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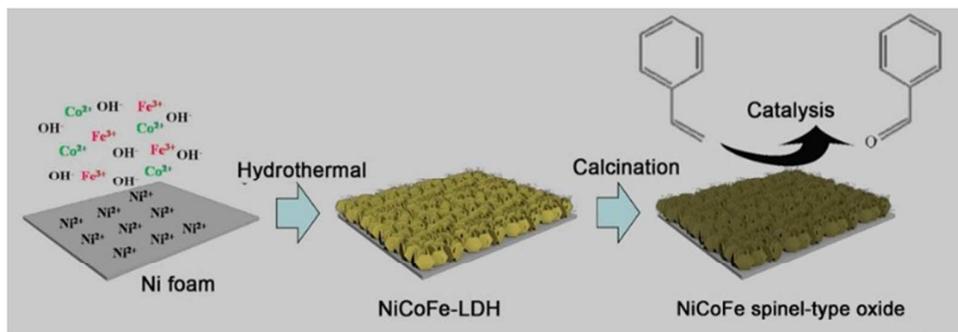
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Graphical abstract:

NiCoFe spinel-type oxide nanosheet arrays derived from layered double hydroxides (LDH) were used as structured catalyst, which exhibited excellent catalytic activity towards the oxidation of styrene.



ARTICLE

NiCoFe spinel-type oxide nanosheet arrays derived from layered double hydroxides as structured catalysts

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Immobilization of catalysts is a trend in future industrial catalysis and environmental protection. Here, NiCoFe spinel-type oxide nanosheet arrays were fabricated by using layered double hydroxides (LDH) as precursors and investigated as structural catalyst for alkenes oxidation. The NiCoFe spinel-type oxide nanosheet arrays exhibited high catalytic activity (72% conversion) and selectivity (64% for benzaldehyde) at 12h towards the oxidation of styrene by *tert*-butyl hydroperoxide (TBHP). These good catalytic performances were mainly attributed to the unique nanosheet array structure and the substitution of cobalt. This strategy can be extended to other spinel-type oxide nanoarrays on metallic substrates and offers new opportunities for the design of new types of highly efficient structured catalysts.

1 Introduction

Structured catalysts have attracted a great deal of interests due to their unique physical and chemical properties. Compared with conventional particle catalysts, structured catalysts are generally characterized by the small pressure drop and controllable mass transport during reaction process, as well as good thermal and mechanical properties. Combined with their properties of easy separation and recycle, these advantages make them superior to conventional particle catalysts and thus preferable in many industrial applications with respect of the environment protection and from the energy economic point of view.¹⁻³ However, traditional structured catalyst is commonly made by applying catalytically active component to an inert monolith structure, which results in a heterogeneous distribution and leaching of the active component during catalytic reactions.⁴ Nanoarrays, as a new kind of structured catalyst, offer the possibility to solve this problem. Firstly, uniform nanoarrays with catalytically active components grown directly on a substrate could offer good thermal and mechanical stabilities of the catalyst, ideally avoiding the leaching of the active materials even under harsh reaction conditions. Secondly, the nanoarray structure can effectively increase the specific surface area of the catalysts, enhancing the accessibility of the reactant to the catalytic site and favoring molecular diffusion.^{5,6} Moreover, nanoarrays with the faces of the crystallites perpendicular to the substrate may also have enhanced catalytic efficiency relative to the powdered form because of the high availability of the active sites located on the edges of the crystallites. In addition, fabrication of nanoarrays makes it possible to combine the catalytic activity of materials and the architecture advantage of nanoarrays together to obtain catalysts which are easy to remove at the end of the reaction. Therefore, a uniform nanoarray directly grown on a metal substrate, with large surface area, should be an ideal

architecture for structured catalyst. For example, we have constructed hierarchical $\text{Co}_{3-x}\text{Fe}_x\text{O}_4$ nanoarrays on an iron substrate, which showed excellent catalytic activity and stability for styrene oxidation.⁷ Co_3O_4 nanostructure arrays grown on ceramic cordierite honeycombs were also reported to exhibit high performance in NO oxidation with a NO conversion of about 80% at 275°C, which is better than the powder counterpart.⁸

