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Preparation of supported Co catalysts from Co–Mg–Al layered double hydroxides for carbon dioxide reforming of methane

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ABSTRACT

Mg(Al)O mixed oxide-supported Co catalysts were prepared by using Co–Mg–Al layered double hydroxides (LDHs) as precursors and their structural and catalytic properties for CH₄–CO₂ reforming were studied. Upon calcination and reduction, Co–Mg–Al LDHs were decomposed to Mg(Co, Al)O mixed oxides and gave rise to highly dispersed Co metal particles with the mean size of ~9–10 nm. The catalytic activity, stability, and coke resistance of Co/MgAl increased with the increase of Co loading. The 12%–15%Co/Mg₃Al catalysts showed high and stable activity as well as less coke deposition during 30 h of reaction at 1023 K. Sintering of Co particles was not clearly observed, indicative of good thermal stability of Co particles, and this could be attributed to the strong metal-support interaction between Co particles and Mg(Al)O. It was also found that the optimum LDHs-Co/MgAl catalyst exhibited superior coke resistance than the LDHs-Ni/MgAl catalyst. Particularly during 25 h of reaction at 873 K, the 12%Co/Mg₃Al catalyst showed much higher catalytic stability and much less coke deposition as compared to the 12%Ni/Mg₃Al catalyst, highlighting the great potential of using Co instead of Ni as an active catalyst for the CH₄–CO₂ reforming.

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Introduction

Carbon dioxide reforming of methane to synthesis gas is an attractive technology from the viewpoint of energy and environmental concern [1–3]. Both methane and carbon dioxides are two greenhouse gases and also two of cheap and abundant carbon-containing resources and the resulted synthesis gas is a valuable feedstock for hydrogen production and Fischer–Tropsch synthesis to produce clean fuels. Owing to its highly endothermic nature, carbon dioxide reforming of methane can be also used as a chemical energy transmission system

(CETS), in which solar energy is used to drive the endothermic forward reaction [4,5]. For example, by using parabolic trough as solar collector, methane reforming could be operated at a low temperature of 823–873 K, which was reported to upgrade 10–15% of the fuel [5]. It is well known that Group VIII metals are more or less catalytically active toward the CH₄–CO₂ reforming [6–8]. Generally, noble metals such as ruthenium and rhodium show high catalytic performance, but their industrial application is greatly limited due to the high cost and low availability of noble metals. From the viewpoint of industrial application, non-precious metals such as nickel and cobalt are more preferable. So far, much attention has been

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paid to nickel-based catalysts because of their comparable activity with noble metals [2,7,8], while cobalt is usually reported to be less effective than nickel [8–10]. The common problem of Ni and Co catalysts is the deactivation caused by coke deposition, sintering of metal particles, and/or metal oxidation, and for this reason considerable efforts have been made to improve the catalytic performance [11–19].

Using layered double hydroxides (LDHs) as precursors have been proved to be an effective way for the preparation of supported metal catalysts [20–24]. LDHs are a class of two dimensional anionic clays that consist of positively charged brucite-like layers and exchangeable interlayer anions, whose formula can be expressed by $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$. In a previous study [24], we have prepared various Ni/MgAl catalysts by calcination and reduction of Ni-Mg-Al LDHs. The LDHs-Ni/MgAl catalysts showed well-dispersed Ni metal particles and the catalyst with suitable Ni loading (12 wt%) showed good catalytic activity and stability for the CH_4 - CO_2 reforming at 1023 K. However, the LDHs-Ni/MgAl catalyst was rapidly deactivated at a low temperature of 873 K due to serious coke deposition. In the present work, a series of Co/MgAl catalysts with different Co loadings were prepared from Co-Mg-Al LDHs and their catalytic performance for the CH_4 - CO_2 reforming was investigated. It was found that the optimum LDHs-Co/MgAl catalyst exhibited superior catalytic performance than the LDHs-Ni/MgAl catalyst particularly in terms of low-temperature catalytic stability and coke resistance, highlighting the great potential of using Co instead of Ni as an active catalyst for the CH_4 - CO_2 reforming.

