Hydrothermal synthesis of graphene-LaFeO₃ composite supported with Cu-Co nanocatalyst for higher alcohol synthesis from syngas

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Abstract

The composite of graphene and a perovskite-type oxide (PTO) should be an attractive new material, owing to the special properties of graphene and the flexibility of PTO. Both graphene and PTO are promising support for some metallic nanoparticles. Therefore, in this work, taking LaFeO₃ as the representative for PTO, a novel composite of graphene sheets-LaFeO₃ has been prepared by using hydrothermal synthesis, and bimetallic nanoparticles of Cu-Co have been loaded on the composite. The resultant catalyst is applied to higher alcohols synthesis (HAS) from syngas. The morphology, structure and the state of the bimetallic composite catalyst are characterized by using techniques of SEM, TEM, AFM, XRD, TPR, Raman and N₂ adsorption-desorption. For the graphene-LaFeO₃ support, the graphene sheets are embedded into the bulk LaFeO₃ or uniformly deposited on the surface of the LaFeO₃ grains, resulting in high specific surface area. And the mass transferring ability of the bimetallic catalyst is optimized by uniform mixing of graphene and LaFeO₃ and the formation of the mesopores. For the active component, the Cu-Co alloy nanoparticles are highly dispersed on the graphene-LaFeO₃ composite, which leads to the high activity, high selectivity and

excellent stability to higher alcohols.

Key words: graphene, LaFeO_3 , perovskite-type oxide, CuCo alloy, higher alcohols synthesis

1. Introduction

With declining fossil fuel resources, the alternative commercial energy sources, such as higher alcohols from coal or biomass via syngas, have been studied extensively in the recent years as clean, sustainable and transportable fuel alternatives. The key challenge for higher alcohol synthesis (HAS) [1] is to develop a catalyst with qualified performance, and the catalytic conversion from syngas to higher alcohols is considered to be the most efficient way for producing C_{2+} alcohols (alcohols with two or more than two carbon atoms in one molecule), to be used as fuel additives, gasoline blends and alternative transportation fuel.

The catalysts reported for HAS include modified Fischer-Tropsch (FT) catalysts, modified methanol catalysts, molybdenum based catalysts and rhodium based catalysts. The modified FT catalysts, mainly include Cu-Co and Cu-Fe based catalysts [2], generally generate $\text{C}_1\text{--C}_6$ linear alcohols. The modified methanol catalysts produce a mixture of methanol and comparatively small part of C_{2+} alcohols. Similar to modified FT catalysts, Mo-based catalysts [3] mainly produced $\text{C}_1\text{--C}_5$ straight chain alcohols, while which possess very good anti-sulfur ability and run under much high pressure. Rhodium-based catalysts [4] show high selectivity to ethanol, but in a high-cost. Among all of the four categories of alcohol catalysts, the improvement on their stability, reactivity and the selectivity to C_{2+} alcohols is still a major challenge for the commercialization of HAS technologies.

It is expected that remarkable improvement on the selectivity and the stability may be achieved by using supported bimetallic Cu-Co catalysts. For example, Cu-Co/ZnO shows high C_{2+} oxygenate selectivity [5], in which ZnO support, to some extent, improves the dispersion of Co and the interaction between cobalt and copper, while improvement on the stability of the catalyst is needed. Subramanian et al.[6] prepare a series of Cu-Co bimetallic catalysts with different structures and find that Cu-Co mixed nanoparticles in atomic distance is beneficial for higher alcohols formation owing to the synergy between Cu and Co. It is widely accepted that either nanoparticles of Cu-Co alloy are formed or the two nanometal particles of copper and cobalt are fully in contact, the high selectivity to C_{2+} alcohols would be obtained; and the strong interaction between Cu-Co and support is the key for improving the stability for HAS catalyst [7, 8].

Perovskite-type oxides (PTOs), the general formula ABO_3 , have been extensively studied as catalysts mainly for oxidation reactions [9]. Previously, our research group found that $LaFeO_3$ with perovskite structure supported Cu-Co showed high selectivity to C_{2+} alcohols and very good stability, owing to the formation of bimetallic Cu-Co nanoparticles and the interaction between the nanoparticles with the support [10]. Escalona et al. study $LaFe_{1-x}Co_xO_3$ for CO hydrogenation to produce hydrocarbons, and similar viewpoints are raised, in which metal alloy of Co-Fe is formed and the anti-sintering ability of the metal nanoparticles is very good [11]. However, the lower specific surface area of PTOs is the major disadvantage, which leads to relatively low activity. For example, Ding et al.[12] prepare high-purity $AFeO_3$ (A: La, Sm, Eu, Gd) materials and the specific surface area is in the range of 2-3 m^2/g .

PTOs with high specific surface area can be made, while the preparation methods are complex. For example, using template-based method PTOs with specific surface area exceeding 100 m^2g^{-1} can be made, as for $Co/LaFe_{0.7}Cu_{0.3}O_3$ catalyst [13], in which, the Cu-Co alloy nanoparticles are uniformly disperses on $LaFeO_3$ support. And the strong interaction between Cu-Co and $LaFeO_3$ effectively improved the anti-sintering ability of the Cu-Co nanoparticles in the catalysts, resulting in a good stability for HAS reaction.

Graphene (GE), a two-dimensional sheet of sp^2 -bonded carbon atoms in honeycomb-like network, is kind of much attractive material due to its high mechanical strength, high surface area and excellent stable chemical property [14]. Recently, much effort has been focused on the synthesis of graphene-based composites by using graphene oxide (GO) solution. The composites, often with hierarchical ordering, have been assembled using nano- or microscale templates, such as polymers [15], emulsions[16], silica [17, 18], titania[19, 20] and iron oxide [21]. In detail, Y. Liu et al.[17, 18] prepare meso-macroporous graphene- SiO_2 composites, showing an excellent catalytic activity, high selectivity and good stability in the CO oxidation in hydrogen rich gases. Zhou et al.[22] reported that the graphene-wrapped Fe_3O_4 anode material exhibit much better performance in the reversible capacity and the cyclic stability than those without graphene. Wan et al.[23] prepared graphene oxide- TiO_2 composites, in which graphene oxide play an important role in structural integrity and stability, and the tunable pore sizes by adjusting the starting compositions. However, to the best of our knowledge, the modification or functionalization of PTOs including $LaFeO_3$ with graphene for gas-solid catalytic application has not been reported in the open literatures. There are a few attempts to combine PTOs with CNTs (carbon nanotubes) for use in metal-air batteries, for instance, Weidenkaff et al.[24] prepare $Ln_{1-x}A_xCoO_3$ ($Ln=Er, La$; $A=Ca, Sr$)/CNTs composite material. GE is closely related with CNT, that

is, a CNT can be made by rolling a GE sheet.

GE tends to interact with metals, owing to π electrons from the sp^2 hybrid of the carbon atoms [25], which can stabilize the metallic nanoparticles including copper and cobalt. The specific surface area of GE is high, and as inserting GE sheets into the grains of a PTO the resultant composite should have high specific surface area. Thus, if nanoparticles of Cu-Co alloy are loaded on the GE-PTO composite, the catalyst should show excellent performance for HAS including activity, selectivity to C_{2+} alcohols and stability.

GE is an attractive new material, and PTOs are a kind of mixed metal oxide which have extensive application areas. In the formula ABO_3 of PTOs, A and B sites ions can be substituted by other metal ions, generating $A_{1-x}A'_xB_{1-y}B'_yO_3$ and so on. It is known that about 90% metal ions in the Periodic Table can be served as the ions of the PTOs' lattice [26]. Therefore, the preparation of GE-PTOs composite is attractive and of great value.

In this work, a method for preparing GE-LaFeO₃ composite was reported, in which LaFeO₃ is a PTO. Cu-Co/GE-LaFeO₃ was used as the catalyst for HAS. The details of the preparation, the characterization of the composite and the catalytic performance of the catalyst for HAS were discussed. This preparation method should be extendable for preparing other GE-PTOs composites.

