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JOURNAL OF RARE EARTHS
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JOURNAL OF RARE EARTHS, Vol. 28, No. 5, Oct. 2010, p. 747

Influence of copper content on structural features and performance of pre-reduced $LaMn_{1-x}Cu_xO_3$ ($0 \le x < 1$) catalysts for methanol synthesis from CO_2/H_2

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Received 13 April 2010; revised 14 May 2010

Abstract: A series of pre-reduced $LaMn_{1-x}Cu_xO_3$ ($0 \le x < 1$) catalysts for methanol synthesis from CO_2 hydrogenation were prepared by a sol-gel method. The catalytic performances were strongly dependent on the copper content. XRD investigation revealed that the single perovskite structure could be preserved after being reduced, when the substitution for Mn by Cu was less than 50%. The Cu-doped (x=0.5) $LaMnO_3$ was much more active than the other catalysts for reaction, showing CO_2 conversion up to 11.33% and methanol selectivity close to 82.14%. The structural features of samples ($x \le 0.5$) were studied. It was determined that copper existed as Cu^+ species under reduction conditions. H_2 was adsorbed on Cu^+ sites and CO_2 was activated on the medium CO_2 active species in the lattice. The strong interaction between Cu^+ and Mn inhibited the further reduction from Cu^+ to Cu^0 and made the fine dispersion of medium basic site to adsorb CO_2, contributing to reactivity.

Keywords: $LaMn_{1-x}Cu_xO_3$ perovskite; sol-gel method; CO_2 hydrogenation; methanol; rare earths

It is well known that carbon dioxide emissions have induced global warming. The technologies of exploitation and fixation of CO_2 as the major strategies have received much attention at present. Indeed, catalytic hydrogenation of carbon dioxide to methanol is one of the attractive approaches, since methanol is a key material for many chemicals, as well as an alternative energy substitute for the oil-based fuels of automobiles[1].

Considerable research efforts have been directed to development of catalysts which show high activity towards methanol synthesis from carbon dioxide hydrogenation[2–6]. $AB_{1-x}B_x'O_3$ (A and B (B') are usually a lanthanide and transition metal, respectively, and x is the substitution degree) perovskite-type oxides have been reported to catalyze many reactions after being reduced under proper conditions. Activity is governed by nature of the cation in position B and related to reducibility. Meanwhile, the partial substitution of B-sites gives rise to a modification in catalytic behavior for some reactions. Compared with conventional preparation methods, this method could lead to a fine particle size and a high dispersion of active sites. For example, Navarro et al.[7] added Ru to $LaCoO_3$, which increased activity and stability of $LaCoO_3$-derived catalyst for hydrogen production by oxidative reforming of diesel. Araujo et al.[8] also pointed out that $LaNi_{1-x}Ru_xO_3$ was active in methane reforming with CO_2 and was not accompanied by coke deposition. Tien-Thao et al.[9] found that $LaCo_{1-x}Cu_xO_{3-\delta}$ catalysts featured higher-alcohol in CO hydrogenation. The addition of copper into $LaCoO_3$ framework led to changes in product distribution of reaction. Petrović et al.[10] studied the Pd-doped perovskite phase $LaTi_{0.5}Mg_{0.5}O_3$ catalysts. They found that Pd content in the mixed perovskite had a little influence on activity of methane oxidation over high temperature, connected with particle size effects and metal-perovskite interactions.

