

# TPR, TPO and TPD Examination of $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-y}$ Mixed Oxide Catalyst Prepared by Co-precipitation Synthesis

Albin Pintar\*, Jurka Batista, Stanko Hoever

Laboratory for Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, P.O. Box 660, SI-1001 Ljubljana, Slovenia

This is a condensed article submitted to Micromeritics. The full version of this article can be found on our website at [www.micromeritics.com/applications/articles.aspx](http://www.micromeritics.com/applications/articles.aspx)

## Introduction

The use of  $\text{CeO}_2$  and  $\text{CeO}_2$ -containing materials as a component of heterogeneous industrial catalysts or as a support for transition metals is based on superior chemical and physical stability, high oxygen mobility, and high oxygen vacancy concentrations, which are characteristic for the fluorite-type oxides (economically and technologically most important application is the use of ceria in the three-way automotive exhaust catalysts as a thermal stabilizer and oxygen storage medium [1]). In this work, we report on the characterization of a  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-y}$  mixed oxide catalyst (prepared by a co-precipitation method and will be referred to as CuCe-1) TPR, TPO, and TPD. These techniques will be demonstrated as an efficient set of tools to obtain information about the redox behavior of this solid. This information is important for designing CuO-CeO<sub>2</sub> catalysts that can replace the expensive noble metal catalysts in a number of down-stream processes, including the production of H<sub>2</sub>-rich gas streams from fossil and renewable fuels for use as a fuel for the proton exchange membrane fuel cells (PEMFC).

## BET, TPR, TPO, and TPD Measurements

Single-point BET surface area, temperature-programmed reduction (TPR) with hydrogen, temperature-programmed oxidation (TPO) with oxygen, temperature-programmed desorption (TPD) of hydrogen, temperature-programmed desorption of oxygen, and hydrogen pulse chemisorption measurements of CuCe-1 sample were performed by means of an automated catalyst characterization system (Micromeritics' AutoChem II 2920), which incorporates a thermal conductivity detector (TCD).

The TPR measurements were carried out following activation and after cooling the sample in helium flow to 0 °C. Then the TPR experiments were performed up to a temperature 400 °C at which the sample was maintained for 30 min. In order to verify that mass transfer limitations do not affect the TPR measurements, we have carried out TPR experiments at different sample loadings (*i.e.*, 0.10 and 0.25 g).

The TPO experiments were performed following TPR after cooling the samples in H<sub>2</sub>(5 vol. %)/Ar flow to 0 °C. After that O<sub>2</sub>(10 vol. %)/He gas mixture

was passed over the samples which were heated to 400 °C and then held at 400 °C for 1 h. To examine the reproducibility of TPR profiles after the reoxidation, the sample was cooled in helium flow to 0 °C at the end of the TPR-1/TPO cycle and then the second reduction run (TPR-2) was carried out under the same reaction conditions as the first run.

The TPD-H<sub>2</sub> was performed following the TPR experiments after cooling the reduced sample in H<sub>2</sub>(5 vol. %)/Ar gas mixture flow to -20 °C. After that the TPD-H<sub>2</sub> experiment was carried out up to a temperature of 650 °C, at which the sample was held for 30 min.

The TPD-O<sub>2</sub> was carried out on the activated sample, which was cooled in O<sub>2</sub>(10 vol. %)/He gas mixture flow to -20 °C. The TPD-O<sub>2</sub> measurement was performed up to a temperature of 400 °C, at which the sample was held for 6 h. The hydrogen pulse chemisorption measurements of CuCe-1 sample were applied after TPD-O<sub>2</sub> measurements to find out whether a chemisorption of hydrogen occurred at temperature close to 0 °C (*i.e.*, during TPR runs). The sample was degassed and cooled under

flowing argon to  $-5\text{ }^{\circ}\text{C}$ , at which pulses of  $\text{H}_2$  (5 vol. %)/argon were injected into a stream of Ar flowing through the sample bed.

