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# Structural sensitivity of mesoporous alumina for copper catalyst loading used for NO reduction in presence of CO

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## ABSTRACT

Copper oxide supported on mesoporous alumina pre-treated at different temperatures was examined for catalytic reduction (SCR) of NO with CO. About 4.5% copper oxide was loaded on mesoporous alumina using wet impregnation method. Detailed investigations concluded that the activity of Cu/m-Al<sub>2</sub>O<sub>3</sub> is strongly influenced by the active Cu phase present on bulk copper aluminate. The Copper phase on the catalyst was strongly affected by pre-treatment temperature of the host material. The optimal pre-treatment temperature of the support was found to be around 900 °C. The reaction mechanism on the catalyst surface was suitably described using L-H mechanistic model with the reduced Cu<sup>δ+</sup> sites generated on the catalyst surface post CO oxidation playing a critical role in NO reduction.

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## 1. Introduction

Suppressing NO<sub>x</sub> and SO<sub>x</sub> released from sources like power plant, biogas production, and automobiles has been among the strategic focus for preventing global climate change. Selective catalytic reduction (SCR) technology using urea or ammonia as the reducing agent in presence of catalyst has been the most promising and efficient technology for NO<sub>x</sub> removal (Schnelle and Brown, 2001). Various metal and metal oxides like Pt, Rh, Pd, V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, CuO etc. have been studied for NO<sub>x</sub> reduction using NH<sub>3</sub>, Hydrocarbon or CO (Fujii et al., 2003; Chafik et al., 2000; Kondarides et al., 2000; Cordoba et al., 2005; Cónsul et al., 2008; Khalfallah Boudali et al., 2009; Haneda et al., 1999; Hu et al., 2000; Xiaoyuan et al., 2004; Bellido and Assaf, 2009; Bera et al., 1999; Patel et al., 2011, 2013, 2014). Among all, copper oxide (CuO) was found to be economical and effective catalyst for selective reduction of NO using various reducing agents. Cu zeolites were studied by Iwamoto

et al. for the NO reducing using hydrocarbon with 100% conversion at 450 °C (Iwamoto et al., 1986). Shimizu et al. (1998) examined the activity of various transition metals supported on alumina for NO reduction using C<sub>3</sub>H<sub>6</sub>. It is reported that Cu/Al<sub>2</sub>O<sub>3</sub> with the high Cu loading is found to be highly active even at low operating temperatures. Activity of the catalyst increased with higher copper loading on the alumina support due to the formation of surface and bulk Cu<sup>2+</sup> species dispersed on tetrahedral and octahedral sites of alumina phase. (Shimizu et al., 1998, 2000).

In previous investigation reported by our group on copper catalysts supported on mesoporous alumina for N<sub>2</sub>O reduction, Zhu et al. (2003a) found that calcination temperature of mesoporous alumina strongly influences its crystalline structure which in turn plays important role in determining the type of Cu species present on its surface post catalyst impregnation. In this paper, we extend that investigation to study the reduction of NO in the presence of CO over a series of

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mesoporous alumina (m-Al<sub>2</sub>O<sub>3</sub>), which were synthesised at different temperatures. The study focuses on the influence of phase transition of m-Al<sub>2</sub>O<sub>3</sub> on the catalytic activity of supported CuO for NO reduction. We further propose a kinetic mechanism for simultaneous CO oxidation and NO reduction on the catalyst.

## 2. Experimental

### 2.1. Synthesis of mesoporous alumina and CuO/mesoporous alumina

Mesoporous alumina (MA) was synthesised following the procedure described elsewhere (Sun et al., 2009). In a typical synthesis, 0.1 mol of aluminium sulphate (Al<sub>2</sub>SO<sub>4</sub>) and 6.38 g of P123 (non-ionic triblock copolymer surfactant) were dissolved in 20 mL of distilled water. The resultant mixture was stirred for 24 h at 40 °C. Ammonia (approx. 0.3 mol) was added into the solution to raise the pH to 8 and subsequently followed by heating the solution at 100 °C for 24 h. The solution is then washed and filtered to remove ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). The resulting solid was dried and calcined at 550 °C, 900 °C and 1200 °C, respectively.

The prepared samples were named as m-Al<sub>2</sub>O<sub>3</sub>-x, where x stands for the sample calcination temperature in °C. Copper oxide was loaded on the m-Al<sub>2</sub>O<sub>3</sub> by impregnating the above three samples with an aqueous solution of copper nitrate at room temperature. The solution is then dried at 100 °C and calcined at 350 °C in air for 5 h. The copper loaded samples in the present manuscript are identified with the prefix "Cu/".

