Green Chemistry



View Article Online

PAPER



Cite this: DOI: 10.1039/c6gc02065h

Hierarchically nanostructured $MnCo_2O_4$ as active catalysts for the synthesis of *N*-benzylideneaniline from benzyl alcohol and aniline[†]

Xiubing Huang, Liping Liu, Hongyi Gao, Wenjun Dong, Mu Yang and Ge Wang*

A facile and scaled-up synthesis route to hierarchically nanostructured transition metal oxides with desirable properties is of great practical importance because of their excellent performance as heterogeneous catalysts in organic synthesis. In this work, hierarchically nanostructured $MnCo_2O_4$ nanorods with multinanopores have been prepared by a facile co-precipitation method using oxalic acid as a precipitant and through their consequent removal by calcination. When evaluated as catalysts for the synthesis of *N*-benzylideneaniline from benzyl alcohol and aniline, the as-prepared hierarchically nanostructured $MnCo_2O_4$ -500 nanorods possessed high conversion (90.9%) of benzyl alcohol and selectivity (95.4%) of *N*-benzylideneaniline at 60 °C even under air for 15 h, which can be attributed to the appropriate and similar ratios of Mn^{2+}/Mn^{3+} (1.36 : 1) and Co^{2+}/Co^{3+} (1.35 : 1) with excellent synergistic effects. The proposed mechanism reveals that the benzyl alcohol is initially dehydrogenated to benzaldehyde which then reacts with another molecule of aniline to form *N*-benzylideneaniline. The $MnCo_2O_4$ -500 nanorods can also be easily recycled without significant loss in catalytic activity for at least 4 cycles. Our findings could provide some guidance on the design of nanostructured spinel-type metal oxide catalysts with better synergistic effects in organic synthesis.

Received 27th July 2016, Accepted 8th November 2016 DOI: 10.1039/c6gc02065h

www.rsc.org/greenchem

1. Introduction

Metal oxides have been widely investigated and used in various fields of chemistry, especially as catalysts in heterogeneous catalysis, due to their excellent redox properties, thermal stability, chemical stability, easy recovery and reusability.¹ Among the various kinds of metal oxides, spineltype transition metal oxides with the formula of AB_2O_4 containing 3d metal ions, have been reported as electro-catalysts for oxygen reduction reactions $(ORR)^{2-5}$ and catalysts for gas oxidation (*e.g.*, CO, toluene).⁶⁻⁹ However, the catalytic activity of spinels in organic chemistry has been rarely reported and demonstrated.¹⁰ If spinel-type transition metal oxides could exhibit excellent catalytic activity in organic reactions at low temperature, they might be promising candidates to substitute transition metal complexes and supported noble metals. New findings regarding organic reactions catalysed at low temperature by spinels are believed to lead to new applications of transition metal oxides.

In the organic reaction community, imines are a class of nitrogen-containing compounds which are important intermediates in the synthesis of various pharmaceutical and agricultural chemicals via versatile transformations (reduction, addition, condensation, and multicomponent reactions).¹¹ Therefore, the efficient and diverse synthesis of imines is of great importance and has economic benefits in the organic synthesis community. Traditionally, imines are synthesized via the condensation reaction of aldehydes or ketones with amines. Recently, several alternative approaches have also been reported, such as the dimerization of primary amines,^{12,13} the oxidation or dehydrogenation of secondary amines,^{14,15} the direct coupling of alcohols and amines,¹⁶⁻²⁰ and the hydroamination of alkynes with amines.²¹ Among these methods, the oxidative coupling of alcohols and amines is one of the most promising approaches due to the easily available and inexpensive alcohols, as well as clean by-products (e.g., water). Various homogeneous and heterogeneous catalysts have been reported for the oxidative coupling of alcohols and amines, such as a homogeneous Ru complex under a N₂ atmosphere,^{22,23} and heterogeneous catalysts based on Au,^{24,25} Pd,²⁶⁻²⁸ or Pt.²⁹ However, the requirement of high temperature (>100 °C), usage of noble metal species or low

Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, 100083, China. E-mail: gewang@mater.ustb.edu.cn

 $[\]dagger$ Electronic supplementary information (ESI) available: O₂-TPD profiles, FT-IR results, cycling test results, XRD and SEM images of MnCo₂O₄-500 after the 1st catalytic cycle. See DOI: 10.1039/c6gc02065h

activity limit the wide applications. Therefore, the development of inexpensive and effective spinel-type catalysts under mild reaction conditions (such as air, low temperature) is desirable.

Among the spinel-type candidates, CoMn₂O₄ and MnCo₂O₄ have been widely investigated in the field of Li-ion batteries and as electrocatalysts in Li-air batteries due to their synergistic effect between manganese and cobalt in which manganese can transport more electrons while cobalt can display a higher electronic conductivity.³⁰ Compared with simple metal oxides, such as manganese oxide and cobalt oxide, spinel oxides (e.g., $CoMn_2O_4$) might also display higher thermal stability, higher activity and better selectivity because of the synergistic effect of the transition metal elements on the oxygen and/or electronic mobility.^{31,32} The redox couples $(Co^{3+}/Co^{2+} \text{ and } Mn^{3+}/Mn^{2+})$ in the spinels (e.g., MnCo₂O₄) could provide an intermediate redox potential for electron transfer. In addition, with the development of nanomaterials, hierarchically nanostructured materials with micrometer dimensions but internally composed of nanometer-sized regions or domains, display their advantages in the structure stability and a large amount of active sites.33-36 Herein, in this work, we chose a model reaction: the synthesis of N-benzylideneaniline (abbr. NBA) from benzyl alcohol (abbr. BA) and aniline, to demonstrate the high catalytic activity of hierarchically nanostructured MnCo2O4 nanorods with nanopores even at low temperature (60 °C) under air. The effects of the composition $(MnCo_2O_4 \text{ and } CoMn_2O_4)$ and calcination temperature (500 and 600 °C) on the physicochemical properties and their catalytic performance were also investigated.