Previously, we have shown that carbon dioxide hydrogenation to methanol over the pre-reduced $LaCr_{0.5}Cu_{0.5}O_3$ catalyst. It was found that the reduced Cu-based $LaCr_{0.5}Cu_{0.5}O_3$ catalyst displayed high catalytic performance in comparison with 13% $Cu/LaCrO_3$. Copper is assumed as an active metal for the formation of alcohols (mainly methanol) but manganese is not a typical catalyst for propagation of hydrocarbon chain of products[11]. The chemical stability of $LaMnO_3$ perovskite phase is higher than that of $LaCrO_3$, due to its lower electronegativity[12]. This leads to the assumption that a combination of Mn and Cu element in the desired perovskite structure could be a promising catalyst precursor for the synthesis of methanol form CO_2/H_2. At present, the substitution of Mn by Cu in $LaMnO_3$ has been reported to catalyze the reactions of oxygenate synthesis from syngas and reduction of NO by CO or propene. Partial Cu substitution can enhance the abundance of anion vacancies and the mobility of lattice oxygen in lanthanites, contributing to a significant improvement in catalytic performance[11,13,14]. The present work was to investigate the effect of copper content on structural features and catalytic behavior for CO_2 hydrogenation to methanol over the pre-reduced $LaMn_{1-x}Cu_xO_3$ catalysts ($0 \le x < 1$). The structural properties of

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DOI: 10.1016/S1002-0721(09)60193-9

catalysts were characterized by X-ray diffraction (XRD), X-ray electron spectroscopy (XPS), temperature programmed desorption (H_2/CO_2-TPD) and Raman measurements.

1 Experimental

1.1 Catalyst preparation

$LaMn_{1-x}Cu_xO_3$ oxides with $0 \le x < 1$, were prepared by a sol-gel method using citric acid as a complexing agent. The amounts of precursor salts ($La(NO_3)_3 \cdot nH_2O$ ($La_2O_3 \ge 44\%$), $Mn(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$) along with citric acid were dissolved in water at a molar ratio of 2:1 (metal cations:citric acid). The total metal cation concentration was fixed to be 0.2 mol/L. The solution was heated to 150 ºC until it was ignited. The resulting powder was finally calcined in air at 400 ºC for 2 h and then at 800 ºC for 4 h.

1.2 Catalyst reaction

The methanol synthesis reaction was carried out in a fixed-bed flow reactor. Prior to the reaction, the precursor of catalyst (0.5 g) was pre-reduced with pure H_2 at 350 ºC for 2 h under atmospheric pressure. Then the reactor was cooled to 200 ºC and the reaction gas was admitted at the pressure of 2 MPa. The reaction of CO_2 hydrogenation was tested at 250 ºC. A CO_2-H_2 reaction mixture in the molar ratio equal to 1:3 was fed at a space velocity (GHSV) of 2400 ml/(h·g). The products were analyzed by an on-line gas chromatograph (GC-950) using TDX-01 column and GDX-401 column, connected to TCD and FID, respectively. The former column was used for the separation of N_2, CO and CO_2, while the latter was used for the separation of methane and methanol. Conversion and selectivity values were calculated by the internal standard and mass-balance methods.

1.3 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Panalytical X'Pert Pro X-ray diffractometer with Cu Kα radiation, in the step mode (0.0167°, 15 s) in the range $20° < 2\theta < 80°$. The voltage and current were 40 kV and 30 mA, respectively.

X-ray photoelectron spectroscopy (XPS) measurements were done on a Quantum 2000 Scanning ESCA microprobe instrument with Al Kα radiation (15 kV, 150 W, $h\nu$=1486.6 eV) under ultrahigh vacuum (10^{-7} Pa), calibrated internally by the carbon deposit C(1s) (E_b=284.8 eV).

H_2-temperature-programmed desorption (H_2-TPD) was conducted on Micromeritics AutoChem 2920 II instrument connected to a ThermoStar GSD 301 T2 mass spectrometer. About 100 mg of the catalyst sample was used for each test. The precursor of catalyst was firstly pre-reduced *in situ* in the TPD equipment by pure H_2 at 350 ºC for 2 h, followed by switching to a H_2 (99.999%, purity) stream for adsorption at 45 ºC for 1 h. The H_2 desorption was then performed from 50 to 700 ºC at a rate of 10 ºC/min. CO_2-TPD was carried out under the same condition as H_2-TPD, conducting from 50 to 450 ºC.

Confocal Raman microspectroscopy was conducted at room temperature with Renishaw UV-Vis Raman 1000 System, equipped with a CCD (charge couple device) detector and a Leica DMLM microscope. The line at 514.5 nm of an Ar^+ laser was used for excitation. The laser power was reduced to ~1.0 mW for ensuring that no sample damage was caused by the laser irradiation.