### Results and Discussion

Interaction of hydrogen with  $\text{Cu}_x\text{Ce}_{1-x}\text{O}_{2-y}$  mixed oxides during TPR involves the adsorption of hydrogen on all active sites of the cerium oxide surface, storage of hydrogen in the host oxide, and reduction of the CuO component [2]. The qualitative and quantitative characterization of reducibility and reoxidability of different types (*i.e.*, well-dispersed, bulk-like) of copper ions present in the prepared CuCe-1 mixed oxide are determined by TPR and TPO measurements carried out in the temperature range from 0 to  $400\text{ }^{\circ}\text{C}$  (Figure 1). Fig. 1a confirms that highly dispersed copper ions in nanocrystalline  $\text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-y}$  can be readily reduced and oxidized at temperatures as low as  $200\text{ }^{\circ}\text{C}$  [3]. The extent of further reoxidation of  $\text{Cu}^0$  to  $\text{Cu}^{2+}$ , partial consumption of hydrogen stored in reduced samples, and storage of oxygen during the TPO run are illustrated in Fig. 1b.

Evidently, the total hydrogen

consumption of CuCe-1 solid is larger than the value expected for a complete reduction of the CuO component to  $\text{Cu}^0$  (Table 1). The additional hydrogen consumption may be due to surface reduction of  $\text{CeO}_2$  [2]. During the reduction process, storage of hydrogen in the oxide, mainly in the bulk (*i.e.*, formation of bronze-like species) and further reaction of these activated hydrogen species with the lattice oxygen ions at  $T > 230\text{ }^{\circ}\text{C}$  can take place [4].

Fig. 1a shows that the CuCe-1 sample starts to be reduced at temperatures below  $100\text{ }^{\circ}\text{C}$ . The reduction steps as well as the simultaneous incorporation of hydrogen into the catalyst structure is completed at temperatures below  $250\text{ }^{\circ}\text{C}$ . Data shown in Table 1 confirm that in the performed TPR analysis complete reduction of CuO phases was obtained. At least two peaks could be distinguished on the TPR profile of CuCe-1: a very small peak with a maximum at  $T = 90\text{ }^{\circ}\text{C}$  and a large reduction peak with a maximum at  $155\text{ }^{\circ}\text{C}$  (Fig. 1a). The total hydrogen uptake obtained from the integrated area is  $36.2\text{ ml H}_2/\text{g}_{\text{solid}}$ ,

which is higher than the equivalent stoichiometric total oxygen consumption of  $15.3\text{ ml O}_2/\text{g}_{\text{solid}}$  (Table 1).

Subsequently, deconvolution of TPR profile illustrated in Fig. 1a was performed. Three peaks were sufficient to accurately describe  $\text{H}_2$  consumption during the reduction of CuCe-1 sample. This suggests that the reduction of intermediate  $\text{Cu}^+$  phases to  $\text{Cu}^0$  proceeds much faster in comparison to the  $\text{Cu}^{2+} \rightarrow \text{Cu}^+$  reduction step. The mathematical analysis of TPR profile illustrated in Fig. 1a reveals that the storage of  $\text{H}_2$  into the catalyst structure occurs in parallel to the reduction of CuO (or  $\text{Cu}_2\text{O}$ ) phases. It is interesting to note that the amount of  $\text{H}_2$  incorporated into the catalyst structure, calculated by means of the performed deconvolution analysis, is in good agreement with the results of TPR analysis (Table 1).

Fig. 1b shows a profile obtained during the TPO analysis of pre-reduced CuCe-1 sample. It should be noted that no oxygen was consumed at  $T \leq 0\text{ }^{\circ}\text{C}$ . It was also verified by means of pulse chemisorption measure-

**Table 1.** Results of TPR-1, TPO, TPR-2, TPD- $\text{H}_2$  and TPD- $\text{O}_2$  analyses of CuCe-1 mixed oxide sample.

