Partial oxidation of methane over Ni/Mg/Al/La mixed oxides prepared from layered double hydrotalcites

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ABSTRACT

A series of Ni/Mg/Al/La mixed oxides prepared by thermal decomposition of layered double hydrotalcites (HT) were characterized by XRD, ICP, EXAFS, TGA, TPR-H_2, SEM, and N_2 adsorption/desorption technique. The results revealed the formation of periclase-type catalysts with mesoporous structure, and the addition of La^{3+} lowered the phase crystallization with the formation of small oxide particles. Such catalysts had both high activities and stabilities toward partial oxidation of methane (POM). The catalyst containing 6.5 mol.% La^{3+} showed the highest performance at 1053 K with CH_4 conversion of 99%, CO selectivity of 93% and H_2 selectivity of 96%, which could be attributed to the presence of highly dispersed nickel and then the resistance to coke formation due to the promotion effect of lanthanum.

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1. Introduction

Synthesis gas was of great importance in chemical industry mainly because syngas ($H_2 + CO$) was the feedstock for methanol and Fischer–Tropsch synthesis. An important industrial route for syngas production was through steam reforming of methane (SRM). However, this process was highly endothermic and required heating of large quantities of steam. Furthermore, the Ni-based catalysts typically used for this process were deactivated easily owing to the carbon deposition. Catalytic partial oxidation of methane (POM), in the presence of O_2, offered the greatest potential to synthesis gas or hydrogen due to mild exothermicity, and could be conducted in small reactors ideal for decentralized applications. Therefore, POM had been receiving significant attention for its industrial prospect [1–9].

Supported nickel catalysts normally prepared by wet impregnation were considered to be active toward the reaction [10]. However, this method led to some heterogeneity in the distribution of active metal on the surface and then a low dispersion of metallic species which favored the coke formation. Moreover, POM was an exothermic reaction, which required the high stability of catalysts to avoid sintering of active phase.

Hydrotalcite-type (HT) compounds had many practical applications as catalysts or catalyst precursors [11,12]. In particular, the Mg/Al mixed oxide obtained of HT precursors presented high surface area, basic properties and small crystal sizes. HT compounds were considered as suitable precursors of nickel catalysts [13–16], allowing homogeneous distribution of nickel inside the structure of the precursors and then leading to the well dispersed and stable metal nickel particles. Besides,

the rare-earth oxides like La_2O_3 had a beneficial effect on the nickel dispersion, and the catalysts promoted with lanthanum toward methane reformation presented good conversion levels and lower carbon formation than unprompted catalysts [17–20]. Besides, the materials modified by lanthanum derived from HT precursor might show the tunable basicity and then led to a new economical approach to the catalyst for POM. Even so, no systematic study of HT derived catalysts for POM was carried out in terms of the resistance of lanthanum to carbon formation and active metal sintering as well as a detailed understanding of the effect of lanthanum on the catalysts structure and catalytic performances. Thus, the Ni/Mg/Al/La mixed oxides were derived from layered double HT precursors by traditional co-precipitation method to improve catalytic activity and stability of nickel catalysts for POM, and the effect of La^{3+} on the catalysts structure and catalytic activity was investigated in detail in the present work.

