# Development, Synthesis, and Study of Nanomaterials of Titania Doped by Zirconium for Selective Hydrogenation of 2-Methyl-3-Butyn-2-ol in a Microcapillary Reactor

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Abstract—An ordered mesoporous titanium—zirconium  $Ti_xZr_{1-x}O_2$  matrix for introducing catalytic nanoparticles was synthesized by self-assembly using titanium isopropoxide and zirconium oxychloride as precursors and amphiphilic triblock copolymer F127 as a template. The process of self-assembly occurs without the addition of an acid to preserve the morphology and structure of the catalytic nanoparticles. When controlling the initial molar ratios of the copolymer to metal precursors, titanium—zirconium nanocomposites with controlled texture and composition were obtained in a wide range of titania content, from 15 to 80 mol % TiO<sub>2</sub>. The structural and phase properties of the composites were studied by X-ray diffraction, low-temperature nitrogen adsorption, and transmission electron microscopy. Composites have an ordered mesoporous structure, a high specific surface area, a large pore volume, and a uniform pore size distribution. Catalytic coatings of 1 wt % Pd–Zn/Ti<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> (x = 1.0, 0.8, 0.5) on the inner surface of a capillary reactor were prepared by the dip-coating method using a colloidal solution of Pd–Zn nanoparticles. The developed catalytic coatings based on titanium–zirconium composites exhibit high activity and selectivity (> 96%) in the hydrogenation of 2-methyl-3-butyn-2-ol.

*Keywords:* mesoporous structure, titanium–zirconium composites, Pd–Zn nanoparticles, selective hydrogenation, 2-methyl-3-butyn-2-ol

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## INTRODUCTION

World technical progress has led to serious global environmental problems. To solve them, work is currently underway to develop environmentally friendly and efficient processes. In this context, processes in microstructured reactors are a key technology. A microreactor with a catalyst located on its walls provides several orders of magnitude greater a surface-tovolume ratio than periodic reactors and maintains better heat and mass transfer [1, 2]. In microreactors, reactions are controlled by kinetics and this leads to an increase in the selectivity of product formation, while the laminar flow allows precise control of the contact time [3, 4]. Moreover, the continuous operation of microreactors allows simple and fast process optimization and, hence, lower costs [5]. To create highly efficient capillary reactors, reproducible methods for the deposition of a porous catalytic coating are developed [6, 7]. Multicrystalline oxide coatings have high mechanical strength and thermal stability compared to titania-based coatings [8]. Mixed oxides TiO<sub>2</sub>-ZrO<sub>2</sub> are widely used as catalysts and supports with metals,

oxidation of volatile organic compounds [9]. Such improved mixed oxides of titanium and zirconium combine the advantages of TiO<sub>2</sub> (active catalyst and support) and the acid-base properties of ZrO<sub>2</sub> and expand their use by creating new catalytic sites due to strong metal-support interaction. The most commonly used methods for obtaining mixed oxides  $TiO_2$ -ZrO<sub>2</sub> are coprecipitation and the sol-gel method. One of the significant advantages of the solgel method is the fact that multicomponent singlephase metal oxides can be formed at relatively low temperatures compared with the solid-phase reaction [10]. TiO<sub>2</sub>– $ZrO_2$  composites have a high specific surface area, pronounced acid-base surface properties, high thermal stability, and mechanical strength [11– 13]. In recent years, a number of structured materials have been obtained by combining the sol-gel method with surfactants. Amphiphilic surfactant molecules self-organize into various structures. The evaporation-

nonmetals, and metal oxides for various catalytic reactions, namely dehydrogenation, oxidation, hydroge-

