Articles

Novel CH₄ Combustion Catalysts Derived from Cu–Co/X–Al (X = Fe, Mn, La, Ce) Hydrotalcite-like Compounds

Jie Cheng, Junjie Yu, Xiaoping Wang, Landong Li, Jinjun Li, and Zhengping Hao*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences,
Beijing 100085, P.R. China

Received January 8, 2008. Revised Manuscript Received April 28, 2008

Novel Cu₁Co₂/X_{0.2}Al_{0.8} well-mixed oxides (where X = Fe, Mn, Ce, La) were synthesized by calcinations of corresponding hydrotalcite-like compounds at 800 °C for 4 h. Their catalytic performance for the methane combustion was investigated. The oxides and their precursors were characterized by X-ray diffraction (XRD), thermogravimetry–differential scanning calorimetry (TG-DSC), temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and N₂ adsorption/desorption techniques. The derived oxides are mainly of spinel and tenorite phase, with surface area of 10–30 m²/g, where new phase CeO₂ and LaCoO₃ are segregated in Ce- and La-containing oxides, respectively. The catalytic activities of the catalysts are related to the redox properties of the metal cations and the species in the surface. Incorporation of the Mn and Fe element is helpful to the reduction of the oxide catalysts, which may lead to the enhancement of the catalytic activity. Among the catalysts investigated, Cu₁Co₂/Mn_{0.2}Al_{0.8} gives the highest catalytic activity. Light-off and complete oxidation temperature was centered at about 374 and 496 °C, respectively. The less active was Cu₁Co₂/Fe_{0.2}Al_{0.8}. The intensities of surface oxygen species over Mn- and Fe-containing oxides are much higher than other catalysts, implying the higher activity of surface oxygen for the methane combustion.

Introduction

The catalytic combustion of CH₄ has attracted considerable attention due to its potential application for power and heat generation with ultralow emissions of NO_x, CO, and unburned hydrocarbons.^{1,2} Nevertheless, there remains a major problem for the application of catalytic combustion unsettled, namely, the scarcity of robust and stable catalysts for catalytic combustion under severe hydrothermal conditions. Extensive efforts have been made to develop suitable catalysts and overcome these key obstacles for commercial applications.^{3,4} Generally, catalysts contain noble metals such as Pd and Pt are well-known to be active for methane combustion at low temperature, but they are

expensive and poorly stable because of sintering and volatilization of the active phase at moderate-high temperatures.^{5–7} Recently, alternative high stable catalytic materials based on single and doped transition metal oxides,⁸ perovskites,^{9,10} and hexaaluminates^{11–13} have been tested for the methane combustion.

(5) Persson, K.; Ersson, A.; Jansson, K.; Iverlund, N.; Jaras, S. *J. Catal.* **2005**, 231 (1), 139–150.

(6) Persson, K.; Ersson, A.; Jansson, K.; Fierro, J. L. G.; Jaras, S. G. *J. Catal.* **2006**, 243 (1), 14–24.

(7) Persson, K.; Jansson, K.; Jaras, S. G. *J. Catal.* **2007**, 245 (2), 401–414.

(8) Liotta, L. F.; Di Carlo, G.; Pantaleo, G.; Deganello, G. *Appl. Catal., B* **2007**, 70 (1–4), 314–322.

(9) Chiarello, G. L.; Rossetti, I.; Forni, L. *J. Catal.* **2005**, 236 (2), 251–261.

(10) Fabbri, L.; Kryukov, A.; Cappelli, S.; Chiarello, G. L.; Rossetti, I.; Oliva, C.; Forni, L. *J. Catal.* **2005**, 232 (2), 247–256.

(11) Zarur, A. J.; Ying, J. Y. *Nature* **2000**, 403 (6765), 65–67.

(12) Teng, F.; Xu, J. G.; Tian, Z. J.; Wang, J. W.; Xu, Y. P.; Xu, Z. S.; Xiong, G. X.; Teng, F. *Chem. Commun.* **2004**, (16), 1858–1859.

* Corresponding author. E-mail: zpinghao@rcees.ac.cn. Tel.: +86-10-62849194. Fax: +86-10-62923564.

