



Effect of surface Lewis acidity on selective catalytic reduction of NO by C₃H₆ over calcined hydrotalcite



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ABSTRACT

The selective catalytic reduction (SCR) of NO by C₃H₆ has been studied over a series of calcined hydrotalcite, which were prepared by four different methods to obtain various Lewis acid sites. The catalysts have been investigated by X-ray powder diffractometer, N₂ adsorption, Temperature-programmed desorption of NH₃ (NH₃-TPD), pyridine adsorption FTIR (Py-FTIR), Temperature-programmed desorption of NO + O₂ (NO + O₂-TPD) and *in situ* FTIR techniques. The Lewis acid sites could be changed with the transformation of the crystalline structure from the mixed oxides of MgO and Al₂O₃ to spinel phase. It is demonstrated that Lewis acid sites play an important role in determining the catalytic performance of SCR by C₃H₆ over calcined hydrotalcite catalysts. Various nitrate species as the key intermediate species for SCR could form at Lewis acid sites during the process of the reaction under lean-burn condition.

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1. Introduction

Selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) is a potential method to remove NO under rich-O₂ condition. For this reaction, several studies have been carried out on the role of Lewis acid sites in this reaction over recent years [1,2]. Based on these literatures, there have been different opinions concerning the role of Lewis acid site in the process for SCR. On one hand, Capek [1] proposed that Lewis acid sites were most likely the only active sites for HC-SCR. On the other hand, the result of Ma [2] claimed that Lewis acid sites might not contribute to catalytic activity for HC-SCR. Owing to the complexity of the process for HC-SCR with different catalysts, reductants and reaction conditions, there has been no generally accepted mechanism on what roles Lewis acid sites play in the reaction.

In the past decade, hydrotalcite (HT) materials have been found important applications in preparing catalysts because of their small crystallite, high surface area and well thermal stability [3]. These catalysts have been used in many fields, such as catalysts for trans-

esterification [4], hydrogen production [5], alcohols oxidation [6], SO₂ removal [7,8] and NO_x removal [9,10]. Among them, Cu-Mg-Al, Co-Mg-Al [11], La-Mg-Al [10], Ru-Mg-Al [9], Mn-Mg-Al [12], Co-Ce [13] and K/Mg-Al [14] catalysts derived from their corresponding hydrotalcite-like compounds have been reported to exhibit excellent performance in selective catalytic reduction (SCR) of NO_x and NO_x storage reduction (NSR) as well as high catalytic activity for soot combustion with NO_x/O₂. These observations indicate that the Mg-Al hydrotalcite mixed oxides seems to be promising catalysts for NO_x reduction under lean-burn conditions. Furthermore, it is found that Lewis acid sites could be observed on the Mg-Al mixed oxide catalyst derived from HT [15]. A comprehensive analysis about the effect of Lewis acid sites on the HC-SCR over Mg-Al mixed oxide catalyst under lean-burn conditions is essential for obtaining an optimized performance in the practical HC-SCR application.

In this study, we tried to show that the effect of Lewis acid sites on SCR over calcined hydrotalcite. Various processes show a potential to change the Lewis acid sites of the catalysts. Therefore, four different methods including typical coprecipitation [16], homogeneous precipitation [17], hydrothermal [18] and homogeneous precipitation combined with hydrothermal [19] have been employed to prepare the precursors. These obtained catalysts are thereafter comparatively tested in SCR of NO by C₃H₆ under lean-burn conditions, and characterized by XRD, N₂ adsorption, NH₃-TPD, FTIR and NO + O₂-TPD. Particular attention is paid to

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elucidate the relationship between Lewis acid sites and catalytic performance.

2. Experimental

2.1. Catalyst preparation

For all preparations, magnesium nitrate and aluminum nitrate mixed with deionized water to obtain the salt solution with a special salt ions ratio of Mg:Al = 3:1, which was the typical ratio for HT and a promising ratio for NO_x reduction. The common coprecipitation [16] was carried out as follow. The solution of metal nitrates and 2 M NaOH solution were dropwise added into 0.5 M Na₂CO₃ under vigorous stirring simultaneously, while the pH was maintained 10 ± 0.5. The resulting suspension was then aged at 60 °C for 4 h. All the precipitates were centrifuged, washed and dried at 80 °C overnight. Subsequently, the resulting HTs were calcined at 800 °C for 4 h to obtain MgAl mixed oxide catalysts, which were denoted as Cop.

For comparison, the urea was used as the base retardant, while the most simple and convenience method was the homogeneous precipitation [20]. The procedure was adding the solution into a beaker, which was mixed by metal nitrates and urea solution (urea/salt ions = 3.3), then stirred at 90 °C for 24 h. The obtained catalysts were denoted as Ure. To investigate the effect of the synthesis condition, hydrothermal [21] and homogeneous precipitation with hydrothermal treatment [19] were also employed. For hydrothermal method, the metal nitrates and urea solution mentioned above was added into a stainless-steel Teflon-lined autoclave heating at 90 °C for 24 h, while for the method of homogeneous precipitation with hydrothermal treatment, the same process was used except the mixture solution needs to be stirred in a beaker at 90 °C for 24 h before hydrothermal treatment. These two corresponding catalysts were sequentially denoted as Hyt and UH.