2. Experimental

2.1. Sample preparation

Hierarchically nanostructured CoMn₂O₄ or MnCo₂O₄ were prepared by a co-precipitation method using oxalate acid as a precipitant. In a typical procedure, 22.5 mmol of H₂C₂O₄·2H₂O was dissolved in a mixed solution of 25 mL of ethanol and 25 mL of deionized water at room temperature under vigorous magnetic stirring. Then 4.5 mmol of Co(NO₃)₂·6H₂O and Mn(CH₃COO)₂·4H₂O were dissolved in 25 mL of deionized water, which was added to the oxalate acid solution at one time under vigorous stirring. After stirring at room temperature for 6 h with parafilm, the mixtures were kept still in a drying oven at 50 °C for 10 h. After filtration, the powder was dried at 80 °C for 12 h. The oxalate precursors were referred to as CoMn₂O₄-P and MnCo₂O₄-P. Then the final products were obtained by calcination at different temperatures (i.e., 500 and 600 °C in this report) for 4 h. The resulting products were referred to as CoMn₂O₄-T or MnCo₂O₄-T, in which T represents the calcination temperature.

2.2. Characterization

The thermal decomposition was analyzed by thermogravimetric analysis (TGA) on a NETZSCH STA449C instrument (NETZSCH-Geraetebau GmbH, Selb, Germany) in air with an increasing rate of 10 °C min⁻¹. Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a PANalytical Empyrean Reflection Diffractometer with Cu Ka irradiation $(\lambda = 1.541 \text{ Å})$. High-resolution transmission electron microscopy (HRTEM) images were observed on a JEOL JEM-2011 operated at an accelerating voltage of 200 kV. The morphologies of all samples were observed on a JEOL JSM-6700 Field Emission Scanning Electron Microscope (FESEM) operated at 20 kV. Nitrogen adsorption-desorption isotherms were measured at 77 K with a Micromeritics ASAP-2020 analyser (Micromeritics Instrument Corp., USA). Each sample (200 mg) was degassed at 120 °C for 12 h under vacuum before an adsorption measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. X-ray photoelectron spectroscopy (XPS) data were obtained on an ESCA Lab220i-XL electron spectrometer from VG Scientific using 300 W Al Ka radiation and for peak calibration adventitious C 1s was set at 284.9 eV. Fouriertransform infrared (FT-IR) spectra were collected on a Nicolet 6700 Fourier spectrometer using KBr pellets for all the powders. Oxygen temperature-programmed desorption (O2-TPD) was carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics). Before O2-TPD experiment, 30 mg of the sample was preheated at 120 °C in He flow of 30 mL min⁻¹ for 1 h, followed by cooling in He flow to 40 °C and purging with 20 vol% O_2 -He (40 mL min⁻¹ for 1 h), and then changing to He flow (40 mL min⁻¹) for 40 min to remove O_2 . Then, the heating rate was 10 °C min⁻¹ and the temperature range was from room temperature to 900 °C. The oxygen concentration in the effluent was continuously monitored by a thermal conductivity detector. The amount of O₂ desorbed from the catalyst was quantified by calibrating the peak area against that of a standard O_2 pulse (50.0 µL). The peak area is integrated by using the trapezoid integration method.

2.3. Catalyst test

A typical procedure for N-benzylideneaniline (NBA) formation from benzyl alcohol and aniline is as follows: a catalyst (35 mg) was added to a mixture of benzyl alcohol (0.5 mmol) and aniline (1.0 mmol) in toluene (2.0 mL) in a 25 mL double necked round bottom flask fitted with a reflux condenser under 1 atm O2. The resulting mixture was vigorously stirred at 700 rpm at controlled temperature. After reaction for 15 h, the reaction mixture was filtered and the liquid was transferred to a vial. The products were analyzed using gas chromatographymass spectrometry (GC-MS, Agilent 7890/5975C-GC/MSD) with an HP-5 capillary column. The conversion and yield of the imine products were determined based on benzyl alcohol by GC using decane as an internal standard. The products were also identified using standard compounds. The reusability test of MnCo₂O₄-500 was conducted as follows: the catalyst was collected by centrifugation and washing with ethanol three times to remove the products, followed by calcination at 400 °C in air for 4 h. After this treatment, the obtained catalyst was tested for reaction the second time.

3. Results and discussion

The thermal behaviour of CoMn₂O₄-P and MnCo₂O₄-P solids by thermogravimetric analysis (TGA) is shown in Fig. 1. There are two obvious major weight loss steps. The first weight loss (about 20 wt%) below 250 °C can be attributed to the loss of chemically combined water in CoMn₂O₄-P and MnCo₂O₄-P, indicating there are 2 crystalline water molecules in these precursors, similar to that of manganese oxalate dihydrate and cobalt oxalate dihydrate.37,38 The second prominent weight loss between 250 and 300 °C is about 35 wt%, which corresponds to the thermal decomposition of manganese and cobalt oxalates into $CoMn_2O_4$ or $MnCo_2O_4$ in the presence of an air stream.^{37,38} Note that the weight of these two precursors will be almost stable after 300 °C, indicating that oxalate has been completely decomposed before 300 °C. Based on the TGA results, 500 and 600 °C were chosen as the optimal temperatures to investigate the effects of calcination temperature on the morphology and their catalytic properties. As a result, the thermal decomposition of CoMn₂O₄-P and MnCo₂O₄-P was carried out at 500 or 600 °C for 4 h in static air to ensure the formation of pure-phased CoMn₂O₄ and MnCo₂O₄ with good crystallinity.