(1) Arai, H.; Fukuzawa, H. *Catal. Today* **1995**, 26 (3–4), 217–221.

(2) Eguchi, K.; Arai, H. *Catal. Today* **1996**, 29 (1–4), 379–386.

(3) Choudhary, T. V.; Banerjee, S.; Choudhary, V. R. *Appl. Catal., A* **2002**, 234 (1–2), 1–23.

(4) Gelin, P.; Primet, M. *Appl. Catal., B* **2002**, 39 (1), 1–37.

tion but they show lower catalytic activity and higher light-off temperature than noble metal catalysts.

Hydrotalcite-like compounds (HTLcs) are known as anionic clays or layered double hydroxides (LDHs) and are widely used as adsorbents, ion exchanges, base catalysts, and precursors of mixed oxides for various catalytic applications.^{14–19} HTLcs can be chemically expressed in a general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} represents any divalent metal cation, M^{3+} represents any trivalent metal cation, A^{n-} is an anion (inorganic or organic), and x can have values between approximately 0.25 and 0.33.¹⁵ Due to the possibility of obtaining well homogeneous oxides, HTLcs is used as precursor for the catalysts more than as layered material itself. Moreover, a large spectrum of structural textural and compositional modifications are possible for HTLcs, allowing a fine-tuning and control of the related catalytic activity.²⁰ For example, the three typical components required for a methane combustion catalyst could be all designed in an HTI compound. Jiratova et al.²¹ investigated the catalytic activity of nickel and manganese containing mixed oxides derived from HTLcs in the methane combustion. Our recent studies have shown that Cu- and Co-containing oxide catalysts calcined from MgAl-HTLcs perform well for catalytic combustion of methane.²² However, to the best of our knowledge, with much research on the improvement of methane combustion catalysts through substitution of M^{2+} (Mg^{2+}) by cations such as Cu and Co, modifying the catalysts by replacement of M^{3+} (Al^{3+}) with others seems to draw less attention. In this regard, we designed and prepared a series of CuCoXAl mixed oxide catalysts (where $X = \text{Fe, Mn, Ce, La}$) from the corresponding HTLcs precursors and investigated their catalytic performances in methane combustion.

Experimental Section

Material Preparation. Four $\text{Cu}_1\text{Co}_2/\text{X}_{0.2}\text{Al}_{0.8}$ HTLcs were prepared with a constant-pH coprecipitation method where X represents Fe, Mn, La, and Ce and is denoted as CCXA-HT. For the sake of comparison, Co_3/Al_1 -HT (CA-HT) and $\text{Cu}_1\text{Co}_2/\text{Al}_1$ -HT (CCA-HT) were prepared similarly. In brief, a mixed salt solution (100 mL) and a mixed basic solution (100 mL) were simultaneously added dropwise into 100 mL doubly distilled water within 1 h at constant pH (10 ± 0.5) under vigorous mechanical stirring. The mixed salt solution contains a total cation concentration of 1.0 M from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with the designed molar ratio. All these chemicals in purity of 99% were supplied from Beijing Chemical Industry Company. The basic solution consists of NaOH and Na_2CO_3 with $[\text{OH}^-] = 2.0 \text{ M}$ and $[\text{OH}^-]/[\text{CO}_3^{2-}] = 16$. Precipitates were aged in suspension at room

temperature for 4 h with stirring in the static air and then filtered and thoroughly washed with doubly distilled water. The cake was dried at 70 °C for 12 h and again at 120 °C overnight. These HTLcs were calcined at 800 °C for 4 h to derive $\text{Cu}_1\text{Co}_2/\text{X}_{0.2}\text{Al}_{0.8}$ mixed oxide catalysts (denoted as CCXAO, CAO, and CCAO, $X = \text{Fe, Mn, Ce, La}$). The oxide catalysts were then crushed and sized in 20–40 mesh for sorption experiments and kept in a desiccator to avoid reconstruction of the hydrotalcite-like structure.