Among the various nanoarrays, layered double hydroxides (LDH) nanoarrays and their derivative have attracted intense interests due to their specific structures and properties. LDHs are also called hydrotalcite-like materials, representing a category of layered materials whose composition can be expressed as the general formula of $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}(\text{A}_{x/n})^{n-} \cdot y\text{H}_2\text{O}$. In the last few years, LDH and derived spinel-type oxide nanoarrays have been widely studied for various applications, such as supercapacitor,⁹ anti-corrosion coatings for metals,¹⁰ and as components in optical, electrical, magnetic devices.¹¹⁻¹³ For example, CoAl-LDH@poly nanoplatelets with core/shell structure on a flexible Ni foil substrate was prepared as a high performance pseudocapacitor.⁹ A porous ZnO/ZnAl₂O₄ nanosheet film was fabricated from a ZnAl-LDH film on a Zn-covered stainless steel substrate and used as an anode material for Li-ion batteries.¹⁴ Particularly, LDH nanoarrays are ideal precursors to obtain various substituted spinel-type oxides catalysts with regular compositions and ordered prearrangement of metal cations. After controlled thermal decomposition, LDH lose their layered structure and form spinel-type oxides with high thermal stability, large specific surface area, and high metal dispersion, all of which are very important attributes for catalysts.¹⁵ As results, compared with the materials prepared by conventional techniques, the spinel-type oxide nanoarrays as a new kind of structured catalysts derived from LDH precursors are generally characterized by higher activity and longer lifetimes.¹⁶ Duan et

al. fabricated a MgAl-LDH film on PAO/Al substrate and activated the as-prepared film by a calcination/rehydration procedure to prepare an LDH-based structural catalyst for the conversion of acetone to diacetone alcohol.¹⁷ Basile et al. prepared a NiAl spinel-type oxide film by the calcination of NiAl-LDH film on the surface of FeCr alloy foams, which was demonstrated as new active and stable Ni steam reforming catalyst.¹⁸

Herein, we reported a nanosheet array structured catalyst of NiCoFe spinel-type oxide, which was synthesized from NiCoFe-LDH, and their catalytic activity in alkenes oxidation by organic peroxides. NiCoFe-LDH nanosheet arrays with uniform morphology and ordered structure were firstly prepared on three-dimensional nickel foam substrate by a simple urea precipitation method. After calcination, NiCoFe spinel-type oxide nanosheet arrays with the same morphology were obtained. The spinel-type oxide nanosheet arrays exhibited high catalytic activity (72% conversion) and selectivity (64% for benzaldehyde) for oxidation of styrene by *tert*-butyl hydroperoxide (TBHP) at 12h, which was mainly attributed to the direct contact of the nanosheet arrays with the underlying substrate, the small size of nanosheets, and the substitution of Co in the spinel-type oxide.

2 Experimental section

2.1 Synthesis of NiCoFe spinel-type oxide nanosheet arrays

All chemicals were analytical grade, purchased from Beijing Chemical Reagents Company and used without further purification.

In a typical synthesis, 2 mL of aqueous cobalt nitrate solution (1 mol/L), 2 mL of aqueous ferric nitrate solution (1 mol/L) and 10 mL aqueous urea solution (1 mol/L) were first mixed and stirred for 2 min to form a homogeneous solution. 26 mL of distilled water was then added to the mixture under stirring. The resulted 40 mL of homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 50 mL. The pH value of the solution was 1.92. Nickel foam was carefully cleaned with HCl, absolute ethanol, and distilled water. After immersing the cleaned nickel foam substrate in the homogeneous solution, the autoclave was sealed and maintained at 100°C for 12 h and then allowed to cool down to room temperature naturally. The pH value turned to be 6.87 after reaction indicating the deposition of the metal ions. The substrate was taken out, washed for several times with distilled water, and dried at 70°C for 2 h to get NiCoFe-LDH. NiCoFe spinel-type oxide nanosheet arrays was obtained by calcining NiCoFe-LDH in air at 350°C for 3 h. The existence of Ni in our samples is based on the *in situ* dissolving of Ni²⁺ from the nickel substrate during the hydrothermal reaction.

NiFe-LDH nanosheet arrays were also prepared by using similar process for compare. Typically, 0.5 mL of aqueous ferric nitrate solution (1 mol/L) and 10 mL aqueous urea solution (1 mol/L) were first mixed and stirred for 2 min to form a homogeneous solution. 26 mL of distilled water was then added to the mixture under stirring. The resulted 40 mL of homogeneous solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 50 mL. The cleaned nickel foam was immersed in in the homogeneous solution and the autoclave was sealed and maintained at 100°C for 12 h. NiFe spinel-type oxide nanosheet arrays was obtained after calcining the obtained sample in air at 350°C for 3 h.

