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Effect of composition and calcination temperature of ceria-zirconia-alumina mixed oxides on catalytic performances of ethanol conversion

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Abstract. In the present study, we investigated the effect of preparation method, phase composition and calcination temperature of the (Ce-TZP) – Al_2O_3 mixed oxides on their structural features and catalytic performance in ethanol conversion. Ceria–zirconia–alumina mixed oxides with different (Ce+Zr)/Al atomic ratios were prepared via sol–gel method.Catalytic activity and selectivity were investigated for ethanol conversion to acetaldehyde, ethylene and diethyl ether.

1. Introduction

With increased availability and decreased cost, ethanol is potentially a promising molecule for the production of a variety of value-added chemicals [1]. Catalysts and catalytic processes for ethanol conversion to other chemicals such as hydrogen [2], ethyleneand small oxygenates like acetaldehyde is a subject of great interest [3], especially the research of suitable catalysts, supporting materials, operating conditions for high ethanol conversion, and hydrogen selectivity. In considering the reaction of dehydration: the climbing ethylene price and decreased bioethanol cost make bioethanol-to-ethylene conversion very attractive, especially from nonfood biomass feedstock [4].

Receiving ethylene and ether from alcohols on oxide supported catalysts is of particular interest because bio-ethanol, obtained by the fermentation of biomass, is more environmental friendly. This process is also open opportunities for utilization of renewable resources and by-products of chemical processes, such as glycerol. For increasing activity oxide catalysts for this reactions are usually promoted by active metals[5-7].The nature of the active site metal has a strong impact on the selectivity and activity of the ethanol conversion [8-11]

However, the expensive cost of noble metals still limited the widespread application of these catalysts. In this regard, mixed oxides are considered promising catalysts in dehydration and dehydrogenation of alcohols. Metal oxides and their combinations, such as ZrO_2, Al_2O_3 and CeO_2, were found to show high catalytic activity in acid-base and oxidation–reduction reactions, comparing to supported catalysts [12-13].For example supported and modified CeO_2–ZrO_2 and ZrO2-Al2O3 model catalysts have been extensively studied recently [14-16] as a tree way catalyst (TWC).

The aim of this work was the synthesis and study of the catalytic activity of(Ce -TZP)-Al_2O_3systemsin different composition and calcination temperature in the conversion of ethanol.

2. Materials and methods

Sample powders (Ce+Zr)/Al with 25, 50 and 75 wt.% atomic ratios (A10-CZ, A20-CZ, A50-CZ) were prepared by sol-gel method from the precursor solutions $ZrOCl_2$, $Al(NO_3)_3$, $Ce(NO_3)$. Precipitation was carried out with aqueous ammonia at 250ºC for 120 minute. Oxides samples were obtained at 180ºC and 500ºC. The catalysts were characterized by XRD, ASAP and N2-adsorption. Microscopic study of the composites microstructure with/without modifying was carried out by atomic forcemicroscope ”NEXT” (NTMDT) and scanning electron microscope «LEO1420" (CARL ZEISS).Ethanol conversion was carried out at 200°C-400°C with chromatography analysis of gas mixture (FID, helium as a carrier gas). Catalytic activity and selectivity were investigated for conversion of ethanol to acetaldehyde, ethen and diethyl ether (DEE).

3. Results and discussion

As it seen from the XRD pattern (Figure 1) on freshly prepared catalytic systems at 180°C crystalline phases are not identified. At T=180ºC powder contains a substantially amorphous phase, with appearing of tetragonal ZrO_2. At 400ºC begins the formation of the tetragonal pseudo-cubic phase. And at T= 500ºC phase composition of the powder is represented by a crystalline phase of the solid solution based on t-ZrO_2 and amorphous Al_2O_3. This corresponds with the literature data [17-18].