The XRD patterns of final samples are shown in Fig. 2. All of the reflections in Fig. 2(I) could be indexed as the bodycentered-tetragonal CoMn₂O₄ phase (space group *I*41/*amd* (141), JCPDS no. 77-0471) with a distorted spinel structure owing to the well-known Jahn–Teller effect of Mn(m). All of the reflections in Fig. 2(II) could be indexed as the face-centered-cubic MnCo₂O₄ phase (space group *Fd3m* (227), JCPDS no. 23-1237) with a typical spinel structure. These oxides were regarded as



Fig. 1 TGA curves of $CoMn_2O_4$ -P and $MnCo_2O_4$ -P in air with an increasing rate of 10 °C min⁻¹.



Fig. 2 XRD patterns of CoMn₂O₄-500 (a), CoMn₂O₄-600 (b), MnCo₂O₄-500 (c) and MnCo₂O₄-600 (d).

spinel-type oxides with mixed metal valences, in which cobalt and manganese ions are distributed at tetrahedral and octahedral stacking interstices.³⁹ In addition, the broadening peaks of CoMn₂O₄-500 (Fig. 2a) and MnCo₂O₄-500 (Fig. 2c) indicate a nano-crystalline nature with relatively poor crystallinity after calcination at 500 °C for 4 h. Increasing the calcination temperature to 600 °C would result in enhanced intensity and sharpened XRD diffraction peaks, suggesting a bigger nanocrystal size and better crystallinity of CoMn₂O₄-600 (Fig. 2b) and MnCo₂O₄-600 (Fig. 2d). Their average particle size was estimated from peaks (211) for CoMn₂O₄ oxides in Fig. 2(I) and (311) for MnCo₂O₄ oxides in Fig. 2(II) according to the Scherrer equation, as summarized in Table 1. The average particle sizes for CoMn₂O₄-500 and CoMn₂O₄-600 were 19.7 and 41.3 nm, respectively, while the average particle sizes for MnCo₂O₄-500 and MnCo₂O₄-600 were 9.0 nm and 15.2 nm, respectively, further demonstrating their nano-crystalline nature.

The morphology and microstructure of the as-prepared samples were further demonstrated by FESEM. The typical low magnification FESEM image of $CoMn_2O_4$ -500 in Fig. 3a displays that the sample is composed of spindles with a

Table 1 The textural properties of as-prepared samples

Green C	hemistry
---------	----------

Materials	Surface area ^{<i>a</i>} $(m^2 g^{-1})$	Pore volume ^b $(cm^3 g^{-1})$	Average pore size ^c (nm)	Average particle size ^d (nm)	Ratio of Co ²⁺ /Co ³⁺ e	Ratio of Mn ²⁺ /Mn ^{3+ e}
MnCo ₂ O ₄ -500	77.9	0.29	7.2	9.0	1.35	1.36
MnCo ₂ O ₄ -600	38.6	0.20	9.2	15.2	1.30	1.62
$CoMn_2O_4$ -500	55.5	0.25	9.3	19.7	1.92	0.78
$CoMn_2O_4$ -600	20.3	0.15	16.5	41.3	2.00	1.31

^{*a*} Calculated by the BET method. ^{*b*} Accumulated pore volume from the N_2 adsorption branch with P/P_0 lower than 0.997. ^{*c*} Obtained from the N_2 adsorption branch by the BJH method. ^{*d*} Calculated from the XRD results based on the Scherrer equation. ^{*e*} Calculated based on the area of the deconvoluted peaks in the XPS spectrum.



Fig. 3 FESEM images of $CoMn_2O_4$ -500 (a), $CoMn_2O_4$ -600 (b), $MnCo_2O_4$ -500 (c) and $MnCo_2O_4$ -600 (d). Insets of (a) and (b) are their high magnification images.

micrometer size (4 µm and 2.5 µm in the long and short axes, respectively), which were composed of nanorods along the long axis with nanopores on them, as shown in the inset of Fig. 3a. Increasing the calcination temperature to 600 °C could maintain the spindle morphology, as shown in Fig. 3b. Compared with CoMn₂O₄-500, there is a completely different morphology in MnCo₂O₄-500 (Fig. 3c), which is nanorods with nanopores on them but with a different degree of aggregation. MnCo₂O₄-600 could also possess the nanorod morphology. However, some dispersive nanoparticles were observed in Fig. 3d for MnCo₂O₄-600, which is maybe due to the quick decomposition of oxalate at higher calcination temperature. The results indicate that hierarchically nanostructured CoMn₂O₄-500 and MnCo₂O₄-500 with nanopores have been prepared, which may not only provide a large amount of active sites for catalytic reactions, but also remain stable during the catalytic reactions.