2. Experimental

2.1 Preparation of GE and the GE-LaFeO₃ (LFO) composite

The graphite oxide (GO) was synthesized from oxidation of flake graphite according to the Hummers method.[27] Flake graphite powder and NaNO₃ were added into concentrated H₂SO₄ in the condition of iced bath. Then, KMnO₄ was added gradually under vigorous stirring, and maintained the stirring at 2 °C for 0.5 h. After that, the deionized water was slowly added into the solution and the mixture was stirred at 40 °C for 4 h. Then, the mixture was stirred at 98 °C for 15min, and then, H₂O₂ (30 wt.%) and deionized water were added and stirred for 40 min. The resultant graphite oxide solution was filtered and washed with deionized water for several times until to near-neutral pH. The obtained GO solution was ultrasonic treated for 30 min. The layers of unexfoliated graphite oxide were separated out by using centrifugation at 3000 rpm for 5 min. After that, the suspension containing GO was centrifuged at 8000 rpm for 10 min, and it was freeze-dried overnight. The obtained suspension with GO (1.25 mg/ml) was then used for the following preparation of GE-LFO

composites.

Hydrothermal synthesis of GE-LaFeO₃ was carried out in a stainless steel autoclave. The typical synthesis procedure was as follows: first, Fe(NO₃)₃·9H₂O was dissolved in 150ml GO suspension (1.25 mg/ml). Then, other reactants were added into the solution in the sequence of La(NO₃)₃·6H₂O, NaOH and Na₂CO₃ with stirring, and the molar ratio of La:Fe:NaOH:Na₂CO₃ was 1:1:80:20. The obtained mixture was transferred into the autoclave, and was heated to desired temperatures (such as 300 °C or other temperatures) for 2-48h. After cooling, the product is filtered and washed with deionized water. Lastly, the product was dried at 100 °C in air. The prepared graphene-LaFeO₃ oxide composite is signed as GE-LFO.

2.2 Preparation of Cu-Co/x% GE-LFO composite catalysts

The GE-LFO supported bimetallic Cu-Co catalysts were prepared as follows. The particles of the GE-LFO were impregnated with an aqueous solution of Cu(NO₃)₂·3H₂O and Co(NO₃)₂·6H₂O by wet co-impregnation method. The impregnated samples were freeze-dried for 12 h in vacuum. The obtained Cu-Co/GE-LFO composite was labeled as Cu-Co/x%GE-LFO, where x stand for the weight of graphene in the composite. In all samples, the total loading amount of Cu and Co was kept constant at 10% by weight in calcined catalyst, and the molar ratio of Cu/Co constant at 1:2. The weight fraction of Cu+Co and geraphene was defined as

$$(Cu + Co) \% = \frac{[M]_{Cu} + [M]_{Co}}{[M]_{Cu} + [M]_{Co} + [M]_{GE} + [M]_{LFO}}$$

$$GE \% = \frac{[M]_{GE}}{[M]_{GE} + [M]_{LFO}}$$

in which [M]_{Cu}, [M]_{Co}, [M]_{GE}, and [M]_{LFO} are the weight of metal copper, metal cobalt, graphene and LaFeO₃ support, respectively.

2.3. Characterizations of Prepared Catalysts

The morphology of samples was examined using a scanning electron microscopy (SEM; JEOL, JSM-6700F, 5 kV) and a transmission electron microscope (TEM; JEOL, JEM-2100F, 200 kV). The BET

specific surface areas and pore volumes of samples were obtained by using the N₂ adsorption isotherms at 77 K on a Micromeritics ASAP 2020 apparatus. And the GE-LFO support was calcined in N₂ at 600°C before testing. Crystallographic information of the samples was collected using powder X-ray diffraction (XRD; Bruker, D8 Advance X-ray diffractometer, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$). Raman spectra of samples were collected using a DXR Raman microscope (Thermo Scientific), including a 780-nm excitation laser. AFM observation was conducted for dispersed samples dropped on freshly cleaved mica surfaces (Tip mode, Agilent 5500, USA). The results were acquired at an X-ray power of 250 W and an energy step of 0.1 eV. The vibrational characteristics of powders were investigated using Renishaw inVia Raman microscope, Leica DMLM, RL663 laser. The results were acquired at an X-ray power of 250 W and an energy step of 0.1 eV. The vibrational characteristics of powders were investigated using Renishaw inVia Raman microscope, Leica DMLM, RL663 laser. Temperature programmed reduction (TPR) experiments were carried out on a quartz reactor with a reduction gas mixtures of 5 vol. % H₂/Ar at a heating rate of 10 °C min⁻¹. Before TPR tests, the sample was reduced in a gas mixture of 5 vol. % H₂/Ar at 600 °C for 2 h and then oxidized in air at 150 °C for 1 h to form copper and cobalt oxides.

Catalytic performance tests were evaluated in a stainless-steel fixed-bed continuous-flow reactor and gas chromatograph (GC) combination system. In each run, 800 mg catalyst was loaded into the reactor and then reduced at 400 °C for 3 h in the presence of H₂ with a flow rate of 30 mL/min. After reduction, the reactor was cooled to room temperature, and the pressure was increased to 3 MPa by feeding the syngas mixture (H₂/CO/N₂=8:4:1, where N₂ was used as the internal standard gas for analyzing the reacted gases). The gas hourly space velocity was set at 3900 mL g_{cat}⁻¹ h⁻¹. The gas chromatograph was equipped with two packed columns. Off-gases, such as CO, H₂, N₂, CH₄ and CO₂, were separated online by using a TDX-01 packed column (2 m) connected to a TCD detector. The condensed liquid products of alcohols and hydrocarbons were collected and analyzed off-line using a Porapak Q column (3 m) connected to a FID detector.

The activity of catalyst was evaluated by CO conversion (X_{CO}) and the product selectivity (S_i). The formulas were shown as below:

$$\text{CO conversion(\%): } X_{\text{CO}} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100$$

$$\text{Product selectivity (\%): } S_i = \frac{nC_i}{\sum_{i=1}^6 nC_i} \times 100$$

Where $[\text{CO}]_{\text{in}}$ and $[\text{CO}]_{\text{out}}$ are the moles of CO in the feed stream and in the off-gas, respectively. n and C_i represent the number of carbon atoms and moles of a carbon-containing product, respectively.

3. Results and discussion

3.1 SEM images

The morphology of prepared LFO and GE-LFO composites at different hydrothermal temperature are shown by SEM images in Fig. 1. As can be seen from Fig.1 (a, b), the sample prepared at 275 °C exhibited the random and messy amorphous forms, and most of the particles are La_2O_3 and $\text{FeO}(\text{OH})$ with only a little LFO formed. With hydrothermal temperature increasing, the LFO and GE-LFO composites are successfully synthesized by a simple and direct hydrothermal synthesis method, see Fig. (c, d, e, f, g,). The size of the pure LFO with perovskite structure that in a smooth orthorhombic shape of Fig.1 (c,d) mainly ranged from 4 to 5.5 μm which can be seen from the particle size distributions in Fig. 1(c) obtained by measuring more than 150 particles. The cubic grains are LaFeO_3 with perovskite structure, which has been proved by XRD results, the details will be addressed in the following section 3.5.

For 1%GE-LFO, doping GE did not influence the morphology of LFO at all, but the particle size distributions of GE-LFO slightly increase to the range of 5 to 7 μm , see Fig. 1(e). As the content of GE increased from 1% to 5%, the surface of the cubic grains turned from smooth to rough, which may indicate that the surface of the cubic grains were covered by wrinkle GE film, see Fig. 1(g). Measurement of energy dispersive spectroscopy (EDS) on a representative area in Fig.1 (g) was taken place, and the results indicate that the composites are consisted of C, O, Fe, La, in which carbon element is up to 14.76% on the selected area in SEM image in the Fig. 1(i). This suggests that the grains are composed of LFO and GE, for that the contaminated carbon could not reach this high content.

