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NICKEL-DOPED ALUMINA

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ABSTRACT

Alumina powders, pure and doped with nickel, were synthesized by sol gel method and calcined at 500°C in order to obtain mesoporous structures with a high specific surface area, well adaptable to catalytic application. XRD analysis showed that the addition of Ni^{2+} affect the structural properties of the synthesized oxides. In order to test electrochemical activity of introduced nickel GCE modified with synthesized material was tested in 0.1 M NaOH solution without and with methanol.

INTRODUCTION

Transition aluminas are important in the of various catalysis fields because of their high specific surface areas, surface property and crystalline structure [1–4]. The role of alumina in the catalyst system is often assumed to be purely physical acting as an inert solid onto which a catalyst can be dispersed. However, the surface of alumina is chemically reactive and acts as a catalyst for many acid/base reactions [1,5]. The surface reactivity of an alumina phase depends on the preparation conditions and sample history. There are various crystal structures for alumina and the obtained phases depend on the precursor, additives and the calcinations conditions. The sol–gel process is the most studied chemical method to prepare nanostructured materials [6]. This process allows the easy preparation of very diverse mesoporous structures.

The aim of this paper was to investigate the chemical state of Ni in alumina doped samples and its effect on structure and texture of alumina-based electrodes on electrochemical response.

EXPERIMENTAL

Alumina powders, pure and doped with nickel, were synthesized by sol gel method [7] and calcined at 500°C in order to obtain materials with different structural and textural properties. Samples were denoted as A-500, A10-

500, A20-500, A40-500, to indicate temperature of calcinations and the amount of nickel added to sample. The X-ray powder diffraction measurements were performed on a PHILIPS 1050 X-ray diffractometer using Ni-filtered Cu Kα radiation and Bragg-Brentano focusing geometry. The patterns were taken in the 5–90 °2θ range with the step length of 0.058 °2θ and exposure time of 5 s per step. The drop of dispersion of investigated sample in 5 wt. % Nafion was applied on the surface of glassy carbon electrode. The electrochemical response of samples was tested by cyclic voltammetry in 0.1 M NaOH with and without methanol. All potentials are reported versus Ag/AgCl (3 M KCl) reference electrode, and platinum rod served as counter electrode.

RESULTS AND DISCUSSION

Introduction of nickel species in alumina matrix resulted in materials with different properties from starting alumina. In order to test electrochemical activity of introduced nickel GCE modified with synthesized material was tested in alkaline solution (Fig. 1a and b). Cyclic voltammograms recorded in 0.1 M NaOH for A10-500 only showed current rise at high anodi potential due to oxygen evolution reaction. With increase of Ni content in sample characteristic Ni(II) → Ni(III) pair of peaks appeared at potential range 0.3 - 0.6 V vs. Ag/AgCl electrode and was well pronounced for A40-

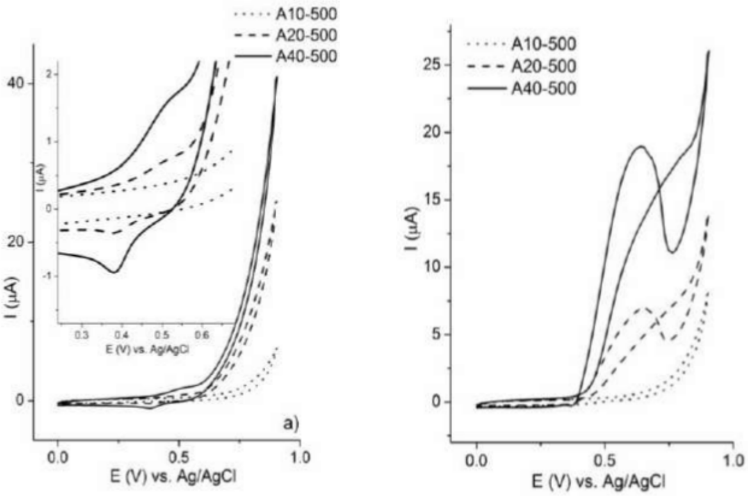

Figure 1. Cyclic voltammograms of alumina samples recorded at 50 mVs^{-1} in 0.5 M NaOH without methanol (left) (Inset: enlarged part of CV in potential range 0.25 V – 0.6 V) and with methanol (right).