2 Results and discussion

2.1 XRD analysis

Fig. 1 depicts the main characteristics of fresh (a) and reduced (b) $LaMn_{1-x}Cu_xO_3$ perovskites ($0 \le x < 1$). For the fresh $LaMn_{1-x}Cu_xO_3$ series ($x \le 0.5$), as shown in Fig. 1(a), the only phase was a single perovskite phase (JCPDS 01-075-0440), indicating the substitution of Cu in Mn site when Cu content was less than 0.5[15]. The phase composition was changed in the used catalyst with x=0.7, the oxygen vacancies were so high that La_2CuO_4 phase appeared, besides a remaining Mn-Cu perovskite phase. Meanwhile, copper oxide phase characterized by two strong reflections at 2θ=35.62° and 38.76° were clearly observed with the substitution for Mn by 90% Cu, implying that a noticeable number of copper ions was still located out of the perovskite lattice. This result accorded with the literature findings reported by Porta et al.[16].

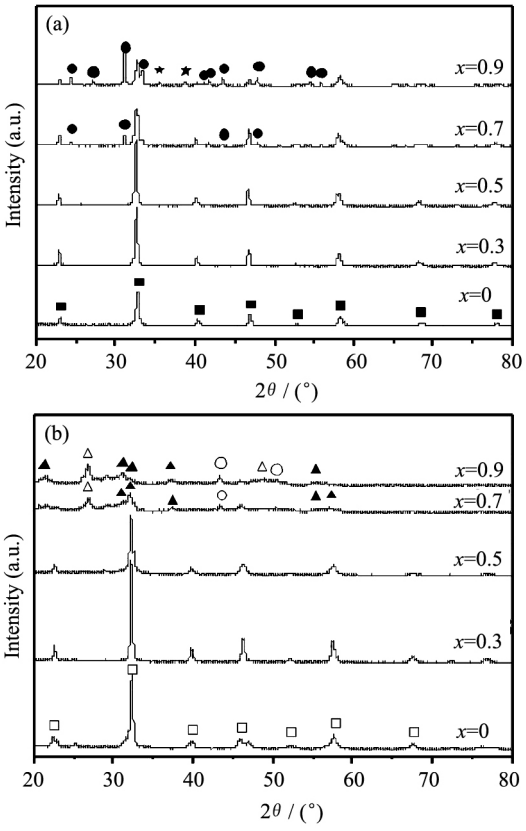

Fig. 1 XRD patterns of the fresh (a) and reduced (b) $LaMn_{1-x}Cu_xO_3$ (■) $LaMnO_3$; (●) La_2CuO_4; (★) CuO; (□) $La_{1-x}Mn_{1-z}O_3$; (▲) $LaMnO_3$; (△) La_2O_3; (○) Cu

Moreover, the substitution of Mn with Cu in perovskites has led to a decline in the diffraction lines. It was attributed to the difference between ionic radii of Cu^{2+} (0.0730 nm) and Mn^{3+} (0.0645 nm), leading to a little change in unit cell of perovskite lattice[17]. The main diffraction peak at 2θ=32.80° with x=0 shifted to the lower angle 2θ=32.63° and 32.58° with x=0.3 and x=0.5, respectively. XRD patterns were also obtained for catalysts reduced at 350 ºC, as shown in Fig. 1(b). The only reduction product was also a perovskite-like single phase $La_{1-x}Mn_{1-z}O_3$ (JCPDS 00-051-1516) when $x\leq$ 0.5. The main diffraction line at 2θ shifted to the much lower angle 32.32º, 32.26º and 32.15° with x=0, x=0.3, and x=0.5, respectively. And along with the increase of Cu doping, the intensity of diffraction peaks of $La_{1-x}Mn_{1-z}O_3$ weakened gradually, while the line width broadened slightly. The XRD patterns of the reduced catalysts showed some weak reflection lines of $LaMnO_3$ (JCPDS 01-085-2219), La_2O_3 (JCPDS 01-089-4016) and Cu (JCPDS 01-089-2838) phases, when the substitution for Mn by Cu was prepared up to 90%.