The SEM-EDS mapping images of Fig. 1(k) can be used to further prove the homogeneous mixing of

GE and LFO in the synthesized composites. The elements of carbon (C K) in GE and lanthanum (La K) and iron (Fe K) in LaFeO_3 have been detected. The element distributions of La and Fe were overlapped perfectly in the cubic particles, and the distribution of C matched well with the distribution of La and Fe suggesting that GE and LFO were uniformly mixed, see the yellow arrows directed in Fig. 1(k). However, for a few grains, elements of La and Fe were detected, while carbon can hardly be seen, as shown by the red arrows in Fig. 1(k). Likely, the grains on which carbon was not detected were not covered by GE. And the GE was also found being inserted into the LFO grains, which could not be well detected by EDS, which was a surface detection technique with limited depth resolution.

The generally used methods for preparing PTOs are co-precipitation and citric acid complexation, in which high temperature calcination in air is necessary in order to form the perovskite structure via solid chemical reactions. The high temperature calcination is also necessary for preparing PTOs via other methods, and generally, the calcination temperature is higher than 700 °C [28]. In the reduction atmosphere the oxides may be reduced, thus PTOs can't be obtained. Furthermore, carbon-based GE is not stable and likely air-combusted under elevated temperatures. Therefore the conventional PTO preparation methods are not successfully applied in the preparation of the GE-doped PTO composites. The current hydrothermal synthesis approach, occurred at much lower temperatures and mild oxidation atmospheres, made synthesis of PTO-GE composites successfully.

PTOs are a class of mixed oxide with formula of ABO_3 , and most of metal ions can be acted as the A and/or B site ions. PTOs can be used or potentially used as catalyst, electrolyte material, ceramics material and so on. Therefore, preparation of GE-PTOs composite is of great significance, and here at the first time, we proposed a preparation method.

3.2 Morphology of the catalysts from TEM images

Fig.2 TEM images of (a, c) 1%GE-LFO; (b) bright-field STEM image of LFO nanoparticle; (b') indexed fourier transforms (FFT) image of red box; (d) Multiple lattice spacing of LFO; (e) Cu-Co/ 1%GE-LFO and (f) STEM-EDS line scan profile of three nanoparticles; Scale bar: 1 μm for (a, c); 5nm for(b); 200 nm for (e).

In order to further insights into the morphology and crystal structure of the prepared GE-LFO nanostructures, and the dispersion degree of loaded Cu-Co nanoparticles on GE-LFO composite, the TEM

results were provided as shown in Fig. 2. The morphology of LaFeO_3 still resembles a cubic shape in micron-size, as in Fig. 2 (a, c). As the red arrows directed in Fig. 2(a) and Fig. 2(c), the crimp layer and the thin film were supposed to be graphene, coinciding well with SEM images presented in the Fig. 1(g). The bright-field STEM image recorded from the individual cubic LFO particle was shown in Fig. 2(b), and the unidirectional alignment of the lattice fringes confirmed LFO being in perovskite structure. The corresponding indexed fourier transforms (FFT)s image was shown in Fig. 2 (d), indicating that the crystal lattice spacing of LFO was 0.2745 nm, which was much close to the theoretical value of 0.2776 nm for the crystalline plane [1 1 0] of LFO (JCPDS Card No. 01-075-0541).

The morphologies of loaded Cu-Co nanoparticles on the composite of GE-LFO can clearly be observed from Fig. 2(e). The metal particles were highly and homogeneously dispersed with an average particle size of 10 nm. The high dispersion may be attributed to the following two reasons. For the bimetallic nanoparticles that dispersed on GE, the polar groups (hydroxyl, epoxide, carbonyl and carboxyl) on GO can offer the anchoring points for copper and cobalt ions in the impregnation process. The anchored copper and cobalt ions should be highly and uniformly dispersed, and migration and agglomeration could be prevented owing to the anchor. After reduction, GO changed to GE and the ions of the metals became to metal nanoparticles, and the metal nanoparticles of Cu-Co should be anchored on the surface of GE, for that metal nanoparticles tend to interact with GE[29]. For the metal nanoparticles of Cu-Co supported on LFO, the metal nanoparticles should be also highly dispersed. Both copper and cobalt ions can be acted as the ions of LFO lattice, suggesting that copper and cobalt species incline to interact with the support of LFO. What is the more important is that the interaction between Cu-Co nanoparticles and GE, and the interaction between Cu-Co nanoparticles and LFO would hinder the sintering of Cu-Co nanoparticles, which improve the stability of the catalyst.

Besides, the highly dispersion of Cu-Co nanoparticles, the alloy formation of Cu-Co is other main reason for the followed high catalytic performance of CO hydrogenation. The alloy states can be clearly shown in the Fig.2 (f), a line profile analysis of STEM. The intensity peaks of Cu and Co were synchronous with each other in each of the nanoparticles from the line profiles of Fig.2 (f), in three continuous nanoparticles, proving that the bimetallic Cu-Co held an alloy structure.

3.3 AFM results

The topography cross-sections of functionalized GE layers and the three-dimensional images of GE-LFO composite are shown by atomic force microscopy (AFM) in Fig. 3. As can be seen from Fig. 3(a) and corresponding cross-section results of Fig. 3(a', a''), the thickness of the graphene sheet obtained is about 1.28 nm. This value is, somewhat, larger than the theoretical thickness of a single carbon-atom layer. The reasons are attributed to the intrinsic out-of-plane deformation of graphene, or the roughness on scales smaller than the AFM probe which will lead to an overestimate of the sheet thickness when cannot reach the lowest points. While, the nano-scale thickness of GE is still thin enough for micrometer-scale GE-LFO composites.

From Fig. 3(b) and the corresponding three-dimensional image of GE-LFO in Fig. 3(c), it is seen that GE sheets were embedded in cubic LFO phase, which seems like that GE sheets were inserted into the bulk LFO, see the red arrow indicated in Fig. 3 (b). From Fig. 3 (c), it is shown that a surface of the cubic LFO was covered by a wrinkle GE layer, as the yellow arrow directed, in according with the SEM results of Fig.1 (g). On the whole, GE sheets were either embedded into the bulk LFO or deposited on the surface of the cubic LFO.

3.4 The results derived from N₂ adsorption-desorption

Nitrogen adsorption-desorption isotherms of the GE-LFO composite and the corresponding BJH pore size distribution are shown in Fig. 4. For the pure LaFeO₃, the isotherm was classified as type II, with an H3 little hysteresis loop. And the hysteresis loop that located in high pressure is related to the macropores, which was formed by the stacking of LaFeO₃ grains. In all cases, except for the line of pure LaFeO₃, the isotherms can be classified as Type IV, according to IUPAC definitions, which highly related to the properties of mesoporosity. The Type H4 loops at P/P₀ range of 0.8-1.0 present the formation of narrow slit-like pores,[30] which should be ascribed to the separation of graphene from the LaFeO₃ perovskite oxide.

During the high temperature calcination in N₂, the separation of the LFO particles and GE would take place, in the composite GE sheets were covered on or embedded in the LFO grains as stated above, therefore resulting in the interspaces between GE and LFO. LFO is metal oxide and GE is carbon sheets, the chemical bond formation between them is not favored; resultantly, in the high temperature calcination, shrinkage of the accumulated LFO particles would happen, and LFO and GE would split off, leaving the interspaces. These

interspaces produced the 5-8 nm slit-like mesopores for GE-LFO composites, in according well with Fig.1 (h) and Fig. 3 (b) and (c). By comparing the pore size distribution profiles of pure LaFeO_3 shown in Fig.4 (b), the mesopores existed in GE- LaFeO_3 composites and not existed in the pure LFO.

To be sure, the mesopores at 3.5nm -12.5 nm are slit-like pores ascribed from the separation of LFO and the GE sheets, the similar phenomenon was found and discussed in our previous work for GE- SiO_2 composite[17, 31]. Speculatively, the BET surface areas and slit-like mesopores of the composite materials could be adjusted by regulating the content of the GE and/or the calcination temperature.