Material Characterization. The crystal structure of the prepared materials was measured on a Rigaku powder diffractometer (D/max-RB) using Cu K α radiation ($\lambda = 0.15418 \text{ nm}$) in the 2θ range of 10–70° at scanning rate of 4°/min. The tube voltage and current were set at 40 kV and 30 mA, respectively. The textural properties of the derived oxides (CCXAOs) were analyzed by N_2 adsorption/desorption at liquid nitrogen temperature (77 K) in a Quantachrome NOVA 1200 gas absorption analyzer. The specific surface area was calculated with the BET equation, and the pore volume and pore size distribution were obtained with the BJH method from the adsorption isotherm. The thermal decomposition and stability of CCXA-HTs was investigated with thermogravimetry (TG, Setaram, Labsys). In a typical measurement, 20–30 mg of HT sample was heated in an Al_2O_3 crucible at a constant heating rate of 10 °C/min from 25 to 1000 °C, with air purging at a flow rate of 30 mL/min. Temperature programmed reduction (TPR) was performed for all the CCXAO catalysts on a conventional TPR apparatus equipped with a thermal conductivity detector (TCD). In general, catalyst samples (50 mg each) were placed in a quartz reactor land sandwiched between two quartz wool plugs. Prior to each TPR run, the catalyst was heated up to 500 °C under an O_2 flushing (40 mL/min). After a 30 min pretreatment in O_2 flow at 500 °C, the reactor bed temperature was then lowered down to room temperature by keeping the same flow rate of oxygen. Then N_2 was fed to the reactor at 50 mL/min for 1 h at room temperature to purge away any residual oxygen. The catalyst was then heated to 750 °C at a constant heating rate of 10 °C/min and reduced in a reducing environment (5% H_2 in N_2 at a flow rate of 50 mL/min). During the heating, H_2 consumption was monitored by the TCD detector. X-ray photoelectron spectroscopy (XPS) experiments were performed on the ESCALAB 200R (Fisons Instruments) analyzer. Various CCXAO samples were separately placed onto a sample holder and degassed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-9} Torr. The sample (typically 50 mg) was then exposed to radiation from an Al K α source (1486.6 eV) equipped with a monochromator, and emitted electrons were collected. The apparatus was calibrated with respect to the Au 4f_{7/2} peak. In the event of a charge effect, an internal reference, such as C_{1s} (BE = 284.6), was used.

Catalytic Activity Test. The catalytic activity evaluations for the methane combustion on CCXAO oxide catalysts were carried out in a tubular plug flow reactor at atmospheric pressure. A mixture of CH_4 :air in a volume ratio of 1:99 at a total flow rate of 400 mL/min passed through the catalyst bed (0.5 g catalyst diluted with similar volumed silica). The gas hourly space velocity (GHSV) was kept at approximately 60 000 h⁻¹. The system was heated externally via a tubular furnace. The reactants and products were online analyzed by a GC equipped with flame ionization detection (FID). CO and CO_2 were catalytically converted to CH_4 by a Ni catalyst prior to the FID measurements. The methane conversion rate was calculated based on the integrated GC peak areas. The catalysts activity was characterized by T_{10} , T_{50} , and T_{90} representing the temperature of methane conversion rates of 10, 50, and 90%, respectively.

Results

Transformation of Hydrotalcites to Mixed Oxides. The X-ray diffraction of HTLcs (dried at 110 °C) is shown in Figure 1A. All the compounds show the typical diffraction peaks at $2\theta = \sim 11^\circ$, 23° , and 34° , attributed to the (003), (006), and (012) crystal planes in the layered structure with a rhombohedral symmetry (3R) (JCPDS 51-0045 and 37-0630). The in-plane

(13) Teng, F.; Liang, S. H.; Gauge, B.; Zhu, Y. F.; Xu, J. G.; Wen, G. D.; Tian, Z. J.; Wang, Z. M.; Yang, X. M.; Xiong, G. X. *J. Phys. Chem. C* **2007**, *111* (29), 10941–10947.

(14) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11* (2), 173–301.

(15) Yu, J. J.; Jiang, Z.; Zhu, L.; Hao, Z. P.; Xu, Z. P. *J. Phys. Chem. B* **2006**, *110* (9), 4291–4300.

(16) Li, L. D.; Yu, J. J.; Hao, Z. P.; Xu, Z. P. *J. Phys. Chem. C* **2007**, *111* (28), 10552–10559.