2.2 Reaction activity

The catalytic performances of catalysts for CO_2 hydrogenation to methanol are summarized in Table 1. The major product was methanol, and the by-products were CO and methane, of which CO was the major one due to "reverse-water-gas-shift (RWGS) reaction". It was found that the substitution of Mn by Cu in the perovskite had an influence on the catalytic behavior that the selectivity of CH_3OH and the conversion of CO_2 were improved significantly. Firstly, the catalytic activity of Cu-doped $LaMnO_3$ was much higher than that of undoped $LaMnO_3$ for hydrogenation of carbon dioxide, especially to produce methanol. Secondly, the yield of methanol did not always increase with the increasing substituted Cu-containing and it was up to the highest value when x=0.5, with the CO_2 conversion of 11.33% and methanol selectivity of 82.14%. Lastly, the selectivity of methanol over catalysts with $x\leq$0.5 was much higher than that over catalysts with x>0.5. Therefore, the characterizations of $LaMn_{1-x}Cu_xO_3$ ($x\leq$0.5) would be further studied as follows, in view of the complexity of phases when x=0.7 and 0.9.

2.3 XPS investigations

XPS spectra of $LaMn_{1-x}Cu_xO_3$ (x=0.3 and 0.5) before and after being reduced are presented in Fig. 2 (a) and (b), providing direct experimental evidence about valence states of Cu species. Cu^{2+} had the BE of Cu $2p_{3/2}$ band above 933.5 eV

Table 1 Performance of catalysts for CO_2 hydrogenation*

$LaMn_{1-x}Cu_xO_3$	X_{CO2}/%	S_{MeOH}/%	S_{CO}/%	S_{CH4}/%
x=0.9	1.28	9.32	46.12	44.56
x=0.7	3.79	36.17	36.34	27.49
x=0.5	11.33	82.14	13.83	4.03
x=0.3	3.94	68.1	26.38	5.52
x=0	0.83	0	55.83	44.17

* Reaction conditions: P=2 MPa, GHSV=2400 ml/(h·g), CO_2:H_2=1:3 (molar ratio)

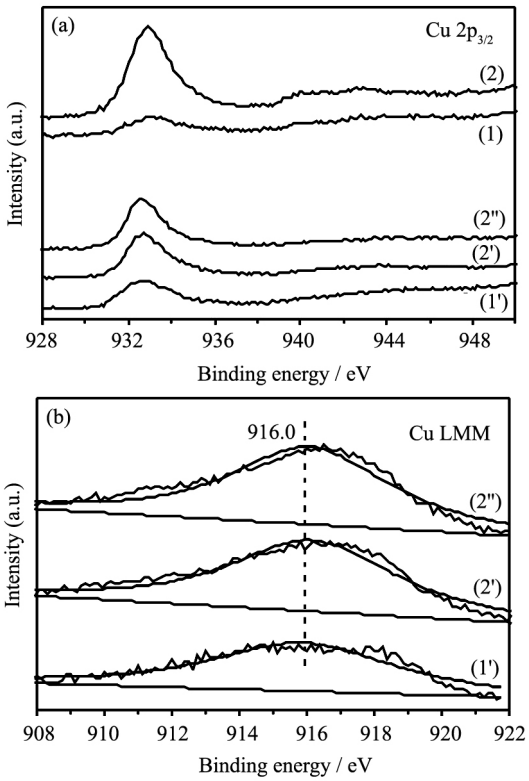

Fig. 2 XPS-Auger spectra of Cu 2p3/2 (a) and Cu LMM (b)
(1) the fresh $LaMn_{0.7}Cu_{0.3}O_3$; (2) the fresh $LaMn_{0.5}Cu_{0.5}O_3$; (1') the reduced $LaMn_{0.7}Cu_{0.3}O_3$ for 2 h; (2') the reduced $LaMn_{0.5}Cu_{0.5}O_3$ for 2 h; (2") the reduced $LaMn_{0.5}Cu_{0.5}O_3$ for 11 h