The most probable mesoporous sizes were 5.5, 6.6 and 7.8 nm for 1%GE-LFO, 3%GE-LFO and 5%GE-LFO, respectively. The increase of the mesoporous size with the increasing of the GE content may be attributed to the increase of the folding, stacking and wrinkles of the GE sheets with the increasing of the GE content.

The specific surface area, pore volumes and the most probable mesopore size of the composite derived from those isotherms are summarized in Table 1. The specific surface area of sample are 7, 12, 31 and 53 m^2/g for LaFeO_3 , 1% GE- LaFeO_3 , 3% GE- LaFeO_3 and 5% GE- LaFeO_3 , respectively. The BET surface areas of the composite increased with the increase of GE content, suggesting that the surface of GE sheets were not enclosed by LaFeO_3 particles and there are slit pores between GE and LaFeO_3 , agreeing with the above statement.

The specific surface area of 5%GE-LFO was up to 53 m^2/g , which more than eight times higher than that of pure LaFeO_3 . The specific surface area of the well-organized micro spherical LaFeO_3 nanoparticles is 8.5 m^2/g prepared with hydrothermal method [32, 33], which is close to 7 m^2/g of this work. In order to prepare LaFeO_3 with high surface area, sol-gel method was used, and the specific surface area of the resulted LaFeO_3 is 16.5 m^2/g^{-1} [34]. By comparing, it can be said that the specific surface area of the prepared GE-LFO is high.

Correlating with above mentioned SEM and TEM AFM results, which exhibited representative and local images of GE-LFO composite, while, the N_2 adsorption-desorption isotherms showed the overall property of the composite. The N_2 adsorption-desorption results further prove that the graphene sheets were embedded

into the bulk LFO or uniformly covered on the surface of the cubic LaFeO_3 oxide.

3.5 XRD results

The crystallinity and phase purity of the prepared GE-LFO and formation mechanism of LFO sample were investigated by using the powder XRD patterns, as shown in Fig. 5. For all prepared LFO and GE-LFO, the diffraction peaks can be indexed to the orthorhombic perovskite structure of LaFeO_3 (JCPDS 00-037-1493) with lattice constants of $a = 5.565 \text{ \AA}$, $b = 7.838 \text{ \AA}$ and $c = 5.577 \text{ \AA}$. The sharp and strong diffraction peaks suggest that LFO samples were highly crystallized. No peaks corresponding to FeO(OH) , La_2O_3 and other iron or lanthanum containing species can be detected, which further confirms the presence of single-phase LaFeO_3 . The average crystallite size calculated from Scherrer formula is 144 nm after 48h hydrothermal period.

As for GE-LFO composites prepared at 300°C , the sharp and strong diffraction peaks of LFO obviously appeared (Fig. 5 a), indicating that the content of GE and reaction time did not influence the crystal phase of LFO at all. Separately, the presence of GE in 1%GE-LFO, 3%GE-LFO and 5%GE-LFO composite had little effect on the orthorhombic crystal phase of LFO from Fig. 5(a), which agrees with the report of [24] and [35]. In [24] and [35], the composites of carbon nanotubes with metal oxide were made, and found that carbon nanotubes had little effect on the phase of the metal oxides.

The state of bimetallic Cu-Co in Cu-Co/GE-LFO catalyst after different treatment was show in Fig.5 (b). Compared to the fresh Cu-Co/GE-LFO catalyst, the Cu-Co/GE-LFO-after reduction exhibited the diffraction peaks of $\text{Co}_{0.52}\text{Cu}_{0.48}$ alloy (JCPDS 00-50-1452), which was confined in the diffraction peaks between Co (111) at 44.2° and Cu (111) at 43.3° [36]. The formation of Cu-Co alloy would be further supported by the following TPR results. Additional, compared with the reduced Cu-Co/GE-LFO catalysts, the diffraction peaks corresponding to $\text{Co}_{0.52}\text{Cu}_{0.48}$ alloy is weakened and evidently moved to lower 2θ value after the reaction, caused by the separation of some cobalt from $\text{Co}_{0.52}\text{Cu}_{0.48}$ to generate Co_2C , as shown in the Fig. 5(b). For the used catalyst, at 2θ of 42.5° , a weak diffraction peak corresponding to Co_2C was observed. The formation of Co_2C can improve the selectivity to higher alcohols in the catalytic performance.

3.6 TPR results

The TPR-H₂ tests were carried out to further probe the possibility of Cu-Co alloy formation and the reducibility of the oxidized Cu-Co species. Generally, no significant hydrogen uptake was noticeable on LaFeO₃ support. Dacquin [37] and Faye [38] pointed out that Fe³⁺ remains unchanged inside the perovskite structure up to 700 °C in TPR process. For the TPR profile of monometallic Co/LFO, there were two H₂ consumption peaks, one was at T_{max}=456 °C and the other was at T_{max}=614 °C in the Fig. 6(a). The low-temperature peak was likely associated with the reduction of Co³⁺ to Co²⁺ with the subsequent structural change to CoO, and the higher temperature peak to the reduction of Co²⁺ to metallic cobalt[39].

As for the bimetallic Cu-Co/LFO catalyst, an overlapped reduction peaks from 320 °C to 500 °C and a tailing reduction peak from 520 °C to 620 °C can be clearly observed in Fig.6 (b). Separately, for the overlapped peak with reduction peak at 359 °C could be assigned the reduction of Cu²⁺ to Cu⁰ and Co³⁺ to Co²⁺, at the same time some of the Co³⁺ would be reduced to Co⁰. Seen from Fig. 6a and Fig. 6b, adding copper into Co/LFO leads to a shift of the reduction for cobalt ions to lower temperature, the similar phenomenon is reported in[40]. Huang et al. [41] find that adding copper ions into the perovskite lattice promoted the reduction of cobalt ions. Wang et al. [8] ascribe the shift of the reduction peaks to the lower temperature with increasing Cu content in Cu–Co-oxide/Al₂O₃ to the hydrogen activation on the reduced copper sites. Namely here for Cu-Co%GE-LFO, metallic cobalt is formed under the catalyzing of the metal copper nanoparticles, hence, the metallic cobalt species should be nearby a nanoparticle of metallic copper, thus the metallic cobalt would tend to interact and link with the nanoparticle of copper to form a bimetal alloy nanoparticle.

Similarly, tailing peak at 596 °C is attributed to the reduction of Co²⁺ or Co³⁺ to Co⁰, which is lower than that of monometallic Co/LFO, this is likely also attributed to the catalyzing of metallic copper for cobalt ions reduction.

For Cu-Co/3%GE-LFO and Cu-Co/1%GE-LFO catalyst of Fig.6 (d, c), the TPR profile is much similar to each other, except that the reduction peak about 20 °C to lower temperature for Cu-Co/3%GE-LFO. While, compared with Cu-Co/LFO catalyst in Fig.6 (b), the doping GE led to a significant difference for TPR profiles, lowered the reduction peak obviously. The main reason may be attributed to higher dispersion of Cu-Co particles in the GE containing catalysts, owing to the higher specific surface area of GE-LFO composite, see Table 1.

Compared with Cu-Co/LFO, for Cu-Co/GE-LFO the broad hydrogen consumption peaks for the reduction of Co^{2+} or Co^{3+} to metallic cobalt shifted to a lower temperature of around 580 °C. The shift may be due to the higher dispersion of copper and cobalt species in the GE containing catalysts. At the same time, the hydrogen consumption reduced as compared to that of Cu-Co/LFO, this reduction indicates that more cobalt and copper are in interaction and most of the copper and cobalt can be reduced together at lower temperatures, accordingly less mono cobalt metal was formed. The TPR results suggest that Cu-Co alloy is more likely to be formed as copper and cobalt supported on GE than supported on LFO. In Cu-Co/GE-LFO, Cu-Co particles were supported on the surface of both GE and LFO.

