibited better catalytic performance than the Al-Co spinel. This was due to the substitution of Al with Ga in the Al-Co spinel, resulting in better low-temperature reducibility, higher surface oxygen percentage and Co^{3+} concentration in the Ga-Co spinel, as well as better adsorption/desorption capacities for the oxygen and toluene. Furthermore, the Ga-Co spinel that employed LDH as the catalyst precursor also demonstrated excellent stability and no catalyst deactivation was observed during the 50 h on stream at $300\text{ }^{\circ}\text{C}$.

Experimental Section

The Ga-Co LDH and Al-Co LDH composite with Ga: Co and Al: Co molar ratio of 1: 2 was prepared by co-precipitation method (see details in the **Supporting Information, S1**). Before reaction, the prepared Ga-Co LDH and Al-Co LDH were calcined at $500\text{ }^{\circ}\text{C}$ for 3 h in muffle and the calcined catalyst was marked as Ga-Co spinel and Al-Co spinel, respectively. Meanwhile, in order to compare the Ga-Co spinel structure is formed without the catalyst precursor (LDH), Ga-Co spinel was prepared according to the traditional citrate sol-gel method to make a comparison (SI). The resultant sample was labeled as Ga-Co sol-gel. Catalytic evaluation and material characterization are provided in detail in the **SI**.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: layered double hydroxides • oxidation • spinel oxides • toluene • VOCs

