

Comparing Catalytic Properties of Copper Loaded CeO₂ and SnO₂ Oxides Catalysts for CO oxidation

B. Šmíd,² P. Hanyš,^{1,2} K. Frey,³ T. Mori,¹ M. Takahashi,¹
I. Matolínová,² and V. Matolín²

¹Nano-Ionics Materials Group, Fuel Cell Materials Center, National Institute for Materials Science,
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, Fax: +81-298-860-4667

²Department of Surface and Plasma Science, Faculty of Mathematics and Physics,
Charles University, V Holešovičkách 2, 180 00 Prague 8, Czech Republic

³Department of Surface Chemistry and Catalysis Institute of Isotope,
H-1121 Budapest Konkoly Thege u. 29-33, Hungary

Abstract. Catalytic properties of systems composed of copper loaded CeO₂ and SnO₂ were examined. Catalysts were prepared using a conventional impregnation method. After preparation the samples were calcined in oxygen respectively reduced in hydrogen. Treatments were carried out at 400 °C resp. 300 °C for 2 hours. The amount of copper in prepared samples was 8 at. % in both cases. Morphology and particle size were observed using Scanning Electron Microscopy (SEM). Crystal phases were characterized by X-Ray Diffraction method (XRD). The CO oxidation reaction was performed in a flow micro-reactor in the mixture of He, O₂ and CO, where the catalyst was deposited on a silicon oxide chip ensuring a very reliable catalyst temperature control. It can be expected that nano-structured copper loaded oxide catalysts could be used for removing CO produced in a wet reforming reaction for fuel cell applications.

Key words: nano-sized catalytic systems, copper, ceria, tin oxide, CO oxidation

1. INTRODUCTION

Oxide supported metallic particles have found wide range of applications in the field of catalysis, gas sensing or fuel cell materials [1,2]. The reducibility of such oxides provides them for taking an active part in the catalytic process. Cerium oxide (ceria) supported systems have attracted much attention as the CO oxidation catalyst in the recent years [1,3-5]. Cerium dioxide (CeO₂) is an important catalyst in many chemical reactions, e.g. the NO reduction under oxidation conditions or CO oxidation under reducing conditions in automotive exhaust catalysts [1].

The remarkable redox ability of CuO-CeO₂ at the lower temperature was found to play an essential role in CO oxidation reaction [3, 4]. It was shown the catalytic behavior of CuO-CeO₂ greatly depends on the preparation routes [5]. The catalysts for fundamental studies are prepared by various conventional techniques such as impregnation, ion exchange, anchoring/grafting, spreading and wetting, hydrolysis, and homogeneous deposition-precipitation [6]. Presently, it is a new trend regarding novel chemical techniques of synthesis that can lead to ultra fine, high-surface-area catalysts for heterogeneous catalysis [7].

SnO₂ was still extensively used in gas sensing studies and doping by various metals is a common way to enhance the sensitivity and/or selectivity of the SnO₂ gas sensors [8-12]. Addition of a small amount of suitable metal can increase a number of oxygen vacancies, which strongly affects the sensing properties of the material [13-15]. The Cu and CuO doped SnO₂ have been frequently studied [16-18] due to the exquisite sensitivity of the system towards H₂S gas, which was shown to be primarily due to a dominant role played by the spill-over mechanism [18].

In this paper, copper impregnated CeO₂ nano-catalytic system is investigated and compared with copper loaded SnO₂ system.

2. EXPERIMENTAL DETAILS

2.1 Preparation of catalysts

For preparation powder catalysts we used commercial CeO₂ powder (99.5 % min, Alfa Aesar, John Matthey Company) or SnO₂ powder and Cu (II) acetate monohydrate ((C₂H₃O₂)₂·H₂O, purity: 99.99+%, Sigma Aldrich Company) as starting materials. Cu loaded CeO₂ and SnO₂ were prepared by impregnation method. The copper acetate and CeO₂ or SnO₂ were mixed with ethanol in a magnetic stirrer and dried in a flow of nitrogen. Then copper impregnated CeO₂ was calcined in a flow of oxygen or reduced in a mixture of hydrogen and helium (10 % of H₂ and He in balance) at 300 °C for 2 hours, copper impregnated SnO₂ was calcined and reduced at 400 °C for 2 hours.

