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Lanthanum-promoted copper-based hydrotalcites derived mixed oxides for NO_x adsorption, soot combustion and simultaneous NO_x-soot removal

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ABSTRACT

La-promoted Cu-based hydrotalcites derived mixed oxides were prepared and their catalytic activities for NO_x adsorption, soot oxidation, and simultaneous NO_x-soot removal were investigated. The catalysts were characterized by XRD, DTG, BET, FTIR, H2-TPR, TPD and TPO techniques. The oxides catalysts exhibited mesoporous properties with specific surface area of 45–160 m^2/g. The incorporation of La and Cu decreased the amount of basic sites due to the large decrease in surface areas. Under O_2 atmosphere, La incorporation is dominant for soot oxidation activity, while Cu favors high selectivity to CO_2 formation. A synergetic effect between La and Cu for catalyzed soot oxidation lies in the improved redox property and suitable basicity. The presence of NO in O_2 significantly promoted soot oxidation on the catalysts with the ignition temperature decreased to about 300 °C. In O_2/NO atmosphere, NO_2 acts as an intermediate which oxidizes soot to CO_2 at a lower temperature with itself reduced to NO or N_2, contributing to the high catalytic performance in simultaneous removal of NO_x and soot.

1. Introduction

Diesel engines have been widely used for a long time in power generation, land vehicles and marine power plant because of the high efficiency of the engines, their low-operating costs, high durability and reliability. With the expansion, however, diesel engine exhausts have caused serious problems to global environment and human health due to the emission of nitrogen oxides (NO_x) and soot particulates. In order to meet the more stringent legislation limits on NO_x and particulate, catalytic after treatment processes for reducing the emission of both harmful substances must be developed because the emissions cannot be avoided by engine modification alone. Over the past decades, selective catalytic reduction (SCR) and NO_x storage catalysts (NSC) systems have been proposed for NO_x elimination, while catalyzed diesel particulate filter (CDPF) appears to be an effective solution for soot removal [1–5].

Considering the pollutants emitted from diesel engines as a whole, two promising after treatment alternatives have been put forward. One is the catalytic direct conversion of NO_x and soot particulates through redox reactions between both pollutants. Soot can be eliminated by catalytic combustion with NO_x and/or O_2 in diesel particulate filters (DPF), in which NO_x can also be reduced by soot forming N_2 and CO_2 simultaneously [6]. Perovskites, spinels, iron oxides, Co-K supported catalysts and Cu ion exchanged zeolites [7–12], *etc.* are active catalysts for this reaction. The other is the combination of NO_x traps and oxidation catalysts, also called diesel particulate-NO_x reduction (DPNR) system, which has been developed by Toyota Company [13]. Several catalysts have been investigated to fulfill this aim, including noble metal [14], perovskite [15], rare earth metal oxides [16], mixed metal oxides [17,18], and so on. These two types of after treatment technologies are ambitious, while the exigent research subject now is to develop more active catalysts possessing low-temperature activity for both soot oxidation and NO_x reduction.

Recently, a type of well-dispersed oxides derived from hydrotalcite-like compounds (HT or HTLCs) have received increasing attention [19–23], which are excellent catalysts or catalyst supports owing to their large surface areas, basic properties, high metal

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dispersions and good thermal stability. These physicochemical properties depend on incorporated cations, contents and calcined temperature. Such mixed oxides containing transition metal also show redox properties and have been applied in many reactions such as selective catalytic reduction of NO_x [24,25], NO_x storage and reduction [26,27], catalytic oxidation of CO [28,29], catalytic combustion of methane and VOCs (Volatile Organic Compounds) [30–32]. In our previous works [33,34], Cu-based mixed oxides derived from HTLCs displayed good activities for catalytic oxidation of soot and simultaneous NO_x-soot removal due to the higher redox properties and surface areas. On the other hand, rare earth ions such as La, Ce and Sm, as catalyst additive components, not only may improve the low temperature activity of the catalyst and the reduction ability for NO_x, but may also improve the stability of the catalyst [35,36]. In particular, La supported materials [37,38] have also proved to be very active and stable catalysts for the catalytic abatement of soot and NO_x. Considering the high price of lanthanum oxide, it is more practical from an industrial point of view to reduce the content of rare earth metals in catalysts. Thus, a more efficient catalyst of La-promoted Cu-based mixed oxides from HTLCs is designed to involve different redox sites and basic properties needed for good performance on soot oxidation and NO_x reduction.

The present paper deals with the physicochemical characterization and catalytic performances of La-promoted Cu-based hydrotalcites derived mesoporous mixed oxides as catalyst for the adsorption of NO_x, oxidation of soot and simultaneous NO_x-soot removal. Especially, the *in situ* FTIR tests with the soot–catalyst mixture were carried out in the presence of O_2 and $NO + O_2$, respectively, to explore possible intermediates generated during soot oxidation.

