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Loading oxide nano sheet supported Ni–Co alloy nanoparticles on the macroporous walls of monolithic alumina and their catalytic performance for ethanol steam reforming

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ABSTRACT

The nanoparticles of Ni–Co alloy/MgAlO_x nanosheets were supported on monolithic macroporous γ -Al₂O₃ by calcining and reducing a layered double hydroxide which contains elements of Mg, Ni, Co and Al. This precursor was in situ grown on the macropores' walls of the γ -Al₂O₃ support by sharing the sole Al source. The catalysts and their precursors were characterized by using the techniques of XRD, TPR, TEM, SEM, ICP-OES, TG and N₂ adsorption/desorption. The results indicate that small Ni–Co alloy nanoparticles were highly dispersed on the MgAlO_x nanosheets and the porous structure with the open access of active sites should be beneficial for the mass transfer. The resultant catalysts exhibited excellent catalytic performance for ethanol steam reforming. The new preparation approach described here provides a practical and efficient method to support nanobimetallic catalysts. The results suggest that this type of material possesses tremendous potential for future applications.

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Introduction

In recent years, bimetallic catalysts have drawn great attention due to their superior catalytic performance. Zhang et al. [1] found that the activity and thermal stability of SBA-15

supported Au–Cu alloy nanoparticles (NPs) are higher than that of the corresponding monometallic catalysts for CO oxidation with or without the presence of H₂. The Ni–Co bimetallic catalyst also shows better catalytic performance than the mono Ni- or Co-based catalysts for steam reforming of ethanol (SRE) [2]. The addition of Co can reduce the carbon

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deposition and alleviate the sintering of the active Ni species. It is generally attributed to the electronic and/or geometric modification by guest metals [3] as well as the synergistic effects between the two metals [4,5].

Layered double hydroxides (LDHs) consisting of positively charged hydroxide layers and exchangeable interlayer anions can be expressed by the formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_x/n \cdot mH_2O$ [6,7]. The M^{2+} and M^{3+} ions occupy the octahedral sites in a brucite-like layer and the A^{n-} anion is located in the hydrated interlayer galleries. The structure and properties of LDHs have a wide interest in heterogeneous catalysts acted as catalyst precursors and catalyst supports [8,9]. In particular, the highly uniform distribution of metal ions in the layer of LDHs can be maintained in the corresponding oxidized and/or reductive products due to the topotactic transformation [10–12], which favors the formation of alloy.

There are some reports of supported nano-bimetallic catalysts which have been obtained by treating LDHs precursors due to the uniform distribution of flexible and tunable metal ions in the hydroxide layers. Tomishige et al. [13] successfully prepared uniformly dispersed Ni–Fe alloy NPs supported on Mg–Al mixed metal oxides by calcination and reduction of a NiFeMgAl-LDH precursor. This product shows higher catalytic activity and better stability than the supported monometallic Ni for the steam reforming of toluene. Co–Fe alloy NPs dispersed on MgO, with narrow particle size distribution, also can be obtained by thermal reduction of MgCoFe-LDH precursor [14].

Macroporous materials have great potential application in heterogeneous catalysts. This is due to the high specific surface area and enhanced mass transfer, such as the three-dimensional macroporous catalyst for the preferential oxidation of CO in hydrogen-rich gases [15,16]. In addition, the monolithic macroporous materials have benefits which include minimum pressure drop, low mass transfer resistance and easy catalyst separation and recyclability [17–21]. Al_2O_3 is one of the most important support materials and there are many reports related to macroporous $\gamma-Al_2O_3$ [15,16,22]. However, the macroporous $\gamma-Al_2O_3$ supported nano bimetallic catalysts have yet to be reported up to now.

It is difficult to obtain the interaction between two metal components in an alloy or other state when using traditional preparation methods. Such as the generally used impregnation method, due to the difference of preferential adsorption of metal precursors on the support or aggregation of precursors during drying and calcinations [23,24], the loaded two metal components are far more likely to form monometallic NPs separately.

