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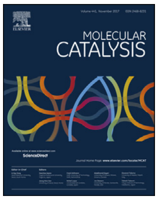

Editor's choice paper

Mechanistic investigations on NO reduction with CO over Mn/TiO_2 catalyst at low temperatures

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ABSTRACT

A series of titania-supported transition metal oxide catalysts were evaluated for NO reduction with CO as reductant at low temperature (200 °C) in the presence of excess oxygen. Among the investigated systems, MnO_x/TiO_2 has been found to be the preeminent catalyst. *In situ* FT-IR and transient studies were carried out in order to identify the chemisorbed species which could act as catalytic intermediates, and in consequence to propose the low temperature reduction of NO pathway over the Mn/TiO_2. The NO adsorption and NO + O_2 co-adsorption of *in situ* FT-IR experiments revealed the formation of surface reaction intermediate N_2O species along with the formation of monodentate and bidentate nitrates, whereas CO adsorption on the catalyst leads to the formation of carbonate species. Interestingly, in the case of NO and CO co-adsorption over MnO_x/TiO_2, the formation of CO_2 (CO oxidation with gas phase oxygen) is inhibited due to the surface reaction competition between NO and CO. The formation of N_2O as an intermediate was evident from the occurrence of peaks at 1286 and 1335 cm^{-1} region. There is no formation of NO_2 as a surface intermediate or gas phase stable product in the present *in situ* Fourier transform infrared spectroscopy (FT-IR) and transient mass spectroscopic studies, respectively. Remarkably, a neat absorption peak at 2178 cm^{-1} ascribed to the isocyanate (–NCO) species was not observed during *in situ* infrared spectroscopic studies of NO + CO and CO + NO co-adsorptions. Based upon this evidence it is proposed that the formation of NCO^- species from the reaction between CO and N_{ads} is completely forbidden over the Mn/TiO_2 catalysts. These results indicate that the reaction mechanism follows a different pathway for our catalyst, from that of the other metal based catalysts. The role of lattice oxygen in the reaction mechanism is substantiated by isotopic labeling and transient analysis studies. Lewis acid sites act as the active sites for the reaction.

1. Introduction

The chemistry of reducing NO to nitrogen has attracted considerable interest of many researchers due to its adverse effect on the environment. For decades, it was accomplished by using noble metal and metal oxide catalysts at elevated temperatures using reductants like NH_3, urea, hydrocarbons etc. [1–3]. For economical reasons, continuous efforts were made to replace noble metal based catalysts with transition metal based catalysts and to develop catalysts capable of operating at relatively low temperatures [4]. Although NH_3 is the most widely used reductant so far, recently, CO has attracted to a great extent of interest due to the socio-economic concerns associated with ammonia [5]. Using CO as reductant has several important advantages like; it can be produced onsite for the cases of coal or natural gas utilization (stationary sources), or it is part of the exhaust stream due to incomplete combustion of liquid fuels (mobile sources), thereby eliminating the costly steps of purchasing, transporting, and storing the reductant [6].

Several catalytic systems are reported for the selective catalytic reduction (SCR) of NO, but most of them are active at relatively high temperatures (≥300 °C) [7–11]. Our research findings reveal that MnO_2/TiO_2 is a versatile catalyst for SCR of NO with NH_3 at low temperatures and industrially relevant conditions [1,12]. In view of this, we have examined several transition metal-based catalysts for SCR of NO with CO to find out the most viable catalyst system [6,8]. Moreover, the reaction mechanism, another important

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aspect of the process, is still a matter of great interest. There are of course discrepancies and many controversial considerations in the open literature regarding the mechanism of NO + CO reaction. Some researchers reported that over some metal based catalysts, the isocyanate (–NCO) species is the intermediate that is formed during the NO reduction by CO [13–18]. In contrast, it was also suggested that NO dissociation and the direct formation of N_2 is the important step. Other reports in the open literature propose that N_2O was observed as a reaction intermediate over Pt- and Rh-based catalysts [19–21]. In view of these, combined *in situ* FT-IR and transient analysis of products experiments were performed to elucidate the reaction mechanism for the reaction over our MnO_x/TiO_2 catalyst. A series of probable elementary steps were proposed as the possible mechanism for the reaction. We found that the reaction mechanism over our catalyst follows a different pathway from that of the noble metal based catalysts. Another interesting observation is that the presence of NO in the reaction mixture hinders the CO oxidation to CO_2. Moreover, there is no evidence about NO_2 and isocyanate (–NCO) species formation in the present study. We propose that the NO adsorption and its subsequent dissociation occur on the reduced manganese sites leads to the formation of N_2O. Thereafter, N_2O dissociates into molecular nitrogen and oxygen. During the process, reduced manganese sites act as the active sites for NO dissociation.

2. Experimental

2.1. Catalyst synthesis

Wet impregnation method was adopted to prepare a series of anatase titania (Hombikat UV 100 from Sachtleben Chemie) supported transition metal oxide (M = Cr, Mn, Fe, Ni, Cu; 10 wt.%) catalysts. The transition metal oxides were deposited on titania using dilute solutions of their nitrate precursors. In a typical synthesis, 50 ml deionized water was added to a 100 ml beaker containing a measured quantity of support. The mixture was heated to 70 °C under constant stirring. Then, a predetermined amount of nitrate precursor was added to the solution and the mixture was evaporated to dryness. The paste thus obtained was further dried overnight at 110 °C, ground and calcined at 400 °C for 2 h in a continuous flow of air and at 500 °C for 4 h in a continuous flow of air.