Experimental

Catalyst preparation

Co-Mg-Al LDHs were synthesized by co-precipitation of the corresponding metal nitrates as reported previously [24]. In brief, a 100 mL aqueous solution containing the desired amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added drop-by-drop into a 100 mL aqueous solution of Na_2CO_3 under stirring at room temperature and $\text{pH} = 10 \pm 0.5$. The precipitate was filtered, washed with de-ionized water, and dried at 373 K for 12 h. Subsequently, the obtained Co-Mg-Al LDHs were calcined in air at 1073 K for 5 h. The prepared samples are denoted as $x\text{Co}/\text{Mg}_3\text{Al}$, where x represents the weight percentage of Co in the calcined sample ($x = 6, 9, 12, 15$ wt%) and 3 refers to the molar ratio of (Co + Mg)/Al, which was kept constant for all samples. The Co loading was varied from 6% to 15% since lower or higher Co loadings would probably cause rapid deactivation by oxidation of Co metal or coke deposition [25]. The molar ratio of (Co + Mg)/Al was fixed to 3 since it was reported to be a suitable composition for Ni-Mg-Al LDHs to achieve high metal dispersion and catalytic activity [26].

Catalyst characterization

N_2 adsorption (77 K) was conducted on a Micromeritics ASAP 2020 to measure the BET specific surface area of the samples. Prior to N_2 adsorption, the sample was treated in vacuum at

453 K for 4 h. Powder X-ray diffraction (XRD) measurements were carried out on a PANalytical X'PertPro diffractometer with Co $K\alpha$ radiation ($\lambda = 0.179$ nm) at 40 kV and 40 mA. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEM-2100 (JEOL) microscope operated at 200 kV. Field emission scanning electron microscopy (FE-SEM) was performed on a Hitachi-S4800 operated at 5.0 kV.

Temperature-programmed reduction (H_2 -TPR), temperature-programmed oxidation (O_2 -TPO), and CO chemisorption were conducted on a Micromeritics AutoChem 2920 equipped with a thermal conductivity detector (TCD). For H_2 -TPR, 100 mg of sample was pretreated with 3% O_2 /Ar gas at 773 K for 0.5 h. The H_2 -TPR profile was recorded in a 10% H_2 /Ar mixed gas (30 mL min^{-1}) from ambient temperature to 1273 K by 10 K min^{-1} . For O_2 -TPO, 100 mg of sample was pre-reduced with H_2 at 1073 K for 0.5 h. The TPO profile was recorded in a 3% O_2 /Ar mixed gas (30 mL min^{-1}) from ambient temperature to 1273 K by 10 K min^{-1} . The amount of O_2 consumption was used to calculate the Co reduction degree, assuming that $3\text{Co}^0 + 2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4$. For CO chemisorption, 100 mg of sample was pre-reduced with H_2 at 1073 K for 0.5 h. CO adsorption was performed at ambient temperature by pulse method using 5% CO/He gas.

To measure the coke deposition on the spent catalysts, O_2 -TPO was carried out on the Micromeritics AutoChem 2920 connected to a mass spectrometer (Hiden Analytical HPR20). 100 mg of catalyst was used and TPO was performed in 3% O_2 /Ar gas (30 mL min^{-1}) from ambient temperature to 1273 K by 10 K min^{-1} . The mass signal of $m/e = 44$ was used to monitor the CO_2 formed.

Catalytic reaction

CH_4 - CO_2 reforming was conducted using a fixed-bed quartz tube reactor (6 mm i.d.) operated at atmosphere pressure. 50 mg of catalyst with particle size of 0.3–0.6 mm was used. The catalyst was pre-reduced with H_2 (30 mL min^{-1}) at 1073 K for 0.5 h. After the catalyst was cooled to the reaction temperature, the reactant gas mixture ($\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:2$, $\text{WHSV} = 60,000$ mL $\text{g}^{-1} \text{h}^{-1}$) was introduced into the reactor to start the reaction. The reactor exit gas was analyzed by an online TCD gas chromatography (Shimadzu GC-2014). The catalyst activity was tested by increasing the reaction temperature step-by-step from 773 K to 1073 K; at each temperature the activity was evaluated for 1 h. The catalytic stability of catalyst was tested at 1023 K for 30 h or at 873 K for 25 h. After reaction, the reactant gas was stopped and the catalyst was cooled down to ambient temperature in N_2 flow and then taken out of the reactor for further characterization.

Results and discussion

Structural and physicochemical properties of the LDHs-Co/MgAl catalysts

Fig. 1 shows the XRD patterns of the 12%Co/ Mg_3Al catalyst during the preparation, while those of other samples are presented in Figs. S1–S3 (Supplementary Material). The as-

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