nation, hydroprocessing,  $deNO_x$  and photocatalytic

induced self-assembly process (EISA) includes the natural and spontaneous ability of surfactants to organize themselves in various forms through hydrogen bonds and  $\pi - \pi$  interactions, as well as electrostatic and van der Waals forces. Cooperative nucleation and aggregation leads to the formation of an organic-inorganic hybrid structure. The removal of surfactant molecules leads to the formation of a mesoporous material. The EISA process was developed to produce thin films of structured silica and was first proposed by Brinker [14, 15] and Stucky [16]. Over the past decade, the main efforts have been focused on the synthesis of ordered mesoporous TiO<sub>2</sub>-ZrO<sub>2</sub> composites for use in photocatalysis [17–21]. Currently, it remains important to obtain catalytic mesoporous coatings based on mixed  $TiO_2$ -ZrO<sub>2</sub> oxides with an integrated active ingredient for the selective hydrogenation of acetylene alcohol. Such a mesoporous structure with a large specific surface area and connected pores improves the catalyst properties, since it provides access to the active component of reactants and reaction products. The introduction of zirconia into the titania matrix contributes to the preservation of the ordered mesoporous structure of titania [22]. In this case, the particles of the active component are in the mesoporous space of the nanostructured support, which limits their growth in the course of the catalytic reaction and, consequently, increases the stability of the catalyst. In order to prevent the dissolution of metal nanoparticles, the synthesis of such coatings should be carried out at low acidity of the sol.

This work is devoted to the synthesis and study of the physicochemical properties of mesoporous titania-zirconia composites, as well as catalytic coatings based on them. Titania-zirconia composites with different Ti : Zr ratios were obtained by the EISA method without addition of acid using the amphiphilic Pluronic F127 triblock copolymer as a structure-forming additive. The catalytic properties of Ti<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>-based coatings (x = 1.0, 0.8, 0.5) with Pd-Zn-embedded nanoparticles were studied in the selective hydrogenation of 2-methyl-3-butyn-2-ol (MBY).

#### **EXPERIMENTAL**

## Synthesis of $Ti_x Zr_{1-x}O_2$ Composites

For the synthesis, we used Pluronic F127 ( $M_{av} = 12600$ , EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>) (Sigma-Aldrich Chemical Inc.), zirconium oxychloride (ZrOCl<sub>2</sub> · 8H<sub>2</sub>O) (Vekton), titanium tetraisopropoxide (Ti[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>O]<sub>4</sub>) (Acros), methanol (99.8%), and ethanol (99.9%) (Baker). The mesoporous TiO<sub>2</sub>-ZrO<sub>2</sub> composites were synthesized by the sol-gel method in the presence of a template. The molar ratio of reagents was Pluronic F127 : [(CH<sub>3</sub>)<sub>2</sub>O]<sub>4</sub>Ti : ZrOCl<sub>2</sub> · 8H<sub>2</sub>O : alcohol = 0.0112 : 0-1 : 1-0 : 34. Pluronic F127 with a

weight of 0.85 g was dissolved in 2 mL of a mixture of ethanol and methanol (volume ratio, 1 : 1) at room temperature. Ti[CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>O]<sub>4</sub> and ZrOCl<sub>2</sub> · 8H<sub>2</sub>O were added to the solution (overall Ti + Zr amount, 6 mmol) with intense stirring. After stirring for 2 h at room temperature, the homogeneous sol was transferred to an oven to evaporate the solvent. After two days of aging at 303 K and a relative humidity (RH) 50%, the gel was dried at 373 K for 1 day. Then, the temperature was slowly raised from room temperature to 673 K (heating rate, 1 K/min) and calcined at 673 K for 2 h in air. High-temperature treatment (873, 1073 K) was carried out in air for 1 h at a heating rate of 5 K/min.

## Synthesis of $Pd-Zn/Ti_xZr_{1-x}O_2$ Coatings

Mesoporous films doped with nanoparticles were obtained by one-step synthesis using a precursor solution according to the procedure described in [23]. The colloid solution of Pd–Zn nanoparticles (molar ratio, Pd: Zn = 1: 1) stabilized by polyvinylpyrrolidone  $(M_{\rm av} = 50000, \text{Acros})$  was prepared by the reduction of Pd(CH<sub>3</sub>COO)<sub>2</sub> (46.5% Pd, Aurat) and ZnCl<sub>2</sub> (98%) salts in an ethylene glycol solution [24]. The catalysts  $Pd-Zn/TiO_2$ ,  $Pd-Zn/Ti_{0.8}Zr_{0.2}O_2$ , and Pd- $Zn/Ti_{0.5}Zr_{0.5}O_2$  were synthesized in the form of powder and films on the inner surface of a capillary. The weights of catalytic films Pd-Zn/TiO<sub>2</sub>, Pd-Zn/Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>, and Pd-Zn/Ti<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> were 1.95, 3.85, and 6.50 mg, respectively.