2. Experimental

2.1. Catalyst preparation

The hydrotalcites precursors with different metal atomic ratio listed in Table 1 were prepared by co-precipitation of an aqueous solution of suitable metal nitrates with an aqueous solution of 2 M NaOH and 1 M Na_2CO_3. The two solutions were mixed under vigorous stirring at 25 °C with the pH maintained constant at 10.0 ± 0.5. The resulting slurry was aged in the mother liquor at 80 °C for 18 h. It was then filtered and washed with distilled water until the pH of the filtrate was around 7. The precipitate was then dried at 100 °C for 12 h to obtain HTLCs. Samples are denoted according to the metal constituents in the initial mixture. Mg_3Al_1-HT, $Mg_3Al_{0.9}La_{0.1}$-HT, $Cu_2Mg_1Al_1$-HT and $Cu_2Mg_1Al_{0.9}La_{0.1}$-HT (marked as MA-HT, MAL-HT, CMA-HT and CMAL-HT, respectively) were similarly prepared.

The corresponding mixed oxides were obtained by thermal decomposition of hydrotalcites precursors at 800 °C in air for 5 h, referred as to MAO, MALO, CMAO and CMALO, respectively.

2.2. Catalyst characterization

XRD was conducted with a BRUKER-AXS D8Adance X-ray Diffractometer using Cu Kα radiation, at 40 KV and 40 mA, in the scanning angle (2θ) range of 5–80° at a scanning speed of 4°.

Thermogravimetric analysis was carried out using a Perkin-Elmer Pyris Diamond TG/DTA, with air as carrier gas (100 ml/min) at a heating rate of 10 °C/min from 25 to 900 °C.

N_2 adsorption–desorption isotherms were performed using a Micromeritics ASAP 2020 surface area analyzer after outgassing at 300 °C for 5 h prior to analysis. The specific surface areas were calculated with the BET equation on the basis of the adsorption data.

Infrared spectra were recorded on a Bruker Tensor 27 spectrometer. The samples were prepared in the form of pressed wafers (2% of sample in KBr).

Temperature-programmed reduction with H_2 (H_2-TPR) experiments were performed in a quartz reactor with a thermal conductivity detector (TCD) to monitor the H_2 consumed. A 50 mg sample was pretreated *in situ* at 500 °C for 1 h in a flow of O_2 and cooled to room temperature in the presence of O_2. TPR was conducted at 10 °C/min up to 900 °C in a 30 ml/min flow of 5 vol.% H_2 in N_2.

Temperature-programmed desorption (TPD) of carbon dioxide for determination of basicity was carried out using 50 mg of a catalyst on the same fixed-bed microreactor as used in H_2-TPR. Prior to CO_2 desorption all catalysts were pretreated under He (50 ml/min) to 800 °C for 1 h. Then, after cooling the sample, the adsorption of CO_2 at room temperature was performed until surface saturation was reached. The excess of CO_2 was removed by He flowing 1 h through the catalyst layer. After the TCD baseline leveled off, TPD was conducted at a heating rate of 10 °C/min in a flow of He (50 ml/min) from room temperature to 800 °C.

The *in situ* FTIR spectra were recorded on a Bruker Tensor 27 spectrometer over 400–4000 cm^{-1} after 32 scans at a resolution of 4 cm^{-1}. The mixture of soot and catalyst in tight contact was pressed into a thin self-supporting wafer with a thickness of 7.5 mg/cm^2. The wafer was loaded into an *in situ* infrared transmission cell which is capable of operating up to 500 °C and equipped with gas flow system. All experiments were performed in the flow of 100 ml/min with the heating rate of 5 °C/min.

2.3. Catalytic activity testing

NO_x adsorption experiments were carried out in a fixed bed micro reactor connected to a chemiluminiscence NO_x analyser (42i-HL, Thermo Environmental). The catalysts (100–200 mesh, 50 mg) were pretreated *in situ* at 500 °C for 1 h in He. After cooled to 100 °C, a feed gas containing 1000 ppm NO + 5 vol.% O_2 in He (100 ml/min) was introduced and NO_x adsorption was started at a heating rate of 10 °C/min until 700 °C.

The temperature-programmed oxidation (TPO) reactions were conducted in a fixed bed micro reactor consisting of a quartz tube (6 mm i.d.). Printex-U from Degussa is used as model soot. The soot was mixed with the catalyst in a weight ratio of 1:9 in an agate mortar for 30 min, which results in a tight contact between soot and catalyst. A 50 mg sample of the soot/catalyst mixture was pretreated in a flow of He (50 ml/min) at 200 °C for 1 h to remove surface-adsorbed species. After cooling down to room temperature, a gas flow with 5 vol.% O_2 in He or 1350 ppm NO + 5 vol.% O_2 in He (100 ml/min) was introduced and then TPO was started at a

Table 1
Compositions and lattice parameters of the synthesized hydrotalcites.

Samples	Metal molar ratio in solution	Lattice parameter (Å)		FWHM of (003) peak (2θ)	ACS[a] (nm)
		a	*c*		
MA-HT	Mg:Al = 3:1	3.060	23.366	0.664	12.5
MAL-HT	Mg:Al:La = 3:0.9:0.1	3.061	23.355	0.714	12.0
CMA-HT	Cu:Mg:Al = 2:1:1	3.072	22.712	0.683	11.6
CMAL-HT	Cu:Mg:Al:La = 2:1:0.9:0.1	3.062	21.422	1.005	11.8

[a] Average crystallite size calculated from *d* (003) and *d* (006) planes using Debye–Scherrer equation.