2.2. Catalyst characterization

2.2.1. X-ray diffraction

X-ray powder diffraction patterns were recorded on a Siemens D500 diffractometer using a Cu K_α radiation source (wavelength 1.5406 Å). An aluminium holder was used to support the catalyst samples. The scanning range was 5°–80° (2θ) with a step size of 0.05° and a step time of one second. The XRD phases present in the samples were identified with the help of JCPDS data files.

2.2.2. Temperature programmed reduction (H_2-TPR)

The temperature-programmed reduction (H_2-TPR) experiments were carried out from 70–900 °C on a Micromeritics AutoChem 2910 instrument using 50 mg of calcined catalyst. Prior to the analysis the catalysts were pretreated at 250 °C for 2 h in ultra high pure helium (30 ml min^{-1}, Wright Brothers) stream. The TPR runs were carried out with a linear heating rate (10 °C min^{-1}) in a flow of 4% H_2 in Ar (Matheson) with a flow rate of 25 ml min^{-1}. The hydrogen consumption was measured quantitatively by a thermal conductivity detector.

2.2.3. In situ *FT-IR studies*

FT-IR spectra were recorded using a Bio-Rad (FTS-40) spectrometer. Circular self-supporting thin wafers (8 mm diameter) consisted of 8–12 mg of material were used for this study. The wafers were placed in a high-temperature cell with CaF_2 windows and purged with ultra high purified (UHP) grade helium (30 ml min^{-1}, Wright Brothers) at 200 °C for 2 h to remove any adsorbed impurities and cooled to 50 °C. The background spectra of the solids prior to gas adsorption were collected during the cooling process and subtracted from consequently recorded spectra. The atmospheric CO_2 and H_2O vapor are both strong IR absorbers. Both occur in air and in the optical light path and contribute to any IR absorption signal measured. For this reason, we have recorded the air spectrum by running it with no sample and stored as a BLANK spectrum. The blank spectrum and background spectrum were then subtracted by the computer program, leaving the net sample spectrum. Any suspected changes in H_2O vapors and atmospheric CO_2 were corrected by updating the blank spectrum at regular intervals. On the other hand, the optical path was also purged with dry air to eliminate the interferences from the large CO_2 band (atmospheric) and H_2O vapors and obtain more stable environment. This eliminates the necessity of correcting for the blank signal derived from impurities in the air. Afterward, CO (1% in He, Matheson), NO (2% in He, Matheson) and pure O_2 (Wright Brothers) were introduced into the cell at 30 ml min^{-1} for 1 h at 50 °C to ensure complete saturation of the sample and then physisorbed gas was removed by flushing the wafer with helium for 3 h at 50 °C. The same procedure was followed for the adsorption of single gas and for the adsorption of multiple gases, as helium flowed for 3 h at 50 °C between gas adsorption steps. The FT-IR absorption spectra were collected after desorbing the adsorbed gas at temperatures ranging from 50 to 200 °C in a continuous helium flow. Sixteen scans were averaged for each normalized spectrum at a resolution of 2 cm^{-1}. To get the information about the presence of different acid sites on the catalyst and their nature, NH_3 (4% in He, Matheson) adsorption was also performed in similar manner.

2.3. Reaction procedure

The SCR of NO with CO was carried out at atmospheric pressure in a fixed bed quartz reactor (i.d. 6 mm). A measured amount of catalyst (0.1 g in dry basis, 80–120 mesh) was placed in the reactor in between two glass wool plugs. Oxygen (4% in He, Wright Brothers), carbon monoxide (1% in He, Matheson) and nitric oxide (2.0% in He, Matheson) were used as received. The inlet concentrations of NO and CO were 400 ppm 2 vol.% of oxygen was fed into the reaction stream. All the experiments were conducted at the gas hourly space velocity of 50,000 h^{-1}. The reaction temperature was measured by a type K thermocouple inserted directly into the catalyst bed. Prior to the catalytic experiments, the catalyst was activated *in situ* by passing (2 vol.%) oxygen for 2 h at reaction temperature. The reactants and products were analyzed *on-line* using a Quadrapole mass spectrometer (MKS PPT-RGA), and a chemiluminescence detector (Eco Physics CLD 70S).

The isotopic labeling experiments were carried out to investigate the interaction of catalyst lattice oxygen with the gas phase oxygen. 150 mg of the catalyst was pretreated at 200 °C temperature with 2 vol% of unlabeled oxygen (4% $^{16}O_2$ in He, Wright Brothers) for 2 h. The purpose of the pretreatment was to remove the OH-groups from the catalyst surface. Following this, the system was flushed with helium (Wright Brothers) with the flow rate of 85 ml/min to remove unlabeled oxygen completely from the reactor. Thereafter, 20,000 ppm of labeled oxygen (4% $^{18}O_2$; 99 atom% in He, Isotech) was introduced to the system at 200 °C and the a.m.u. for $^{16}O_2$ (32), $^{16}O^{18}O$ (34), and $^{18}O_2$ (36) were followed with a mass spectrometer (MKS PPT-RGA). The signal of the cross labeled oxygen ($^{16}O^{18}O$) was corrected from the interference with the labeled oxygen. The normalized concentrations were calculated by divid-

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