3.7 Raman

Raman spectroscopic technology was generally used to determine electronic structure of carbon products, the structure distortion (order-disorder effects in the lattice) and oxygen motion of perovskite oxide materials, and the Raman spectrum are shown in Fig.7. Compared with Raman spectroscopy of LaFeO_3 (Fig.7 a) and graphene (Fig. 7b), all of the composite of GE-LFO keep the properties of both GE and LFO. In detail, five vibrational bands at 220, 284, 402, 490 and 604 cm^{-1} were observed. The absorptions at 284 and 490 cm^{-1} corresponds to A_g and B_{3g} assigned modes. Two-photon scattering and impurity related scattering were observed at 604, 402 and 284 cm^{-1} , which were in good agreement with the values reported for LaFeO_3 [32]. No other peaks corresponding to LaO_x and FeO_x were found, agrees with XRD results above.

The well-known G peak (at $\sim 1590 \text{ cm}^{-1}$) is usually assigned to characteristic for sp^2 -hybridized carbon-carbon bonds in graphene, and D band (at $\sim 1350 \text{ cm}^{-1}$) exhibits a common feature for sp^3 defects in carbon. The prominent D band is an indication of disorder of the GO, originating from defects associated with vacancies, grain boundaries, and amorphous carbon species [42]. Generally, the intensity ratio of the D band to the G band was used to reflect the order of defects in GO or graphene. Compared to GO, GE-LFO composites showed two differences in the Raman spectra. Firstly, the calculated I_D/I_G for GE-LFO samples were lower than that of GO, indicating a lower density of defects in GE of GE-LFO. Secondly, the I_D/I_G ratio for GO, 1%GE-LFO, 3%GE-LFO and 5%GE-LFO were 1.59, 1.51, 1.42 and 1.23, respectively, which decreased with the increase of GE contents. This may imply that the increasing GE content, to some extent, was able to rectify the biased aromatic structures by repairing defects and reducing graphene oxide. While, compared to reduction

treatment of the hydrothermal treatment, the chemical reduction was always associated with an increase of the I_D/I_G ratio because of the fragmentation of sp^2 domains, as the report of [43]. And the decreasing of I_D/I_G ratio in the composites suggests that the current hydrothermal method resulted in more graphene content without decreasing the average size of the sp^2 domain and retained large sp^2 domains. The revealed lower defect levels in the NaOH hydrothermal treated GO samples was consistent to the Sun's work [44].

3.8 Proposed mechanism for GE-LFO formation

Based on all collected characterization information, the following reaction mechanism of current the hydrothermal method was proposed, as shown in Fig. 8.

Firstly, the surface of GO generally possesses many functional groups, carbon vacancy defect and surface dangling bonds. It offers the anchoring points for Fe^{3+} and La^{3+} adsorption on the both sides of GE. After the treatment of ultrasonic, the Fe^{3+} and La^{3+} uniformly dispersed and intercalated between the sheets of GO to form stable metal-GO. Upon adding NaOH, La^{3+} and Fe^{3+} ions are transformed into small amorphous $La(OH)_3$ and $Fe(OH)_3$ precipitates at the adsorption site of GO, as shown in the Equation 1.

Secondly, in the 270 °C hydrothermal condition, small crystallines of $LaFeO_3$, $FeO(OH)$ and La_2O_3 are formed. They, together with the former precipitated $La(OH)_3$ and $Fe(OH)_3$ and ions of Fe^{3+} , La^{3+} , OH^- and water, are in an equilibrium state. The equilibrium is in a dynamic balance, with both crystallizing and dissolving, as shown in the Equation 2. This was supported by results of SEM and XRD. For example, SEM images in the Fig.1(a,b), revealed the formation of a few of $LaFeO_3$ particles, but many $FeO(OH)$ and La_2O_3 particles under the 270 °C hydrothermal condition. With the growth of $LaFeO_3$ crystalline, the layers of GO further expanded. On this occasion, the growth of $LaFeO_3$ crystals is mainly controlled by the intrinsic crystal structure anisotropy, i.e. the dominate crystal growth and agglomeration. During this phase, hydrothermal synthesis significantly reduced and broken down C-O bonding or other functional groups, thereby converting GO to graphene and formatting dangling bonds will further provide the adsorb site for LFO on graphene oxide. Perera et al [45] has proved that graphene oxide has a ~70% reduction of oxygenated species after alkaline hydrothermal treatment by XRD and Raman. Similarly, Shen et al.[46] also prove that graphene oxide could be well reduced under the hydrothermal condition[47, 48], which also has proved by our above mentioned Raman

results. $4\text{La}(\text{OH})_3 \downarrow + 4\text{Fe}(\text{OH})_3 \downarrow \rightleftharpoons 4\text{La}^{3+} + 4\text{Fe}^{3+} + 24\text{OH}^- \rightleftharpoons 2\text{LaFeO}_3 + 2\text{FeO}(\text{OH}) + \text{La}_2\text{O}_3 + 11\text{H}_2\text{O}$ (Equation 2)

Lastly, with the hydrothermal temperature going on, at 300 °C, impurity FeO(OH) and La₂O₃ will dissolve to form pure and crystalline LaFeO₃ particles, which means that the equilibrium of moved to the right (Equation 3). And the residual dangling bonds on the reduced graphene will further contact with LaFeO₃ oxide, which the volume keeps go increasing (micron order). Then, the graphene and LaFeO₃ could mix homogeneously. A possible formation mechanism for GE-cubic LFO is the dissolution-recrystallization from an amorphous structure (Fig.1 a, b) to a well-crystalline product (Fig. 1c,d), as originally proposed by Rossetti et al.[49]. It is observed that the strain in the *c*-axis direction is much higher than that in the *a*-axis direction while the domain sizes for both directions are similar. Additional, In the LFO perovskite structure, the [100] plane has the lowest surface energy and in turn the slowest planar growth rate. Thus, the equilibrium shape is cubic, as observed in other perovskites such as PbTiO₃.[50, 51]

Then, there are two kinds of GE exist in the cubic shaped composites, one is the GE sheets inserted in the LFO grains and sandwiched between the LFO particles, and the other is the graphene dispersed or covered on the outside surfaces of GE-LFO composite grains.

3.10 Catalytic performance of Cu-Co/GE-LFO

The catalytic performance of Cu-Co/GE-LFO for HAS from syngas were investigated, and the selectivities and CO conversions are summarized in Table 2. Over all of the four Co-Cu/GE-LFO catalysts, the detected products include ROH (ethanol, methanol, propanol and butanol), hydrocarbons (HCs) and CO₂, and the relative proportion of ROH/HCs were found to be highly GE dependent. The conversion of CO and the selectivity to ROH increased with increasing GE content, the ROH selectivities over Cu-Co/LFO, Cu-Co/1%GE-LFO, Cu-Co/3%GE-LFO and Cu-Co/5%GE-LFO were 49.4, 51.4, 53.4 and 56.9%, respectively. Oppositely, the selectivity to CO₂ and HCs decreased with the increase of GE content, and the selectivity to HCs over Cu-Co/LFO, Cu-Co/1%GE-LFO, Cu-Co/3%GE-LFO and Cu-Co/5%GE-LFO are 40.1, 39.0, 38.3 and 35.2%, respectively. Among those, Cu-Co/5%GE-LFO exhibited the best catalytic performance with the lowest CO₂ and hydrocarbon selectivity and the highest alcohols selectivity.

Up to now, the catalytic mechanism over the graphene-based catalysts used for gas-solid catalytic reaction has not been reported yet. While, based on the above mentioned characterization results and catalytic results, we can draw some main reasons that is highly related to very good catalytic performance for HAS over Cu-Co/GE-LFO catalysts.