Hydrogen production from bio-ethanol is a green and environmental route to sustainable energy. The steam reforming of ethanol (SRE) for hydrogen production is attractive owing to its high hydrogen yield and renewability of ethanol. However, the critical problem of Ni-based catalysts is deactivation resulted from carbon deposition and/or the sintering of metallic nickel nanoparticles [25].

In this work, in attempts to alleviate this problem, a method for loading Ni–Co alloy/MgAlOx on the walls of macroporous Al_2O_3 was presented by using NiCoMgAl-LDH as the precursor. NiCoMgAl-LDH precursors were *in situ* grown on the wall of the macroporous Al_2O_3 support by sharing aluminum element

from the support. The textural and structural features of the resultant catalysts were studied, and their catalytic performances for SRE were investigated. Another significance of this work is that this preparation scheme can be extended for loading other bimetallic nanoparticles, for that many transitional metal ions can be served in LDHs.

Experimental

Preparation of samples

Preparation of monolithic macroporous $\gamma-Al_2O_3$

The monolithic macroporous Al_2O_3 was prepared according to the preparation method reported previously by our group in Ref. [18]. Briefly, Al_2O_3 hydrosols were imbibed into the macroporous polystyrene monolithic foams. The imbibed samples were dried at 60 °C for 12 h. The imbibing and drying procedures were repeated several times. After repeats of imbibing-drying, the samples were calcined in a flowing air furnace with a heating rate of 1 °C min⁻¹ to 600 °C. Thus, the samples of monolithic macroporous $\gamma-Al_2O_3$ were obtained.

Loading MgNiCo/Al-LDH on monolithic macroporous $\gamma-Al_2O_3$
 $Mg(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and urea were dissolved in 20 mL deionized water. The total concentration of metal ions M^{2+} (Ni^{2+} , Co^{2+} , Mg^{2+}) was 1 M, and the concentration of urea was 3 M. The molar ratios of $Mg^{2+}:Ni^{2+}:Co^{2+}$ in the initial solution were 4:4:0, 4:2:2 and 4:0:4 for $Mg_4Ni_{4-x}Co_x$ with $x = 0, 2$ and 4, respectively. 1 g monolithic macroporous $\gamma-Al_2O_3$ was then impregnated under vacuum in the above solution for 1 h to let macropores be infiltrated with the solution. The remainder of the solution along with the impregnated monolithic macroporous $\gamma-Al_2O_3$ was then transferred into a 100 mL Teflonlined stainless-steel autoclave. The autoclave was sealed, maintained at 120 °C for 24 h, and then cooled to room temperature by using cooling water. The monolithic macroporous $\gamma-Al_2O_3$ was then rinsed several times with deionized water under ultrasonication. The resultant samples were dried at 80 °C for 12 h. The MgNiCo/Al-LDH sheets were then synthesized on the monolithic macroporous $\gamma-Al_2O_3$. The three precursors were labeled as Mg_4Ni_4 , $Mg_4Ni_2Co_2$ and Mg_4Co_4 corresponding to $Mg_4Ni_{4-x}Co_x$ of $x = 0, 2$ and 4, respectively.

Synthesis of hierarchical NiCo-alloy/MgAlOx supported on monolithic macroporous $\gamma-Al_2O_3$

After calcination at 750 °C for 2 h with a heating rate of 1 °C min⁻¹, the $Mg_4Ni_{4-x}Co_x$ was transformed into mixed metal oxides. The corresponding samples were named as Mg_4Ni_4 -cal, $Mg_4Ni_2Co_2$ -cal and Mg_4Co_4 -cal corresponding to the calcined $Mg_4Ni_{4-x}Co_x$ with $x = 0, 2$ and 4, respectively. The calcined samples were reduced at 750 °C for 2 h in 5% H_2/Ar , and named as Mg_4Ni_4 -re, $Mg_4Ni_2Co_2$ -re and Mg_4Co_4 -re, respectively.

Characterization

The phase structure analyses of the catalysts were determined by the X-Ray Diffraction (XRD) technique which was

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