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Catalytic combustion of propane over mixed oxides derived from $Cu_xMg_{3-x}Al$ hydrotalcites

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ABSTRACT

Cu-based mixed oxides ($Cu_xMg_{3-x}AlO$-800s, $x = 0$, 0.5, 1.0, 1.5, 2.0 and 3.0) were prepared by calcinations of corresponding $Cu_xMg_{3-x}Al$ ternary hydrotalcites ($Cu_xMg_{3-x}Al$-HTLCs) at 800 °C and used for catalytic combustion of propane. The $Cu_xMg_{3-x}Al$ ternary hydrotalcites and derived combustion catalysts were well characterized to investigate the dependence of the performance of propane catalytic combustion with their structure and components. The results showed that Cu can replace Mg in a wide range of Cu/Mg ratios to form $Cu_xMg_{3-x}Al$-HTLCs with the unique layered structure of hydrotalcite, though the Cu substitution significantly deteriorates the thermal stability of the $Cu_xMg_{3-x}Al$-HTLCs. It was found that calcinations at 800 °C completely transformed the $Cu_xMg_{3-x}Al$-HTLCs to $Cu_xMg_{3-x}AlO$-800 mixed oxides, containing spinel, periclase and tenorite oxide phases. The TPR results revealed those catalysts derived from hydrotalcites were easier to be reduced than the simply mixed oxides, this was due to the strong interactions among the components existing in the $Cu_xMg_{3-x}AlO$-800 materials. The $Cu_xMg_{3-x}AlO$-800 catalysts exhibit superior catalytic activity in propane combustion to Pd/Al_2O_3 and the mechanically mixed oxides. The excellent activities of the $Cu_xMg_{3-x}AlO$-800 were attributed to the strong interaction among the component oxides as observed by the XRD, TG-DSC and TPR characterizations.

1. Introduction

Liquefied Petroleum Gas (LPG) has been extensively applied in the fuel-powered vehicles because of its attractive features, such as clean combustion, high energy–density, simple storage and ready for use in transportation [1]. To remote areas where natural gas is not readily available, LPG can replace natural gas because it is easy to convey through the established infrastructure [2]. However, the exhaust gas from LPG combustor (e.g. LPG Engines and burners) still contains a significant amount of hydrocarbons, which are hazardous to the environment and contribute to atmospheric greenhouse gas effects [3,4]. The primary source of emitted hydrocarbons from LPG burners or engines are low-carbon organic compounds in which propane is the most abundant and is rather difficult to eliminate [4]. Catalytic combustion represents a promising and low-cost technology for both energy efficacy and control of organic pollutant emissions, however, such techniques are highly dependent on the effectiveness of the combustion catalyst [4–8]. In order to meet the even tighter environmental legislations, it has become necessary to develop efficient catalysts for catalytic combustion of the emitted propane from LPG combustors [4,8]. In addition, the suitable catalysts are also highly desired for the propane-fueled solid oxide fuel cells since they share the same requirements [9,10].

The typical catalysts for propane abatement are usually based on costly noble metals (Pt, Pd, Rh, etc.) which are subjected to deactivation due to sintering and catalyst poison [4,11]. Intensive studies have been conducted to explore cost-effective and robust transition metal (TM) catalysts for complete oxidation of propane, such as TM (TM = Mn, Fe, Co, Ni or Fe)-doped ZrO_2 [8], lanthanum-based perovskites [12–14], etc. Among those transition metal oxides, copper oxide based catalysts exhibit excellent activity and has been used in catalytic combustion of methane and VOCs (Volatile Organic Compounds) [5,6,15,16]. Recently, it has been found that the mixed oxides derived from thermal decomposition of corresponding hydrotalcite precursors are a class of novel catalysts with large surface area and high thermal stability [6,17–20]. In the past decade, the Cu-based oxides derived from Cu-containing hydrotalcites were found to be highly active in the catalytic combustion of toluene [21] and methane [6,19], catalytic removal of NO_x [22–24], and catalytic oxidation of soot from diesel exhausts [25,26]. Considering the excellent activity and stability of the Cu-based mixed oxide derived from Cu-based hydrotalcite, it may be expected that these materials will perform well in the catalytic combustion of propane.

