

Structural and Catalytic Properties of Copper Oxide/Nickel Oxide Modified Zirconia Prepared by Sol-Gel Technique

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Single and two-phase materials involving zirconia have been widely investigated because of their interesting catalytic, electronic and mechanical properties (1). It is now well established that these properties are very sensitive to the methods of preparation and subsequent heat treatments (2). This paper reports that by using sol gel technique it is possible to prepare solid solutions of CuO and NiO with zirconia even though they are insoluble at higher temperatures. Such metastable solid solutions have been found to be fairly stable at temperatures less than 600 °C. It has been shown that it is possible to use these metastable solid solutions for variety of applications such as catalytic oxidation of hydrocarbon. Extensive investigation of CuO-ZrO₂ system reported earlier (3) has shown that it is possible to obtain stabilized zirconia with CaF₂ structure by replacing Zr⁴⁺ by Cu²⁺ in the lattice of ZrO₂. The reported increase in the catalytic activity of this composition was suggested to be due to easy electron conduction because of the presence of Cu in the lattice and an increase in the mobility of oxygen due to the oxygen ion vacancies. The introduction of CeO₂ in this composition has found to increase the catalytic activity for oxidation of methane as shown in the Fig. 1. Presence of cerium is expected to increase the electron transport due to Ce³⁺/Ce⁴⁺ redox reaction.

In this paper we also report the stabilization of ZrO₂ by the addition of NiO in the lattice by sol-gel technique. The results show that it is possible to obtain cubic (fluorite) phase of ZrO₂ using sol-gel technique. Using the above technique, it is possible to introduce Ni²⁺ in the lattice of ZrO₂ at least up to 15mol%. Such stabilized cubic phase is found to be fairly stable below 600 °C. Heating them above 600 °C, however, results in the transformation to the monoclinic phase and subsequent precipitation of separate NiO phase. XPS of Ni 2p core level for various compositions of Ni in ZrO₂ prepared by sol-gel technique is shown in Fig. 2. It shows that at small concentrations of NiO (2 mol%), all Ni²⁺ goes in the lattice of zirconia substitutionally. At higher concentrations appearance of a second peak indicates that Ni²⁺ is also present in another position, possibly interstitially. Above 10mol% NiO, however, peaks correspond only to pure NiO indicating that NiO is present as a second phase largely covering each zirconia particle. These results are consistent with the lattice constant measurements obtained by x-ray diffraction (Fig. 3). Lattice constant is found to decrease linearly with increase in the concentration of NiO up to about 15mol% NiO. The extent of decrease, however, does not correspond to the one expected, if all Ni ions are around to go substitutionally in ZrO₂ lattice. The XPS spectra also give evidence of interaction of Ni²⁺ ions with oxygen vacancies. Composition with 20mol% NiO also gives fluorite structure corresponding to the stabilized zirconia. Its lattice constant, however, is not consistent with composition containing < 15% NiO. Heating the composition at 1000 °C for more than 12 hours did not show any trace of monoclinic but highly stable cubic fluorite phase. This therefore is expected to be a very good anode material for SOFC. The stabilized fluorite structure

at temperature <600 °C of composition less than 15mol% NiO suggest the possible use of these compositions for low temperature catalytic reactions, particularly hydrocarbon oxidation. Further investigations on catalytic and electronic properties of these compositions are in progress.

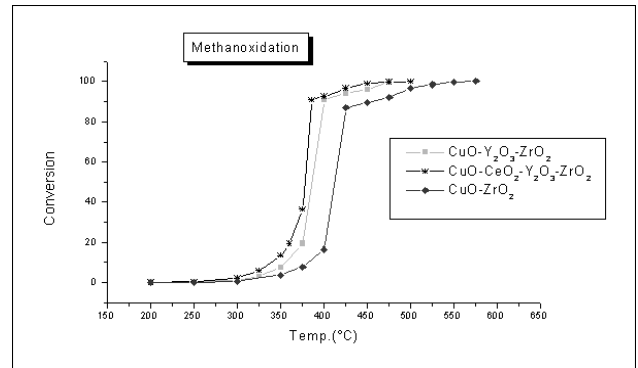


Fig. 1 Catalytic activity of methane combustion

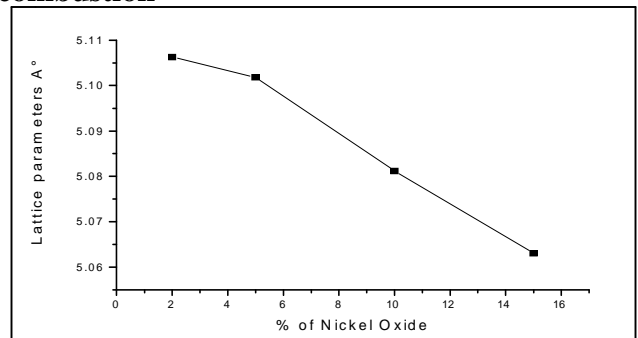


Fig. 2 Variation of lattice constant Vs NiO%

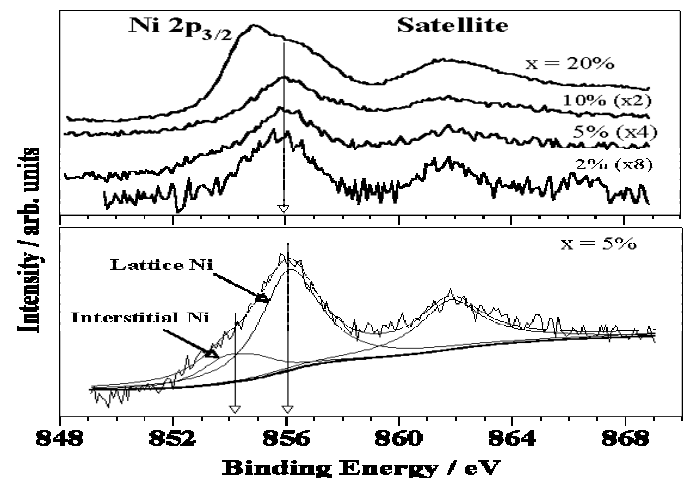


Fig. 3 XPS spectra of NiO/ZrO₂ samples

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