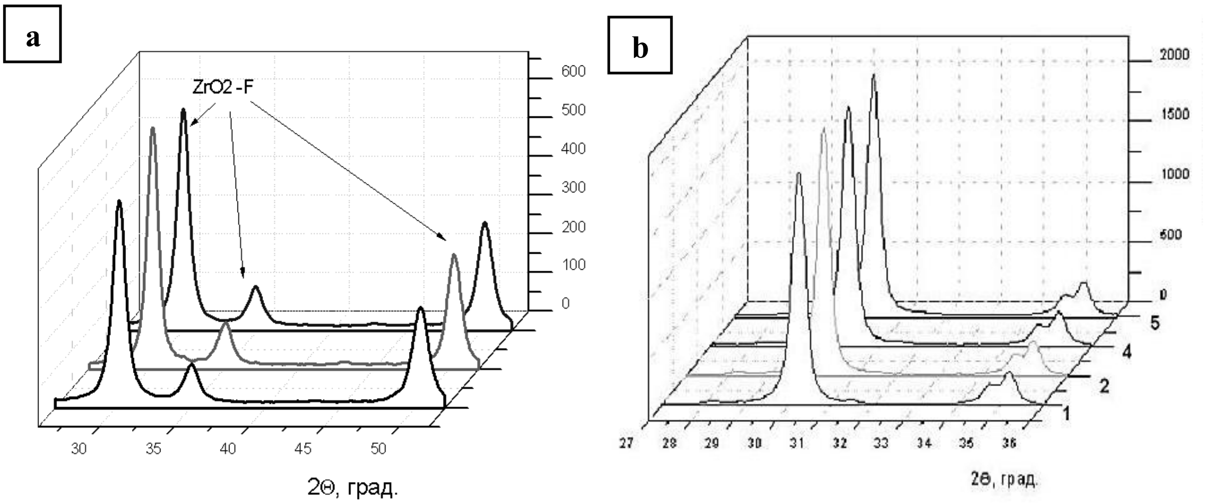

Figure.1 XRD patterns for oxide samples obtained at 180°C (a) and 500°C (b)

The observed differences in phase formation during heat treatment result in different grain size compositions in the microstructure of the compositesthat shown on figure 2(b) and [19-20].On the AFM images (Fig. 2) morphology of surface it could be identified 1-2 μm big grains of α - Al2O3 phase (corundum) with habit close to hexagonal drowned in solid solution of ZrO2 with smooth surface.

The main reaction was dehydration (as well as intramolecular dehydration) with selectivity for olefin and ether 60%. Alcohol dehydrogenation proceeds in parallel (less than 10% conversion). The selectivity is correlated with the catalyst composition and depends on calcination temperature.

Calcination temperature of the catalyst significantly affects the selectivity of the reaction of intermolecular dehydration. For example, for a mixed oxide system with composition A50-CZ selectivity after calcination increases 5 times, and for the sample with the smallest amount of aluminum A10-CZ the selectivity is 5 times less, as illustrated the diagram on Figure 3.