with a shake-up peak and it was absent on the reduced surface. Since the BE of Cu $2p_{3/2}$ bands in Cu^0 (932.67 eV) and in Cu^+ (932.4 eV) are almost the same, they can be distinguished by different kinetic energy of the Cu LMM line position in metal (918.65 eV) and Cu_2O (916.8 eV)[18]. The result indicated that the chemical state of copper existed as Cu^+ species after the Cu-doped $LaMnO_3$ being reduced for both 2 and 11 h. That was why there was no Cu^0 peak in XRD patterns of the reduced catalysts. In numerous studies, it has been confirmed that the stabilization of the Cu^+ ions on the support favors the hydrogenation of CO_2[19]. The Cu^+ ions could also be stabilized on the surface of perovskite. According to Fujita et al.[20] the presence of Cu^+ accelerated the reduction of CO_2 to CO (RWGS) besides methanol, which would explain why the $LaMn_{0.5}Cu_{0.5}O_3$ catalyst was less selective towards methanol, compared with the $LaCr_{0.5}Cu_{0.5}O_3$ catalyst, as reported in the case of $LaCr_{1-x}Cu_xO_3$[21].

2.4 CO_2-TPD

Fig. 3 depicts CO_2-TPD profiles of the reduced $LaMn_{1-x}Cu_xO_3$ (x=0, 0.3 and 0.5) and the fresh $LaCr_{0.5}Cu_{0.5}O_3$, detecting concentration of surface basic sites and basic strength. The first main TPD peak around 100 ºC appeared for all the samples, originating from weak CO_2 adsorption. The subsequent peak was found in the range from 250 to 350 ºC, corresponding to medium basic sites[22]. It was also observed that the second desorption peak shifted to the high temperature with the increasing copper content. The TPD

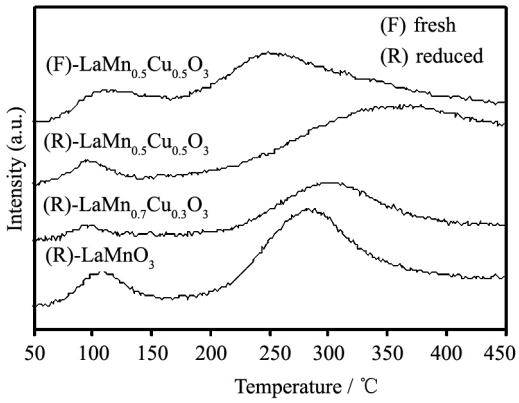

Fig. 3 CO_2-TPD profiles of the reduced $LaMn_{1-x}Cu_xO_3$ (x=0, 0.3 and 0.5) and the fresh $LaMn_{0.5}Cu_{0.5}O_3$

profiles of the fresh $LaMn_{0.5}Cu_{0.5}O_3$ showed a desorption peak around 250 ºC, lower than those of the reduced $LaMn_{1-x}Cu_xO_3$. This result disclosed an interaction between Cu^+ and Mn. And the interaction increased with the Cu content. It was found that the area of medium CO_2 desorption peak for x=0.5 was larger than those for x=0 and 0.3. As the medium CO_2 active species can be better dispersed on the surface of catalyst over x=0.5, the better the dispersion, the more the adsorption of CO_2.

2.5 Raman data

Fig. 4 shows Raman spectra of $LaMn_{1-x}Cu_xO_3$ (x=0, 0.3 and 0.5) compounds after being reduced, measured at room temperature, which displays peaks located around 530 and 660 cm^{-1}. According to lattice dynamic calculations, the peaks at 530 and 660 cm^{-1} are associated with bending- and stretching-like vibrations of the $Mn(Cu)O_6$ octahedra, respectively[23]. It is noted that the intensity of Raman spectra over $LaMn_{0.5}Cu_{0.5}O_3$ was much higher than that over $LaMn_{0.7}Cu_{0.3}O_3$. This result might be due to the stronger interaction between Mn/Cu ions over $LaMn_{0.5}Cu_{0.5}O_3$ than that over $LaMn_{0.7}Cu_{0.3}O_3$, as Minh et al.[24] observed over $LaMn_{1-x}Ni_xO_3$, which was in agreement with conclusion of CO_2-TPD data. This interaction may be responsible for the harder Cu reduction process ($Cu^+ \rightarrow Cu^0$).