Fig. 4 represents the TEM images of the as-prepared samples at low and high magnification. Since the micrometersize spindles and rods of the as-prepared samples have been determined by FESEM images, only parts of the as-prepared samples were detected by the TEM technique. Fig. 4a and c show the top parts of a spindle as indicated in Fig. 3a and b for CoMn₂O₄-500 and CoMn₂O₄-600, respectively. It clearly shows that CoMn₂O₄-500 (Fig. 4a) possessed hierarchical nanostructures in which the nanorods were composed of nanocrystals with secondary nanopores among them. The high magnification image of CoMn₂O₄-500 (Fig. 4b) reveals its poly-crystalline nature with poor crystallinity, in agreement with the XRD results in Fig. 2. The lattice fringes with an interplanar distance of 0.28 nm and 0.45 nm correspond to the (200) and (101) planes of CoMn₂O₄, respectively. Increasing the calcination temperature results in a bigger crystal size with better crystallinity, as shown in the low (Fig. 4c) and high (Fig. 4d) magnification TEM images for CoMn₂O₄-600. However, CoMn₂O₄-600 still possesses the hierarchical nanostructures with fewer pores (Fig. 4c). The low and high magnification of MnCo₂O₄-500 and MnCo₂O₄-600 are represented in Fig. 4e-h, indicating that MnCo₂O₄ has a nanorod morphology with a less-uniform size. MnCo₂O₄-500 also shows a hierarchically nanoporous structure, and these pores are randomly arranged but distributed among the small primary nanoparticles (Fig. 4e). The high magnification of MnCo₂O₄-500 in Fig. 4f displays its small primary poor-crystalline nanoparticles with the diameters ranging from 5 to 10 nm. The nanoparticle size and crystallinity increased when the heating temperature elevated to 600 °C, while some nanopores among nanoparticles disappeared, as shown in Fig. 4g for MnCo₂O₄-600. The distinct lattice fringes with an interplanar distance of 0.24 nm and 0.29 nm correspond to the (311) and (220) planes of MnCo₂O₄, respectively.

The hierarchically nanostructured nature of nanopores of the as-prepared CoMn₂O₄ and MnCo₂O₄ was further demonstrated by N₂ adsorption-desorption measurements at 77 K, as shown in Fig. 5, with the inset displaying their corresponding BJH adsorption pore-size distribution. All the samples exhibit a typical type II with a H3 hysteresis loop, which is characteristic of macroporous materials. According to the pore size distribution curves obtained from BJH adsorption isotherms, as shown in the inset of Fig. 5, these as-prepared materials are composed of mesoporous and macroporous structures, which are consistent with the FESEM/TEM results (Fig. 3 and 4). The BET specific surface areas, pore volumes and average pore size of the samples are summarized in Table 1. The BET specific surface areas of CoMn₂O₄-500, CoMn₂O₄-600, MnCo₂O₄-500 and $MnCo_2O_4$ -600 were 55.5, 20.3, 77.9 and 38.6 m² g⁻¹, and their corresponding pore volumes were 0.25, 0.15, 0.29 and



Fig. 4 Low magnification (a, c, e, g) and high magnification (b, d, f, h) TEM images of $CoMn_2O_4$ -500 (a, b), $CoMn_2O_4$ -600 (c, d), $MnCo_2O_4$ -500 (e, f) and $MnCo_2O_4$ -600 (g, h).

 $0.20 \text{ cm}^3 \text{g}^{-1}$, respectively. These results indicate that increasing the calcination temperature would result in less BET specific areas and pore volumes because of the growth of nanocrystals. In addition, the BET specific areas and pore volumes of CoMn_2O_4 were a bit smaller than those of MnCo_2O_4 obtained from the same calcination temperature, which may be due to the smaller crystal size in MnCo_2O_4 samples than that in CoMn_2O_4 . The hierarchically mesoporous/macroporous structures indicate good morphological stability and abundant catalytic active sites, thus possibly improving the reversibility and catalytic activity.



Fig. 5 N₂ adsorption/desorption isothermal curves of CoMn₂O₄-500, CoMn₂O₄-600, MnCo₂O₄-500 and MnCo₂O₄-600. Inset is their pore size distribution curves.

To obtain more detailed information about the elemental composition and valence values, X-ray photoelectron spectroscopy (XPS) analysis was carried out for the hierarchically nanostructured $CoMn_2O_4$ and $MnCo_2O_4$, and the Co 2p XPS and Mn 2p XPS spectra are shown in Fig. 6 and 7, respectively. All of the Co 2p spectra in Fig. 6 are well deconvoluted by considering two spin–orbit doublets characteristic of Co^{2+} and Co^{3+} and two shakeup satellites.⁴⁰ Two Co 2p3/2 and Co 2p1/2 peaks located at around 780.2 and 795.4 eV are accompanied by two prominent shake-up satellite peaks (around 786.6 and 803.1 eV) in Fig. 6a and b, indicating the dominating presence of the $Co(\pi)$ in $CoMn_2O_4$ -500 and $CoMn_2O_4$ -600, the shake-up satellite peaks are not obvious, indicating a smaller portion of Co^{2+} , as shown by the calculated ratio of Co^{2+}/Co^{3+} in Table 1 based on the



Fig. 6 Co 2p XPS spectra of hierarchically nanostructured CoMn₂O₄-500 (a), CoMn₂O₄-600 (b), MnCo₂O₄-500 (c) and MnCo₂O₄-600 (d).



Fig. 7 Mn 2p XPS spectra of hierarchically nanostructured $CoMn_2O_4$ -500 (a), $CoMn_2O_4$ -600 (b), $MnCo_2O_4$ -500 (c) and $MnCo_2O_4$ -600 (d).

area of the deconvoluted peaks. The Mn 2p spectra in Fig. 7 display two main spin-orbit lines of 2p3/2 at around 642.0 eV and 2p1/2 at around 653.5 eV with a separation of 11.5 eV. After refined fitting, the spectrum can be deconvoluted into four peaks, in which the two peaks at around 641.8 and 653.4 eV can be assigned to the existence of Mn(II), while the other two peaks at around 643.7 and 654.2 eV are characteristic of the Mn(III) cation.⁴² The results indicate that the Mn element exists as mixed Mn^{2+} and Mn^{3+} in both hierarchically nanostructured MnCo₂O₄ and CoMn₂O₄ after calcination at 500 and 600 °C. The results in Table 1 show that the portion of Mn²⁺ increased with the calcination temperature increasing from 500 to 600 °C while the ratio of $\text{Co}^{2+}/\text{Co}^{3+}$ is relatively stable with the increase of the calcination temperature. As is known, electron transfer was important for the catalytic reaction. Thus, we speculate that the redox couples of Mn^{3+}/Mn^{2+} and Co^{3+}/Co^{2+} as well as hierarchical nanostructures may facilitate the oxide's role as an electron relay system for diverse intermediate steps in the reaction of adsorbed species, providing an excellent catalytic activity and stability.