Analyses	CuCe-1	Analyses	CuCe-1
<i>TPR-1</i>		<i>TPD-<math>\text{H}_2</math> up to 650! C</i>	
total $\text{H}_2$ uptake, $\text{ml/g}_{\text{solid}}$	36.2	desorbed $\text{H}_2$ , $\text{ml/g}_{\text{solid}}$	4.7
stored $\text{H}_2$ (HSC <sub>1</sub> ), $\text{ml/g}_{\text{solid}}$	15.0 (41 %) <sup>a</sup>	rest of $\text{H}_2$ , $\text{ml/g}_{\text{solid}}$	10.3
<i>TPO</i>		<i>irreversibly captured <math>\text{H}_2</math>, %</i>	
total $\text{O}_2$ uptake, $\text{ml/g}_{\text{solid}}$	15.3		69
partial $\text{O}_2$ uptake, $\text{ml/g}_{\text{solid}}$	4.8 (31 %) <sup>b</sup>	<i>TPD-<math>\text{H}_2</math> up to 400! C</i>	
remained $\text{H}_2$ , $\text{ml/g}_{\text{solid}}$	5.4 (36 %) <sup>c</sup>	desorbed $\text{H}_2$ , $\text{ml/g}_{\text{solid}}$	3.9
<i>TPR-2</i>		rest of $\text{H}_2$ , $\text{ml/g}_{\text{solid}}$	11.1
total $\text{H}_2$ uptake, $\text{ml/g}_{\text{solid}}$	36.2	irreversibly captured $\text{H}_2$ , %	74
stored $\text{H}_2$ (HSC <sub>2</sub> ), $\text{ml/g}_{\text{solid}}$	15.0	<i>TPD-<math>\text{O}_2</math> up to 400! C</i>	
HSCC, $\text{ml/g}_{\text{solid}}$	$\nabla 20.4$	desorbed $\text{O}_2$ , $\text{ml/g}_{\text{solid}}$	0.8

<sup>a</sup>Part of  $\text{H}_2$  consumed for incorporation into the catalyst structure.

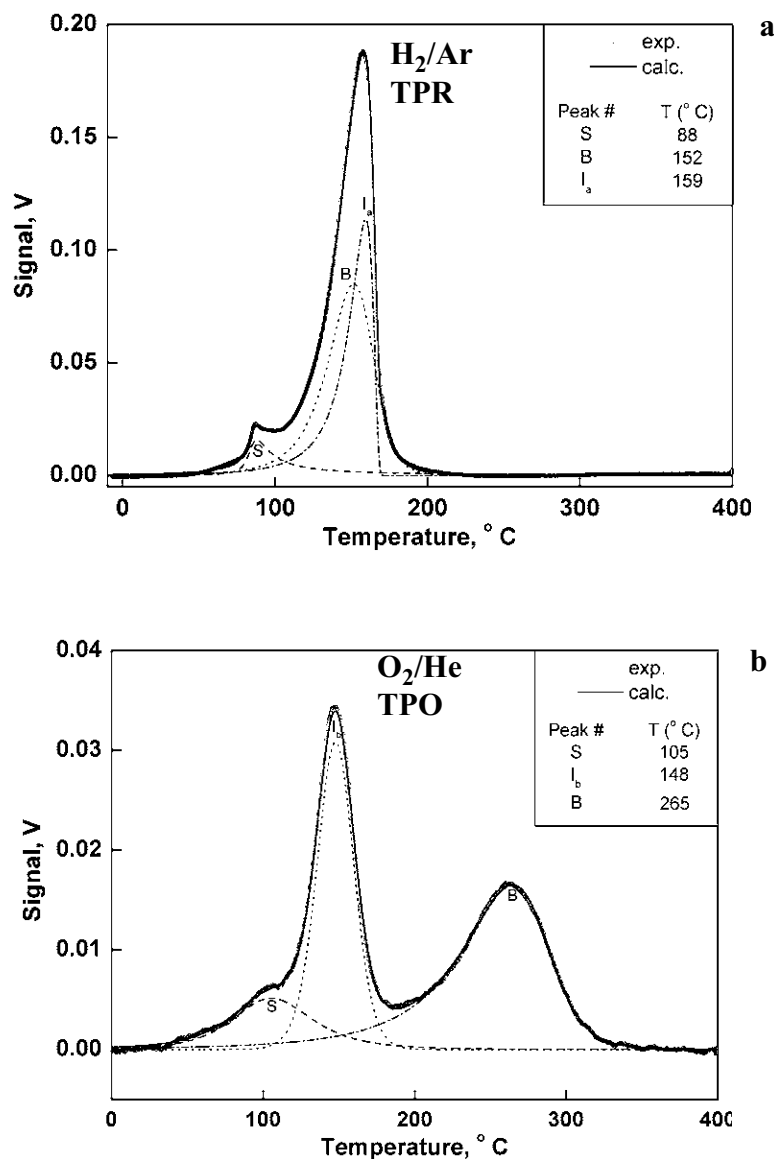
<sup>b</sup>Part of  $\text{O}_2$  consumed in a reaction with  $\text{H}_2$  stored in the catalyst structure.