Firstly, whatever bimetallic Cu-Co nanoparticles are supported on either GE or LFO of the GE-LFO composite, Cu-Co would show high selectivity to higher alcohols. No reports can be found on Cu-Co supported on GE for HAS, while there are a few reports on Cu-Co supported on CNTs for HAS. Dong et al.[52] show that $\text{Co}_3\text{Cu}_1/\text{CNT}$ catalyst achieved high selectivity to $\text{C}_2\text{-C}_8$ alcohols. The addition of CNTs to Co_3Cu_1 led to an increase concentration of Co-species like $\text{CoO}(\text{OH})$, which closely associated with the higher alcohol generation. This was very similar to the cases of HAS over the Co-Mo-K/CNT catalyst [53]. The authors pointed out that the addition of a minor amount of CNTs to $\text{Co}_1\text{Mo}_1\text{K}_{0.05}$ catalyst caused little change in the apparent activation energy for HAS, but led to an increase of surface concentration of the two kinds of catalytically active species, $\text{CoO}(\text{OH})/\text{Co}_3\text{O}_4$ and Mo^{4+} , which are closely associated with the alcohols generation. The properties of GE are much like CNTs, hence the mechanism for HAS over Cu-Co/GE and over Cu-Co/CNTs may be similar. The Cu-Co/LFO is highly active and selective for HAS reaction, details of which was reported in our previous work of [10].

Secondly, the mesoporosity of GE-LFO composite contributed to the high conversion of CO. As the AFM, TEM and N_2 adsorption-desorption results shown, graphene sheets were inserted into LaFeO_3 grains, and GE sheets and LFO particles were separated in the calcination treatment at 600°C in N_2 , leaving the slit-like mesopores. The mesoporosity provided with well passes for the reaction molecules transferring.

Thirdly, TEM, XRD and TPR results indicated that Cu-Co was in the state of alloy and highly dispersed on GE-LFO support, which generally led to the high selectivity to higher alcohols. For Cu-Co bimetallic alloy, it is accepted that metal copper can activate CO non-dissociatively and subsequently generate methanol, while metal cobalt enables the dissociative CO adsorption and C-C chain growth. Then, Cu and Co work cooperatively to generate higher alcohols, thus the synergistic catalyzing of Cu and Co resulted in the high selectivity to higher alcohols.

Compared with some representative excellent catalysts reported in literatures [10, 52, 54-56] (Table 3),

Cu-Co/GE-LFO in this study was still one of the best catalysts for HAS with a much higher selectivity to higher alcohols and relatively good activity.

Results of the stability test of Cu-Co/5%GE-LFO catalyst are shown in Fig. 9. In the running period of 160 h, the catalyst maintains its good activity and excellent selectivity to the higher alcohol. CO conversion is around 54.2%, the selectivity to alcohols and to HCs are 55.8% and 36.2%, respectively, and the mass fraction of C₂₊ alcohols in total alcohols was stable at about 80%.

The excellent stability of Cu-Co/GE-LFO is highly related the interaction between Cu-Co nanoparticles and GE/LFO. Sintering of metal nanoparticles is the most probable reason for the deactivation of Cu-Co catalyst for HAS [7]. GE also tends to interact with metal nanoparticles of Cu-Co, so Cu-Co supported on GE should also be highly anti-sintering. Copper and cobalt ions can act as the lattice ions of LFO, indicating that copper and cobalt species incline to interact with LFO. This interaction contributes the high anti-sintering ability for Cu-Co nanoparticles. The first-principles calculations on the strong interaction of metal (such as Ni, Co, Ru, Pd, and Ti nanoparticles) and GE indicated a shift of the Pauli-exclusion-induced energy-level and a hybridization of states' repulsive interactions, leading a band gap opening with metallic gap states [57]. The obtained theoretic results match well the practical test result of metal-graphene interaction studied by TEM.[25]

4. Conclusions

The bimetallic Cu-Co alloy supported on a composite consisted of graphene sheet and LaFeO₃ with perovskite structure was prepared by a simple hydrothermal method combined with impregnation method. As for the novel graphene-LaFeO₃ composite, the graphene sheets were embedded into LaFeO₃ grains or deposited on the surface of LaFeO₃ grains uniformly from SEM and AFM characterizations. And the BET results exhibit high specific surface area of graphene-LaFeO₃ composite, which favors the homogeneous dispersion of Cu-Co nanoparticles and the formation of Cu-Co alloy. Slit-like mesopores that exist between the graphene sheets and LaFeO₃ provided with well porous network for transmitting the reactant gases. The prepared Cu-Co/graphene-LaFeO₃ showed very good activity and selectivity to C₂₊ alcohols, owing to the formation of Cu-Co alloy. The strong interaction between Cu-Co alloy and graphene-LaFeO₃ support

restrained the sintering and agglomerating of the nanoparticles, resulting in the very good stability. Significantly, this designing scheme may be applied for preparing other graphene-perovskite-oxide composite, to note that a lot of transitional metal ions can act as the lattice ions of a perovskite-type oxide.

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Notes and references

- [1] P. Forzatti, E. Tronconi, I. Pasquon, Higher alcohol synthesis, *Catal. Rev.*, 33 (1991) 109-168.
- [2] K. Xiao, X. Qi, Z. Bao, X. Wang, L. Zhong, K. Fang, M. Lin, Y. Sun, CuFe, CuCo and CuNi nanoparticles as catalysts for higher alcohol synthesis from syngas: a comparative study, *Catal. Sci. Technol.*, 3 (2013) 1591-1602.
- [3] S. Zaman, K.J. Smith, A review of molybdenum catalysts for synthesis gas conversion to alcohols: catalysts, mechanisms and kinetics, *Catal. Rev.*, 54 (2012) 41-132.
- [4] D. Mei, R. Rousseau, S.M. Kathmann, V.-A. Glezakou, M.H. Engelhard, W. Jiang, C. Wang, M.A. Gerber, J.F. White, D.J. Stevens, Ethanol synthesis from syngas over Rh-based/SiO₂ catalysts: A combined experimental and theoretical modeling study, *J. Catal.*, 271 (2010) 325-342.
- [5] X. Mo, Y.-T. Tsai, J. Gao, D. Mao, J.G. Goodwin, Effect of component interaction on the activity of Co/CuZnO for CO hydrogenation, *J. Catal.*, 285 (2012) 208-215.
- [6] N.D. Subramanian, G. Balaji, C.S. Kumar, J.J. Spivey, Development of cobalt–copper nanoparticles as catalysts for higher alcohol synthesis from syngas, *Catal. Today*, 147 (2009) 100-106.
- [7] G. Liu, Y. Geng, D. Pan, Y. Zhang, T. Niu, Y. Liu, Bi-metal Cu–Co from LaCo_{1-x}Cu_xO₃ perovskite supported on zirconia for the synthesis of higher alcohols, *Fuel Process. Technol.*, 128 (2014) 289-296.
- [8] J. Wang, P.A. Chernavskii, A.Y. Khodakov, Y. Wang, Structure and catalytic performance of alumina-supported copper–cobalt catalysts for carbon monoxide hydrogenation, *J. Catal.*, 286 (2012) 51-61.
- [9] R.Z. Wei Yang, Biaohua Chen, Nicolas Bion, Daniel Duprez, Sébastien Royer, Activity of perovskite-type mixed oxides for the low-temperature CO oxidation: Evidence of oxygen species participation from the solid, *Journal of Catalysis*, 295 (2012) 245-258.
- [10] Y.Z. Fang, Y. Liu, L.H. Zhang, LaFeO₃-supported nano Co-Cu catalysts for higher alcohol synthesis from syngas, *Appl. Catal. A: Gen.*, 397 (2011) 183-191.
- [11] N. Escalona, S. Fuentealba, G. Pecchi, Fischer–Tropsch synthesis over LaFe_{1-x}Co_xO₃ perovskites from a simulated biosyngas feed, *Appl. Catal. A: Gen.*, 381 (2010) 253-260.
- [12] J. Ding, X. Lü, H. Shu, J. Xie, H. Zhang, Microwave-assisted synthesis of perovskite ReFeO₃ (Re: La, Sm, Eu, Gd) photocatalyst,

Mat. Sci. Eng. B-Solid, 171 (2010) 31-34.

