

УДК539.2

doi: 10.18101/ 978-5-9793-0898-2-5-8

**SYNTHESIS OF MESOPOROUS  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$   
SOLID SOLUTION AND  $\text{VO}_x$  LOADED CATALYSTS  
FOR OXIDATIVE DEHYDROGENATION OF PROPANE**

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Mesoporous nanostructured  $\text{VO}_x/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts have been prepared by the surfactant-assisted method of nanoparticle assembly. The textural and structural properties of the prepared nanocatalysts were characterized by different methods.

**Keywords:** catalysts, nanostructure, mesopore, solid solution, phase transition.

Работа посвящена синтезу оксидных катализаторов  $\text{VO}_x/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  химическим методом. Текстульные и структурные свойства катализаторов были исследованы различными методами.

**Ключевые слова:** катализаторы, наноструктура, мезопора, твердый раствор, фазовый переход.

## 1. Introduction

Ce-Zr-O solid solutions have attracted much attention as supports of copper oxide and precious metal oxidation catalysts because the addition of  $ZrO_2$  to  $CeO_2$  can control the structure or the sites of  $CeO_2$  crystallite, which leads to the improvement in oxygen storage capacity (OSC), redox property, thermal resistance of  $CeO_2$  and promotion of metal dispersion [1,2]. The effect of various preparation methods and different Ce/Zr ratio on the catalytic activity was investigated by many research groups [3]. However, little attention has been paid to the formation of mesoporous structure of Ce-Zr-O catalyst supports, though the mesoporous structure would give rise to well-dispersed and stable metal catalyst particles on the surface upon calcinations and reduction because of its abundant pores and large surface, exhibiting a great potential in further improving the catalytic performance. In this paper the high-surface area mesoporous  $Ce_xZr_{1-x}O_2$ , which were prepared by a surfactant-assisted method of nanocrystalline particle assembly, supported vanadium oxide were characterized by different methods. The catalytic properties of the  $VO_x/Ce_xZr_{1-x}O_2$  nanocatalysts were evaluated by oxidative dehydrogenation of propane using a microreactor-GC system.  $N_2$  adsorption-desorption isotherms revealed a mesoporous nanocatalyst system with high-surface area and uniform pore-size distribution. The results of catalytic activity measurements showed that these mesoporous nanostructured  $VO_x/Ce_xZr_{1-x}O_2$  catalysts were very active for oxidative dehydrogenation of propane. The catalytic behavior depended on the  $VO_x$  loading amount, the calcination temperature, the Ce/Zr ratio of supports, the surface area and the particle size of the catalyst.

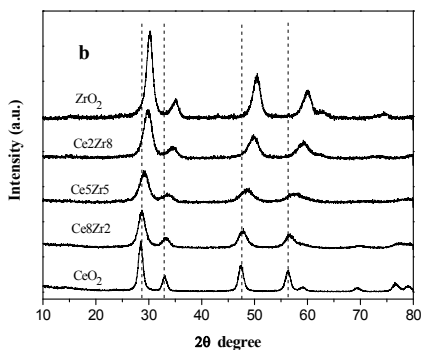
## 2. Experimental

The ceria-zirconia mixed oxide  $Ce_xZr_{1-x}O_2$  ( $x=0, 0.2, 0.5, 0.8, 1$ ) were synthesized using a surfactant-assisted method of nanoparticle assembly. The supported vanadia catalysts were prepared by wet impregnation method using Ammonium metavanadate ( $NH_4VO_3$ ) solution. The catalytic properties of the  $VO_x/Ce_xZr_{1-x}O_2$  nanocatalysts were evaluated by oxidative dehydrogenation of propane using a microreactor-GC system. The textural and structural properties of the prepared  $VO_x/Ce_xZr_{1-x}O_2$  nanocatalysts were characterized by means of XRD,  $N_2$  sorption, TEM,  $H_2$ -TPR, UV-vis, Raman and XPS.