Thermogravimetric and differential thermal analysis (TG-DTA) of as prepared catalysts was performed with TG-DTA 6200 device (Seiko Instruments Company). The temperature rate was set up from ambient temperature to 1000 °C with the heating rate 5 °C·min⁻¹ in flowing air atmosphere. The determined temperatures for decomposition of starting materials are 300 °C and 400 °C for copper loaded CeO₂ and SnO₂ powders, respectively.

2.2 Evaluation of catalytic activity

The CO oxidation reaction was examined using a micro catalytic flow reactor composed of a copper base plate with built-in heating system and thermocouple. The amount 2 mg of tested powder catalyst was placed on a silicon chip (~15x15 mm² in

size), soluted by several drops of ethanol and then carefully dried to create homogeneous layer. The wafer is covered by a sealing and quartz glass with two gas inlets, into which gas input and output is connected.

During reaction experiments, the sample was heated from room temperature up to 300 °C with the heating rate 10 °C per minute. For the measurements of the activity of catalysts we used the mixture of oxygen with helium (4 % of O₂ and He in balance) and carbon monoxide. The flow rates, controlled by Omega FMA6500 digital mass flow controllers and mixed before entering the micro reactor, were as follows; CO: 3 ml.min⁻¹, O₂ with He: 37.5 ml.min⁻¹. It means the flow rate of O₂ was 1.5 ml.min⁻¹, we used the stoichiometric ratio of CO:O₂ 2:1 and the total flow rate was 40.5 ml.min⁻¹. The output of the micro reactor with outlet gas is connected by a needle valve with the UHV (Ultra High Vacuum) chamber equipped by a Pfeiffer Prisma QME200 Quadrupole Mass Spectrometer for gas analysis.

2.3 Structure observation

Particle morphology and nanostructure of obtained powders were observed by two field emission SEM instruments (S-4800 and S-5000, Hitachi). SEM observations were performed with the gun voltages of 10 kV resp. 20 kV. Prior to SEM observation, powder samples were dispersed into ethanol ultrasonically, with the suspensions on to a thin layer of aluminium foil. A small portion of the foil with the sample on it was cut and placed onto a sample plate with carbon sticker.

Crystal phases of specimens were analyzed by XRD (RINT 2500 HF, Rigaku X-ray diffractometer, operated condition: 40 kV, 300 mA, and Cu-K α radiation). The crystallite size was calculated using Sherrer's formula, defined as follows:

$$D = (K\lambda) / (B \cos\theta) \quad (1)$$

where D is the crystallite size, K is the constant depended on crystallite shape (we used 0.9), λ is the wavelength of the incident X-rays (0.15406 nm), B is full width of half maximum (FWHM) of integral breadth and θ is the diffraction angle.

3. RESULTS AND DISCUSSION

3.1 Crystal size and crystal phases

Copper loaded CeO₂ samples

Fig. 1 shows XRD patterns of copper impregnated CeO₂ samples calcined and reduced at 300 °C for 2 hours. The XRD spectra containing characteristic fluorite peaks of CeO₂ point to well crystallized powders. From the Sherrer's formula (1) and FWHM of (111), (200), (220), (311) and (400) peaks, we determined the crystallite size of CeO₂. The calculated CeO₂ particle size of the calcined and reduced samples at 300 °C was approximately 56 nm and 51 nm, respectively. After calcination procedure the XRD spectrum shows CuO patterns, while in the case of the reduced sample there are metallic copper peaks. The CuO average particle size calculated from (111) and (-111) peaks is 25 nm (see Fig. 1 b) and Cu average particle size in calculated from (111) and (200) peaks is around 62 nm (see Fig. 1 a).

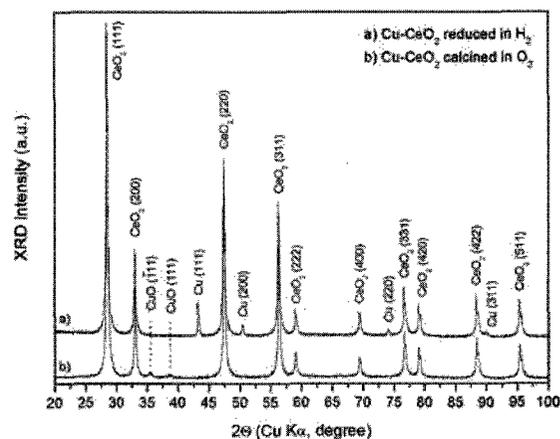


Fig. 1 X-ray diffraction patterns of copper loaded CeO₂ (a) reduced in hydrogen and (b) calcined in oxygen; all treatments were carried out at 300 °C for 2 hours.