As shown in the O₂-TPD results in Fig. S1,† O₂ desorption in these as-prepared samples starts at low temperatures around 60 °C, indicating their potential catalytic activity at low temperatures. The peaks of oxygen desorption at around 110 °C and 340 °C were due to the desorption of weakly adsorbed oxygen species (*e.g.*, O^{2-} , O_2^{2-} , or O^{-}) and the peaks at higher temperatures (*e.g.*, 420 and 860 °C) can be attributed to the desorption of lattice oxygen in these samples. MnCo₂O₄-500 and CoMn₂O₄-500 display a higher oxygen desorption amount than that of MnCo₂O₄-600 and CoMn₂O₄-600 in the low temperature range, maybe due to their higher surface areas.

The catalytic activities of the as-prepared samples were evaluated using a model reaction: the synthesis of *N*-benzylideneaniline (NBA) from benzyl alcohol and aniline. Initially, the catalytic activity of the as-prepared materials for

the synthesis of NBA from benzyl alcohol and aniline was investigated at 80 °C under 1 atm O2 for 12 h (entries 1-4 in Table 2). Only NBA and benzaldehyde were detected as the products, and there were no N-phenylbenzylamine and N.Ndibenzylaniline formed during the catalytic reaction, indicating the excellent selectivity for the synthesis of NBA. Among these as-prepared catalysts, MnCo₂O₄-500 showed the best catalytic performance with a high conversion (97.8%) of BA and a high selectivity (96.4%) of NBA. The catalytic activity of MnCo₂O₄-500 and MnCo₂O₄-600 (Table 2 entries 1 and 2) also indicates the advantages of a hierarchical nanostructure with high surface areas for a superior catalytic performance. Even though the BET surface area (*i.e.*, 55.5 m² g⁻¹) of CoMn₂O₄-500 is higher than that (*i.e.*, 38.6 m² g⁻¹) of MnCo₂O₄-600, the catalytic activity of CoMn₂O₄-500 is lower than that of MnCo₂O₄-600, as shown in entries 2 and 3 in Table 2, indicating the great influence of the composition on the catalytic activity. The initial reaction rates by the BET surface area of these catalysts for the first 1 h have been calculated to be around 0.112, 0.068, 0.049, and 0.057 mmol (m² h)⁻¹ for MnCo₂O₄-500, MnCo₂O₄-600, CoMn₂O₄-500, and CoMn₂O₄-600, respectively, further demonstrating the best catalytic performance of MnCo₂O₄-500. During the catalytic reactions, Co^{3+} and Mn^{3+} tend to accept electrons from benzyl alcohol at first and then transmit these electrons through the action of Co²⁺ and Mn^{2+} . With the change of the molar ratio of Mn^{2+}/Mn^{3+} and Co²⁺/Co³⁺ in the as-prepared catalysts, the electronic acceptance and transmission ability should change at the same time. Only when these two redox couples reached equilibrium at the same time, the as-prepared CoMn₂O₄ or MnCo₂O₄ could show the best catalytic performance. Thus the reason for the highest catalytic performance of MnCo₂O₄-500 may be that the best synergistic effect arose from appropriate and similar ratios of Mn^{2+}/Mn^{3+} (1.36:1) and Co^{2+}/Co^{3+} (1.35:1).⁴³

 Table 2
 N-Benzylideneaniline (NBA) synthesis from benzyl alcohol (BA) and aniline over the as prepared catalysts under various conditions

Entry	Catalyst	Т (°С)	Oxidant	Time (h)	Conv. of BA (%)	Select. of NBA (%)
1	MnCo ₂ O ₄ -500	80	O ₂	12	97.8	96.4
2	MnCo ₂ O ₄ -600	80	O_2	12	73.9	85.4
3	CoMn ₂ O ₄ -500	80	O_2	12	67.1	53.4
4	CoMn ₂ O ₄ -600	80	O_2	12	54.4	74.2
5	MnCo ₂ O ₄ -500	80	Air	12	93.9	92.8
6	MnCo ₂ O ₄ -500	60	Air	15	90.9	95.4
7	MnCo ₂ O ₄ -500	80	N_2	12	35.7	91.9
8	MnCo ₂ O ₄ -500	60	O_2	15	97.8	96.0
9	2^{nd} MnCo ₂ O ₄ -500	60	O_2	15	96.0	95.1
10	3 rd MnCo ₂ O ₄ -500	60	O_2	15	96.2	96.2
11	4 th MnCo ₂ O ₄ -500	60	O_2	15	95.8	96.0
12	No catalyst	60	O_2	15	_	_
13	Co_3O_4	60	O_2	15	_	_
14	MnO_2	60	O_2	15	_	_
15^a	$MnCo_2O_4-500$	60	Air	15	88.9	95.8

Catalytic conditions: 35 mg catalyst, benzyl alcohol (0.5 mmol), aniline (1.0 mmol), toluene (2.0 mL), 1 atm. ^{*a*} Scaled-up test: 140 mg catalyst, benzyl alcohol (2.0 mmol), aniline (4.0 mmol), toluene (8.0 mL), 1 atm.

