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Promoting effect of CeO_2 in a Cu/CeO_2 catalyst: lowering of redox potentials of Cu species in the CeO_2 matrix

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The promoting effect of CeO_2 in a Cu/CeO_2 catalyst for CO oxidation and NO reduction compared to CuO and Cu/ZrO_2 is deduced to be based on lowering of redox potentials of copper species in the Cu/CeO_2 matrix in relation to CuO and Cu/ZrO_2.

CeO_2 is an active support for precious metal as well as base metal catalysts and is widely used as a promoter for three way catalysts (TWCs). The promoting effect of CeO_2 is largely attributed to enhancement of metal dispersions, surface segregation of active metal, oxide ion defects for oxygen mobility and oxygen storage capacity (OSC).[1–5] Enhancement of catalytic activity by CeO_2 is observed in terms of reduction in the reaction temperature and decrease in activation energy. Complete CO oxidation over pure CeO_2 occurs above 500 °C while the temperature is brought down to 150 °C over Cu/CeO_2.[6–8] In contrast, 100% CO conversion occurs at 225 °C over bulk CuO. There seems to be an electronic interaction between Cu and CeO_2 which plays a vital role for the lowering of the reaction temperature and enhancement of the catalytic activity. Similar effects are also seen over Pt/CeO_2 and Pd/CeO_2 catalysts.[9] Several studies exist on the metal–support interaction and its effects on catalytic activity.[10–12] However, the exact nature of the interaction between metal ions and CeO_2 is not yet fully understood. We consider it worthwhile to investigate the Cu–CeO_2 interaction by electrochemical methods which can provide the redox properties of Cu species in a CeO_2 matrix. Here, we report for the first time, cyclic voltammetry and temperature programmed reaction (TPR) studies of a Cu/CeO_2 catalyst in comparison with CuO and Cu/ZrO_2. We show that the redox potentials of the Cu^{2+}/Cu^+ and Cu^+/Cu^0 couples in a CeO_2 matrix are lower than those in CuO and ZrO_2 matrices. The catalytic properties are consistent with the electrochemical behavior.

5% Cu/CeO_2 catalyst was prepared by the solution combustion method.[8] For the preparation of 5% Cu/ZrO_2 by this method, carbohydrazide (CH) was used as the fuel along with zirconyl nitrate and copper carbonate at 400 °C. X-Ray diffraction studies have shown that Cu^{2+} ions are substituted for Ce^{4+} to lead to a $Ce_{1-x}Cu_xO_{2-\delta}$ solid solution. Cu is in a +2 oxidation state as seen from X-ray photoelectron spectroscopy of the Cu 2p core level region as well as by electron paramagnetic resonance (EPR) spectra of Cu/CeO_2.[8]

Electrochemical studies were carried out with a CH-660A Electrochemical Analyzer (CH Instruments, USA) using a three-electrode cell configuration. The working electrodes were made by mixing 65 wt% graphite and 35 wt% Cu based materials. The mixture was ground thoroughly and 10 mm pellets of 1.5 mm thickness were prepared and subsequently mounted on a glass tube using conductive silver paint (Eltecks Corporation, India). Cu wire was used as the current collector. The electrode was polished to give a shining mirror finish using fine grade emery (SiC) paper. The counter electrode used was a Pt foil and saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte solution was 0.05 M sodium sulfate (Na_2SO_4). The electrolyte was degassed by bubbling with N_2 prior to the measurement. In most cases the electrodes were cycled from +1.6 to −0.8 V at different scan rates. All experiments were performed at ambient temperature (*ca.* 25 °C).

The gas–solid reactions were carried out in a home-made TPR system equipped with a quadrupole mass spectrometer QXK300 (VG Scientific Ltd., England) using a packed bed tubular reactor.[8,9] Typically 0.1–0.2 g of the catalyst was loaded in a quartz tube reactor of 20 cm length and 6 mm diameter and the reactor was heated from 30 to 750 °C at a rate of 15 °C min^{-1}. The reactant gases were passed over the catalyst at a flow rate of 25 μmol s^{-1}.

The cyclic voltammogram of the Cu/CeO_2 electrode in 0.05 M Na_2SO_4 solution is shown in Fig. 1. The voltammogram obtained for the CuO electrode is also shown for comparison. The voltammograms consist of two cathodic and two anodic peaks for both bulk CuO and 5% Cu/CeO_2 samples in the scan range of 1.6 to −0.8 V *vs.* SCE. The Ce^{4+}/Ce^{3+} redox couple is not observed in the potential range studied. Similar voltammograms were observed for 5% Cu/ZrO_2 (not shown). The first peak labeled A is attributed to the reduction of Cu(II) to Cu(I) and the second peak B is due to reduction of Cu(I) to Cu(0) in all three cases.[13] The reduction potential values of $Cu^{2+} \rightarrow Cu^+$

