Research Article

Catalytic Combustion of Low Concentration Methane over Catalysts Prepared from Co/Mg-Mn Layered Double Hydroxides

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A series of Co/Mg-Mn mixed oxides were synthesized through thermal decomposition of layered double hydroxides (LDHs) precursors. The resulted catalysts were then subjected for catalytic combustion of methane. Experimental results revealed that the Co_{4.5}Mg_{1.5}Mn₂LDO catalyst possessed the best performance with the $T_{90} = 485^{\circ}\text{C}$. After being analyzed via XRD, BET-BJH, SEM, H₂-TPR, and XPS techniques, it was observed that the addition of cobalt had significantly improved the redox ability of the catalysts whilst certain amount of magnesium was essential to guarantee the catalytic activity. The presence of Mg was helpful to enhance the oxygen mobility and, meanwhile, improved the dispersion of Co and Mn oxides, preventing the surface area loss after calcination.

1. Introduction

Low concentration methane such as coal mine methane is usually emitted directly into the atmosphere or burned immediately due to its low calorific value, resulting in either greenhouse effect or a huge waste of resource. Moreover, NO_x can be also produced during thermal combustion. Therefore, it is necessary to develop a cost-effective technology for capturing and utilizing the low concentration methane.

So far, a number of studies have focused on the catalytic oxidation of methane, especially on the noble metal catalysts [1–4]. Nevertheless, noble metal catalysts normally show some shortcomings for real application like volatility, high sintering rates, poisoning in the presence of disturbing compounds, and high price [5]. As such, the mixed metal oxide catalysts have been attracting rising concern recently for methane catalytic combustion [6, 7]. And some reporter showed that the activity of mixed metal oxide catalysts was not necessarily worse than noble metal catalysts for VOCs catalytic oxidation [8–10].

Layered double hydroxides (LDHs) are known as a series of anion layered compounds whose chemical composition can be represented as $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+}[\text{A}_{x/n}^{n-} \cdot y\text{H}_2\text{O}]^{x-}$. M^{II} and M^{III} are bivalent and trivalent metal cations, Aⁿ⁻ is an *n*-valent anion, and the values of *x* usually range from 0.20 to 0.33. After thermal decomposition, LDHs could be potential materials for total oxidation catalysts due to their large surface area, high metal dispersion, small crystallite size, and stability against sintering [11]. Up to now, a lot of efforts have been dedicated to developing the LDHs catalysts for volatile organic compounds (VOCs) degradation and the methane catalytic combustion [5, 12].

In light of the above points, we synthesized a series of LDHs related catalysts, in which the transition metals Co and Mn were induced as bivalent and trivalent metal cations, respectively, for the methane catalytic combustion. Then, the catalysts were characterized by various methods to show the relationships between the chemophysical properties of the catalysts and their performances.

2. Experimental Section

2.1. Catalyst Preparation. The LDHs precursors Co/Mg-Mn were prepared by coprecipitation method at a constant pH value (10 ± 0.5). Mixed salt solution (100 mL) and 2 M NaOH (100 mL) solution were added dropwise into 100 mL 0.45 M Na_2CO_3 solution simultaneously under vigorous mechanical stirring at 60°C in water bath for 1 h. The mixed salt solution consists of a total cation concentration of 2 M from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2$ with $(\text{Mg} + \text{Co})/\text{Mn} = 3.0$. The addition of the alkaline solution and the pH value were controlled by a pH meter. Precipitates formed were aged with the mother liquid overnight at 60°C under vigorous stirring and then filtered and thoroughly washed with distilled water to $\text{pH} = 7.0$. After that, the resulting solid (LDHs precursors) was dried at 100°C for 12 h. Then, these LDHs precursors (denoted as $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$) were calcined at 600°C for 4 h to derive Co/Mg-Mn mixed oxide catalysts (denoted as $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$). Finally, the oxide catalysts were crushed and sized in 40–60 mesh for activity test and characterizations.