The catalytic conditions (e.g., catalyst amount, temperature, time, gas atmosphere) for the activity of MnCo₂O₄-500 were further investigated in order to obtain a more comprehensive and deeper understanding. The catalytic activity over $MnCo_2O_4$ -500 was dependent on the catalyst amount at 80 °C reaction temperature using 35 mg catalyst for 12 h under 1 atm O2 and is shown in Fig. 8. The conversion of BA and selectivity of NBA both smoothly increased with the increase of the catalyst amount and showed the highest conversion (97.8%) and selectivity (96.4%) with 35 mg of $MnCo_2O_4$ -500, as shown in Fig. 8a. The catalytic activity dependent on the reaction temperature using 35 mg of MnCo₂O₄-500 under 1 atm O₂ for 12 h in Fig. 8b indicates that the conversion of BA and selectivity of NBA also increased with the reaction temperature and showed the highest conversion and selectivity at 80 °C, but the conversion and selectivity at 60 °C were also as high as 95.9% and 95.0%, respectively. The results indicated that a relatively high catalytic performance can also be achieved using MnCo₂O₄-500 at low temperature (e.g., 60 °C). We



Fig. 8 Catalytic activity dependent on the catalyst amount at 80 °C (a) and reaction temperature using 35 mg of $MnCo_2O_4$ -500 (b). Catalytic conditions: benzyl alcohol (0.5 mmol), aniline (1.0 mmol), toluene (2.0 mL), 12 h, 1 atm O_2 .

further investigated the catalytic activity over 35 mg of $MnCo_2O_4$ -500 at 60 °C dependent on the reaction time under 1 atm O_2 , as shown in Fig. 9 (black curve). The conversion of BA can reach 97.8% at 15 h and 98.3% at 16 h. After the removal of the catalyst from the hot mixture after 3 h, the leaching test results that are shown in Fig. 9 (red curve) demonstrated the heterogeneous property of the catalytic reaction.

MnCo₂O₄-500 also showed excellent catalytic activity (90.9% of conversion and 95.4% of selectivity) under an air atmosphere at 60 °C for 15 h (Table 2 entry 6). At 80 °C under air, MnCo₂O₄-500 can obtain a higher conversion (93.9%) but a bit lower selectivity (92.8%) within 12 h (Table 2 entry 5), which is comparable with the reported results (Table S1⁺). During the catalytic process, benzaldehyde was observed at the initial stage and the amount slowly decreased with the reaction time, indicating that benzaldehyde is an intermediate and the reaction should proceed in two consecutive steps (Scheme 1): (i) the oxidation of benzyl alcohol to benzaldehyde and (ii) the further NBA formation of benzaldehyde with aniline.¹⁶ The controlled experiment under N2 (Table 2 entry 7) demonstrated that oxygen plays an important role in the oxidation of benzyl alcohol to benzaldehyde. To further support the mechanism, FT-IR absorption measurements were conducted, as shown in Fig. S2.† In the mixture of MnCo₂O₄-500 and benzyl alcohol at room temperature, the bands of benzyl alcohol can be



Fig. 9 Catalytic activity of $MnCo_2O_4$ -500 dependent on the reaction time (a) and leaching test (b). Catalytic conditions: 35 mg of $MnCo_2O_4$ -500, benzyl alcohol (0.5 mmol), aniline (1.0 mmol), toluene (2.0 mL), 60 °C, 1 atm O₂.



Scheme 1 Reaction pathway for NBA synthesis from benzyl alcohol and aniline.

Paper

observed, in which the –OH stretch of pure $MnCo_2O_4$ -500 was shifted to 3367 cm⁻¹ from 3425 cm⁻¹, indicating the adsorption of benzyl alcohol by hydrogen bonding with $MnCo_2O_4$ -500. In addition, the CH₂ bend and C–O stretch can be observed at 1451 and 1010 cm⁻¹, respectively, but no C=O stretch was observed, suggesting that almost no oxidation occurred at room temperature. However, after heat treatment at 60 °C under air for 1 h, the intensity of the –OH and C–O stretches, and the CH₂ bend decreased. In addition, new peaks for the in-plane C–H bend from the –CH=O group at 1403 cm⁻¹ and the C=O stretch at 1706 cm⁻¹ of benzaldehyde were observed, demonstrating the oxidation of benzyl alcohol on the catalyst surface during the heat-treatment at 60 °C under air.

As shown in Fig. 9 and Table 2 entry 8, MnCo₂O₄-500 shows 97.8% conversion of BA and 96.0% selectivity of NBA at 60 °C under O₂ for 15 h. In addition, MnCo₂O₄-500 can be reused without significant loss of the conversion of BA and selectivity of NBA for at least four cycles (as shown in Table 2 entries 8-11 and Fig. S3[†]). Similar XRD patterns of fresh MnCo₂O₄-500 and those after the 1st catalytic cycle shown in Fig. S4[†] suggest the relatively good phase stability during the catalytic reaction, even though there are some changes in the nanorod morphology (Fig. S5[†]). Controlled experiments (Table 2 entries 12-14) demonstrated the catalytic activity and synergistic effect of Mn and Co in MnCo₂O₄-500. To demonstrate the testing efficiency and possible scalability, a 4-fold scale reaction was carried out and the catalytic activity (Table 2 entry 15) was similar to that of a smaller scale (Table 2 entry 6). Generally, NBA formation can easily proceed upon heating in the presence of benzaldehyde and aniline. NBA formation from benzaldehyde and aniline with/without MnCo2O4-500 has also been carried out under 1 atm O2 at 60 °C and the results demonstrated that NBA can be formed even without MnCo₂O₄-500, but the conversion of benzaldehyde without MnCo₂O₄-500 is only a bit smaller than that with MnCo₂O₄-500, indicating that the formation of benzaldehyde from benzyl alcohol (step 1) is the rate-determining step.