(17) Yu, J. J.; Tao, Y. X.; Liu, C. C.; Hao, Z. P.; Xu, Z. P. *Environ. Sci. Technol.* **2007**, *41* (4), 1399–1404.

(18) Yu, J. J.; Wang, X. P.; Li, L. D.; Hao, Z. P.; Xu, Z. P. *Adv. Funct. Mater.* **2007**, *17* (17), 3598–3606.

(19) Yu, J. J.; Wang, X. P.; Tao, Y. X.; Hao, Z. P.; Xu, Z. P. *Ind. Eng. Chem. Res.* **2007**, *46* (17), 5794–5797.

(20) Centi, G.; Perathoner, S. *Micropor. Mesopor. Mat.* **2008**, *107* (1–2), 3–15.

(21) Jiratova, K.; Cuba, P.; Kovanda, F.; Hilaire, L.; Pitchon, V. *Catal. Today* **2002**, *76* (1), 43–53.

(22) Jiang, Z.; Hao, Z. P.; Yu, J. J.; Hou, H. X.; Hu, C.; Su, J. X. *Catal. Lett.* **2005**, *99* (3–4), 157–163.

Figure 1. XRD patterns of samples CCXA-HTs (A) and oxide catalysts CCXAOs (B) where the hydrotalcite-like phase was marked as “H”, spinel as “S”, tenorite as “T”, LaCoO₃ as “+”, and CeO₂ as “#”.

X-ray diffraction from plane (110) and (113) can also be noted at $\sim 60^\circ$ and $\sim 61^\circ$ for all HTlcs. These characteristic diffraction peaks reveal a quite good dispersion of metal ions in the hydroxide layers.

The XRD patterns of the derived mixed oxides (Figure 1B) show the complete transformation from the hydrotalcite to the oxide phase. For sample Co₃Al oxide, diffraction peaks with 2θ at $\sim 31^\circ$, 36° , 39° , 45° , 55° , 59° , and 65° were observed that are only attributed to a spinel phase (Co₂AlO₄, JCPDS 38-0814; CoAl₂O₄, JCPDS 44-0160 and 82-2246; Co₃O₄, JCPDS 74-2120). With the introduction of copper, the diffraction peaks at 36° and 48° are ascribed to the tenorite (JCPDS 34-0394). It is hard to distinguish CuAl₂O₄ phase because its diffractions are very similar to CoAl₂O₄ and Co₂AlO₄. However, we can deduced that there should existed the CuAl₂O₄ phase since the spinel formation rate follows the sequence CoAl₂O₄ < CuAl₂O₄,²³ and the cobaltic oxide can enhance the formation of CuAl₂O₄ at 800 °C, which could be attributed to an effective increase in the mobility of CuO species, facilitating its diffusion into the interior of Al₂O₃ grains.²⁴ When Fe or Mn is included, the mixed oxide is of spinel phase and tenorite and no crystalline Fe or Mn phase is detected. For oxide CCCAO, a new phase (CeO₂, JCPDS 34-0394, marked with “#” in Figure 1B) is

Figure 2. Thermogravimetry–differential thermogravimetry (TG-DTG) profiles of catalysts CCXA-HTs in air.

Figure 3. Temperature dependence of methane catalytic combustion on oxide catalysts CCXAOs.

segregated. Similarly, CCLAo has LaCoO₃ (JCPDS 48-0123) as the segregated phase (marked with “+” in Figure 1B).

Figure 2 presents the weight loss rates of these hydrotalcite-like compounds during heating in air, revealing the transformation of these CCXA-HTs into the corresponding oxides. In general, the thermal decomposition (weight loss) of the hydrotalcites consists of three steps. The first step occurs at 100–250 °C for all HT samples, mainly ascribed to the loss of interlayer and adsorbed water molecules. The second step of the weight loss at 250–300 °C consists of dehydroxylation of interlayer hydroxyl groups and decomposition of interlayer carbonate and traced nitrate, resulting in the collapse of the

(23) Bolt, P. H.; Habraken, F. H. P. M.; Geus, J. W. *J. Solid State Chem.* **1998**, 135 (1), 59–69.