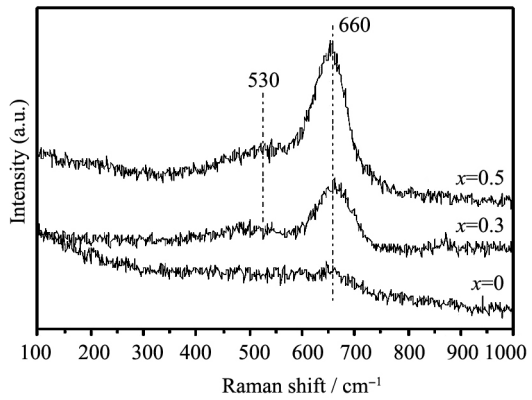

Fig. 4 Raman spectra of the reduced $LaMn_{1-x}Cu_xO_3$ (x=0, 0.3 and 0.5)

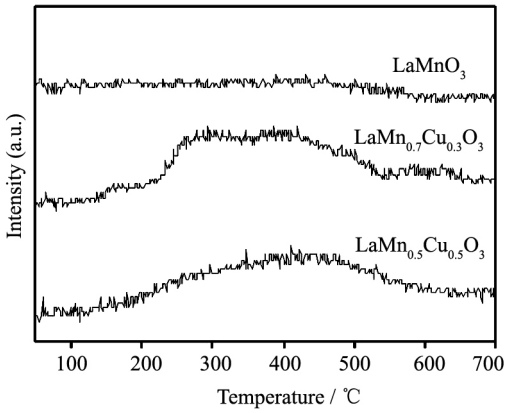

Fig. 5 H_2-TPD spectra of the reduced $LaMn_{1-x}Cu_xO_3$ (x=0, 0.3 and 0.5)

2.6 H_2-TPD spectra

Fig. 5 shows the TPD spectra taken on the reduced $LaMn_{1-x}Cu_xO_3$ (x=0, 0.3 and 0.5) catalysts. With the increasing temperature, no desorption peak appeared for $LaMnO_3$, while a much broader signal in the range of 200–600 ºC was monitored over $LaMn_{0.7}Cu_{0.3}O_3$ and $LaMn_{0.5}Cu_{0.5}O_3$. It could be assigned to desorption of strongly adsorbed species in the form of dissociatively adsorbed hydrogen[25]. This result suggested that H_2 might be adsorbed on the Cu^+ sites.

3 Conclusions

According to the catalyst characterizations, copper was assumed as an active metal for the formation of methanol, and its active oxidation state was Cu^+. When less than 50% Cu was doped into $LaMnO_3$, the perovskite structure was maintained. H_2 was adsorbed on Cu^+ sites and CO_2 was activated on medium CO_2 active species in the lattice. Then the interaction between Cu^+ and Mn occurred. It made a fine dispersion of active sites to adsorb much CO_2 and inhibited the further reduction from Cu^+ to Cu^0, contributing to reactivity of methanol. The catalytic behavior of $LaMn_{0.5}Cu_{0.5}O_3$ was higher than those of $LaMn_{0.7}Cu_{0.3}O_3$. This phenomenon was assigned to its stronger interaction between Cu^+ and Mn. However, the Cu-undoped $LaMnO_3$ had no reactivity to methanol, due to its poor adsorption of hydrogen. And the reason why $LaMn_{0.3}Cu_{0.7}O_3$ and $LaMn_{0.1}Cu_{0.9}O_3$ displayed poorer catalytic performance to methanol could be attributed to that they had no complete perovskite structure and there was no interaction between Cu and Mn to improve the reactivity.

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