2.2. Catalytic Activity Testing. The catalytic activity tests of methane were performed in a fixed bed with an inside steel tube reactor operated at atmospheric pressure. 0.5 g catalyst diluted with equal volume silica sand was used during the test with a gas mixture of $\text{CH}_4:\text{O}_2:\text{N}_2 = 1.6:16:144$ at a total flow rate of around 160 mL/min passing through the reactor. The gas flow rate was controlled by mass flow meter. The internal diameter of the reactor is 8.20 mm and the length is 450 mm. Catalytic activity tests were carried out with a gas hourly space velocity (GHSV) of $25,000 \text{ h}^{-1}$, at the temperature ranging from 350 to 600°C . The reactants and products were online analyzed by Agilent GC and equipped with flame ionization detection (FID). Before each test, the catalysts were preheated at 500°C for 30 min and then cooled to 350°C to start the test. The methane conversion rate was calculated based on the integrated GC peak areas.

2.3. Catalytic Characterization. X-ray diffraction patterns (XRD) were recorded using a Rigaku D/Max RA diffractometer to identify the crystal structure of the samples with the monochromatic $\text{Cu K}\alpha$ radiation at 2θ ranging from 5 to 80° with a scanning rate of $4^\circ/\text{min}$. The textural properties of the derived oxides were analyzed by N_2 adsorption/desorption at 77 K in a JW-BK132F static adsorption analyzer. Before each test, the catalyst was pretreated at 100°C for 3 h in vacuum. The specific surface area was calculated with the BET equation, and the pore volume and pore size distribution were obtained by the BJH method. The micromorphology characteristics were examined by scanning electron microscope (SEM: Ultra 55, Carl Zeiss AG, USA). A custom-made TCD setup was employed to run the temperature programmed reduction (TPR) test by using 50 mg catalysts. Prior to the test, a preheat treatment was performed in $5\% \text{ O}_2/\text{He}$ at 500°C for 2 h. Then, the sample was cooled down to 100°C and kept at this temperature for 30 min. After that, TPR tests were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ with 30 mL/min

FIGURE 1: XRD patterns of the $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$ precursors (H: hydrotalcite-like compounds; #: MnCO_3 ; ?: unidentified phases).

$6\% \text{ H}_2$ balanced with He going through. X-ray photoelectron spectroscopy with $\text{Al K}\alpha$ X-ray ($h\nu = 1486.6 \text{ eV}$) radiation operated at 150 W (Thermo ESCALAB 250Xi, USA) was used to investigate the surface atomic state of the sample. All the binding energies obtained were corrected using the C 1s level at 284.8 eV as an internal standard.

3. Results and Discussions

XRD patterns of all the $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$ precursors and calcined mixed oxides are exhibited in Figures 1 and 2, respectively. From Figure 1, a well-crystallized LDHs phase ($2\theta = 11.5^\circ, 23^\circ, 34^\circ$) could be detected in all the samples except the $\text{Co}_6\text{Mn}_2\text{LDH}$. Meanwhile, the reflections corresponding to MnCO_3 (PDF-No. 44-1472) also appeared in the former three samples [13]. However, the intensity referred to $\text{Co}_6\text{Mn}_2\text{LDH}$ sample was particularly low. And its crystallized phases could not be identified based on the phase analysis software, Jade5. The similar finding had been also reported by Kovanda et al. [14] in their study regarding Co and Mn containing layered double hydroxides. After calcination at 600°C for 4 h, spinel-type mixed oxides were formed in all the samples including $\text{Co}_6\text{Mn}_2\text{LDO}$. Such samples probably consist of one or mixture of MnCo_2O_4 (PDF number: 23-1237), CoMn_2O_4 (PDF number: 01-1126), Mg_6MnO_8 (PDF number: 19-0766), Co_3O_4 (PDF number: 43-1003), and MgCoMnO_4 (PDF number: 39-1157), considering that their peaks were almost superimposed. At low Co loading content ($\text{Co}_{1.5}\text{Mg}_{4.5}\text{Mn}_2\text{LDO}$), MnCo_2O_4 could be the main phase. And, with the increase of Co content, the peaks would gradually shift to higher angle range. For the sample $\text{Co}_6\text{Mn}_2\text{LDO}$, the obtained phases were mainly Co_3O_4 phase. Compared with the other three samples, it could be also found that the signal of Mg-free sample ($\text{Co}_6\text{Mn}_2\text{LDO}$) became sharper and higher, indicating that the primary particle size was probably larger than the others. For instance, the primary particle size calculated by Scherrer

FIGURE 2: XRD patterns of the $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$ samples (◆: MnCo_2O_4 phases; ♥: Co_3O_4).

equation increased from 8.1 nm for $\text{Co}_{4.5}\text{Mg}_{1.5}\text{Mn}_2\text{LDO}$ to 12.9 nm for $\text{Co}_6\text{Mn}_2\text{LDO}$.