# Study of Physicochemical Properties of $Ti_x Zr_{1-x}O_2$ Composites and Pd–Zn/ $Ti_x Zr_{1-x}O_2$ Catalysts

The phase composition of the samples was studied by X-ray diffraction (XRD). Powder XRD patterns were recorded using a HZG-4C diffractometer (Freiberger Prazisionmechanik, Germany) with  $CoK_{\alpha}$ radiation in the range  $4^{\circ} < 2\theta < 50^{\circ}$  with a counter rate of 1°/min. Transmission electron microscopic (TEM) images were obtained using a JEM-2010 instrument (JEOL, Japan) operating at 200 kV with a resolution of 0.14 nm. Nitrogen adsorption and desorption isotherms at 78 K were measured using an ASAP 2400 analyzer (Micromeritics, USA). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) theory. The pore volume and pore size distribution were obtained using the Barrett–Jovner–Halenda model (BJH) from the desorption branch of isotherms. The content of Pd, Zn, Ti, and Zr in powder catalysts was found by X-ray fluorescence (XRF) spectroscopy using a VRA-30 analyzer (ThermoFisher Scientific, Switzerland) with a Cr anode of an X-ray tube. The catalyst content in the microcapillary reactor was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an OPTIMA 4300 DV instrument (Perkin



**Fig. 1.** XRD patterns in the region of low angles for  $TiO_2$ – ZrO<sub>2</sub> composites with different Ti : Zr ratios calcined at (a) 673 and (b) 873 K: (*1*)  $Ti_{0.15}Zr_{0.85}O_2$ ; (*2*)  $Ti_{0.30}Zr_{0.70}O_2$ ; (*3*)  $Ti_{0.70}Zr_{0.30}O_2$ .

Elmer, USA). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed using a Q-1500 derivatograph (MOM Budapest, Hungary). The measurements were carried out at a heating rate of 10 K/min from 293 to 873 K in an air atmosphere.

#### Catalytic Tests

The catalyst in a microcapillary reactor was preliminarily reduced in situ in a flow of hydrogen (2 mL/min) at a temperature of 573 K for 2 h. A description of the equipment for carrying out the reaction in a microcapillary reactor and the experimental technique are given in [25]. The capillary was placed in a thermostatic oven at 313 K. Hydrogen and a solution of MBY or 2-methyl-3-buten-2-ol (MBE) in methanol were fed to a T-shaped mixer, the inner diameters of the inlet and outlet tubes were 250 µm before the capillary. The flow rate was varied from 5 to  $100 \,\mu$ L/min, the gas flow was 6 mL/min. Three to five samples were taken after the system reached a steady state for 20 min, diluted with methanol (5:1) and analyzed using a Kristall 2000M gas chromatograph (Khromatek, Russia) equipped with a capillary column with a stationary SKTFT-50X phase; diameter, 0.22 mm; length, 30 m (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences); a flame ionization detector. The carbon balance for these systems was  $100 \pm 2\%$ , i.e., the major products were 2-methyl-3butyn-2-ol (MBY), 2-methyl-3-buten-2-ol (MBE), and 2-methyl-2-butanol (MBA). The conversion x, selectivity to MBE  $S_{\text{MBE}}$ , product yield Y, reactor productivity Q, catalyst productivity A were calculated as follows:

$$x = \frac{(C_{\rm MBY,0} - C_{\rm MBY})}{C_{\rm MBY,0}} \times 100,$$
  

$$S_{\rm MBE} = \frac{C_{\rm MBE}}{(C_{\rm MBY,0} - C_{\rm MBY})} \times 100,$$
  

$$Y = \frac{C_{\rm MBE}}{C_{\rm MBY,0}} \times 100,$$
  

$$Q = \frac{(C_{\rm MBY,0} - C_{\rm MBY})v_{\rm I}YM}{\rho} \times 100,$$
  

$$A = \frac{(C_{\rm MBY,0} - C_{\rm MBY})v_{\rm I}YM}{\rho m_{\rm Pd}} \times 100,$$

where  $C_{\text{MBY},0}$  is the initial concentration of MBY;  $C_{\text{MBY}}$  and  $C_{\text{MBE}}$  are the current concentrations of MBY and MBE, respectively;  $v_{\text{liquid}}$  is flow rate of liquid; *m* is the molecular weight of MBY;  $\rho$  is the density of a liquid; and  $m_{\text{Pd}}$  is the weight Pd.