- [13] D.P. Guilong Liu, Ting Niu, Ang Cao, Yizhi Yue and Yuan Liu, Nanoparticles of Cu–Co alloy supported on high surface area LaFeO₃—preparation and catalytic performance for higher alcohol synthesis from syngas, RSC Adv., 5 (2015) 31637-31647.
- [14] A.K. Geim, Graphene: status and prospects, Science, 324 (2009) 1530-1534.
- [15] A.J.P. Jemma L. Vickery, Stephen Mann, Fabrication of Graphene–Polymer Nanocomposites With Higher-Order Three-Dimensional Architectures., Adv. Mater., 21 (2009) 2180-2184.
- [16] N.D. Petkovich, A. Stein, Controlling macro- and mesostructures with hierarchical porosity through combined hard and soft templating, Chemical Society reviews, 42 (2013) 3721-3739.
- [17] T. Niu, G.L. Liu, Y. Liu, Preparation of Ru/graphene-meso-macroporous SiO₂ composite and their application to the preferential oxidation of CO in H₂-rich gases, Appl. Catal. B: Environ., 154-155 (2014) 82-92.
- [18] T. Niu, W.W. Zhao, G.L. Liu, A. Cao, L.H. Zhang, Y. Liu, The graphene-meso-macroporous SiO₂ supported Pt–Ni alloy nanocatalyst for preferential oxidation of CO in H₂-rich gases, Int. J. Hydrogen Energy, 39 (2014) 18929-18939.
- [19] F. Zou, Y. Yu, N. Cao, L. Wu, J. Zhi, A novel approach for synthesis of TiO₂–graphene nanocomposites and their photoelectrical properties, Scripta Mater., 64 (2011) 621-624.
- [20] C.A.C. Timothy N. Lambert, Bernadette Hernandez-Sanchez, Ping Lu,, A.A. Nelson S. Bell, Thomas Friedman, Timothy J. Boyle, David R. Wheeler, and Dale L. Huber, Synthesis and Characterization of Titania-Graphene Nanocomposites, J. Phys. Chem. C, , 113 (2009) 19812–19823.
- [21] F. Li, J. Zhao, Z. Chen, Fe-Anchored Graphene Oxide: A Low-Cost and Easily Accessible Catalyst for Low-Temperature CO Oxidation, The Journal of Physical Chemistry C, 116 (2012) 2507-2514.
- [22] G. Zhou, D.-W. Wang, F. Li, L. Zhang, N. Li, Z.-S. Wu, L. Wen, G.Q. Lu, H.-M. Cheng, Graphene-Wrapped Fe₃O₄ Anode Material with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries, Chem. Mater., 22 (2010) 5306-5313.
- [23] M.L. Lei Wan, Dongying Zhou, Liying Zhang, Weimin Cai, Preparation and Characterization of Free-standing Hierarchical Porous TiO₂ Monolith Modified with Graphene Oxide, Nano-Micro Lett., 4 (2012) 90-97.
- [24] A. Weidenkaff, S.G. Ebbinghaus, T. Lippert, Ln_{1-x} A_x CoO₃ (Ln= Er, La; A= Ca, Sr)/Carbon Nanotube Composite Materials Applied for Rechargeable Zn/Air Batteries, Chem. Mater., 14 (2002) 1797-1805.
- [25] R. Zan, U. Bangert, Q. Ramasse, K.S. Novoselov, Metal-graphene interaction studied via atomic resolution scanning transmission electron microscopy, Nano Lett., 11 (2011) 1087-1092.
- [26] M.A.P.a.a.J.L.G. Fierro, Chemical structures and performance of perovskite oxides, Chemical Reviews,, 101 (2001) 1981-2018.
- [27] O.C. Compton, S.T. Nguyen, Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials, Small, 6 (2010) 711-723.
- [28] J.L.G.F. M. A. Pen, Chemical structures and performance of perovskite oxides, Chemical Reviews, 101 (2001) 1981-2018.
- [29] P.V. Kamat*, Graphene-Based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Carbon Support, J. Phys. Chem. Lett., 1 (2010) 520–527.
- [30] J.-L.S. Wen-Hua Zhang, Lian-Zhou Wang, and Dong-Sheng Yan, Preparation and Characterization of ZnO Clusters inside Mesoporous Silica, Chem. Mater., 12 (2000) 1408–1413.
- [31] T. Niu, C.X. Wang, L.H. Zhang, Y. Liu, Potassium promoted Ru/meso-macroporous SiO₂ catalyst for the preferential oxidation of CO in H₂-rich gases, Int. J. Hydrogen Energy, 38 (2013) 7801-7810.
- [32] K.G. S. Thirumalairajan, I. Ganesh, D. Mangalaraj, C. Viswanathan, A. Balamurugan, N. Ponpandian, Controlled synthesis of perovskite LaFeO₃ microsphere composed of nanoparticles via self-assembly process and their associated photocatalytic activity, Chem. Eng. J., 209 (2012) 420-428.
- [33] Z.L.Z. Gang Xiong, Xujie Yang, Lude Lu, Xin Wang, Characterization of perovskite-type LaCoO₃ nanocrystals prepared by a stearic acid sol–gel process, J. Mater. Sci. Lett., 16 (1997) 1064-1068.
- [34] P.V.B. Gosavi, Rajesh B., Pure phase LaFeO₃ perovskite with improved surface area synthesized using different routes and its characterization, Mater. Chem. Phys., 119 (2010) 324-329.

- [35] S. Lu, Y. Liu, Preparation of meso-macroporous carbon nanotube-alumina composite monoliths and their application to the preferential oxidation of CO in hydrogen-rich gases, *Appl. Catal. B: Environ.*, 111-112 (2012) 492-501.
- [36] J. Su, W. Mao, X.C. Xu, Z. Yang, H. Li, J. Xu, Y.F. Han, Kinetic study of higher alcohol synthesis directly from syngas over CoCu/SiO₂ catalysts, *Aiche J.*, 60 (2014) 1797-1809.
- [37] J.P. Dacquin, M. Cabié, C.R. Henry, C. Lancelot, C. Dujardin, S.R. Raouf, P. Granger, Structural changes of nano-Pt particles during thermal ageing: Support-induced effect and related impact on the catalytic performances, *J. Catal.*, 270 (2010) 299-309.
- [38] J. Faye, E. Guélou, J. Barrault, J.M. Tatibouët, S. Valange, LaFeO₃ Perovskite as New and Performant Catalyst for the Wet Peroxide Oxidation of Organic Pollutants in Ambient Conditions, *Top. Catal.*, 52 (2009) 1211-1219.
- [39] C.-W. Tang, C.-B. Wang, S.-H. Chien, Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS, *Thermochim. Acta*, 473 (2008) 68-73.
- [40] L. Shi, W. Chu, S. Deng, Catalytic properties of Cu-Co catalysts supported on HNO₃-pretreated CNTs for higher-alcohol synthesis, *Journal of Natural Gas Chemistry*, 20 (2011) 48-52.
- [41] L. Huang, M. Bassir, S. Kaliaguine, Reducibility of Co³⁺ in perovskite-type LaCoO₃ and promotion of copper on the reduction of Co³⁺ in perovskite-type oxides, *Appl. Surf. Sci.*, 243 (2005) 360-375.
- [42] C.-Y. Su, Y. Xu, W. Zhang, J. Zhao, X. Tang, C.-H. Tsai, L.-J. Li, Electrical and Spectroscopic Characterizations of Ultra-Large Reduced Graphene Oxide Monolayers, *Chem. Mater.*, 21 (2009) 5674-5680.
- [43] K. Zhou, Y. Zhu, X. Yang, X. Jiang, C. Li, Preparation of graphene–TiO₂ composites with enhanced photocatalytic activity, *New J. Chem.*, 35 (2011) 353-359.
- [44] D. Luo, G. Zhang, J. Liu, X. Sun, Evaluation criteria for reduced graphene oxide, *The Journal of Physical Chemistry C*, 115 (2011) 11327-11335.
- [45] S.D. Perera, R.G. Mariano, K. Vu, N. Nour, O. Seitz, Y. Chabal, K.J. Balkus, Hydrothermal Synthesis of Graphene-TiO₂Nanotube Composites with Enhanced Photocatalytic Activity, *ASC Catal.*, 2 (2012) 949-956.
- [46] J. Shen, M. Shi, B. Yan, H. Ma, N. Li, M. Ye, One-pot hydrothermal synthesis of Ag-reduced graphene oxide composite with ionic liquid, *Journal of Materials Chemistry*, 21 (2011) 7795.
- [47] K.S. Yuxi Xu, Chun Li, Gaoquan Shi Self-assembled graphene hydrogel via a one-step hydrothermal process, *ACS Nano*, 4 (2010) 4324-4330.
- [48] Y. Zhou, Q. Bao, L.A.L. Tang, Y. Zhong, K.P. Loh, Hydrothermal Dehydration for the “Green” Reduction of Exfoliated Graphene Oxide to Graphene and Demonstration of Tunable Optical Limiting Properties, *Chem. Mater.*, 21 (2009) 2950-2956.
- [49] G. Rossetti, D. Watson, R. Newnham, J. Adair, Kinetics of the hydrothermal crystallization of the perovskite lead titanate, *J. Cryst. Growth*, 116 (1992) 251-259.
- [50] J. Moon, T. Li, C.A. Randall, J.H. Adair, Low temperature synthesis of lead titanate by a hydrothermal method, *J. Mater. Res.*, 12 (1997) 189-197.
- [51] J. Moon, J.A. Kerchner, H. Krarup, J.H. Adair, Hydrothermal synthesis of ferroelectric perovskites from chemically modified titanium isopropoxide and acetate salts, *J. Mater. Res.*, 14 (1999) 425-435.
- [52] X. Dong, X.-L. Liang, H.-Y. Li, G.-D. Lin, P. Zhang, H.-B. Zhang, Preparation and characterization of carbon nanotube-promoted Co–Cu catalyst for higher alcohol synthesis from syngas, *Catal. Today*, 147 (2009) 158-165.
- [53] X.-M. Wu, Y.-Y. Guo, J.-M. Zhou, G.-D. Lin, X. Dong, H.-B. Zhang, Co-decorated carbon nanotubes as a promoter of Co–Mo–K oxide catalyst for synthesis of higher alcohols from syngas, *Appl. Catal. A: Gen.*, 340 (2008) 87-97.
- [54] G. Liu, T. Niu, D. Pan, F. Liu, Y. Liu, Preparation of bimetal Cu–Co nanoparticles supported on meso–macroporous SiO₂ and their application to higher alcohols synthesis from syngas, *Appl. Catal. A: Gen.*, 483 (2014) 10-18.
- [55] N.D. Subramanian, G. Balaji, C.S.S.R. Kumar, J.J. Spivey, Development of cobalt–copper nanoparticles as catalysts for higher alcohol synthesis from syngas, *Catal. Today*, 147 (2009) 100-106.
- [56] N. Tienthao, M. Hassanzahediaki, H. Alamdari, S. Kaliaguine, Effect of alkali additives over nanocrystalline Co–Cu-based perovskites as catalysts for higher-alcohol synthesis, *J. Catal.*, 245 (2007) 348-357.