From the activity tests (which will be discussed in Figure 6), we found that the activity of $\text{Co}_6\text{Mn}_2\text{LDO}$ sample was lower than the Mg-containing sample $\text{Co}_{4.5}\text{Mg}_{1.5}\text{Mn}_2\text{LDO}$. To further investigate the reason, we tried to get a clue from the SEM images of their $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$ precursors. The results are shown in Figure 3. From Figures 3(a) and 3(c), the $\text{Co}_{4.5}\text{Mg}_{1.5}\text{Mn}_2\text{LDH}$ samples showed a flake-like morphology and the size of flakes was approximately 400–450 nm. Without addition of magnesium, the sheet structure also appeared in the precursors, but the size and thickness grew larger. At the same time, we could also observe a lot of sintered particles from the image. This was probably attributed to the aggregation of the primary particles, since Mg-free sample should be of smaller primary particle size according to the XRD results in Figure 1. And the aggregation of the particles would lead to the easy sintering of the calcined oxides. This was consistent with the results of the LDO-XRD (Figure 2).

The specific areas of the $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$ precursors and the derived LDO samples are presented in Table 1. It could be observed that the surface area of LDH increased from 49.09 m^2/g to 130.88 m^2/g , which was in accordance with the result of LDH-XRD (Figure 1) that the peaks of the samples were getting broader with the addition of Co, indicating the decreasing of the grain size. However, the Mg-free LDO sample got the greatest loss in surface area (from 130.88 to about 45 m^2/g), together with the decreases of the pore diameter and volume. This fitted well with the result of LDO-XRD (see Figure 2) that the grain size would grow bigger without Mg being involved. According to the literatures [15–17], the alkaline earth could isolate transition metals effectively by strong interaction to reduce the agglomeration of the particles, thus reducing the loss of the specific area after calcination.

H_2 -TPR (see Figure 4) showed the differences in reducibility of the prepared LDO samples caused by the

TABLE 1: Porous properties of the $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$ (a) and LDO (b).

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$S_{\text{BET}}^{\text{b}}$ (m^2/g)	D_p^{b} (nm)	V_p^{b} (cm^3/g)
$x = 1.5$	49.09	43.88	28.66	0.31
$x = 3$	58.07	44.1	26.37	0.29
$x = 4.5$	85.15	50.87	24.36	0.28
$x = 6$	130.89	45.23	20.11	0.23

increasing content of Co. Based on the literatures [18, 19], the broad reduction peaks from 250 to 500°C were the results of overlapping peaks related to the reductions of Co/Mn oxides, which consists of the reduction process of $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}} \rightarrow \text{Co}^0$ in Co_3O_4 phase and Mn^{IV} species reduction. With the increase of Co content, the peaks first shifted to higher temperature and then the peaks shifted obviously to the lower temperature and a shoulder peak appeared at 284°C, which could be assigned to the reduction of $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$ [18], while, for the catalyst $\text{Co}_6\text{Mn}_2\text{LDO}$, the peaks shifted to higher temperature again and an additional peak at about 680°C became more evident. This high temperature peak might be attributed to the reduction of Co-Mn mixed oxide due to the sintering of catalyst in absence of Mg. The possible reason is that the existence of Mg could suppress the sintering and improve the dispersion of the active substance.

Oxygen normally played a very important role in the decomposition of methane according to the catalytic mechanism [20]. As such, the oxygen states on the catalysts herein were investigated by XPS characterization and the binding energies of O1s were given in Figure 5. Generally, there are three different types of oxygen in the catalysts with binding energy of O1s electrons, 529.0–530.0 eV, 531.3–531.9 eV, and 532.7–533.5 eV, which could be ascribed to lattice oxygen (O_a), surface adsorbed oxygen (O_b), and oxygen bonded in OH group (O_c), respectively [21–23]. In case of our catalysts (see Figure 5), oxygen with binding energy of 529.5–530.3 eV was the most intensive form and could be assigned to the lattice oxygen [22]. And oxygen species with binding energy of 531.0–531.5 eV can be attributed to the surface adsorbed oxygen (O_b) which could be considered the most active oxygen [24]. The percentage of O_b in total surface oxygen is listed in Table 2, from which we could clearly notice the tendency that O_b decreased with the introduction of Co, especially for the Mg-free one. In other words, the magnesium was necessary for keeping a certain amount of surface active oxygen possibly due to its well electronic donation property as a typical alkali earth metal. At last, oxygen with binding energy of 532.1–532.9 eV was originated from carbonated species or molecular absorbed water [25].

