

XPS studies of yttria-stabilized zirconia interfaced with Pt nanoparticles for carbon monoxide and ethylene electrooxidation

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Yttria-stabilized zirconia (YSZ) has been extensively studied in fuel cell and gas sensor technologies in the last decades due to its good O^{2-} ionic conductivity at temperatures higher than 400°C. Recently, YSZ has attracted considerable attention as a promising catalyst support in heterogeneous catalysis and electrochemical promotion of catalysis (EPOC). It has been shown that the strong metal-support interaction between Pt nanoparticles and YSZ enhances the catalytic activity of the catalyst for oxidation of volatile organic compounds (VOC) [1]. Moreover, it has been reported recently that Pt nanoparticles (~ 2.5nm) supported on YSZ exhibited high catalytic activity towards CO and C_2H_4 electrooxidation in oxygen-free gas environment at low temperatures [2]. It was proposed that strong metal support interaction (SMSI) between Pt nanoparticles and YSZ results in O^{2-} transfer towards Pt through the triple phase boundary (tpb) and electron transfer from Pt to the support. This charge transfer can affect the catalytic activity of Pt/YSZ for CO and C_2H_4 electrooxidation in the absence of O_2 in the gas feed.

X-ray photoelectron spectroscopy (XPS) has been used as a powerful tool in order to investigate the surface structure of various materials. The main advantage of XPS is that it can give important information concerning the surface composition [3].

In the present study, XPS is applied to investigate the changes in the chemical composition of YSZ support interfaced with Pt nanoparticles of three well defined particle sizes (2.2, 3.8, 4.2 ± 0.5 nm) before and after the reaction of CO and C_2H_4 electrooxidation in oxygen-free gas environment. To this end, XPS measurements of the samples before and after the reaction were performed and a correlation of the surface properties and the catalytic activity takes place.

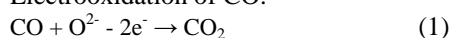
Pt nanoparticles are synthesized using the modified polyol method in ethylene glycol [4]. In this way Pt nanoparticles with three different particle size were prepared: namely 2.2 (Pt/YSZ-1), 3.8 (Pt/YSZ-2) and 4.4 (Pt/YSZ-3) nm. Pt colloids were deposited on YSZ (Tosoh, SSA = 13m²/g). by taking appropriate amount of the colloids and mixing them with 1.5 g of YSZ The total Pt metal loading was 1wt%.

Catalytic activity measurements were carried out at atmospheric pressure in a continuous flow U-shaped quartz reactor in the temperature range of 40 - 400°C. The reactant and product gases were analyzed by an on line

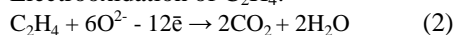
gas chromatograph (GowMac 350) and non-dispersive infrared (NDIR) gas analyzer (HORIBA VA-3001).

It was found that CO and C_2H_4 conversion in the absence of O_2 in the gas feed is strongly particle-size dependent. The lowest catalytic activity is observed for the largest Pt particles and it increases significantly as the Pt particle size decreases. An increase of 30% in CO conversion is observed for temperatures lower than 100°C, whereas C_2H_4 oxidation at Pt YSZ-1 already takes place at temperatures as low as 50°C. High catalytic activity of the smaller Pt nanoparticles can be due to the extended tpb and formation of the larger amount of the galvanic cells allowing the following electrochemical reactions to take place [2]:

Electrooxidation of CO:

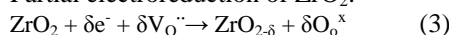


Electrooxidation of C_2H_4 :

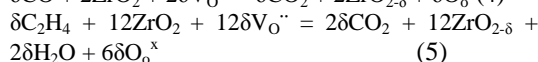
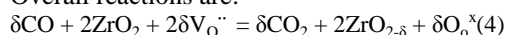


Cathodic reaction at tpb:

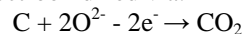
Partial electroreduction of ZrO_2 :



Overall reactions are:



Detailed XPS analysis of the spent catalysts has shown that the signal of C1s peak increases after the reaction. This indicates that the sample is covered by a C-containing deposit. The increase is around 60% in the case of Pt/YSZ-1 but it is only around 30% of the less active sample (Pt/YSZ-3). This might confirm that some carbon deposition is taking place during the reaction. The deposited carbon is electrooxidized via:



On the other hand, the O1s spectrum after the reaction shows an increase in the intensities of the components at higher binding energies. These are characteristic of the chemisorbed oxygen species which increases in the case of the most active sample (Pt/YSZ-1) while it shows no significant changes for the sample with the largest Pt particles (Pt/YSZ-3). Analysis of the characteristic peaks of zirconium and yttrium was carried out and results will be discussed and correlated to the observed catalytic activities.

The need to investigate the effect of the particle size on the surface properties and consequently on the overall performance of the obtained catalysts is of significant importance for the design of "state of the art" catalysts. XPS can give important information towards this direction.

References:

1. P. Vernoux, M. Guth, X. Li, *Electrochem. Solid-St. Lett.* 12 (2009) E9.
2. R.J. Isaifan, E. Baranova, *Electrochem. Commun.*, 27 (2013) 164.
3. S. Ladas, S. Kennou, S. Bebelis, C.G. Vayenas, *J. Phys. Chem.* 97 (1993) 8845.
4. E. Baranova, C. Bock, D. Ilin, D. Wang, B. Macdougall, *Surf. Sci.*, 600 (2006) 3502.