2.2 Characterization

Powder X-ray diffraction (XRD) was performed on a Shimadzu XRD-6000 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range from 10° to 70°. The size and morphology of as-synthesized samples were monitored by using scanning electron microscopy (SEM, Zeiss Supra 55) and transmission electron microscopy (TEM, Hitachi H-800). The composition of the products was characterized by means of high-resolution transmission electron microscopy (HRTEM, JEM 2100), energy dispersive X-ray analysis (EDXA) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). Samples for TEM and HRTEM were prepared by scraping the NiCoFe spinel-type oxide from the substrate and ultrasonicated in ethanol, after which the suspension was dropped onto a carbon-enhanced copper grid and dried in air.

2.3 Catalytic reaction

Styrene oxidation was carried out in a 50 mL two-necked round bottom flask with a flask condenser. 1.14 mL of styrene, 1.56 mL of *tert*-butyl hydroperoxide (TBHP, 65 wt.%), 10 mL of acetonitrile and 0.1 g NiCoFe spinel-type oxide (or NiFe spinel-type oxide) nanosheet arrays catalyst were successively added into the flask under stirring. Then the mixture was heated to 80°C in an oil bath for 12 h. The catalytic reaction was monitored by carefully withdrawing small amounts of the reaction liquid every 2 h with a microsyringe from the flask. The products were identified and quantified using a gas chromatograph (GC-SP-6890, SE-30 capillary column, 30 m \times 0.32 mm) with a flame ionization detector, nitrogen as carrier gas and a constant oven temperature (120°C). Both the injector and detector temperature were 300°C. The reactant conversion and product selectivity were calculated as follows:

$$\text{Styrene conversion (mol\%)} = \frac{\text{moles of reactant converted}}{\text{moles of reactant in feed}} \times 100$$

$$\text{Product selectivity (mol\%)} = \frac{\text{moles of product}}{\text{moles of reactant converted}} \times 100$$

3 Results and discussion

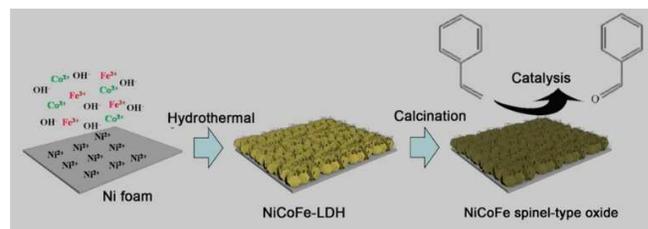


Fig. 1 Schematic illustration of the fabrication procedure of NiCoFe spinel-type oxide nanosheet arrays and their application in oxidation of styrene to benzaldehyde as structured catalyst.

As illustrated in Fig. 1, NiCoFe-LDH nanosheet arrays on a nickel foam substrate were achieved based on the co-deposition of Co²⁺, Fe³⁺ and *in situ* dissolved Ni²⁺ from the nickel foam in CO(NH₂)₂ solution by a hydrothermal reaction. After calcination, NiCoFe spinel-type oxide nanosheet arrays with the same morphology and structure were obtained and used as structured catalyst for the oxidation of styrene. SEM images in Fig. 2 clearly reveal the morphology evolution of the products. Fig. 2a shows the porous and zigzag structure of the nickel

foam. After the hydrothermal reaction of Co^{2+} , Fe^{3+} , nickel foam and urea at 100°C for 12 h, NiCoFe-LDH nanosheet arrays were obtained. As shown in Fig. 2b, hexagonal NiCoFe-