Copper loaded SnO₂ samples

The XRD data from the copper impregnated SnO₂ sample, after calcination (a) and reduction (b) procedures are presented in Fig. 2. After calcination procedure the sample contains nano-crystalline particles of CuO. In the case of reduced sample patterns of the Cu-Sn alloys – concretely Cu₃Sn and Cu₆Sn₅ species – were found in the XRD spectrum.

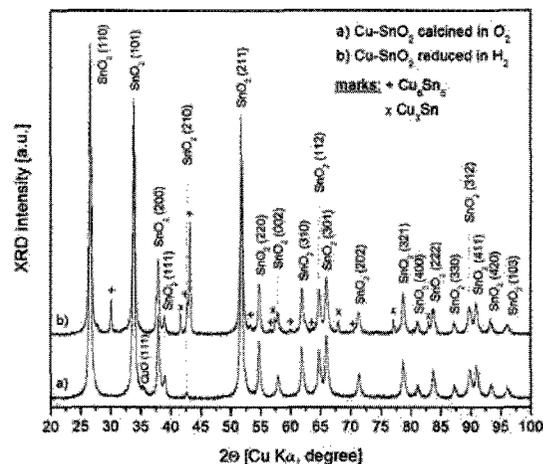


Fig. 2 X-ray diffraction patterns of copper loaded SnO₂ (a) calcined in oxygen and (b) reduced in hydrogen; all treatments were carried out at 400 °C for 2 hours.

The SnO₂ particle size calculated using Sherrer's formula (1) from (110), (101), (211), (200) and (220) peaks was about 45 nm. The particle size of Cu₆Sn₅ species calculated from (-113) peak was about 75 nm. In the case of Cu₃Sn species the particle size calculated from (002c) and (083c) was about 73 nm.

3.2 Particle morphology

For characterization of obtained samples, the particle morphologies were observed using Scanning Electron Microscopy (SEM).

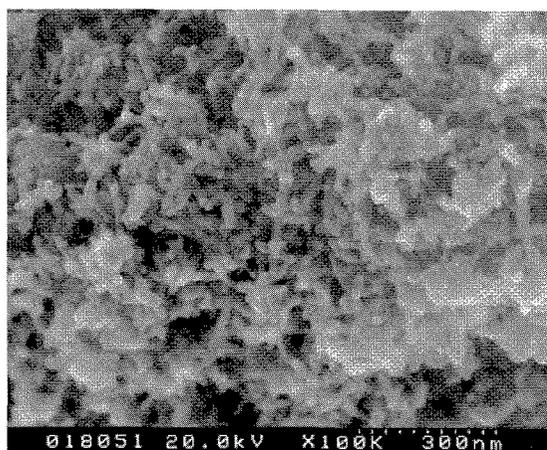


Fig. 3 SEM image of copper loaded CeO_2 calcined at 300°C for 2 hours.

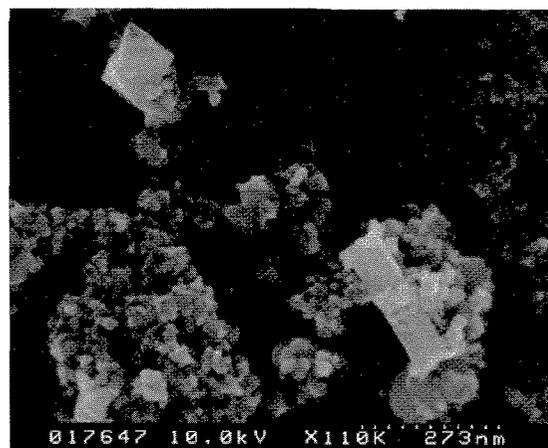


Fig. 4 SEM image of copper loaded CeO_2 reduced in the mixture of hydrogen and helium (10 % H_2 , He in balance) at 300°C for 2 hours.

The SEM images of the calcined and reduced copper loaded ceria are displayed in **Fig. 3** and **4**, respectively. The calcined ceria powder (see **Fig. 3**) contains the elongated particles and particles of non specific shape. From the previous work we know that these elongated particles are created by copper oxide [19]. The diameter of elongated particle is about 30 nm which corresponds very well with the size calculated from XRD data.

