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Selective catalytic reduction of NO with CO using different metal-oxides incorporated in MCM-41

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HIGHLIGHTS

- Metal-oxide catalysts activity correlated with their M–O bond-strength.
- The catalyst ability to release lattice oxygen initiates reaction between NO and CO.
- Ru-MCM-41 is the most efficient catalyst with lowest reaction onset temperature.

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ABSTRACT

Metal oxide doped mesoporous silica (MCM-41) were prepared by a co-precipitation method and utilized for the selective catalytic reduction of nitric oxide with carbon monoxide at temperatures in the range 423–723 K. The supported metal oxides investigated included oxides of ruthenium, copper, cobalt, nickel and iron. This selection offered a wide range of metal–oxygen bond strength within the catalyst. The catalysts were characterized by powder XRD, N_2 sorption analysis and temperature programmed reduction (TPR) in hydrogen. At reaction temperatures less than 550 K the activity of the catalysts was in the order of Ru-MCM-41 > Co-MCM-41 > Ni-MCM-41 ≈ Fe-MCM-41 ≈ Cu-MCM-41. At reaction temperatures above 650 K, the Ru-MCM-41 was still the most active catalyst followed by Cu-MCM-41.

1. Introduction

Although large efforts are currently directed at the development of renewable energy sources, such as solar and wind power, fossil fuels including coal are expected to continue to be an important source of energy for many decades and, consequently, there remains a need to continue research in development of technologies to reduce emissions from fossil fuel combustion. For example, nitric oxides (NO_x) emitted from the combustion of fossil fuels in power stations and automobiles contribute towards negative environmental impacts such as global warming and smog formation. The most commonly used post-combustion technology to reduce NO_x emissions is the selective catalytic reduction (SCR) of NO with ammonia or urea as a reducing agent over, for example, vanadium oxide based catalysts. The cost of such SCR processes is typically high due to the chemical handling requirements and the energy required to operate at high reaction temperatures. Carbon monoxide, which is also present in the flue gases of coal-fired power stations, has potential as an alternative, lower cost reducing agent in SCR processes and low-temperature SCR of NO with CO has been demonstrated over supported noble metal catalysts such as Pd [1] or Rh-based [2], [3] catalysts. Other lower cost materials such as copper oxide, Co–Cr, Ag–Al_2O_3, Fe_2O_3, Cu–ZSM-5, Cr–TiO_2, Mn–TiO_2, Fe–TiO_2 have also been investigated as catalysts for NO reduction [4–11].

Although there has been a large number of investigations of catalytic materials for NO reduction with CO, criteria for designing an optimum catalyst for this reaction is yet to be developed. In a recent study, Reddy and Khanna [12] performed molecular simulations to better understand the mechanisms of the coupled reactions of CO oxidation and NO reduction, and from their simulation results concluded that the capacity of catalyst to provide active intracrystalline oxygen molecules for CO oxidation is an important requisite characteristic for NO + CO reduction catalysts. To further explore Reddy and Khanna's hypothesis about the strength of metal–oxygen bond strength and catalytic activity, we prepared a series of metal oxide catalysts supported on mesoporous silica MCM-41. The catalysts included oxides of ruthenium, copper, cobalt, nickel and iron; the metal–oxygen bond strengths

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in these oxides range from 100 kJ mol^{-1} in RuO_2 [13,14] to 409 kJ mol^{-1} in Fe_2O_3 [13]. Mesoporous silica MCM-41 was selected as a catalyst support in this study based on our previous studies on NO + CO reaction [15,16] in which we reported that the mesoporous structure of MCM-41 facilitated good dispersion of active CuO particles and produced catalysts with good activity.

2. Material and methods

2.1. Catalyst preparation

Mesoporous silica MCM-41 was synthesized using the method described by Kumar et al. [17]. The metal oxides catalyst supported on MCM-41 were prepared by a co-precipitation method using chloride or nitrate salts of metals. The amount of metal-salts used in the preparation was predetermined to ensure that the molar concentrations of respective metals are equal in all the samples. For example, in a typical co-precipitation catalyst synthesis, the desired quantity of $Cu(NO_3)_2{\cdot}3H_2O$ was added to a 120 mL solution containing 2.4 g of dissolved cetyltrimethylammonium bromide (CTABr, 99% Aldrich) and 8 mL of 32 wt%. ammonia solution. To this mixture 10 mL of tetraethyl orthosilicate (TEOS, 98%, Aldrich) was added drop wise and the solution was stirred for 24 h, then filtered to recover a white precipitate. The solids were air dried for 24 h then calcined at 500 °C for 5 h. The synthesized catalysts were carefully stored in desiccator until further use. Hereafter the catalysts will be referred to as X-MCM-41, where X stands for (Cu, Ni, Fe, Co and Ru).