### 2.2. Characterisation of synthesised samples

Nitrogen adsorption–desorption isotherm measurements were carried out on micromeritics Tristar II 3020 at 77 K. The samples were degassed at 200 °C for 24 h prior to nitrogen physisorption analysis. The surface area of the samples was calculated by multi point BET method and the pore size distribution was obtained from the adsorption isotherm by BJH method. The pore volume was estimated at relative pressure of 0.99. Small angle XRD of the samples in the 2θ range of 0.7–4° was recorded by Bruker D8 Advanced Research diffractometer with a Cu-Kα radiation source at 40 kV and 30 mA. Wide angle XRD patterns of the samples were obtained on a Bruker D8 advanced equipped with copper target, graphite monochromators & scintillation counter operated at 40 kV and 30 mA in the 2θ range of 2–90°. X-ray photoelectron spectroscopy (XPS) of catalysts was performed using kratos AXIS ultra X-ray photoelectron spectrometer using monochromatic Al at pass energy of 160 and 40 eV. TEM images were obtained using JEOL JEM1010 electron microscope.

Bulk elemental copper composition of the catalysts was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). In a typical ICP-OES measurement, 20 mg of sample was digested with 5 mL of nitric acid and 2.5 mL of hydrofluoric acid by microwave using a CEM MDS 2000 digester, and elemental concentrations were determined using a Varian Vista Pro ICP-OES. Temperature programmed reduction (TPR) was performed using hydrogen on Belcat instrument. Details of TPR procedure could be found in earlier publications (Patel et al., 2011, 2014).

N<sub>2</sub>O chemisorption test was performed to obtain dispersion of copper catalyst on support material using Belcat

instrument. This method involves three steps (1) reduction of CuO to Cu metal by H<sub>2</sub> (2) occupation of active sites on Cu metal by N<sub>2</sub>O chemisorption and (3) reduction by H<sub>2</sub>. The catalyst was first reduced to Cu<sup>0</sup> metal in a mixture of H<sub>2</sub>/Ar at 400 °C for 45 minutes. The catalysts were then purged with Argon for 30 minutes and cooled to room temperature in the presence of Argon. The chemisorption step was carried out by flowing N<sub>2</sub>O at 90 °C for 30 min followed by purging in an Argon flow. Subsequently the catalyst was cooled followed by reduction under H<sub>2</sub>/Ar while increasing the temperature to 800 °C at a ramp rate of 10 °C/min. The amount of H<sub>2</sub> consumed in this final step was used to calculate the metal dispersion and metal surface area as per equations shown below:

$$D_{\text{Cu}} = \frac{\text{Mol}_{\text{H}_2} \times \text{MW} \times 10^4}{\text{SF} \times w} \quad (1)$$

$$S_{\text{Cu}} = \frac{\text{Mol}_{\text{H}_2} \times \text{SF} \times N_A}{10^4 \times C_M M \times w} \quad (2)$$

$$\phi_{\text{Cu}} = \frac{6000}{S_{\text{Cu}} \times \delta_{\text{Cu}}} \quad (3)$$

where

MW molecular weight of metal (g/mol)

N<sub>A</sub> Avogadro's number

R gas constant, J/K mol

SF stoichiometric factor

C<sub>M</sub> number of Cu atoms per unit surface area (1.4 × 10<sup>19</sup>)

D<sub>Cu</sub> metal dispersion (%)

w %wt of metal

Mol<sub>H<sub>2</sub></sub> moles of H<sub>2</sub> consumed per g of sample

φ<sub>Cu</sub> average particle size of copper (nm)

δ<sub>Cu</sub> density of copper (8.92 g/cm<sup>3</sup>)

S<sub>cu</sub> surface area of copper catalyst (m<sup>2</sup>/g)

### 2.3. Catalytic activity test

The NO reduction reaction in presence of CO was carried out in fixed bed micro reactor at atmospheric pressure in the temperature range of 250–450 °C. 0.1 g of catalyst was packed between quartz wool and placed inside a 0.9 cm ID quartz tubular reactor. The reactor was fed with fixed concentration of NO and CO in Helium mixture at the total flow rate of 80 mL/min. A fixed reaction temperature was maintained until outlet NO concentration reached at constant value. The inlet and outlet concentration of NO was continuously measured by chemiluminescence analyser (Thermo 42i HL).

## 3. Results

### 3.1. Structural characterisation of Alumina and CuO/alumina

Fig. 1 shows the nitrogen adsorption and desorption isotherms on the three m-Al<sub>2</sub>O<sub>3</sub> samples at 77 K while Fig. 2 shows the BJH pore size distribution. The initial two samples exhibited a type IV isotherm as per BDDT classification recognised for mesoporous structure (Sing et al., 1985), while the third sample, i.e. m-Al<sub>2</sub>O<sub>3</sub>-1200, exhibited a type II isotherm, although a small degree of hysteresis was also seen. The textural properties of each of m-Al<sub>2</sub>O<sub>3</sub> samples are summarised in Table 1. In general, the BET specific surface area of the m-Al<sub>2</sub>O<sub>3</sub>

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