<sup>c</sup>Part of  $\text{H}_2$  stored in the catalyst structure after the completion of TPO analysis.

ments carried out at  $T = 0^\circ\text{C}$  that no  $\text{O}_2$  was consumed during the preceding detector stabilization period (5 min), in which a catalyst sample was exposed to the oxygen stream. As Fig. 1b shows, the TPO profile measured during the reoxidation of CuCe-1 sample was satisfactorily simulated by assuming the following processes: (i) reoxidation of the well-dispersed Cu phase; (ii) reoxidation of the segregated Cu phase; (iii) consumption of  $\text{H}_2$  stored in the catalyst structure. The calculated relative surface areas of peaks belonging to the reoxidation of well-dispersed (17 %) and segregated (83 %) Cu phases, are very close to the corresponding TPR-1 values. Furthermore, the calculated relative surface area of the  $I_b$  peak belonging to the consumption of  $\text{H}_2$  stored in the catalyst structure, equals to 35 %, which is close to 31 %, calculated from the results of TPO analysis (Table 1). It is reported in Table 1 that significant amount of hydrogen (36 %) remained captured in CuCe-1 sample after the completion of TPO analysis conducted in the temperature range of 0-400 °C.

The second reduction of catalyst sample examined in this study was performed and compared to those measured during the TPR-1 analysis. It was found that the TPR-2 profile is shifted towards higher temperatures. This shift is the consequence of substantial decrease of the sample volume (up to one third), which occurred during the TPR-1 analysis. Partially, the shift might be attributed also to the fact that the BET surface area drops considerably after TPR-1 analysis (from 44 to 21  $\text{m}^2/\text{g}$ ). However, this cumulative effect was less pronounced for the CuCe-1 sample (a temperature shift of only 5 °C was noted). Interestingly, the same number of peaks (3) was used to satisfactorily simulate

**Figure 1.** TPR-1 (a) and TPO (b) profiles of CuCe-1 sample measured in the temperature range of 0-400 °C and predicted by means of deconvolution method. Operating conditions: 50 ml/min (STP),  $\text{H}_2$ (5 vol. %)/Ar (a),  $\text{O}_2$ (10 vol. %)/He (b), 5° C/min. Sample weight, 250 mg. The initial state of (b) is fresh sample following TPR-1 run, cooling in  $\text{H}_2$ (5 vol. %)/Ar to 0° C and purging at 0° C with pure Ar. Designation of peaks: S – well-dispersed CuO species; B – bulk-like CuO phase;  $I_a$  –  $\text{H}_2$  incorporation in the catalyst structure;  $I_b$  – consumption of  $\text{H}_2$  incorporated in the catalyst structure during the TPR-1 analysis.



the TPR-2 profile by means of the deconvolution method as was in the case of TPR-1 analysis. Although the BET surface area changes considerably during the TPR-1 analysis, these findings suggest that the interface between the CuO and CeO<sub>2</sub> phases is not modified significantly.