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In this paper, $Cu_xMg_{3-x}Al$-HTLCs ($x = 0, 0.5, 1.0, 1.5, 2.0$ and 3.0) were firstly synthesized through co-precipitation at a constant pH. The obtained HTLCs were calcined at 800 °C to form the $Cu_xMg_{3-x}Al$ mixed oxide catalysts, $Cu_xMg_{3-x}AlO$-800s, and used for catalytic combustion of propane. The properties of $Cu_xMg_{3-x}Al$-HTLCs and their derivatives were characterized using XRD, TG-DSC and TPR techniques to explore the correlation between catalytic performance, structure and composition.

2. Experimental

2.1. Catalyst preparation

Six $Cu_xMg_{3-x}Al$-HTLCs ($x = 0, 0.5, 1.0, 1.5, 2.0$ and 3.0) were prepared by co-precipitation at constant pH [17]. Typically, one aqueous solution A (100 mL) containing appropriate amounts of $Cu(NO_3)_2 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with total metal-ion concentration of $1.0\ mol\ L^{-1}$ and another aqueous mixed alkaline solution B (containing i.e., NaOH and Na_2CO_3) were simultaneously mixed into a beaker containing 150 mL distilled water under vigorous stirring. The pH of the solutions was controlled at 10–11 and monitored through a pH meter. The obtained precipitates were aged at room temperature for 24 h prior to filtering and washing to neutral pH, and then were dried in oven at 120 °C for 12 h to receive the $Cu_xMg_{3-x}Al$-HTLCs. The $Cu_xMg_{3-x}Al$-800 mixed oxides catalysts were obtained through further calcinations (heating rate of 5 °C/min) of the $Cu_xMg_{3-x}Al$-HTLCs at 800 °C for 5 h. For comparative study, the PdO/Al_2O_3 catalyst (1 wt.% Pd loading) was prepared by a conventional impregnation method, and subsequently calcined at 800 °C for 5 h. The $CuO/MgO/Al_2O_3$ catalyst (molar ratio 0.5:2.5:1) was also prepared by calcinations of corresponding oxide mixtures of the required amount at 800 °C. All catalyst samples were pressed at 5.0 Mpa and sieved to a size of 20–40 mesh for the activity tests.

2.2. Catalyst characterization

The crystal structure of the prepared materials was determined by continuous scan X-ray diffraction using a Philips X'Pert MPD X-ray diffractometer, employing Cu Kα radiation ($\lambda = 1.5418$ Å), Ni filter, scan speed 2°/min, at 40 kV, 40 mA. The thermal decomposition and stability of $Cu_xMg_{3-x}Al$-HTLCs (40 mg) were studied through thermogravimetry analysis and differential scanning calorimetry (TG and DSC, Seteram, Labsys™, Al_2O_3 crucibles) in the air ramping at 10 °C/min. The specific surface areas of the solid samples were measured by N_2 adsorption at 77 K in a Quantachrome NOVA 1200 Sorptomatic apparatus.

Temperature-programmed reduction (TPR) was performed on all the catalysts (50 mg) on a home-made TPR system. Prior to each TPR run, the catalyst was pre-treated at 500 °C under an O_2 flow (40 mL/min) for 30 min with 10 °C/min ramp. After cooling to room temperature in the same oxygen flow, N_2 was fed to the reactor at 30 mL/min for 1 h at room temperature to purge residual oxygen. The catalyst was then heated to 900 °C at a constant heating rate of 10 °C/min using H_2 (5 vol.%)/N_2 (95 vol.%) under a flow rate of 30 mL/min. A TCD detector was used to record the H_2 concentration in the effluent.

2.3. Catalytic activity test

The catalytic activity evaluations for the propane combustion on the $Cu_xMg_{3-x}AlO$-800s were carried out in a tubular quartz reactor at atmospheric pressure. The catalysts were activated at 500 °C for 1 h in a 100 mL/min air flow. After cooling to 100 °C, a mixture of C_3H_8:O_2:N_2 in a volume ratio of 0.2:1:98.8 at a total flow rate of 1200 mL/min were passed through the catalyst bed (1.0 g 20–40 mesh catalyst diluted with 1.0 g silica sands); the GHSV was approximately $100{,}000\ h^{-1}$. The system was heated externally via a tubular furnace regulated via a thermocouple inserted into the catalyst bed. The reactants and products were analyzed online by a GC (B.F. Tianpu, Beijing Beifen Tianpu Instrument Tech. Co. Ltd.) equipped with a FID. The column was a 60/80 Carboxen 1000. CO and CO_2 were catalytically converted to CH_4 by a Ni catalyst mounted in a catalytic furnace prior to feeding into the FID detector.