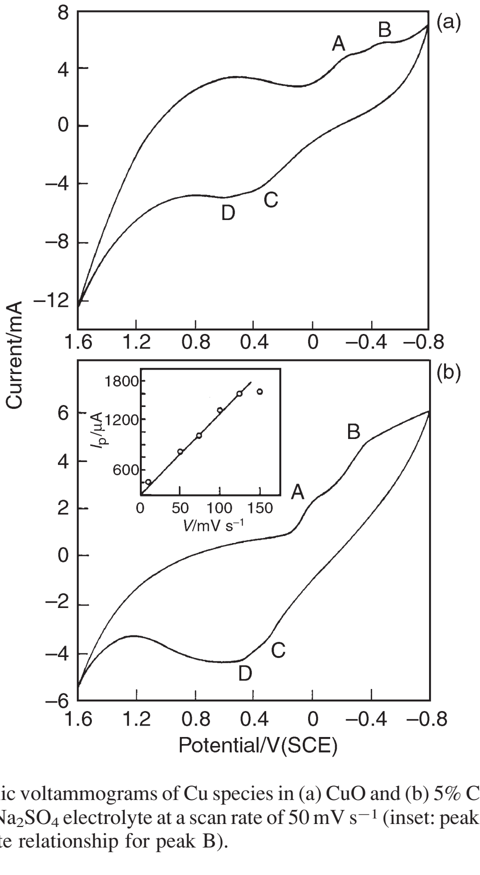

Fig. 1 Cyclic voltammograms of Cu species in (a) CuO and (b) 5% Cu/CeO_2 in 0.05 M Na_2SO_4 electrolyte at a scan rate of 50 mV s^{-1} (inset: peak current *vs.* scan rate relationship for peak B).

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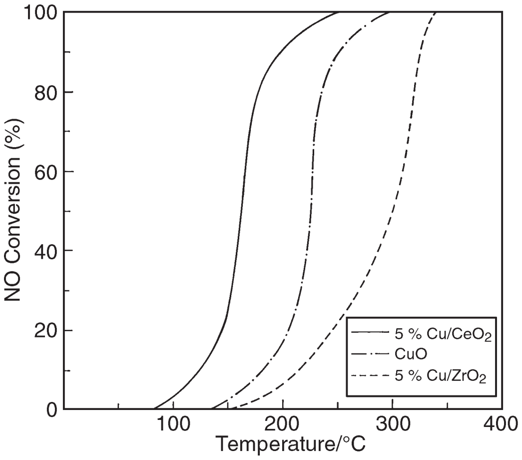

Fig. 2 NO conversion (%) over different Cu based catalysts for NO + NH_3 reaction.

and $Cu^+ \rightarrow Cu^0$ in the CeO_2 matrix are −0.12 and −0.40 V, respectively, whereas the values for the CuO and Cu/ZrO_2 electrodes are −0.28, −0.50 and −0.38, −0.55 V, respectively. Oxidation potential values for $Cu^0 \rightarrow Cu^+$ (peak C) and $Cu^+ \rightarrow Cu^{2+}$ (peak D) in CeO_2 substrate are +0.25 and +0.50 V which are lower than those observed with CuO (+0.36 and +0.60 V) and Cu/ZrO_2 (+0.40 and +0.73 V) electrodes. The potential values indicate that Cu species in a Cu/CeO_2 matrix require less energy to be reduced and oxidized than in the case of pure CuO and Cu/ZrO_2 matrices. The plot of the second peak [B in Fig. 1(b)] as current (I_p) *vs.* scan rate (V) is shown as an inset in Fig. 1(b) for the Cu/CeO_2 system in 0.05 M Na_2SO_4 solution. The linear relationship indicates that the redox active species is surface confined.

NO conversions (%) for the NO + NH_3 reaction over 5% Cu/CeO_2, CuO and 5% Cu/ZrO_2 as a function of temperature are shown in Fig. 2. It is clear that complete NO conversion occurs at 250 °C over 5% Cu/CeO_2 whereas this requires 350 °C over 5% Cu/ZrO_2 with the reaction temperature over CuO lying in between. The reaction temperatures over these catalysts also follows the same trend for NO + CO and CO + O_2 reactions.

NO reduction by NH_3 involves electron transfer from NH_3 to NO. NH_3 is adsorbed on a Cu^{2+} site partially reducing the Cu^{2+} ion. This charge can be transferred to Ce^{4+} which can be picked up by NO to give [N] + [O]. Based on the electronic interaction between Ce 4f, O 2p and Cu 3d orbitals, electron transfer can be facilitated in Cu/CeO_2 as follows:

$$–Ce^{4+}–O^{2-}–Cu^{2+}– + e \rightleftharpoons –Ce^{4+}–O^{2-}–Cu^{+}– \rightleftharpoons –Ce^{3+}–O^{2-}–Cu^{2+}– \rightleftharpoons –Ce^{4+}–O^{2-}–Cu^{2+}– + e$$

Such a scheme involves the redox couples Cu^{2+}/Cu^+ and Ce^{4+}/Ce^{3+}. These couples are available only for Cu/CeO_2 and not for CuO and Cu/ZrO_2 systems. A decrease in redox potentials of Cu species in Cu/CeO_2 as revealed in the voltammograms provides direct evidence of the promoting action of CeO_2. This will result in a decrease in the energy required for the electron transfer from NH_3 to NO and consequently a decrease in reaction temperature.

In conclusion, we have shown the correlation of catalytic properties of Cu/CeO_2 with the electrochemical behavior of the Cu species. The promoting action of CeO_2 is thus deduced to be *via* the lowering of redox potentials of Cu^{2+} ions in the CeO_2 matrix.

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