The catalytic activities of the $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$ samples derived from LDH precursors in methane total oxidation tested within the temperature range of 330–600°C are shown in Figure 6, where the methane conversion is plotted as a function of the reaction temperature. As shown in Figure 6, it could be clearly observed that the T_{90} (defined as 90% methane conversion) went down with the increase of Co content at first and then increased for

FIGURE 3: SEM images of $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDH}$ precursors (a) and (c), $x = 4.5$, and (b) and (d), $x = 6$.

FIGURE 4: H_2 -TPR patterns of $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$ samples.

the $\text{Co}_6\text{Mn}_2\text{LDO}$ sample. The $\text{Co}_{4.5}\text{Mg}_{1.5}\text{Mn}_2\text{LDO}$ catalyst showed the best performance with the $T_{90} = 485^\circ\text{C}$. This result was in agreement with our previous H_2 -TPR characterization where $\text{Co}_{4.5}\text{Mg}_{1.5}\text{Mn}_2\text{LDO}$ exhibits the best low-temperature reducibility. As we know, active oxygen was a critical factor for the catalytic oxidation reaction. The various valences of transition metal Co could supply abundant active oxygen in the catalysts, so the activity improved with the increase of Co at first, but when Mg is totally substituted by Co, the activity decreases because Mg could act as an electronic promoter in the catalysts to guarantee the oxygen mobility which was of

great importance for the catalytic oxidation reactions. The enhanced oxygen mobility after Ca-doping was reported in the literatures, which might indirectly support our assumption [24, 26].

4. Conclusions

A series of Co/Mg-Mn mixed oxide based catalysts were prepared via the calcination of layered double hydroxides with (Co+Mg)/Mn ratio at 3 and Co/Mg ratio from 1.5/4.5

TABLE 2: The amount of the surface elements of $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$.

Sample	Co (%)	Mg (%)	Mn (%)	O (%)	$\text{O}_b/\text{O}_{\text{total}}$
$\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO } x = 1.5$	5.3	27.8	7.4	59.5	23.45
$\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO } x = 3$	11.3	19.6	8.5	60.6	22.59
$\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO } x = 4.5$	16.4	12.6	9.6	61.4	18.70
$\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO } x = 6$	21.3	0	12.5	66.2	13.12

FIGURE 5: O1s XPS patterns of $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$ samples: (a) $x = 1.5$, (b) $x = 3$, (c) $x = 4.5$, and (d) $x = 6$. FIGURE 6: Catalytic activity of $\text{Co}_x\text{Mg}_{6-x}\text{Mn}_2\text{LDO}$ samples (1% vol. CH_4 , 10% vol. O_2 , GHSV = 25000 h^{-1}).

to 6/0, respectively. And then these catalysts were characterized by various methods and tested for their activities for methane catalytic combustion. The typical LDH lamellar structures were identified by X-ray diffraction except for the last $\text{Co}_6\text{Mn}_2\text{LDH}$ sample. But spinel structures were formed in all samples after calcination. The catalytic activities of the prepared catalysts expressed as the methane conversion decreased in the following sequence: $\text{Co}_{4.5}\text{Mg}_{1.5}\text{Mn}_2\text{LDO}$

$> \text{Co}_6\text{Mn}_2\text{LDO} > \text{Co}_3\text{Mg}_3\text{Mn}_2\text{LDO} > \text{Co}_{1.5}\text{Mg}_{4.5}\text{Mn}_2\text{LDO}$. Though the addition of Co would increase the redox ability of the catalyst, a certain amount of magnesium was necessary for high activity. Magnesium oxide would be beneficial to the dispersion of the cobalt and manganese mixed oxides. Furthermore, the existence of Mg could reduce the surface area loss after calcination and increase the surface active oxygen content.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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