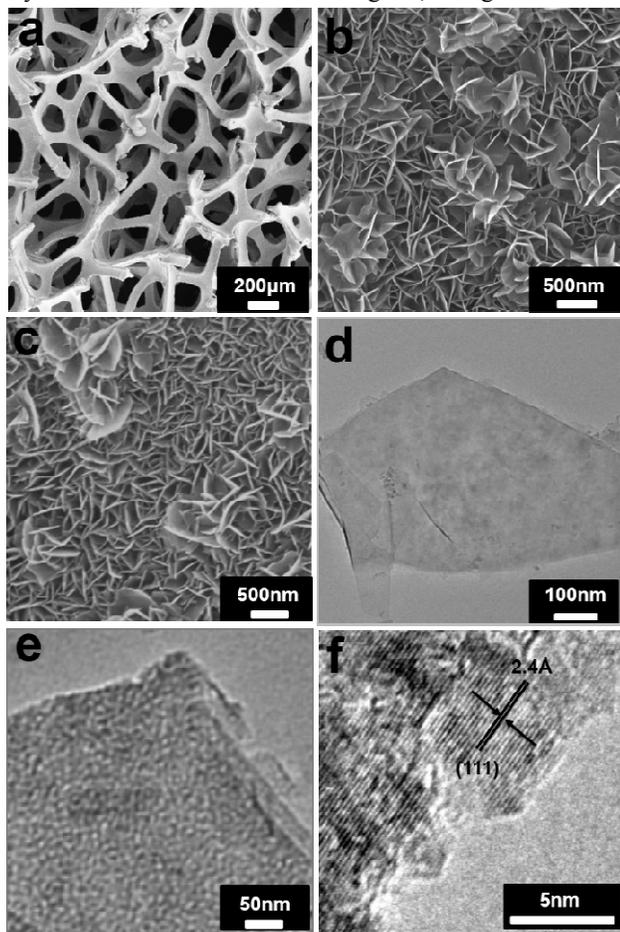


Fig. 2 SEM images of nickel foam (a), NiCoFe-LDH nanosheet arrays (b), and NiCoFe spinel-type oxide nanosheet arrays (c); TEM images of NiCoFe-LDH nanosheet (d) and NiCoFe spinel-type oxide nanosheet (e); (f) HRTEM image of NiCoFe spinel-type oxide nanosheet.

LDH platelets grown perpendicularly to the surface of the substrate are observed, which are about 500 nm in edge length and approximately 10 nm in thickness. NiCoFe spinel-type oxide nanosheet arrays were obtained by calcination of NiCoFe-LDH precursor in air at 350°C for 3 h. As clearly seen in Fig. 2c, the structure of nanosheet arrays is mostly preserved after the calcination treatment. Typical TEM images in Fig. 2d and e show individual nanosheets of NiCoFe-LDH and NiCoFe spinel-type oxide with hexagonal shape, respectively, which are consistent with the SEM images above. However, TEM image in Fig. 2e demonstrates that the ultrathin NiCoFe spinel-type oxide nanosheet consists of numerous interconnected nanoparticles forming a mesoporous structure. HRTEM image of the spinel-type oxide nanosheet in Figure 2f demonstrates the good crystallinity of the material, and the average size of the nanoparticles is about 5 nm. Interplanar distances of 2.4 Å can be determined for a single-crystal particles, corresponding to the (111) plane of the substituted spinel-type oxide. Along with SEM and TEM observations, XRD patterns of NiCoFe-LDH and NiCoFe spinel-type oxide are shown in Fig. 3. As for NiCoFe-LDH precursor, three intense characteristic peaks appearing at 2 theta angles below 35° are attributed to

diffractions of (003), (006) and (012) planes of LDH phase (JCPDF card, No. 51-0463). In the XRD pattern of NiCoFe oxide, no characteristic diffractions of LDH are present,

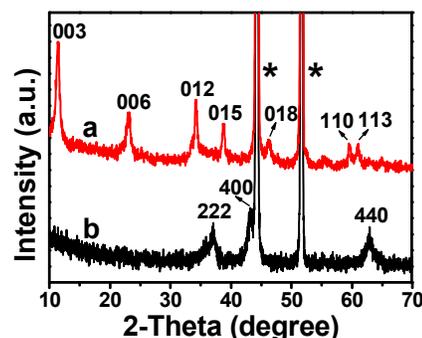


Fig. 3 XRD patterns of the NiCoFe-LDH (a) and NiCoFe spinel-type oxide (b) nanosheet arrays (*: nickel substrate).

