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Oxidation of nitric oxide to nitrogen dioxide over Ru catalysts

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A series of TiO_2 supported catalysts were prepared by impregnation method in a rotary evaporator and evaluated for the oxidation of NO to NO_2. Among all catalysts studied, Ru/TiO_2 catalyst exhibited the best activity and a maximal NO conversion of *c.a.* 94% could be achieved at *c.a.* 275 °C at a high GHSV of 180,000 h^{-1}. For ruthenium catalysts, the effects of supports, ruthenium loadings, pretreatment conditions and experiment conditions (feed gas composition, GHSV) on NO oxidation to NO_2 were investigated in detail. The ruthenium catalysts were characterized by means of X-ray diffraction (XRD), CO pulse chemisorption, transmission electron microscopy (TEM) and temperature-programmed reduction (TPR) techniques. The active ruthenium species for NO oxidation were discussed based on the catalytic and characterization results. Moreover, the reaction mechanism for NO oxidation over Ru/TiO_2 catalyst was studied by means of *in situ* diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS).

1. Introduction

Nitrogen oxides (NO*x*), from stationary and transportation sources, are major air pollutants that greatly contribute to the formation of photochemical smog and acid rain. The removal of NO*x* is always a hot topic forever in the field of environmental catalysis and various techniques have been proposed for the abatement of NO*x* from anthropogenic sources. For example, selective catalytic reduction (SCR) and NO*x* storage-reduction (NSR) are two major techniques for NO*x* abatement in excess oxygen. In the research of SCR and NSR, it is well established that the oxidation of NO to NO_2 is a very important step for the whole reaction. For NSR, NO is first oxidized to NO_2 and then stored on the basic component of catalyst as nitrates [1]. For HC-SCR, NO is oxidized to NO_2, which subsequently reacts with hydrocarbon to give out N_2 [2]. In recent years, the so-called "fast" SCR reaction ($4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$), in contrast to standard ammonia SCR reaction ($4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$), is receiving more and more attention [3–9]. The reaction between equimolar NO–NO_2 and NH_3 is *c.a.* 10 times faster than the reaction between NO and NH_3 at low temperatures (200–300 °C) [10]. Therefore, the fast SCR reaction is considered as a feasible means to boosting the denitrification efficiency at lower temperatures as well as to reducing the catalyst costs of SCR system. It is also noted that most nitrogen oxides from exhaust emissions exist in the form of NO (>90%), so that an upstream pre-oxidation catalyst converting NO to NO_2 is absolutely necessary to realize fast SCR reaction.

In the research of catalysts for NO oxidation, much effort has been focused on supported platinum materials. Pt/SiO_2 [11–13] and Pt/Al_2O_3 [13,14] were reported to be highly active for NO oxidation. The catalytic kinetics and the effects of preparation parameters on activities had been investigated in detail [11–14]. Although supported platinum catalysts show considerable activity for NO oxidation, the high cost of noble metal platinum materials restricts the application of supported Pt catalysts to a great extent. Moreover, the activity loss of supported platinum catalyst in strong oxidizing conditions remains a problem to be solved. Other catalysts, such as supported cobalt catalysts, are now being investigated as alternative catalysts for NO oxidation [15–18].

During the past decades, supported ruthenium materials have been extensively studied as catalysts for a number of reactions, *e.g.* organic synthesis [19], partial oxidation of hydrocarbons [20], Fischer–Tropsch synthesis [21] and ammonia synthesis [22]. Recently, ruthenium catalysts have been applied in the reaction of wet air oxidation of various pollutants [23–25] and complete oxidation of volatile organic compounds [26]. The good redox behaviors of ruthenium catalysts have been proved in these reactions, and supported ruthenium materials are thus expected to be good catalysts for other oxidation reactions. However, up to now, few researches have been focused on the application of ruthenium catalysts in the oxidation of nitric oxide to nitrogen dioxide.

In the present study, the activities of different transition metal catalysts for NO oxidation are investigated and supported ruthenium catalysts are found to be very active for the first time.

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The effects of supports, ruthenium loadings, pretreatment of catalysts and reaction conditions (feed gas composition, GHSV) on NO oxidation are investigated in detail. More important, the active ruthenium species for NO oxidation are discussed based on the catalytic and characterization results.

2. Experimental

2.1. Catalysts preparation

The following oxides were selected as catalyst supports: SiO_2 (Sinopec), Al_2O_3 (Sinopec), ZrO_2 (Sinopec), TiO_2 (Degussa P25, 70% anatase, 30% rutile), TiO_2-Anatase (denoted as TiO_2-A, Fluka), TiO_2-Rutile (denoted as TiO_2-R, Degussa). Diffluent metal salts of analytical agent grade (NH_4VO_3, $CrCl_3$, $MnSO_4$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $PdCl_2$, $RhCl_3$, $RuCl_3$, H_2PtCl_6, $HAuCl_4$) were used as sources for supported materials without further purification.

The catalysts were prepared by impregnating the supports with aqueous solution of metal salt in a rotary evaporator at the constant temperature. In a typical preparation process of Ru/TiO_2, 20 mL $RuCl_3$ aqueous solution (Ru concentration: 1.0 mg/mL) was added to 1 g TiO_2 (P25) support. The impregnated sample was mixed well and then evaporated in a rotary evaporator at constant temperature of 80 °C. The as-prepared samples were carefully washed by distilled water, dried at 100 °C over night and then calcined at 450 °C in flowing air for 4 h. The Pt/TiO_2 sample was further reduced in $5\%H_2/He$ at 450 °C for 1 h prior to catalytic test.