MATLAB was used to calculate the kinetic parameters. The system of differential equations was solved using the function ode45, minimizing the sum of square deviations between the experimental and calculated concentrations at the reactor outlet was performed using the fminsearch function.

## **RESULTS AND DISCUSSION**

## $Ti_x Zr_{1-x}O_2$ Composites

By varying the molar ratio  $\text{Ti}_x \text{Zr}_{1-x} O_2$  (x = 0, 0.15, 0.30, 0.50, 0.70, 0.8, 1), a number of samples were prepared. According to XRD data for  $\text{Ti}_x \text{Zr}_{1-x} O_2$  samples (x = 0, 0.15, 0.30, 0.70) in the region of low angles, a peak is observed at 1.63°, which indicates an ordered structure of pores with a small length (Fig. 1). In the region of high angles, there are anatase peaks (JCPDS 21–1272) of pure TiO<sub>2</sub> and Ti<sub>0.80</sub>Zr<sub>0.20</sub>O<sub>2</sub> (Fig. 2). In [26], it was suggested that ZrO<sub>2</sub> can diffuse into the TiO<sub>2</sub> matrix and there is no ZrO<sub>2</sub> in that case. An





Fig. 2. XRD patterns of TiO<sub>2</sub>-ZrO<sub>2</sub> composites with different Ti : Zr ratios calcined at (a) 673 and (b) 873 K: (1) ZrO<sub>2</sub>; (2)  $Ti_{0.15}Zr_{0.85}O_2$ ; (3)  $Ti_{0.30}Zr_{0.70}O_2$ ; (4)  $Ti_{0.50}Zr_{0.50}O_2$ ; (5) Ti<sub>0.70</sub>Zr<sub>0.30</sub>O<sub>2</sub>; (6) Ti<sub>0.80</sub>Zr<sub>0.20</sub>O<sub>2</sub>; (7) TiO<sub>2</sub>.

increase in the content of Zr inhibits crystallization because samples  $Ti_{0.15}Zr_{0.85}O_2$ ,  $Ti_{0.30}Zr_{0.70}O_2$ ,  $Ti_{0.50}Zr_{0.50}O_2$  and  $Ti_{0.70}Zr_{0.30}O_2$  are in the amorphous state. This phenomenon is probably due to the presence of Ti-O-Zr bonds in the interblock boundaries

KINETICS AND CATALYSIS Vol. 60 2019 No 4



Fig. 3. XRD patterns in the region of low angles for the  $Ti_{0.30}Zr_{0.70}O_2$  composite calcined at (1) 673, (2) 873, and (3) 1073 K.



Fig. 4. Electron microscopic image of  $Ti_{0.30}Zr_{0.70}O_2$  calcined at 673 K. The inset shows the high-resolution image.

that prevent the growth of oxide crystals [27]. The orthorhombic ZrO<sub>2</sub> phase (JCPDS 34-1084) and the monoclinic ZrO<sub>2</sub> phase in trace amounts (JCPDS 37-1484) are formed after calcining the  $Ti_{0.15}Zr_{0.85}O_2$  sample at 873 K. The crystallization of binary oxides occurs at higher temperatures. On XRD patterns in the region of large angles, the samples  $Ti_{0.70}Zr_{0.30}O_2$  and Ti<sub>0.50</sub>Zr<sub>0.50</sub>O<sub>2</sub> after treatment at 873 K contain reflections related to the anatase phase (JCPDS 21-1272) and Ti<sub>2</sub>Zr<sub>2</sub>O<sub>6</sub> (JCPDS 46–1265). Upon the calcination of the  $Ti_{0.30}Zr_{0.70}O_2$  sample at 1073 K, the pore walls crystallize to ZrTiO<sub>4</sub> (JCPDS 34-0415), which is consistent with the literature data [28].