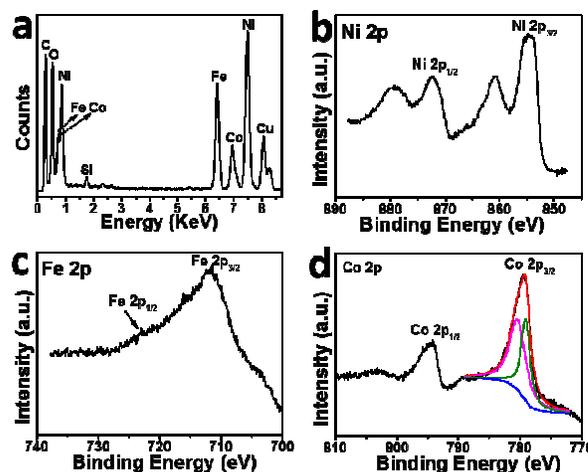


Fig. 4 EDX pattern (a) and XPS spectra (b, Ni2p; c, Fe2p and d, Co2p) of the NiCoFe spinel-type oxide.

indicating that the layered structure of NiCoFe-LDH precursor has been completely destroyed by calcination. The new characteristic diffractions in the pattern demonstrate the presence of spinel-like metal oxide phases. The relative amount of the metal components was measured by energy dispersive X-ray analysis (EDXA) (Fig. 4a), which shows that the atomic ratio of Ni/Co/Fe is around 3.74/1.00/2.11. Based on above results, it is concluded that the substituted spinel-type oxide nanoarrays composed of well-defined porous nanosheets are successfully obtained.

To determine the valent states of the substituted spinel-type oxides, XPS analysis of the sample was carried out and the results were given in Fig. 4b-d. The XPS spectrum in Figure 4b displays that the binding energies are 855.0 eV and 872.3 eV for Ni 2p_{3/2} and Ni 2p_{1/2} which suggested that the valence of Ni is 2+. The binding energy of 711.6 eV accompanied by a peak at binding energy of 724.5 eV in Fig. 4c are for Fe 2p_{3/2} and Fe 2p_{1/2} which indicated the valence of Fe is 3+. The results are quite consistent with the reported value.^{11, 19, 20} From the XPS spectrum of Co 2p in Fig. 4d, it is concluded that the peaks at 779.5 eV and 794.5 eV correspond to Co³⁺ and the peaks at 782.1 eV and 796.8 eV are characteristic of Co²⁺.²¹ Detailed calculation from the deconvoluted peak reveals that the ratio of

$\text{Co}^{3+}/\text{Co}^{2+}$ on the surface of NiCoFe spinel-type oxide is about 1/1.7. Therefore, the NiCoFe spinel-type oxide can be described as Co^{2+} , Co^{3+} substituted NiFe_2O_4 .

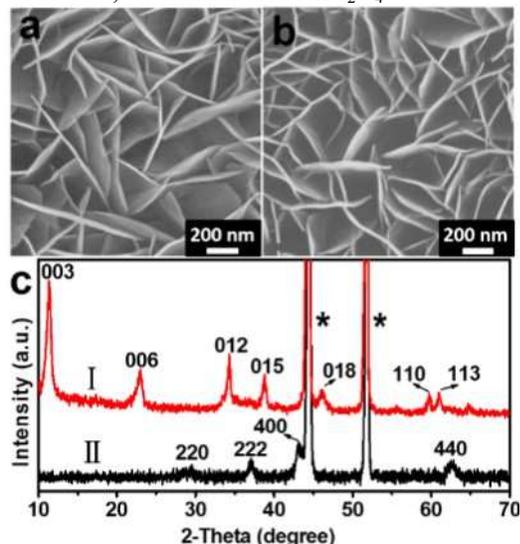


Fig. 5 SEM images of NiFe-LDH nanosheet arrays (a) and NiFe spinel-type oxide nanosheet arrays (b); (c) XRD patterns of NiFe-LDH (I) and NiFe spinel-type oxide (II) nanosheet arrays (*: nickel substrate).

For comparison, NiFe-LDH nanosheet arrays were also prepared by using the similar synthetic process of NiCoFe-LDH without adding $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to the reaction system. NiFe spinel-type oxide nanosheet arrays were obtained after calcining NiFe-LDH in air at 350°C for 3 h. The morphologies and the phases of NiFe-LDH and NiFe spinel-type oxide arrays were almost the same with NiCoFe-LDH and NiCoFe spinel-type oxide, as shown in the SEM images and XRD patterns in Fig. 5.