2. Experimental section

2.1. Catalyst preparation

To prepare the HT precursors, 0.02 mol of $Ni(NO_3)_2$, 0.04 mol of $Mg(NO_3)_2$, x mol of $Al(NO_3)_3$ and y mol of $La(NO_3)_3$ ($y+x=0.02$ mol and $y=0$, 0.005, 0.008, 0.01) were dissolved in 100 ml deionized water as solution A, and the solution B contained 0.16 mol of NaOH and 0.01 mol of Na_2CO_3. The two solutions were added dropwise with stirring to 100 ml deionized water at room temperature and the addition was performed over 30 min with pH = 10 by addition of appropriate amounts of NH_4OH (35% aqueous ammonia solution). The resulting gel-like slurry was transferred into autoclaves and aged for 24 h at 343 K. The solid was filtered out, after previously being washed with deionized water for 24 h then dried for 12 h at 373 K. Thus HT precursors denoted as HTL-z (z = 1, 2, 3, 4 according to y = 0, 0.005, 0.008, 0.01) with different La/Al molar ratios were prepared. Finally, Ni/Mg/Al/La mixed oxides denoted as OML-z series were obtained from HTL-z series calcined in air at 1073 K for 8 h. Scheme 1 shows the preparation process of the catalysts. The pure NiO (p-NiO) obtained from the decomposition of $Ni(NO_3)_2$ after calcination at 1073 K was used for comparison as reference compounds for EXAFS analysis.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) experiments were carried out on a Rigaku Miniflex diffractometer using a Cu target ($\lambda = 1.5418$ Å) with a Ni filter in a 2θ range of 5–70° and the X-ray gun was operated at 50 kV and 30 mA, using a scan speed rate of 0.2°/min. Thermogravimetric analysis (TGA) was carried out on a Setaram TGA-92 thermal analyzer connected to a PC via a TAC7/DX thermal controller. The samples were heated from 303 K to 1073 K at 10 K/min under nitrogen and oxygen stream respectively to analyze the catalysts thermal stability and coke resistivity. The carbon formation rate was calculated by the method provided in Ref. [21]. Elemental chemical analysis was performed using the inductively coupled plasma-optical (ICP) emission spectroscopy (Perkin-Elmer ICP OPTIMA-3000). Temperature-programmed reduction with hydrogen (TPR-H_2)

of the catalysts was performed in the home-built equipment monitored by a thermal conductivity detector (TCD), using 25 mg of catalyst and a temperature ramp from 333 K to 1233 K at 10 K/min, and a flow rate of the 30 ml/min of 10% H_2/N_2 was used, and the maximal temperature (T_M) for reduction profiles was labeled. Besides, to calibrate the amount of H_2 consumption, CuO powder was used as reference. Nitrogen adsorption/desorption isotherms were obtained at 77 K on a Micromeritics ASAP-2000 instrument (Norcross, GA), using static adsorption procedures. Samples were degassed at 623 K for a minimum of 5 h under vacuum (10^{-6} Torr) prior to the measurement. Surface area was measured using the BET method. Scanning electron microscopy (SEM) analyses were performed by means of a JEOL JSM-35C equipment. X-ray absorption fine structure (EXAFS) experiments were carried out on the station of SSRF (Shanghai Synchrotron Radiation Facility), China, and operated at the energy 3.5 GeV and a maximum stored current 300 mA. The finely powdered specimens were directly applied to 3M Scotch tape and then measured at room temperature immediately. The X-ray absorption spectra were collected at the Ni–K edge. EXAFS date was recorded with a Si (111) double-crystal monochromater in transmission mode. Ion chambers before and after the samples were used to measure the incident and transmitted intensities, I_0 and I_1 respectively. EXAFS data analysis was carried out using WinXAS 3.1 provided by SSRF. The fitting process could refer to the previous work which adopting the multiple scattering procedure [22,23], and in the present work, it was carried out in k-space ranges chosen to be from 1.5 to 11 Å to avoid the serious noise signals, and only applied to the first shell (Ni–O) to assure the accuracy of fitting data. The fitting results were obtained both for the data taken by varying EF (correction to E_0), σ^2 (Debye–Waller factors) values and allowing small variations for N (coordination numbers) and R_1 (interatomic distances for Ni–O). The value of S_0^2 was determined to be 0.88 from the fitting of the data for p-NiO, and this value was fixed for other samples. The structural parameters were achieved by nonlinear least-squares fitting in k-space with a k^3 weighting which was used to emphasize the high-energy part of the spectrum. The quality of the fit could be judged from the normalized sum of residuals (R) and reasonable EXAFS fits typically had R values of 20%.

2.3. Catalyst evaluation

Three hundred milligrams of the mixed oxides in powder were used in POM after activation at 1073 K in situ with pure H_2 at 40 ml/min for 4 h. Catalytic tests were performed in a quartz reactor (10 mm diameter) using an oven heated at 1057 K and 957 K, respectively. The reactor was fed with CH_4/O_2 in the ratio of 2/1 for a total flow of 90 ml/min, and the reaction products were analyzed by a TCD gas chromatographs system equipped with 5A molecular sieve and Porapak Q.

3. Results and discussion

3.1. Structure and thermal stability

Fig. 1 gives the XRD patterns of HT precursors. Due to the completely insertion of metallic cations with comparable ionic