2.2. Catalyst characterization

Nitrogen sorption test were carried out at 77 K on a Micromeritics Tristar II 3020 automatic adsorption apparatus. Prior to the N_2 adsorption measurements, samples were degassed under vacuum at 473 K for 24 h. The phase structures of the catalysts were examined by powder X-ray diffraction (XRD) using a Bruker D∗ Advanced Research Diffractometer with a monochromatic Cu-Kα radiation source operated at 40 kV and 30 mA. Two sets of XRD measurements were collected: small angles at 2θ values in the range of (0.7–4) degrees and wide angles at 2θ in the range (2–90) degrees. Inorder to measure the extent of metal loading in the support, a small quantity of sample was carefully dissolved in acid and the sample analysed by ICP.

Temperature programmed reduction (TPR) of the catalysts in hydrogen was performed in a Belcat instrument equipped with a thermal conductivity detector (TCD) to continuously measure the effluent gas compositions. In a typical TPR measurement 50 mg of catalyst was packed between quartz wool in a U-tube reactor (9 mm I.D.). The loaded catalyst was pre-treated in situ at 623 K in a flow of Argon for 1 h and then was cooled to 323 K. The reduction was measured at temperatures from 323 to 923 K using a heating rate of 10 K min^{-1} at 30 mL min^{-1} flow of 5% H_2 in Argon. Water produced during the TPR measurement was trapped in a zeolite column installed between the reactor outlet and the TCD.

2.3. Evaluation of catalyst performance

A fixed bed tubular reactor (9 mm I.D.) mounted inside a vertical furnace was used to conduct the NO + CO reaction. The experimental setup is shown in Fig. 1. The catalyst activity measurements were performed with 0.1 g of catalyst at temperatures from 423 to 723 K; the reaction temperature was measured by a thermocouple located just above the catalyst bed inside the reactor. Prior to the reaction measurement the catalyst was flushed in situ with Argon at 473 K for 1 h. The furnace temperature was adjusted to the reaction temperature and then the reactor was fed with the reactant gas mixture. A feed composition of 250 ppm NO and 750 ppm CO was established by adjusting the feed gas ratio while maintaining a total flow rate of 80 mL min^{-1}. This flow rate was selected to ensure the reaction rate was not limited by external diffusion. At each measurement temperature the reaction condition was maintained until a steady state outlet concentration of NO was observed; typically it took 30 min to achieve this state. The concentrations of NO and NO_2 in the feed (NO_{in}) and reactor effluent (NO_{out}) were measured with a chemiluminescence analyser (Thermo 42i).

The reaction kinetics study was carried out in the same fixed bed reactor described above and by varying the total gas flow rate and/or concentration of reactant in the feed.

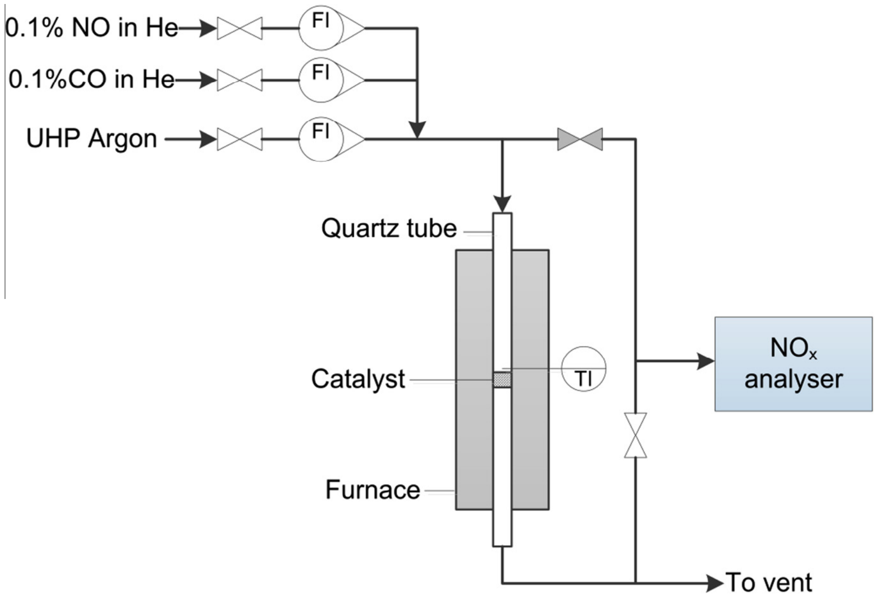

Fig. 1. Schematic of fixed-bed reactor used for selective catalytic reduction of NO with CO. Reactor feed composition controlled by blending gases from cylinders of 0.1% NO in He and 0.1% CO in He.