(24) Deraz, N.-A. M. *Colloids Surf. A: Physicochem. Eng. Aspects* **2002**, 207 (1–3), 197–206.

Figure 4. H₂-TPR profiles of catalysts CCXAOs.

Table 1. Textual Properties, Activities, and Surface Composition of the Oxide Catalysts CCXAOs

sample	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	phase (detected by XRD)	SSA ^a (m ² /g)	pore volume (cm ³ /g)	pore size (nm)	surface composition (mol%)				
								Co	O	Cu	X	Co/Cu
CAO	407	491	560	spinel	30.1	0.062	8.2	19.3	80.7			
CCAO	405	475	589	spinel + tenorite	25.6	0.063	9.9	15.0	75.5	9.5		1.58
CCMAO	374	429	496	spinel + tenorite	20.5	0.052	10.0	13.7	70.5	10.8	5.0	1.27
CCFAO	405	464	532	spinel + tenorite	18.3	0.042	9.2	17.2	68.5	11.5	2.7	1.50
CCLAO	420	489	549	spinel + tenorite + LaCoO ₃	27.5	0.11	15.4	12.9	76.3	7.0	3.8	1.84
CCCAO	410	493	632	spinel + tenorite + CeO ₂	14.2	0.055	15.5	10.5	75.3	12.3	1.9	0.85

^a Specific surface area.

layered structure.^{25,26} A progressive weight loss is observed between 300 and 800 °C, which can be attributed to the phase transitions from HTlcs to spinels.²² In case of Co₃Al and Cu₁Co₂Al, hydrotalcites thermal decomposition between 200 and 300 °C occurred at the two stages. Interestingly, the introduction of Fe, Mn, Ce, and La facilitates the second decomposition stage to some degree and the two steps are partially overlapped because of the lower thermal stability of the hydroxides [Fe(OH)₃, Mn(OH)₃, Ce(OH)₃, La(OH)₃,] and the weak interaction with H₂O with respect to that of Al(OH)₃.¹⁷

Catalytic Activity of Methane Combustion on CCXAO Oxide Catalysts. The catalytic behaviors for methane combustion over Co₃/Al₁, Cu₁Co₂/Al₁, and Cu₁Co₂/X_{0.2}Al_{0.8} catalysts are shown in Figure 3. In this investigation, carbon dioxide is the sole product; carbon monoxide was scarcely detected during oxidation process. The results of the catalytic activity tests are listed in Table 1. CAO and CCAO were also found to exhibit excellent activity for methane oxidation. With the introduction of Mn and Fe into CCAO, the catalytic activity is considerable increased. The lowest T_{10} value (374 °C) was attained by CCMAO, which also showed relatively high activity at a high

Table 2. TPR Peak Maxima and H₂ Uptake (±15%) of CCXAO Catalysts

sample	T (°C)	H ₂ (mL/g)
CAO	257	18
Enter	460	49
CCAO	648	315
	269	86
CCLAO	460	252
	267	87
CCFAO	468	197
	230	80
CCMAO	454	284
	246	70
	359	53
CCCAO	515	204
	230	89
	395	53
	460	162

conversion level (T_{90} = 496 °C). Meanwhile, CCFAO catalyst also possesses the high catalytic activity at high temperature, although its light-off temperature is close to CCAO. On the contrary, both CCCAO and CCLAO catalyst are poorly active at low temperature with respect to CCAO catalyst. Though CCLAO catalyst was less active than the CCCAO catalyst at low temperature, the catalytic activity increased with the rise of the reaction temperature.

(25) Xu, Z. P.; Zeng, H. C. *J. Phys. Chem. B* **2000**, *104* (44), 10206–10214.(26) Xu, Z. P.; Zeng, H. C. *J. Mater. Chem.* **1998**, *8* (11), 2499–2506.