2.2. Catalytic tests

C₃H₆-SCR activity over the catalysts was carried out at atmospheric pressure in a fixed-bed quartz reactor with the diameter of 0.6 mm. 0.2 g catalyst was used in each run with a reaction mixture composed of 1000 ppm NO, 1000 ppm C₃H₆ and 10 vol% O₂ in He. The total flow rate was 100 mL/min, corresponding to a GHSV 30,000 h⁻¹. The reaction products were analyzed by gas chromatography for N₂ and C₃H₆. The concentration of N₂ and N₂O were detected by a 5A zeolite column and a PQ column with thermal conductivity detector (TCD) and C₃H₆ was analyzed by a 6DX-104 column with flame ionization detector (FID). The conversion of NO to N₂ and C₃H₆ to CO_x were calculated according to the following formula:

$$\text{Conversion of NO to N}_2 = 2[\text{N}_2]_{\text{out}}/[\text{NO}]_{\text{in}} \times 100$$

$$\text{Conversion of NO to N}_2\text{O} = 2[\text{N}_2\text{O}]_{\text{out}}/[\text{NO}]_{\text{in}} \times 100$$

$$\text{Conversion of C}_3\text{H}_6 = ([\text{C}_3\text{H}_6]_{\text{in}} - [\text{C}_3\text{H}_6]_{\text{out}})/[\text{C}_3\text{H}_6]_{\text{in}} \times 100$$

$$[\text{N}_2]_{\text{out}} = \text{outlet concentration of N}_2$$

$$[\text{N}_2\text{O}]_{\text{out}} = \text{outlet concentration of N}_2\text{O}$$

$$[\text{NO}]_{\text{in}} = \text{inlet concentration of NO}$$

$$[\text{C}_3\text{H}_6]_{\text{in}} = \text{inlet concentrations of C}_3\text{H}_6$$

$$[\text{C}_3\text{H}_6]_{\text{out}} = \text{outlet concentrations of C}_3\text{H}_6$$

2.3. Characterization methods

XRD patterns of the obtained samples were collected on a Rigaku D/Max 2550VB/PC X-ray powder diffractometer with a Cu K α radiation source ($\lambda = 0.154056$ nm), and operated at a voltage of 40 kV 105 and a current of 100 mA. N₂ adsorption/desorption isotherms were obtained on a NOVA 1200 (Quanta Chrome) equipment, with the samples pretreated at 300 °C for 4 h under vacuum. Surface areas were determined according to the BET method.

NH₃-TPD was conducted with a Chembet PULSAR TPR/TPD (p/n 02139-1). The samples (0.05 g) were loaded into a quartz reactor and heated at 500 °C for 0.5 h. After the samples adsorbing ammonia at 100 °C, the temperature was ramped from 100 °C to 700 °C with a heating rate of 10 °C/min. The FTIR spectra of chemisorbed pyridine (Py-IR) were recorded using a VERTEX 70-FTIR spectrometer. The samples (0.02 g) were pressed into discs and activated by heating in vacuum at 400 °C for 1 h. After cooled to room temperature, the samples were saturated with pyridine vapor for 20 min. The spectra were recorded as the background reference. Afterwards, desorption of pyridine was studied at room temperature, and the spectra was recorded simultaneously.

Calculations based on density functional theory (DFT) were performed with MgO and MgAl₂O₄ models, using the CASTEP code in *Materials Studio* by Accelrys. The Perdew–Burke–Ernzerh of gradient corrected functional (PBE-GGA) was used. The lattice parameters are $a = b = c = 4.22$ Å for MgO, and $a = b = c = 8.08$ Å for MgAl₂O₄, respectively. Two different supercells of MgO (2 × 1 × 1) and MgAl₂O₄ (4 × 2 × 1) are considered to demonstrate the distribution of electron charge density (ECD).

NO + O₂-TPD experiments were carried out in a fixed-bed reactor. Before performing the experiment, 100 mg of sample was pretreated in He flow at 250 °C for 1 h. After the sample was cooled down to room temperature, the He flow was switched to a gas mixture of 2500 ppm NO and 25 vol% O₂ for 1 h. Afterward, reactor was again purged with He gas for another 1 h. Subsequently, the temperature was elevated to 700 °C at the rate of 10 °C/min. The effluent gases were monitored by a quadrupole mass spectrometer (MS) (Ametek, LC-D200M). The NO, O₂ and N₂O were detected and recorded on-line with the mass number of 30, 32 and 44, respectively.

The *in situ* FTIR equipment for monitoring the adsorbed species on the surface of catalysts is the same as mentioned in the chemisorbed pyridine. Spectra were measured with a 100-scan data acquisition at a resolution of 4 cm⁻¹. Prior to each experiment, the catalyst (approximately 20 mg) was pretreated at 400 °C in He for 60 min, and then the background spectrum was collected. Subsequently, the samples were exposed to a flow of 1000 ppm NO and 10 vol% O₂ in He. After that the feed gases were switched to 1000 ppm C₃H₆ and 10 vol% O₂ in He. The total flow rate through the reaction cell was 40 mL/min.

3. Results and discussion

3.1. Catalytic activity

The activity tests of SCR over the obtained catalysts were carried out under O₂-rich condition. Fig. 1 shows the catalytic performance of SCR of NO by C₃H₆ over the four catalysts as a function of temperature. With the increasing temperature, N₂ and N₂O yields enhanced until reaching a maximum. After that, both of them declined. An obvious difference was found that conversion of C₃H₆ increased continuously until complete oxidation. The

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