The oxidation of styrene to benzaldehyde was chosen as a probe reaction to study the catalytic properties of the materials. Benzaldehyde is quite an available chemical that has widespread applications in the production of dyestuffs, perfumes, pharmaceuticals and agrochemicals. It is commercially produced through the catalytic oxidation of toluene to benzoic acid as a by-product which has a low productivity.²² Also, it can be produced by the hydrolysis of benzal chloride. However, the latter method provides benzaldehyde with trace chlorine in it which limits its application in pharmaceuticals and perfumes.²³ Recently, the selective oxidation of styrene with *tert*-butyl hydroperoxide (TBHP) as an oxidant to produce benzaldehyde is of great interest because it is a green process.²⁴ Spinel-type catalysts with high stability and low price have been found to show high selectivity for styrene oxidation to benzaldehyde.^{25,26} However, the reported works based on these catalysts are not efficient, and are hard to separate and recycle.²⁶ The NiCoFe spinel-type oxide nanosheet arrays as mentioned above with the catalytically active component grown directly on a nickel foam substrate may offer the possibility to solve these problems. Fig. 6 shows the catalytic properties of the NiCoFe and NiFe spinel-type oxide nanosheet arrays. NiFe spinel-type oxide nanosheet arrays showed low activity (25% styrene conversion after 6 h, and 36% styrene conversion after 12 h), which is similar with reported spinel-type oxide catalysts.²⁷⁻²⁹ In contrast, the conversion of styrene on NiCoFe spinel-type oxide nanosheet

array catalyst reached 40% after 6 h and increased to 72% after 12 h. The selectivity of benzaldehyde became stabilized at about 64% after 12 h. The specific rate of conversion over NiCoFe spinel-type oxide nanosheet arrays was about 2 times

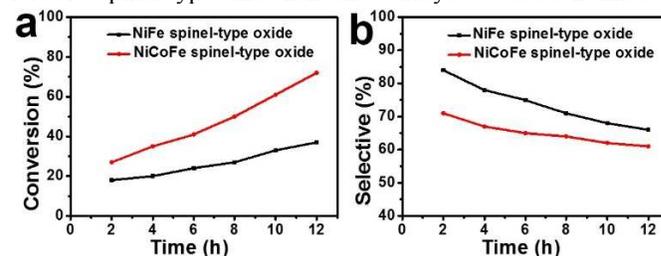


Fig. 6 Styrene conversion (a) and selectivity of benzaldehyde (b) for NiCoFe and NiFe spinel-type oxide catalysts.

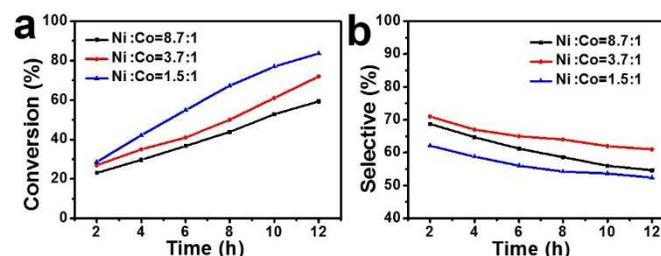


Fig. 7 Styrene conversion (a) and selectivity of benzaldehyde (b) for NiCoFe spinel-type oxide catalysts with different Ni/Co ratio.

higher than that over NiFe spinel-type oxide nanoarrays at 12 h. Moreover, NiCoFe spinel-type oxide catalysts with different Ni/Co ratio were also prepared in a similar synthetic process by changing the amount of Co^{2+} (0.5mmol, 2mmol and 3mmol) added in the hydrothermal system. The Ni/Co ratios determined by EDXA were 8.7:1, 3.7:1 and 1.5:1. Fig. 7 shows the catalytic properties of the NiCoFe spinel-type oxide nanosheet arrays with different Ni/Co ratio. NiCoFe spinel-type oxide with the highest Ni/Co ratio of 8.7:1 showed the lowest catalytic activity (59% styrene conversion after 12 h). As the proportion of Co increased, the styrene conversion was enhanced (Fig. 7a) and NiCoFe spinel-type oxide nanosheet arrays with the Ni/Co ratio of 1.5:1 showed the highest styrene conversion activity of 83% after 12 h. However, further increase the amount of Co^{2+} to a higher level (4 mmol added in the hydrothermal system), the product lost its LDH phase nanosheet morphology and the catalytic activity decreased. Based on above results, it is concluded that the substitution of Co in the spinel-type oxide nanoarrays have a significant influence on the catalytic activity.