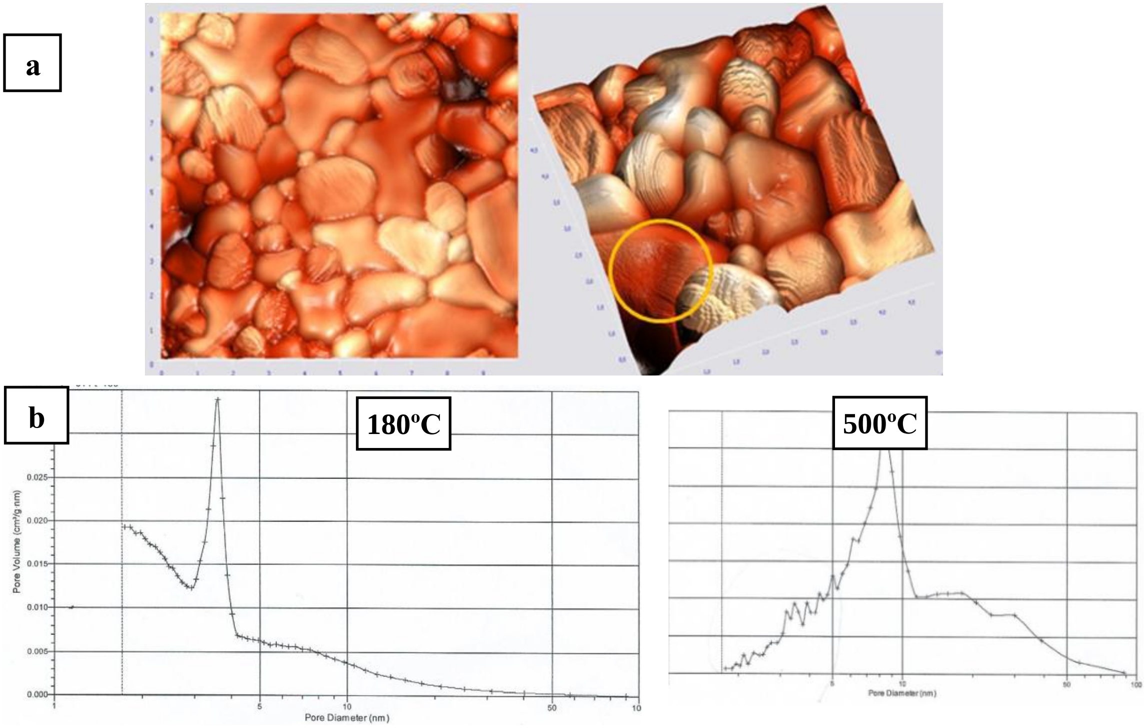

Figure. 2 a) AFM images of the composites (field of view - 10 µm) based on ACZ powders b) Pore volume and pore diameter distribution of amorphous (180°C) and crystalline (500°C) samples.

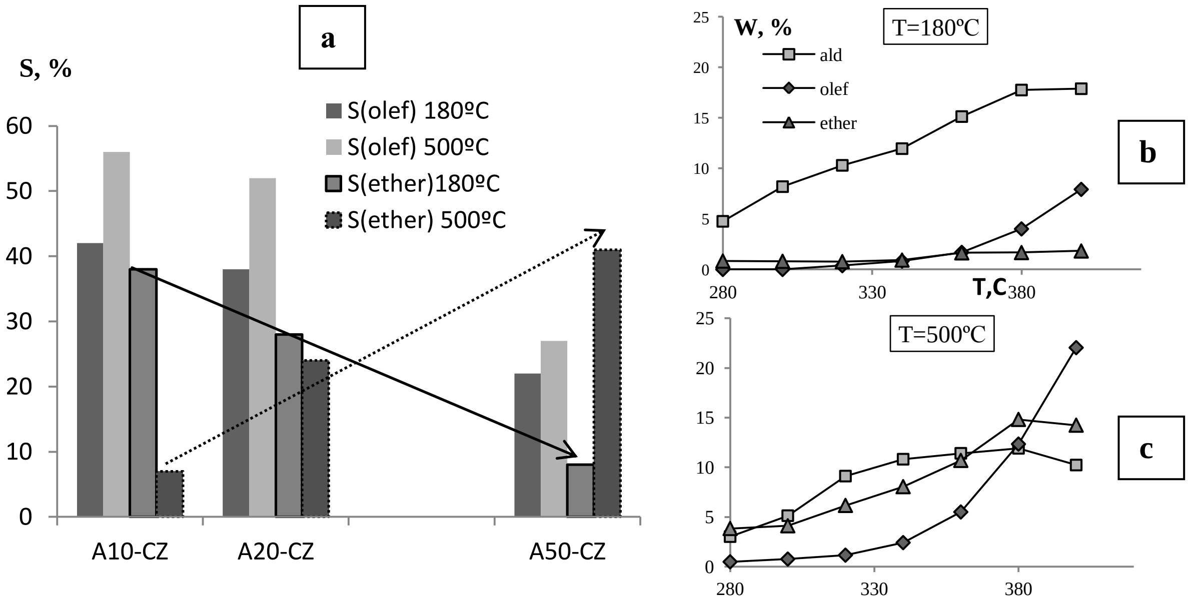

Figure. 3 a)% Selectivityof olefin and ether over samples with different compositions (% Al) obtained at 180ºC and 500ºC; b), c) Temperature dependences for sample A50-CZ obtained at 180ºC and 500ºC

4. Conclusions

Ethanol conversion reaction high selectivity on mixed oxides systems (Ce+Zr)/Al could be achieved by controlling not only the composition of nanopowders but also the calcined temperature.Hence, the preparation technique is of the highest importance for such catalytic systems design.

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