After treatment at 873 K, the mesoporous structure of the  $Ti_{0.70}Zr_{0.30}O_2$  sample is destroyed, while the mesoporous structures of the samples with a higher Zr

Sample	Calcination temperature, K	Specific surface area, m <sup>2</sup> /g	Pore size, nm	Pore volume, cm <sup>3</sup> /g
TiO <sub>2</sub>	673	81.6	7.3	0.098
$Ti_{0.80}Zr_{0.20}O_2$	673	185.5	3.6	0.084
$Ti_{0.70}Zr_{0.30}O_2$	673	156.9	3.7	0.132
$Ti_{0.50}Zr_{0.5}O_2$	673	116.2	3.8	0.136
$Ti_{0.30}Zr_{0.70}O_2$	673	150.4	3.8	0.208
$Ti_{0.30}Zr_{0.70}O_2$	873	103.2	3.7	0.162
$Ti_{0.30}Zr_{0.70}O_2$	1073	79.5	5.1	0.152
$Ti_{0.15}Zr_{0.85}O_2$	673	126.0	3.6	0.187
ZrO <sub>2</sub>	673	65.2	4.9	0.094

 Table 1. Physicochemical properties of  $TiO_2$ -ZrO<sub>2</sub> composites obtained by varying the Ti : Zr ratio and calcination temperature

content are retained  $(Ti_{0.30}Zr_{0.70}O_2 \text{ and } Ti_{0.15}Zr_{0.85}O_2)$ (Fig. 1b). As the temperature increases to 873 K, the peaks in the spectra in the region of large angles become narrower and more intense (Fig. 2b). The crystallite size of the  $Ti_{0.8}Zr_{0.2}O_2$  sample slightly increases from 9 to 15 nm. For  $Ti_{0.15}Zr_{0.85}O_2$ ,  $Ti_{0.50}Zr_{0.50}O_2$ , and  $Ti_{0.70}Zr_{0.30}O_2$ , the crystallite diameter increases from 1.4 to 17 nm, from 1.2 to 15 nm, and from 1.2 nm to 17 nm, respectively. In the case of  $Ti_{0.30}Zr_{0.70}O_2$ , this change is manifested to a lesser extent: the particle size calculated by the Scherrer equation increases from 1.3 to 1.5 nm. Upon calcination at 1073 K, the pore walls of  $Ti_{0.30}Zr_{0.70}O_2$  crystallize to ZrTiO<sub>4</sub>, the crystallite diameter increases to 25 nm. It is obvious that the growth of crystallites leads to the destruction of the mesoporous structure (Fig. 3).

The electron microscopic images of the  $Ti_{0.30}Zr_{0.70}O_2$  sample in the form of a film calcined at 673 K show areas with an ordered pore structure (Fig. 4). The open and regular pore structure provides reagent access to the active component. The cell parameter is 9 nm. The cell walls are in an amorphous state and their thickness is about 5 nm.

The low-temperature nitrogen adsorption isotherms of the mixed  $TiO_2-ZrO_2$  composite with different Ti : Zr ratios are of type IV according to the Brunauer classification with a sharp rise at  $P/P_0 =$ 0.4–0.8, indicating a narrow pore size distribution (Fig. 5a). Hysteresis loops of type H1 are observed, which implies a uniform cylindrical geometry of the pores. Mixed composites have a high specific surface area of 116–185 m<sup>2</sup>/g (Table 1). Pore sizes calculated from nitrogen desorption using the BJH model are in the range 3.6–3.8 nm (Table 1) and do not depend on the Ti : Zr ratio. However, as Ti : Zr increases, the pore size distribution becomes wider (Fig. 5b), which indicates a decrease in their degree of order. The calcu-



**Fig. 5.** Isotherms of low-temperature adsorption of nitrogen (a) and pore size distribution calculated from the desorption branch of the isotherm (b): (*1*) ZrO<sub>2</sub>; (*2*) Ti<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>2</sub>; (*3*) Ti<sub>0.30</sub>Zr<sub>0.70</sub>O<sub>2</sub>; (*4*) Ti<sub>0.70</sub>Zr<sub>0.30</sub>O<sub>2</sub>; (*5*) Ti<sub>0.70</sub>Zr<sub>0.30</sub>O<sub>2</sub>; (*6*) Ti<sub>0.80</sub>Zr<sub>0.20</sub>O<sub>2</sub>; (*7*) TiO<sub>2</sub>.