The propane conversion rate was calculated based on the integrated GC peak areas. The activity on the catalysts was characterized by T_{10}, T_{50}, and T_{90}, which represent the temperatures of propane conversion at 10%, 50%, and 90%, respectively. It is well known that catalytic combustion follows a pseudo first order kinetic mechanism, so its kinetic equation could be written as $\ln[-\ln(1-x)] = f(1000/T)$ [6,17], where x is the degree of propane conversion, and T is the Kelvin temperature at a propane conversion of x. According to the Arrhenus equation, the activation energy (Ea) can be calculated from the $\ln[-\ln(1-x)]$ versus $1/T$ plots. The $\ln[-\ln(1-x)] = f(1000/T)$ can be briefly deduced by combining the integrated equation of first order kinetics, $\ln(C/C_0) = \ln[C_0 \times (1-x)]/C_0 = -kt$, and $\ln k = \ln A - Ea'/RT = \ln A - (Ea'/1000) \times 1000/RT = \ln A - (Ea/R) \times 1000/T = f(1000/T)$, in which C and C_0 are the concentrations at the time t and initial stage respectively, t is reaction time, k is reaction rate constant, Ea′ and Ea are the apparent activation energies with units of J and kJ respectively, R is the gas constant, T is Kelvin temperature, A is the pre-exponential factor. Turnover Frequency (TOF) was calculated at 400 °C on the catalysts in order to compare their specific reactivity. The stability of the optimized catalysts was also studied in the 120 h time on stream reaction.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD analysis of Cu–Mg/Al-HTLCs and derived mixed oxides

The X-ray diffraction patterns of the as-prepared $Cu_xMg_{3-x}Al$-HTLCs are shown in Fig. 1A. The diffraction peaks of the Cu-substituted $Cu_xMg_{3-x}Al$-HTLCs ($x < 3$) can be well indexed to single phased rhombohedral hydrotalcite (JCPDS 22-700) except for the Cu_3Al-HTLC. Besides the hydrotalcite phase in the XRD patterns of Cu_3Al-HTLC, new diffraction peaks corresponding to the malachite $Cu_2(CO_3)(OH)_2$ (JCPDS 75-1163) are observed. No isolated phases of individual Cu, Mg and Al hydroxides are observed in the XRD patterns of $Cu_xMg_{3-x}Al$-HTLCs ($x < 3.0$), suggesting that Cu has been homogeneously incorporated into the matrixes of these $Cu_xMg_{3-x}Al$-HTLCs. As shown in Fig. 1A, the gradual increase of Cu content in these HTLCs leads to the decreased intensity of the symmetric diffraction Bragg peaks at 11°, 22°, 35°, 61° and 63°. While the symmetry of (0 0 1) and (0 0 3) remains unchanged as gradually increasing the Cu content, the symmetry of the diffraction peaks of (0 1 2), (0 1 5), (1 1 0) and (0 1 3) decrease remarkably. At x approaching 2.0, the diffraction peaks of (1 1 0) and (0 1 3) are merged and disappeared when Mg was completely replaced by Cu. The changes of intensity and symmetry of the $Cu_xMg_{3-x}Al$-HTLCs indicate that the crystallinity of the $Cu_xMg_{3-x}Al$-HTLCs dramatically degrades due to the Cu substitution of Mg in the Mg/Al-HTLCs. The changes may be ascribed to the mismatched ion radius between Cu^{2+} and Mg^{2+} ($R_{Mg}^{2+} = 0.078$ nm, $R_{Cu}^{2+} = 0.087$ nm) and the strong interactions among the metal ions in hydrotalcite matrixes due to Jahn–Teller distortion effect of Cu cation [6,27]. The interaction and mismatching effects in the materials lead to more structure defects in $Cu_xMg_{3-x}Al$-HTLCs than in Mg_3Al-HTLC [17], and