Table 3. XPS Results of the CCXAO Catalysts

sample	Co 2p _{3/2}	Co 2p _{1/2}	Co 2p _{3/2-1/2}	Cu 2p _{3/2}	Cu 2p _{1/2}	O _α	O _β	O _β /(O _α + O _β)
CAO	780.4	795.6	15.2			530.2	529.1	20.2
CCAO	780.6	795.6	15.0	934.4	954.0	531.6	529.2	20.6
CCLAO	780.2	795.6	15.4	934.6	954.0	531.4	529.4	18.6
CCFAO	780.2	795.4	15.2	933.4	953.4	531.1	529.3	30.4
CCMAO	780.2	795.4	15.2	933.8	953.4	530.9	529.2	33.5
CCCAO	780.4	795.6	15.2	933.8	953.4	531.1	529.5	19.5

TPR Analysis of CCXAO Oxide Catalysts. The reduction profiles of CCXAO samples are shown in Figure 4. The temperatures of peak maxima along with H₂ uptake are given in Table 2. For CAO, i.e., Co₃Al oxide, the first reduction peak, initiated at 150 °C and ended around 300 °C, is related to the reduction of highly dispersed Co₃O₄ to CoO and Co⁰ on the surface.²⁷ The second peak at 460 °C is attributed to the reduction of bulky Co³⁺ cations in the spinel, and the high temperature at 648 °C is attributed to the reduction of bulky Co²⁺ cations dispersed in the spinel.¹⁵ With the introduction of Cu in HTLcs, there was one diffuse H₂ consumption peak centered at 269 °C for CCAO, initiated at 180 °C and ended around 300 °C. According to Jiang et al.,²² the broad peak shown between 180 and 300 °C can be disintegrated into three peaks centered at 225, 235, and 270 °C, respectively. The peaks at 225 and 235 °C can be assigned to highly dispersed CuO particles supported on the surface of periclase and CuAl₂O₄ spinel, while the peak at 270 °C can be attributed to the reduction of the bulk CuO in the mixed oxides. It is worth to notice that both reduction processes of Cu²⁺ and Co³⁺ take place in the same temperature range.²⁸ Furthermore, the TPR of all the samples containing both Cu and Co shows a peak around 260 °C together with a peak at ca. 460 °C, which could be ascribed to the reduction of Cu and Co species.

For CCMAO and CCCAO catalyst, there was a new diffuse H₂ consumption peak centered at 359 and 395 °C, respectively. The former belongs to the reduction of MnO₂, possibly Mn₃O₄,²⁹ and the latter belongs to CeO₂.

Surface Composition. XPS data provide information about surface composition, obtained from core photoemission intensity data, and information about the chemical state of the elements in near-surface region. Binding energies (BE) of the selected photoemission lines of catalysts are summarized in Table 3. The Co 2p core level and Cu 2p core level are displayed in Figure 5.

The surface compositions of the oxide catalysts CCXAOs are summarized in Table 1. The Co/Cu atomic ratios (based on XPS results) were smaller than the theory ratio of 2, suggesting that the enrichment of Cu on the surface. It is also found that Mn element was enriched on the CCMAO surface.

According to previous XPS studies,^{30,31} the features, such as spin–orbital splitting and shakeup satellite, should be used for identifying the cobalt chemical state. For example, the high spin Co²⁺ compounds such as CoO, Co(OH)₂, and CoAl₂O₄ exhibit a well-defined shakeup satellite structure and high values of Co 2p spin–orbital splitting in the 15.5–16.0 eV range. Contrary to that, the low spin Co³⁺ compounds (Co₃O₄) exhibit very weak satellites and spin–orbital splitting usually close to 15 eV. In Figure 5, the peak of Co 2p_{3/2} for all the samples appeared at around 780.2–780.6 eV (satellite lines are rather weak), the obtained value of the spin–orbit splitting 15.2 ± 0.2 eV corresponds well to the value typical for Co₃O₄ with mixed valence of cobalt.

Figure 5. XPS of Co 2p level (A) and Cu 2p level (B) for CCXAO catalysts.

With the introduction of copper, the presence of satellite peak for Cu 2p_{3/2} core level spectra of all samples show unambiguously the presence of Cu²⁺ on the surface of catalysts. Indeed, when Cu⁺ and Cu⁰ are studied, no satellite peaks are observed. According to Batista's observation,³² only Cu²⁺ species shows a shakeup satellite peak located about 10 eV higher than the Cu 2p_{3/2} transition; this characteristic is used to differentiate between Cu²⁺ and reduced copper.