In the case of copper loaded SnO_2 , between calcined and reduced sample there is almost no difference in particle size and shape as can be seen in **Fig. 5** and **6**. This uniform particle size of calcined and reduced copper loaded SnO_2 sample is in a good agreement with XRD results.

3.3 CO oxidation reaction

The results of investigation of the catalytic properties for CO oxidation reaction over copper impregnated CeO_2 and SnO_2 catalysts are displayed in **Fig. 7**. All lines in this graph are calibrated to the partial pressure of helium.

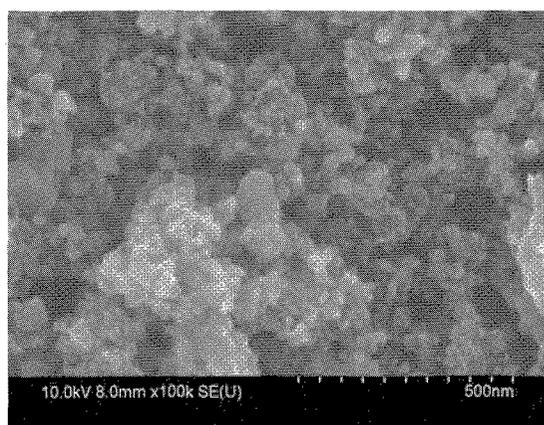


Fig. 5 SEM image of copper loaded SnO_2 calcined at 400°C for 2 hours.

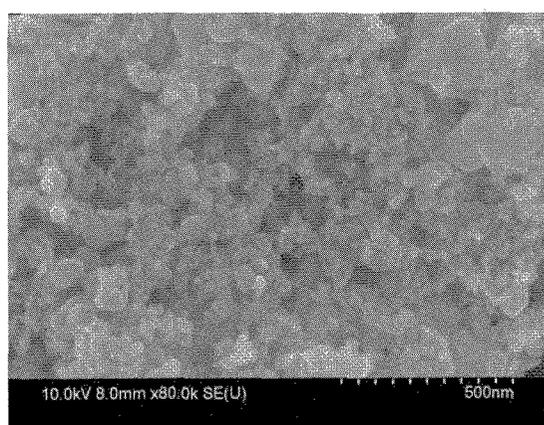


Fig. 6 SEM image of copper loaded SnO_2 reduced in the mixture of hydrogen and helium (10 % H_2 , He in balance) at 400°C for 2 hours.

In the case of copper loaded CeO_2 system, the CO oxidation starts at much lower temperature than in the case of copper loaded SnO_2 . Also the activity of reaction is higher over the first mentioned system. In both cases the powders calcined in oxygen show better properties (start of the reaction at lower temperature and higher activity) than reduced samples; over copper loaded SnO_2 this difference is even more evident.

The reaction curves in **Fig. 7** can be characterized by the reaction temperature T_{50} at 50% yield of CO_2 in CO oxidation reaction. For calcined and reduced copper impregnated CeO_2 powders T_{50} is about 190°C , and the reaction curves start to increase below 100°C .

For the copper impregnated SnO_2 powders it is difficult to determine the characteristic temperature, because the curves do not reach the maximum. The temperature of increasing signal CO_2 is below 200°C and about 240°C for calcined and reduced, respectively.

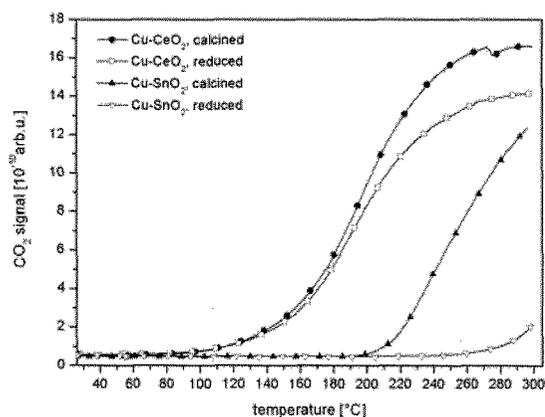


Fig. 7 The CO oxidation reaction over copper loaded CeO₂ catalysts (●) calcined in O₂, (□) reduced in H₂ and copper loaded SnO₂ catalysts (▲) calcined in O₂ and (▽) reduced in H₂.