- [1] a) B. C. McDonald, J. A. de Gouw, J. B. Gilman, S. H. Jathar, A. Akherati, C. D. Cappa, J. L. Jimenez, J. Lee-Taylor, P. L. Hayes, S. A. McKeen, Y. Y. Cui, S.-W. Kim, D. R. Gentner, G. Isaacman-VanWertz, A. H. Goldstein, R. A. Harley, G. J. Frost, J. M. Roberts, T. B. Ryerson, M. Trainer, *Science* **2018**, 359, 760-764; b) J.-H. Park, A. H. Goldstein, J. Timkovsky, S. Fares, R. Weber, J. Karlik, R. Holzinger, *Science* **2013**, 341, 643-647; c) A. C. Lewis, *Science* **2018**, 359, 744-745; d) S. Zhang, J. You, C. Kennes, Z. Cheng, J. Ye, D. Chen, J. Chen, L. Wang, *Chem. Eng. J.* **2018**, 334, 2625-2637.
- [2] a) K. M. Parida, N. Sahu, A. K. Tripathi, V. S. Kamble, *Environ. Sci. Technol.* **2010**, 44, 4155-4160; b) R. Wang, J. Li, *Environ. Sci. Technol.* **2010**, 44, 4282-4287.
- [3] H. Huang, Y. Xu, Q. Feng, D. Y. C. Leung, *Catal. Sci. Technol.* **2015**, 5, 2649-2669.
- [4] a) S. Xie, J. Deng, S. Zang, H. Yang, G. Guo, H. Arandiyán, H. Dai, *J. Catal.* **2015**, 322, 38-48; b) B. Bai, J. Li, *ACS Catal.* **2014**, 4, 2753-2762; c) Y. Wang, C. Zhang, F. Liu, H. He, *Appl. Catal. B: Environ.* **2013**, 142-143, 72-79; d) C. Zhang, F. Liu, Y. Zhai, H. Ariga, N. Yi, Y. Liu, K. Asakura, M. Flytzani-Stephanopoulos, H. He, *Angew. Chem. Int. Ed.* **2012**, 51, 9628-9632; e) L. Torrente-Murciano, B. Solsona, S. Agouram, R. Sanchis, J. M. Lopez, T. Garcia, R. Zanella, *Catal. Sci. Technol.* **2017**, 7, 2886-2896.
- [5] a) M. Romero-Sáez, D. Divakar, A. Aranzabal, J. R. González-Velasco, J. A. González-Marcos, *Appl. Catal. B: Environ.* **2016**, 180, 210-218; b) S. Xie, H. Dai, J. Deng, Y. Liu, H. Yang, Y. Jiang, W. Tan, A. Ao, G. Guo, *Nanoscale* **2013**, 5, 11207-11219; c) U. Menon, V. V. Galvita, G. B. Marin, *J. Catal.* **2011**, 283, 1-9; d) F. Arena, *Catal. Sci. Technol.* **2014**, 4, 1890-1898. e) Q. Yang, D. Wang, C. Wang, F. Li, K. Li, Y. Peng, J. Li, *Catal. Sci. Technol.*, **2018**, 8, 3166-3173.
- [6] a) B. Bai, H. Arandiyán, J. Li, *Appl. Catal. B: Environ.* **2013**, 142, 677-683; b) H. Yi, Z. Yang, X. Tang, S. Zhao, F. Gao, J. Wang, Y. Huang, Y. Ma, C. Chu, Q. Li, J. Xu, *Chem. Eng. J.* **2018**, 333, 554-563; c) G. Li, C. Zhang, Z. Wang, H. Huang, H. Peng, X. Li, *Appl. Catal. A: Gen.* **2018**, 550, 67-76; d) Q. Ren, S. Mo, R. Peng, Z. Feng, M. Zhang, L. Chen, M. Fu, J. Wu, D. Ye, *J. Mater. Chem. A* **2018**, 6, 498-509.
- [7] a) S. Zhao, F. Hu, J. Li, *ACS Catal.* **2016**, 6, 3433-3441; b) S. Zhao, J. Li, *ChemCatChem* **2015**, 7, 1966-1974; c) S. Zhao, K. Li, S. Jiang, J. Li, *Appl. Catal. B: Environ.* **2016**, 181, 236-248.
- [8] Q. Wang, D. O'Hare, *Chem. Rev.* **2012**, 112, 4124-4155.
- [9] J. Feng, Y. He, Y. Liu, Y. Du, D. Li, *Chem. Soc. Rev.* **2015**, 44, 5291-5319.
- [10] G. Fan, F. Li, D. G. Evans, X. Duan, *Chem. Soc. Rev.* **2014**, 43, 7040-7066.
- [11] S. Dagorne, R. Wehmschulte, *ChemCatChem* **2018**, 10, 1-13.
- [12] a) Y. Hou, L. Wu, X. Wang, Z. Ding, Z. Li, X. Fu, *J. Catal.* **2007**, 250, 12-18; b) Y. Hou, X. Wang, L. Wu, Z. Ding, X. Fu, *Environ. Sci. Technol.* **2006**, 40, 5799-5803.
- [13] D. Liu, X. Mo, K. Li, Y. Liu, J. Wang, T. Yang, *J. Power Sources* **2017**, 359, 355-362.
- [14] K. Chakrapani, F. Ozcan, K. F. Ortega, T. Machowski, M. Behrens, *Chemelectrochem* **2018**, 5, 93-100.
- [15] a) R. Birjega, A. Matei, M. Filipescu, F. Stokker-Cheregi, C. Luculescu, D. Colceag, R. Zavoianu, O. D. Pavel, M. Dinescu, *Appl. Surf. Sci.* **2013**, 278, 122-126; b) R. Shannon, *Acta Crystallogr A* **1976**, 32, 751-767.
- [16] a) M. Imran, D. H. Kim, W. A. Al-Masry, A. Mahmood, A. Hassan, S. Haider, S. M. Ramay, *Polym. Degrad. Stabil.* **2013**, 98, 904-915; b) S. Kameoka, T. Tanabe, A. P. Tsai, *Catal. Lett.* **2005**, 100, 89-93; c) Z. Ye, J. M. Giraudon, N. Nuns, P. Simon, N. De Geyter, R. Morent, J. F. Lamonier, *Appl. Catal. B: Environ.* **2018**, 223, 154-166.
- [17] C. Rudolf, B. Dragoi, A. Ungureanu, A. Chiriac, S. Royer, A. Nastro, E. Dumitriu, *Catal. Sci. Technol.* **2014**, 4, 179-189.
- [18] X. Ning, Z. An, J. He, *J. Catal.* **2016**, 340, 236-247.
- [19] H. Wang, W. Yang, P. Tian, J. Zhou, R. Tang, S. Wu, *Appl. Catal. A: Gen.* **2017**, 529, 60-67.
- [20] a) Y. Peng, W. Si, J. Luo, W. Su, H. Chang, J. Li, J. Hao, J. Crittenden, *Environ Sci Technol* **2016**, 50, 6442-6448; b) Y. Wang, L. Guo, M. Chen, C. Shi, *Catal. Sci. Technol.* **2018**, 8, 459-471.
- [21] H. Huang, D. Y. C. Leung, *ACS Catal.* **2011**, 1, 348-354.
- [22] a) Y. Liu, H. Dai, J. Deng, S. Xie, H. Yang, W. Tan, W. Han, Y. Jiang, G. Guo, *J. Catal.* **2014**, 309, 408-418; b) A. Bielański, J. Haber, *Catal. Rev.* **1979**, 19, 1-41; c) X. Wang, W. Zhao, X. Wu, T. Zhang, Y. Liu, K. Zhang, Y. Xiao, L. Jiang, *Appl. Surf. Sci.* **2017**, 426, 1198-1205.
- [23] Y. Mizokawa, H. Iwasaki, R. Nishitani, S. Nakamura, *J. Electron Spectrosc.* **1978**, 14, 129-141.
- [24] X. Duan, M. Pan, F. Yu, D. Yuan, *J. Alloy. Compd.* **2011**, 509, 1079-1083.
- [25] Q. Zhang, S. Mo, B. Chen, W. Zhang, C. Huang and D. Ye, *Mol. Catal.*, **2018**, 454, 12-20.
- [26] Z. Qu, Y. Bu, Y. Qin, Y. Wang, Q. Fu, *Appl. Catal. B: Environ.* **2013**, 132-133, 353-362.
- [27] a) Q. Yang, A. Cao, N. Kang, K. An, Y. Liu, *Fuel. Process. Technol* **2018**, 179, 42-42.; b) F. Liu, L. Zhao, H. Wang, X. Bai, Y. Liu, *Int. J. Hydrogen Energ.* **2014**, 39, 10454-10466.
- [28] J. Deng, L. Zhang, H. Dai and C.-T. Au, *Appl. Catal. A: Gen.* **2009**, 352, 43-49.
- [29] D. A. Aguilera, A. Perez, R. Molina and S. Moreno, *Appl. Catal. B: Environ.*, **2011**, 104, 144-150.

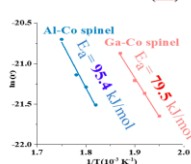
Entry for the Table of Contents

Layout 2:

COMMUNICATION

Periodic Table of the Elements

Traditional

Toluene Oxidation (E_a)

Qilei Yang, Dong Wang, Chizhong Wang, Kezhi Li, Yue Peng*, and Junhua Li

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Promotion effect of Ga-Co spinel derived from layered double hydroxides for toluene oxidation

Graphic Abstract