500 sample. The redox Ni(II) → Ni(III) originates from electroactive layer of $Ni(OH)_2$ that is formed over NiO upon immersion in alkaline solution. The current of oxygen evolution also increased with increase of Ni content, as expected since Ni-based electrodes are good catalyst for the OER [7]. Further testing was performed in the reaction of methanol oxidation from alkaline solution. The current rise due to methanol oxidation was observed at same potential as the formation of NiOOH. There was no current of NiOOH reduction during reverse scan. The same dependence of current of methanol oxidation on Ni content and calcinations temperature as for the current of NiOOH formation was observed. The characteristic feature of recorded voltammograms is hysteresis between the anodic and the cathodic sweeps, in which a higher methanol oxidation charge is observed in the cathodic sweep. The possible explanations for this behavior are: a) different nature of processed occurring in forward and reverse scan; b) the ratio of methanol and supporting electrolyte concentration and c) the difference of the electrode surface in forward and reverse scan.

The electrochemical activity of nickel-doped alumina samples was dictated by the amount of present NiO. XRD patterns of the pure and Ni^{2+}-doped alumina samples, thermally treated at 500°C, show amorphous character (Fig. 2). Only broad peaks with very low intensity, attributed to the γ-Al_2O_3 are observed at 2θ angle of about 38°, 46° and 67.2°, for pure alumina sample. The intensity of these peaks in the doped samples is reduced proportional to the amount of added nickel. XRD data confirmed the formation of the $NiAl_2O_4$ and the oxides of Ni in all the samples. The presence of NiO_2 is observed in the sample A10-500, whereas, in the samples with higher contents of Ni, the formation of NiO is confirmed and its content increases with increasing amount of added Ni^{2+}-ions. The XRD analysis showed that ratio of $NiO/NiAl_2O_4$ changed in same manner indicating that only NiO was electrochemically active. It is unclear how much Ni inside alumina structure affects the electrochemical response of nickel-doped alumina. According to Ojani et al. [8], who investigated Ni

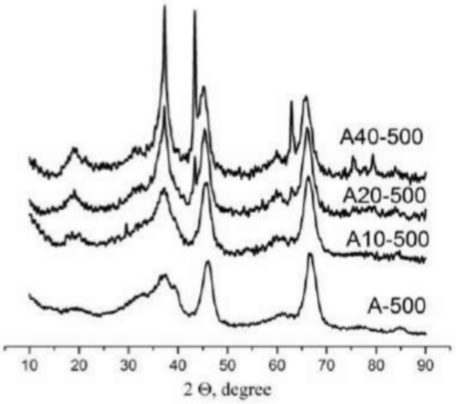

Figure 2. X-ray diffraction patterns of pure and Ni^{2+}- doped alumina samples

modified zeolite Y, the presence of Ni ions inside zeolite cages beside Ni ions present on the surface of the zeolite was essential for good electrochemical activity of NiY. It was proposed that the methanol oxidation takes place on the oxy-hydroxide species formed on the surface of the electrode, while nickel species incorporated in zeolite act as an electron relay to the $Ni(OH)_2$/NiOOH redox system.

CONCLUSIONS

Samples of alumina with different amount of nickel were synthesized by sol gel method and calcined at 500°C. XRD analysis confirmed that all samples have a low ordered structure (almost amorphous), whereby, disorder and crystallites size of the structure of the doped samples are higher in comparison to the structure of the non-doped sample and increase with the Ni^{2+}-content. The electrochemical activity of nickel-doped alumina samples was dictated by the amount of present NiO.

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