To further support the proposed reaction pathway for NBA formation from BA and aniline by a two-step mechanism, the time source of the oxidation of benzyl alcohol over MnCo₂O₄-500 at 60 °C under 1 atm O2 and N2 was investigated, as shown in Fig. 10. The results show that BA can be oxidized to benzaldehyde with the increase of the reaction time at 60 °C under O2, reaching a conversion of 44.8% in 8 h. However, the conversion of BA in the presence of an N2 atmosphere is only about 13.1%, indicating that the benzyl alcohol should be firstly adsorbed onto the surface of MnCo₂O₄-500 and then should react with the active surface oxygen species of MnCo₂O₄-500 to form benzaldehyde. In addition, the conversion of benzyl alcohol in the presence of O₂ is much higher than that under N₂, indicating that O₂ is an indispensable element to obtain a high conversion of BA. In the presence of aniline, the conversion of BA is much higher than that in the absence of aniline, indicating that the formation of NBA would increase the conversion of BA.



Fig. 10 Conversion of benzyl alcohol to $MnCo_2O_4$ -500 dependent on the reaction time under different gases (a) 1 atm O_2 , (b) 1 atm N_2 . Catalytic conditions: 35 mg of $MnCo_2O_4$ -500, benzyl alcohol (0.5 mmol), toluene (2.0 mL), 60 °C.

Table 3 Scope of alcohols for imine synthesis

Entry	Alcohol	Conv. of alcohol (%)	Select. of imine (%)
1	4-Methoxybenzyl alcohol	98.8	94.8
2	4-Methylbenzyl alcohol	98.0	96.4
3	4-Fluorobenzyl alcohol	90.2	92.8

Conditions: 0.5 mmol alcohol, 1.0 mmol aniline, 2.0 mL toluene, 35 mg $MnCo_2O_4\text{-}500,$ 80 °C, 15 h, air.

The scope of alcohols in the MnCo₂O₄-500 catalyzed imine synthesis was examined (Table 3). Substituted benzyl alcohols bearing an electron-donating or -withdrawing group reacted with aniline to afford the corresponding imines with high conversion and selectivity. 4-Fluorobenzyl alcohol (Table 3 entry 3) required a longer reaction time, which could be due to the withdrawing electrons of the fluoro group at the p-position.

4. Conclusions

In summary, we have devised a facile and scaled-up co-precipitation synthesis route using oxalate acid as a precipitant to prepare hierarchically nanostructured $CoMn_2O_4$ and $MnCo_2O_4$ by just tuning the molar ratio of Mn/Co. The obtained $MnCo_2O_4$ -500 has been demonstrated as a reusable and efficient heterogeneous catalyst for the synthesis of *N*-benzylideneaniline of benzyl alcohol and aniline even at 60 °C under air for the first time. The high activity can be attributed to the redox couples (Mn^{2+}/Mn^{3+} and Co^{2+}/Co^{3+}) and the best synergistic effect in $MnCo_2O_4$ -500 is due to the appropriate and similar ratios of Mn^{2+}/Mn^{3+} (1.36 : 1) and Co^{2+}/Co^{3+} (1.35 : 1). These results could give rise to new applications of spinels (*e.g.*, $MnCo_2O_4$) in organic synthesis and bring about the new design of complex metal oxide catalysts with the best synergistic effects.

Acknowledgements

The authors are grateful for financial support from the National Key Research and Development Program of China (no. 2016YFB0701100), 111 Project (no. B13004) and the National Natural Science Foundation of China (no. 51572022).

References

- 1 I. E. Wachs and C. A. Roberts, *Chem. Soc. Rev.*, 2010, **39**, 5002–5017.
- 2 X. M. Zhai, W. Yang, M. Y. Li, G. Q. Lu, J. P. Liu and X. L. Zhang, *Carbon*, 2013, **65**, 277–286.
- 3 H. L. Wang, Y. Yang, Y. Y. Liang, G. Y. Zheng, Y. G. Li, Y. Cui and H. J. Dai, *Energy Environ. Sci.*, 2012, 5, 7931– 7935.
- 4 Y. Y. Liang, H. L. Wang, J. G. Zhou, Y. G. Li, J. Wang, T. Regier and H. J. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 3517– 3523.
- 5 L. Wang, X. Zhao, Y. H. Lu, M. W. Xu, D. W. Zhang, R. S. Ruoff, K. J. Stevenson and J. B. Goodenough, *J. Electrochem. Soc.*, 2011, **158**, A1379–A1382.
- 6 L. Liu and Y. Z. Yang, Superlattices Microstruct., 2013, 54, 26–38.
- 7 N. T. Binh, C. Gennequin, R. Cousin, E. A. Zhilinskaya,
 H. L. Tidahy, N. M. Son, V. T. T. Ha, L. T. Son, N. T. M. Thu,
 P. X. Nui and S. Siffert, *Chim. Oggi*, 2013, 31, 51–54.
- 8 P. S. Arun, B. P. Ranjith and S. M. A. Shibli, *Environ. Sci. Technol.*, 2013, 47, 2746–2753.
- 9 S. A. Hosseini, D. Salari, A. Niaei, F. Deganello, G. Pantaleo and P. Hojati, *J. Environ. Sci. Health, Part A*, 2011, **46**, 291– 297.
- S. S. Acharyya, S. Ghosh, R. Tiwari, B. Sarkar, R. K. Singha, C. Pendem, T. Sasaki and R. Bal, *Green Chem.*, 2014, 16, 2500–2508.
- 11 R. D. Patil and S. Adimurthy, Asian J. Org. Chem., 2013, 2, 726–744.
- 12 X. Lang, H. Ji, C. Chen, W. Ma and J. Zhao, *Angew. Chem.*, *Int. Ed.*, 2011, **50**, 3934–3937.
- 13 F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang and S. Blechert, *Angew. Chem., Int. Ed.*, 2011, **50**, 657– 660.
- 14 S. Furukawa, A. Suga and T. Komatsu, *Chem. Commun.*, 2014, **50**, 3277–3280.
- 15 B. Zhu and R. J. Angelici, *Chem. Commun.*, 2007, 2157–2159.
- 16 M. Tamura and K. Tomishige, Angew. Chem., Int. Ed., 2015, 54, 864–867.
- 17 B. Chen, L. Y. Wang and S. Gao, *ACS Catal.*, 2015, 5, 5851–5876.