It is evident from Table 1 that significant quantities of hydrogen were stored in the structure of CuCe-1 sample during the TPR-1 analysis. It is also shown that hydrogen initially incorporated in CuCe-1 sample was only partially consumed in the subsequent reoxidation step conducted in the temperature range of 0-400 °C. Since the amounts of hydrogen consumed during the TPR-1 and TPR-2 analyses of CuCe-1 sample were found to be equal, this means that the complete hydrogen storage capacity (HSCC) of this solid was not achieved in the first reduction step. On the basis of the performed analysis, it is concluded that the HSCC for CuCe-1 sample is higher than 20.4 ml H<sub>2</sub>/g<sub>solid</sub>.

TPD-H<sub>2</sub> profiles of pre-reduced CuCe-1 sample were measured at temperatures up to 650 °C. This analysis reveals that very small amount of H<sub>2</sub> was physisorbed on the catalyst surface and that the majority of H<sub>2</sub>

stored in the catalyst during the TPR analysis was chemisorbed. H<sub>2</sub> desorption occurred in a wide temperature range, and two wide peaks are noted. Although high temperature of desorption was applied, hydrogen was not completely removed from the structure of CuCe-1 sample, which implies that major part of incorporated H<sub>2</sub> is irreversibly chemisorbed in this solid. For illustration, only about 26 % of hydrogen was desorbed from the CuCe-1 sample in the temperature interval of 0-400 °C.

The TPD-O<sub>2</sub> profile of CuCe-1 sample pre-calcined at 400 °C lies in a very short range of TCD signals, which alludes that in the applied temperature range of 0-400 °C the examined solid exhibits, in comparison to measured TPD-H<sub>2</sub> values, lower ability for the exchange of oxygen. The amount of desorbed oxygen for given temperature range is listed in Table 1. It is seen that TPD-O<sub>2</sub> values are about 3 to 5 times lower compared with TPD-H<sub>2</sub> data obtained in the same temperature range.

In conclusion, the results of this study reveal that despite drastic drop in specific surface area of fresh CuCe-1 sample after the consecutive TPR-H<sub>2</sub>/TPD-H<sub>2</sub> treatments, which implies severe morphological changes of the sample, the redox behavior

remains nearly unchanged as both the total hydrogen consumption and hydrogen storage capacity remain constant during successive TPR cycles (TPR-1/TPO/TPR-2). In the future, determination of specific surface area of CuO in calcined Cu<sub>x</sub>Ce<sub>1-x</sub>O<sub>2,y</sub> catalyst as well as dispersion of Cu<sup>0</sup> in reduced solid will be investigated by means of selective NO and N<sub>2</sub>O chemisorption, respectively [5,6].

## References

- [1] A. Trovarelli, Catal. Rev. - Sci. Eng. 38(4) (1996) 439.
- [2] Krašovec, B. Orel, A.S. Aricó, H. Kim, Appl. Catal. B 28 (2000) 113.
- [3] C. Lamonier, A. Bennani, A. D'Huysser, A. Aboukaïs, G. Wrobel, J. Chem. Soc., Faraday Trans. 92(1) (1996) 131.
- [4] A. Tschöpe, M.L. Trudeau, J.Y. Ying, J. Phys. Chem. B 103 (1999) 8858.
- [5] J.L.G. Fierro, J. Soria, J. Sanz, J.M. Rojo, J. Solid State Chem. 66 (1987) 154.
- [6] R.M. Dell, F.S. Stone, P.F. Tiley, Trans. Faraday Soc. 49 (1953) 195.
- [6] J.C. Kenvin, M.G. White, J. Catal. 130 (1991) 447.

## (Footnotes)

\*Corresponding author.  
Phone: +386-1-47-60-282; fax:  
+386-1-47-60-300. E-mail:  
albin.pintar@ki.si.