4. SUMMARY

We prepared nano-sized copper loaded CeO₂ and SnO₂ catalytic systems using impregnation method. The obtained powders were characterized using XRD, SEM and reaction experiments.

The calcined copper impregnated CeO₂ powder contains elongated particles – CuO – of 25 nm in diameter, while in the reduced sample copper is in a metallic form. The copper loaded SnO₂ after calcination contains nano-crystalline particles of CuO. In the reduced copper impregnated SnO₂ catalyst we found two types of Cu-Sn alloys – Cu₃Sn and Cu₆Sn₅. No Cu-Ce or Cu-Sn species were observed in the calcined samples.

To characterize obtained catalysts, CO oxidation reaction over prepared systems was examined using a micro catalytic flow reactor. The temperature of 50 % CO₂ yield in CO oxidation reaction over copper loaded CeO₂ catalyst is around 190 °C, whilst in the case of copper loaded SnO₂ system T₅₀ is over 240 °C. We suppose that for the low temperature CO oxidation reaction it is responsible the interaction between copper and cerium oxide. For CO oxidation reaction, the copper loaded ceria system is more suitable than copper loaded SnO₂ system.

REFERENCES

- [1] D. R. Mullins, S. H. Overbury and D. R. Huntley, *Surf. Sci.*, **409** (1998) 307.
- [2] T. Mori, Y. Wang, J. Drennan, G. Auchterlonie, J.-G. Lic, T. Ikegami, *Solid State Ionics* **175** (2004) 641-649.
- [3] W. Liu, A. F. Sarofim and M. Flytzani-Stephanopoulos, *Chem. Eng. Sci.*, **49** (1994) 4871.
- [4] W. Liu, M. Flytzani-Stephanopoulos, *J. Catal.*, **153** (1995) 304.
- [5] X. Tang, B. Zhang, Y. Li, Y. Xu, Q. Xin, W. Shen, *Catal. Today*, **93-95** (2004) 191.
- [6] F. J. Janssen, *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knozinger, and J. Weitkamp, Eds., Vol. 4 (1997) 1633.
- [7] P. Bera, S. T. Aruna, K. C. Patil and M. S. Hedge, *J. Catal.*, **186** (1999) 36.
- [8] M. Sauvan, C. Pijolat, *Sensors and Actuators B* **58** (1999) 295.
- [9] O.V. Safonova, G. Delabouglise, B. Chenevier, A. M. Gaskov, M. Labeau, *J. Mat. Sci. & Ing. C* **21** (2002) 105-111.
- [10] B.W. Licznarski, K. Nitsch, H. Teterycz, K. Wisniewski, *Sensors & Actuators B* **79** (2001) 157-162.
- [11] M. Anton, B. Büdy, *Sensors & Actuators, B* **18-19** (1994) 500-501.
- [12] M.N. Rumyantseva, M. Labeau, J.P. Senateur, G. Delabouglise, M.N. Boulova, A.M. Gaskov, *Mater. Sci. Eng. B* **41** (1996) 228-234.
- [13] T. W. Capehart, S.C. Chang, *J. Vac. Sci. Technol. A* **18(2)** (1981) 393.
- [14] A. Galdikas, A. Mironas, A. Šetkus, *Sensors and Actuators B* **26-27** (1995) 29.
- [15] J. Tamaki, T. Maekawa, N. Miura, N. Yamazoe, *Sensors and Actuators B* **9** (1992) 197.
- [16] M.N. Rumyantseva, M. Labeau, J.P. Senateur, G. Delabouglise, M.N. Boulova, A.M. Gaskov, *Mater. Sci. Eng. B* **41** (1996) 228-234.
- [17] J. Tamaki, K. Shimano, Y. Yamada, Y. Yamamoto, N. Miura, N. Yamazoe, *Sensors and Actuators B* **49** (1998) 121-125.
- [18] A. Chowdhuri, V. Gupta, K. Sreenivas, *Sensors and Actuators B* **93** (2003) 572-579.
- [19] B. Šmíd, T. Mori, M. Takahashi, D.-R. Ou, V. Matolin and I. Matolinová, *Advanced Materials Research Vols. 15-17* (2007) 261-266.

(Received January 5, 2007; Accepted September 1, 2007)