- 18 B. Chen, J. Li, W. Dai, L. Y. Wang and S. Gao, *Green Chem.*, 2014, 16, 3328–3334.
- 19 H. Liu, G.-K. Chuah and S. Jaenicke, *J. Catal.*, 2012, **292**, 130–137.
- 20 S. Sithambaram, R. Kumar, Y. C. Son and S. L. Suib, J. Catal., 2008, 253, 269–277.
- 21 R. Severin and S. Doye, Chem. Soc. Rev., 2007, 36, 1407-1420.
- 22 B. Gnanaprakasam, J. Zhang and D. Milstein, Angew. Chem., Int. Ed., 2010, 49, 1468–1471.
- 23 J. W. Rigoli, S. A. Moyer, S. D. Pearce and J. M. Schomaker, Org. Biomol. Chem., 2012, 10, 1746–1749.
- 24 P. Liu, C. Li and E. J. M. Hensen, *Chem. Eur. J.*, 2012, **18**, 12122–12129.
- 25 H. Sun, F.-Z. Su, J. Ni, Y. Cao, H.-Y. He and K.-N. Fan, *Angew. Chem., Int. Ed.*, 2009, **48**, 4390–4393.
- 26 M. S. Kwon, S. Kim, S. Park, W. Bosco, R. K. Chidrala and J. Park, J. Org. Chem., 2009, 74, 2877–2879.
- 27 M. Ousmane, G. Perrussel, Z. Yan, J. M. Clacens,
 F. De Campo and M. Pera-Titus, *J. Catal.*, 2014, 309, 439–452.
- 28 L. L. Zhang, W. T. Wang, A. Q. Wang, Y. T. Cui, X. F. Yang, Y. Q. Huang, X. Y. Liu, W. G. Liu, J. Y. Son, H. S. Oji and T. Zhang, *Green Chem.*, 2013, **15**, 2680–2684.
- 29 W. He, L. Wang, C. Sun, K. Wu, S. He, J. Chen, P. Wu and Z. Yu, *Chem.-Eur. J.*, 2011, 17, 13308–13317.
- 30 F. M. Courtel, H. Duncan, Y. Abu-Lebdeh and I. J. Davidson, J. Mater. Chem., 2011, 21, 10206–10218.
- 31 T.-Y. Wei, C.-H. Chen, H.-C. Chien, S.-Y. Lu and C.-C. Hu, Adv. Mater., 2010, 22, 347–351.
- 32 A. Jha, K. R. Patil and C. V. Rode, *ChemPlusChem*, 2013, **78**, 1384–1392.
- 33 Y.-G. Guo, J.-S. Hu and L.-J. Wan, *Adv. Mater.*, 2008, 20, 2878–2887.
- 34 S. Gao, S. Yang, J. Shu, S. Zhang, Z. Li and K. Jiang, J. Phys. Chem. C, 2008, 112, 19324–19328.
- 35 X. M. Yin, C. C. Li, M. Zhang, Q. Y. Hao, S. Liu, L. B. Chen and T. H. Wang, *J. Phys. Chem. C*, 2010, **114**, 8084–8088.
- 36 L.-Y. Jiang, X.-L. Wu, Y.-G. Guo and L.-J. Wan, J. Phys. Chem. C, 2009, 113, 14213–14219.
- 37 B. Donkova and D. Mehandjiev, *Thermochim. Acta*, 2004, 421, 141–149.
- 38 B. Malecka, E. Drozdz-Ciesla and A. Malecki, J. Therm. Anal. Calorim., 2002, 68, 819–831.
- 39 Y. Xu, X. Wang, C. An, Y. Wang, L. Jiao and H. Yuan, J. Mater. Chem. A, 2014, 2, 16480–16488.
- 40 G. Li, L. Xu, Y. Zhai and Y. Hou, *J. Mater. Chem. A*, 2015, 3, 14298–14306.
- 41 S. A. Needham, G. X. Wang, K. Konstantinov, Y. Tournayre, Z. Lao and H. K. Liu, *Electrochem. Solid-State Lett.*, 2006, 9, A315–A319.
- 42 B. J. Tan, K. J. Klabunde and P. M. A. Sherwood, J. Am. Chem. Soc., 1991, **113**, 855–861.
- 43 X. Shi, F. Zheng, N. Yan and Q. Chen, *Dalton Trans.*, 2014, 43, 13865–13873.