From the XPS spectra of Mn 2p, for the CCMAO catalyst, the binding energy around 642.2 eV could be ascribed to the presence of Mn⁴⁺ species.³³ The Fe 2p spectra recorded for CCFAO sample shows an intense peak at BE of ca. 710 eV

(27) Lucredio, A. F.; Assaf, E. M. *J. Power Sources* **2006**, *159* (1), 667–672.

(28) Rives, V.; Dubey, A.; Kannan, S. *Phys. Chem. Chem. Phys.* **2001**, *3* (21), 4826–4836.

(29) Obalova, L.; Pacultova, K.; Balabanova, J.; Jiratova, K.; Bastl, Z.; Valaskova, M.; Lacny, Z.; Kovanda, F. *Catal. Today* **2007**, *119* (1–4), 233–238.

(30) Khassin, A. A.; Yurieva, T. M.; Kaichev, V. V.; Bukhtiyarov, V. I.; Budneva, A. A.; Paukshtis, E. A.; Parmon, V. N. *J. Mol. Catal. A* **2001**, *175* (1–2), 189–204.

(31) Kosova, N. V.; Devyatkina, E. T.; Kaichev, V. V. *J. Power Sources* **2007**, *174* (2), 735–740.

accompanied by a satellite line visible at BE of 718.4 eV, as is indicative of Fe^{3+} cations.³³ From the XPS spectra of Ce3d, three pairs of peaks (V,U; V'',U''; V''',U''') arise from different Ce 4f electron configuration, suggesting that the oxidation state of cerium was Ce^{4+} species in CCCAO.³⁴ This is also in agreement with the XRD results.

According to the corresponding XPS spectra of O1s, two peaks (O_α and O_β) were displayed, which represent two different kinds of surface oxygen species.³⁵ O_α with BE from 529.15 to 529.31 eV is characteristic of the lattice oxygen (O^{2-}), while O_β with BE of 530.22–531.65 eV belongs probably to the adsorptive O_2 or/and the surface oxygen ions with low coordination. The O1s core level from the XPS spectra of the CCXAO catalysts are summarized in Table 2.

Discussion

As shown in Figure 3 and Table 1, the catalytic activity of CCXAO catalysts for methane combustion obviously varied with the doped metal cations, which indicated that combustion activity is primarily determined by the nature of the metal cation. For the combustion catalyst, although specific area is one of the possible factors influencing catalytic activity, the variation in the catalytic activity could not be interpreted by the variation in the specific area. For example, the activity of CCMAO and CCFAO was much more active than CCLAO and CCCAO, although Mn and Fe doping reduced the surface area of the catalysts, as shown in Table 1.

Catalytic combustion over mixed oxides occurs via a redox mechanism involving reversible variation of the oxidation state of the metal cations in the structure. In methane combustion, the metal cations strongly modify the oxygen desorption and reduction behaviors. In the present study, the redox properties evaluated by TPR, as shown in Figure 4. The reduction at low temperature for catalysts containing Cu species is not active for methane oxidation. However, the redox behaviors were strongly influenced by the copper substitution. For example, the peak at 648 °C for the reduction of bulky Co^{2+} cations dispersed in the spinel is disappeared, the two-step reduction of bulky Co cations are partially overlapped and the reduction of bulky Co^{3+} cations in the spinel is shifted to low temperature. These change are ascribed to the interaction between interaction between Cu and Co ions. The reduction processes of $\text{Cu}^{2+}/\text{Cu}^0$ take place between 200 and 300 °C. The corresponding extraction of Cu^0 atoms from the framework enhances the reduction of $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Co}^{2+}/\text{Co}^0$. Such Cu^0 metal acts as a catalyst for hydrogen dissociation thus providing atomic hydrogen, which facilitates reduction of cobalt ions.³⁶ Velu et al.³⁷ also found that Cu^+ species can be stabilized in the Co-containing materials if they were treated in the reducing atmosphere. The Cu^{2+} species are reduced first to metallic Cu. This metallic Cu can assist the reduction of Co^{3+} to Co^{2+} during which the metallic Cu is partially oxidized to Cu^+ .