2.2. Catalyst characterization

The ruthenium contents in supported ruthenium catalysts were determined by ICP-AES using an Optima 2000 spectrometer. The surface areas of catalysts were analyzed by low temperature N_2 adsorption/desorption using a Quantachrome NOVA-1200 gas absorption analyzer and the specific surface areas were calculated using the BET equation.

The X-ray diffraction patterns of samples were recorded on a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4°/min in $2\theta = 5$–$80°$.

The dispersion of ruthenium on various supports was determined by CO pulse adsorption on a chemisorption analyzer (Chemisorb 2720, Micromeritics). In a typical experiment, *c.a.* 100 mg sample in the quartz reactor was first reduced in $5\%H_2/He$ at 450 °C for 1 h and pretreated in He at 450 °C for 1 h to remove H_2 adsorbed on the surface of samples. After cooling down to room temperature in flowing He, pulses of 5%CO/He were injected to the reactor one pulse per minute until no further changes in signal intensity of outlet CO. The dispersion of ruthenium was calculated assuming the equimolar adsorption of CO on ruthenium metal.

The temperature-programmed reduction experiments of samples were carried out on a chemisorption analyzer (Chemisorb 2720, Micromeritics) with 5 vol.% H_2/Ar at a heating rate of 10 °C/min from 50 to 600 °C. Prior to reduction, the sample (100 mg) was treated in He at 450 °C for 1 h.

Transmission electron microscopy images of samples were acquired on a JEOL 2010 transmission electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the catalyst sample were placed on a carbon-coated copper grid, followed by evaporation at ambient temperature.

2.3. Catalytic oxidation of nitric oxide

The catalytic oxidation of NO was performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, 0.15 g sample (sieve fraction, 0.25–0.5 mm) was placed in a quartz reactor (4 mm i.d.) and pretreated in $5\%O_2/He$ ($5\%H_2/He$ for Pt/TiO_2 sample) at 450 °C for 1 h. After cooling to 150 °C in He, the reactant gas mixture (400 ppm NO, 10% O_2, He balance) was fed to the reactor. The total flow-rate of the gas mixture was kept at 450 mL min^{-1}, corresponding to a GHSV of 180,000 h^{-1}. The inlet and outlet gases were monitored on-line using a gas chromatograph (HP 6820 series, for N_2 and N_2O analysis) and a chemiluminescence NO*x* analyzer (Ecotech EC 9841, for NO and NO_2 analysis).

2.4. In situ DRIFT study of NO and NO–O_2 adsorption

In situ DRIFT studies were performed on the spectrometer (Bruker Tensor 27) with 128 scans at a resolution of 4 cm^{-1}. A self-supporting pellet (*c.a.* 50 mg) made of the catalyst sample was placed in the IR flow cell and the background spectrum was taken at desired temperatures in flowing He. For NO adsorption, 1% NO in He was fed to catalyst cell at room temperature and a series of time-dependent DRIFT spectra of NO adsorption were sequentially recorded. For NO–O_2 co-adsorption, the gas mixture (400 ppm NO, 10% O_2, balance He) was fed to the sample cell at a total flow-rate of 60 mL min^{-1} at 150 °C. After holding this temperature for 20 min, it was stepwise increased to the next designed temperature. The DRIFT spectra were recorded every 25 °C (from 150 to 350 °C) after 20 min of steady state reaction.

3. Results and discussion

3.1. NO oxidation activity over TiO_2 supported catalysts

The temperature dependence of steady-state NO oxidation over a series of TiO_2 supported catalysts is shown in Fig. 1. For reference, the thermodynamic equilibrium for NO–NO_2 under given conditions is also shown in the figure (in dashed). The main product for NO oxidation was NO_2, and the formation of other N-containing product (N_2O, N_2, etc.) could be neglected. The NO conversion to NO_2 over catalysts was kinetically limited at low temperatures and equilibrium-limited at higher temperatures. After reaching thermodynamic equilibrium, if possible, the NO conversion to NO_2 closely followed the thermodynamic equilibrium curve. Among TiO_2 supported transition metal oxides investigated, the best activity was obtained over Co/TiO_2 sample and the activity order was observed as $Co/TiO_2 > Mn/TiO_2 > V/TiO_2 > Cu/TiO_2 > Fe/TiO_2 > Cr/TiO_2 > Ni/TiO_2$. Among TiO_2 supported precious metal or metal oxides studied, Ru/TiO_2 showed the best activity, followed by Rh/TiO_2 and then Pd/TiO_2 and Au/TiO_2. The Pt/TiO_2 catalyst showed good activity at low temperatures (<225 °C), however its activity at high temperatures was observed to be lower than Rh/TiO_2. It should be mentioned that the Pt/TiO_2 was pre-reduced before reaction, considering that Pt metal was reported be more active than Pt oxides [11,14]. Ru/TiO_2 was the most active catalyst among TiO_2 supported catalysts for NO oxidation and a 50% NO conversion to NO_2 was achieved at *c.a.* 250 °C at a very high GHSV of 180,000 h^{-1}. The maximal NO conversion of *c.a.* 94% could be achieved at *c.a.* 275 °C.

The XRD patterns of TiO_2 supported catalysts studied are shown in Fig. 2. Typical diffraction peaks of TiO_2 support corresponding to anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phase were observed, as marked in the XRD patterns. Besides, no diffraction peaks corresponding to the supported phases, neither in metal form nor in oxide form, could be observed. It is deduced that the supported phases are highly dispersed on TiO_2 support. The TEM image of Ru/TiO_2 catalyst is displayed in Fig. 3. It is seen that homogeneous nano-clusters with averages diameters of below 5 nm are evenly dispersed on the surface of TiO_2 support.