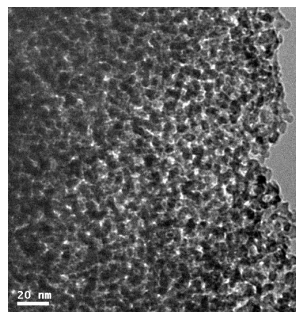
## 3. Results and discussion

The XRD spectra of the Ce/Zr mixed oxides are presented in Fig.1. As the cerium content varies, ceria-zirconia solid solutions exhibit a cu-

bic-tetragonal structural phase transition where the ideal fluorite-type structure has the space group  $Fm-3m$  and the tetragonal phase belongs to the  $P4_2/nmc$  group and has oxygen displacements from an ideal fluorite position. From Fig. 1, it can be seen that ceria and  $Ce_{0.8}Zr_{0.2}O_2$  mixed oxides are crystallized in the cubic fluorite-type structure. After introduction of zirconia in the ceria lattice, the main diffraction peaks for the cerianite structure at  $2\theta \approx 28.6$  and  $47.5^\circ$  are shifted towards higher diffraction angles. This observation was attributed to shrinkage of lattices due to the replacement of  $Ce^{4+}$  (ionic radius 0.098 nm) with a smaller  $Zr^{4+}$  (ionic radius 0.084 nm) in agreement with the Vegard rule. The tetragonal structure typical of  $CeO_2$  was appeared while  $x > 0.5$ . The nitrogen adsorption-desorption isotherms and the corresponding pore size distributions of the  $VO_x/Ce_xZr_{1-x}O_2$  with different  $VO_x$  content revealed that the surfactant-assisted method prepared  $VO_x/Ce_xZr_{1-x}O_2$  catalyst-shave wormhole-like mesoporous structure with high surface area and uniform pore size distribution. Fig.2 shows the TEM micrographs of the sample  $Ce_{0.8}Zr_{0.2}O_2$  calcined at 500 C. The images clearly demonstrate that the  $Ce_{0.8}Zr_{0.2}O_2$  catalysts have a disordered wormhole-like mesopore structure, formed by the agglomeration of the uniform nanoparticles. The accessible pores are connected randomly, lacking discernible long-range order in the pore arrangement among the small  $Ce_{0.8}Zr_{0.2}O_2$  particles, being in well agreement with the  $N_2$  adsorption-desorption isotherms. The  $H_2$ -TPR, UV-vis, Raman and XPS analysis indicated that that different Ce/Zr ratio of supports influenced the formation of vanadium species on the  $Ce_xZr_{1-x}O_2$  surface.



**Fig. 1.** XRD patterns of  $Ce_xZr_{1-x}O_2$  solid solutions.



**Fig. 2.** TEM images of mesoporous  $Ce_{0.8}Zr_{0.2}O_2$ .

The catalytic behavior depended on the  $\text{VO}_x$  loading amount, the calcination temperature, the Ce/Zr ratio of supports, the surface area and the particle size of the catalyst. In oxidative dehydrogenation of propane, additional contribution to propylene formation derives from the contribution of catalytic dehydrogenation of propane, under oxygen-lean condition. The 8VC2Z8 catalyst exhibit a stable catalytic performance in the oxidative dehydrogenation of propane.

#### **4. Conclusions**

Mesoporous nanostructured  $\text{VO}_x/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts with high-surface areas and narrow mesopore size distributions have been prepared by the surfactant-assisted method of nanoparticle assembly. The different Ce/Zr ratio of supports influenced the formation of vanadium species on the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  surface. In combine with results of catalytic performance we suggest that the polyvanadate catalysts are less selective for propylene and more strongly oxidizing toward CO than the catalysts with isolated vanadate species in ODHP. Furthermore, polyvanadate species show high activity to the direct dehydrogenation of propane.

#### **Acknowledgements**

*This work was financially supported by The Research Program of Science and Technology at Universities of Inner Mongolia Autonomous Region (NJZZ16042) and Inner Mongolia Science and Technology Plan (110570).*

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