It is clearly that our NiCoFe spinel-type oxide catalysts show higher selectivity to benzaldehyde than other products for the oxidation of styrene. Besides benzaldehyde and styrene oxide as the main product, phenyl acetaldehyde, 1-phenyl-1, 2-ethanediol and benzoic acid were also detected as by-products with low productivities. This result well coincide with other spinel-type oxide catalysts.²⁷⁻²⁹ As previously reported, the selectivity of oxidation of styrene varies on different catalysts. With spinel-type oxide as the catalysts, it generally show high selectivity to benzaldehyde as listed in Table 1. A free radical mechanism is involved in styrene oxidation over spinel-type oxide catalysts. The trivalent ions on the surface of catalysts are catalytic active sites and they are more inclined to produce benzaldehyde as a main product.²⁷⁻²⁹ Our NiCoFe spinel-type

oxide nanosheet arrays also show a higher catalytic conversion in the oxidation of styrene than previously reported spinel nanoparticles catalysts, as listed in Table 1.

Table 1. Oxidation of styrene with TBHP catalysed by a variety of catalysts.

Catalyst	Reaction time	Styrene conversion (mol%)	Selectivity (mol%)		Ref.
			Benzaldehyde	Styrene oxide	
NiCoFe spinel-type oxide nanosheet arrays	12h	72.0	64.0	16.2	this study
NiFe spinel-type oxide nanosheet arrays	12h	36.0	66.0	20.8	this study
Fe ₃ O ₄ nanoparticles	12h	36.5	68.4	-	27
NiFe ₂ O ₄ nanoparticles	12h	31.4	55.6	-	27
SrFe ₂ O ₄ nanoparticles	18h	50.8	63.7	28.0	28
Mg,Fe _{3-x} O ₄ nanoparticles	12h	32.0	63.2	-	29

Tracing the source of the high catalytic performance of the NiCoFe spinel-type oxide is of great importance for constructing efficient catalysts. Firstly, the Ni foam substrate with micro holes and zigzag flow channels, result in a good mass transport property and large surface area per unit area of the catalyst. Secondly, the NiCoFe-LDH nanosheet arrays are achieved based on the co-deposition of Co²⁺, Fe³⁺ and in situ dissolved Ni²⁺ from the nickel substrate in CO(NH₂)₂ solution by a hydrothermal reaction. The dissolved Ni²⁺ directly joins the nanosheets growth reaction, making the LDH nanoarrays anchored strongly to the nickel substrate. After calcination, the structure of the NiCoFe spinel-type oxide nanosheet arrays grown firmly on the nickel substrate is obtained, which makes sure the active component distributed homogeneously and also ensures that the catalysts have a strong contact with the nickel foam to mitigate leaching during the catalytic reactions process. Thirdly, the nanosheets on the metal substrate are around 500 nm in edge length and 10 nm in thickness which are quite small, so the large surface area of the nanosheet arrays make more chemically active sites exposed, which contribute a lot to the high catalytic activity. Fourthly, the substitution of Co leads to the appearance of new active Co³⁺ sites at the surface of the samples, resulting in a high catalytic efficiency.^{7, 30} Finally, the nanosheet arrays with porous architecture give a rough surface and open spaces, allowing for easy gas diffusion and mass transport, which greatly enhance the high activity. In addition, our NiCoFe spinel-type oxide catalyst with a nanoarray structure can be easily separated and can be directly reused without any treatment. On the basis of the obtained results above, it is concluded that the NiCoFe spinel-type oxide nanosheet arrays as structured catalyst are shown to be attractive for the styrene oxidation reaction and may open up new opportunities for the design of new types of highly efficient structured catalysts.

4 Conclusions

NiCoFe spinel-type oxide nanosheet arrays as structural catalyst for the process of styrene oxidation were fabricated by using layered double hydroxides (LDH) as precursors, which exhibited high catalytic activity (72% conversion) and selectivity (64% for benzaldehyde) at 12h for oxidation of styrene by *tert*-butyl hydroperoxide (TBHP). The high catalytic activity of the NiCoFe spinel-type oxide nanosheet arrays is mainly attributed to the direct contact of the nanosheet arrays with the underlying substrate, the small size of nanosheets with large surface area and the substitution of Co in the spinel-type oxide. This strategy can be extended to synthesize other metal oxide arrays on metallic substrates and offers new opportunities for the design of new types of highly efficient structured catalysts.

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Notes and references

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