Considering the reaction conditions of reducing (CH_4) agents available at reaction temperature, such a redox mechanism could

Figure 6. XPS of Fe 2p level (A), Mn 2p level (B), La 3d (C), and Ce 3d (D) for CCXAO catalysts.

be responsible for the higher activity in the methane oxidation at low temperature over the similar Cu/Co-based mixed oxide catalysts.

On correlating catalytic activity data in Figure 3 with TPR results, the most active CCMAO catalyst contains the optimum amount of components reducible in the temperature region 350–400 °C, the range in which the catalytic reaction proceeds.

(32) Batista, J.; Pinter, A.; Mandrino, D.; Jenko, M.; Martin, V. *Appl. Catal., A* **2001**, 206 (1), 113–124.

(33) Essayem, N.; Martin, V.; Riondel, A.; Vedrine, J. C. *Appl. Catal., A* **2007**, 326 (1), 74–81.

(34) Damyanova, S.; Bueno, J. M. C. *Appl. Catal., A* **2003**, 253 (1), 135–150.

(35) Damyanova, S.; Perez, C. A.; Schmal, M.; Bueno, J. M. C. *Appl. Catal., A* **2002**, 234 (1–2), 271–282.

(36) Tien-Thao, N.; Alamdari, H.; Zahedi-Niaki, M. H.; Kaliaguine, S. *Appl. Catal., A* **2006**, 311, 204–212.

(37) Velu, S.; Suzuki, K.; Gopinath, C. S. *J. Phys. Chem. B* **2002**, 106 (49), 12737–12746.

The active site on CCMAO catalyst is mainly identified as being Mn⁴⁺ of MnO₂. Although MnO₂ is not detected by XRD, it is confirmed by XPS. Meanwhile, XPS results show that replacement of Al³⁺ with manganese could result in an enrichment of Mn on the surface. These results show MnO₂, especially on the surface, is responsible for the high catalytic activity of the CCMAO oxide.

It is generally believed that CH₄ catalytic combustion proceeds by the surface reaction between adsorbed oxygen and methane. There are two oxygen species taking part in this reaction:³⁸ One is the chemisorption oxygen weakly bonded which takes part in the reaction at low temperature. Another is the lattice oxygen bonded which takes part in the reaction at high temperature. The surface or chemisorption oxygen is believed to be more active and reacts with methane at lower temperature than the original lattice oxygen. With a rise of reaction temperature, not only does surface oxygen decrease but lattice oxygen becomes reactive. As a result, the high temperature oxidation is dominantly operated by the lattice oxygen. According to the XPS results, two kinds of oxygen species α and β with different bonding strength seem to coexist at the surface of the CCXAO catalysts. The intensities of O β signal over CCMAO and CCFAO catalysts are much higher

than over other catalysts, implying the higher activity of surface oxygen for methane combustion.

Conclusions

Co₃/Al₁, Cu₁Co₂/Al₁, and Cu₁Co₂/X_{0.2}Al_{0.8} hydrotalcite-like compounds (where X = Fe, Mn, Ce, La) were prepared via a coprecipitation process and identified by their XRD patterns. Their transformation to mixed oxides upon calcinations was also confirmed by XRD patterns and TG analysis. The derived oxides are mainly of spinel and tenorite phase, where new phase CeO₂ and LaCoO₃ are segregated in Ce- and La-containing oxides, respectively. There could be existed the synergetic effect between Cu and Co over Cu/Co-based mixed oxide catalysts. Incorporation of the fourth element has assisted the reduction of metal cations in the oxide catalysts, which could lead to the enhancement of the catalytic performance. Among the catalysts investigated, Cu₁Co₂/Mn_{0.2}Al_{0.8} excels over all other catalysts for the methane oxidation. Meanwhile, oxygen species play a major role in the catalytic combustion of methane. The intensities of surface oxygen species over Mn- and Fe-containing oxides are much higher than other catalysts, implying the higher activity of surface oxygen for the methane combustion.

Acknowledgment. This work was financially supported by the National Basic Research Program of China (No. 2004CB719500) and the Chinese National Science Fund for Distinguished Young Scholars (No. 20725723).

EF8000168

(38) Seiyama, T. *Catal. Rev.—Sci. Eng.* **1992**, 34 (4), 281–300.