[57] P.V.K. Brian Seger, Fuel Cell Geared in Reverse: Photocatalytic Hydrogen Production Using a TiO₂/Nafion/Pt Membrane Assembly with No Applied Bias, J. Phys. Chem. C, , 113 (2009) 18946–18952.

Figure

Fig. 1 SEM images of (a, b) the support which prepared at 275 °C; (c,d) LFO which prepared at 300 °C; (e,f) 1%GE-LFO which prepared at 300 °C; (g) 5%GE-LFO which prepared at 300 °C, corresponding (h) enlarged drawing of GE-LFO's edge; (i) STEM-EDS spectrum of 5%GE-LFO composite; and SEM-EDS mapping images (k) of the GE-LFO composite morphologies; The sample with scale bars of (a, c, e, k) 5 μm, (b, d, f) 20 μm, (g) 2 μm, (h) 100nm.

Fig.2 TEM images of (a, c) 1%GE-LFO; (b) bright-field STEM image of LFO nanoparticle; (b') indexed fourier transforms (FFTs) image of red box; (d) Multiple lattice spacing of LFO; (e) Cu-Co/ 1%GE-LFO and (f) STEM-EDS line scan profile of three nanoparticles; Scale bar: 1 μm for (a, c); 5 nm for (b); 200 nm for (e).

Fig. 3 AFM images of (a)GE; (b)5% GE-LFO; and corresponding three-dimensional image of (c); (a',a'') cross-section analysis of the graphene suspension deposited on freshly cleaved mica substrates

Fig.4 (a) N_2 adsorption-desorption isotherms, (b) BJH mesoporous size distribution curve of LFO(■), 1 %GE-LFO (●), 3%GE-LFO (▲) and 5%GE-LFO (▼)

Fig. 5 XRD patterns of (a) x%GE-LFO composites prepared at different hydrothermal period and (b) the magnified patterns between 31° and 35° of Cu-Co/5%GE-LFO catalyst with different treatment

Fig. 6 TPR profiles of Cu-Co oxides supported on LFO and GE-LFO composites

Fig.7 Raman spectrum of (a) 5%GE-LFO; (b) 3%GE-LFO; (c) 1%GE-LFO; (d) GO and (e) LFO

Fig. 8 The speculated formation mechanism of GE-LFO support

Fig. 9. Conversion of CO, selectivity to alcohols, methane, CO₂ and alcohol distributions over Cu-Co/5%GE-LFO with reaction time on stream at 300 °C, 3 MPa, H₂/CO/N₂ = 8/4/1, 3900 h⁻¹

Table 1. Specific surface area, pore volume and the mesopore size of GE-LFO and Cu-Co/GE-LFO composite derived from N₂ adsorption-desorption

Sample	Specific surface area (m ² /g)	The most probable pore size (nm)	Total pore volum (cm ³ .g ⁻¹)
LaFeO ₃	7	-	0.021
1% GE- LaFeO ₃	12	5.6	0.057
3% GE- LaFeO ₃	31	6.4	0.092
5% GE- LaFeO ₃	53	7.6	0.137
Cu-Co/5%GE-LaFeO ₃	48	7.5	0.131

Table 2 Catalytic performance of CO hydrogenation over Cu-Co/GE-LFO catalysts

Samples	X _{co} %	S _{CO₂} %	Selectivity to HC/%				Selectivity to ROH/%				S _{ROH} %
			C ₁	C ₂	C ₃	C ₄₊	C ₁	C ₂	C ₃	C ₄₊	
Cu-Co/LFO	35.6	10.5	18.2	13.5	6.9	1.5	13.5	20.4	11.7	3.8	49.4
Cu-Co/1%GE-LFO	38.9	9.6	17.9	13.9	5.8	1.4	12.8	21.4	11.3	5.9	51.5
Cu-Co/3%GE-LFO	40.3	8.3	16.3	14.3	6.5	1.2	10.9	23.5	12.2	6.8	53.4
Cu-Co/5%GE-LFO	49.7	7.9	14.5	14.8	4.3	1.6	9.7	26.7	13.1	7.4	56.9

Reaction conditions: 300 °C, GHSV=3900 mL·g_{cat}⁻¹·h⁻¹, 3 MPa, H₂/CO/N₂=8:4:1

Table 3 The comparison of CO conversions and alcohols selectivity over Cu-Co/GE-LFO (this study) and some open-published representative catalysts (in references)

Sample	T(°C)	H ₂ /CO ^a	Pressure(Mpa)	GHSV(h ⁻¹)	X _{co} (%) ^b	S _{ROH} (%) ^c
20%Cu-Co/La ₂ O ₃ -SiO ₂ ⁵³	330	2	3	3900	32.12	39.45
Cu-Co/LaFeO ₃ ¹⁰	300	2	3	3900	56.0	43.0
Co@Cu ⁵⁴	300	2	2	18000	-	41.5
Co ₃ Cu-11%CNT ⁵¹	300	2	5	7000	26.5	49.8
0.75%K-LaCo _{0.7} Cu _{0.3} O ₃ ⁵⁵	275	2	6.8	5000	35.2	48.9
Cu-Co/GE-LFO ^d	300	2	3	3900	49.7	56.9

a Molar ratio.

b CO conversion.

d Catalyst of this work