Fig. 6. Thermal analysis data for the  $Ti_{0.30}Zr_{0.70}O_2$  composite.

lated pore wall thickness is  $\sim$ 5.3 nm, which is consistent with the TEM data.

Thermal analysis curves (TG-DTA) of the  $Ti_{0.30}Zr_{0.70}O_2$  sample during decomposition in air are shown in Fig. 6. The maximum on the TG curve is observed at 567 K, the weight loss is about 50 wt % In the temperature range from 473 to 673 K, the decomposition of Pluronic F127 amphiphilic triblock copolymer proceeds and water is removed, both adsorbed and from the Ti-Zr hydroxide. The exothermic effect at 573 K on the DTA curve refers to the decomposition of F127 and the dehvdration of Ti–Zr hvdroxide. The exothermic effect at 573 K on the DTA curve refers to the decomposition of F127 and the dehydration of Ti-Zr hydroxide. The exothermic effect at 993 K corresponds to the crystallization of the ZrTiO<sub>4</sub> phase, which leads to the destruction of the mesoporous  $Ti_{0.30}Zr_{0.70}O_2$  sample.

# $Pd-Zn/Ti_xZr_{1-x}O_2$ Coatings

Microscopic images of the Pd-Zn/Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> sample in the form of a powder reduced at 573, are shown in Fig. 7. The sample has a homogeneous amorphous worm-like structure with a pore size of 5– 6 nm, which agrees with the data of low-temperature nitrogen adsorption (Fig. 8). The HRTEM images (Fig. 8a) show Pd-Zn nanoparticles, which repeat the pore structure of the support (Fig. 4), with an average diameter of 3.7 nm. The resulting value corresponds to the pore diameter of the original matrix. With the introduction of the active component into the  $Ti_{0.8}Zr_{0.2}O_2$  matrix, a porous system with a larger pore size is formed (5.2 nm instead of 3.6 nm for the carrier). Therefore, we can assume that nanoparticles of the active component are located inside the pores of the support. For samples based on pure titania, the particle size of TiO<sub>2</sub> after reduction at 573 K is 6.5 nm according to TEM data [20]. When zirconia is added to the support matrix, the specific surface area and pore volume increase from 85 to 143  $m^2/g$  and from 0.10 to 0.18  $\text{cm}^3/\text{g}$ , respectively. The walls of the support pores hold embedded nanoparticles and hinder their migration over the support surface. The partial degradation of the mesoporous structure of the undoped matrix leads to sintering and agglomeration of nanoparticles. Thus, in samples based on mixed oxide, the nanoparticles of the active component are sintered to a lesser extent.

A comparative study of the catalytic properties of  $Pd-Zn/Ti_xZr_{1-x}O_2$  (x = 1.0, 0.8, and 0.5) in the MBY hydrogenation reaction was carried out. In earlier publications [23, 25], we showed that the activity and selectivity of the MBY hydrogenation reaction on Pd-Zn/TiO<sub>2</sub> coatings increase with increasing reaction time as a result of the removal of carbonaceous deposits. Similar patterns were observed for titanium-zirconium coatings (Fig. 9). As the reaction time increases



Fig. 7. TEM images (a, b) and histograms of particle distribution over sizes (c) of the  $Pd-Zn/Ti_{0.8}Zr_{0.2}O_2$  powder catalyst reduced at 573 K.



**Fig. 8.** Isotherms of nitrogen adsorption (a) and pore size distribution (b) of  $Pd-Zn/Ti_{0.8}Zr_{0.2}O_2$  powder catalyst reduced at 573 K.

from 1 to 32 h, the reactor productivity rises from 0.8 to 8.6 g/day for Pd– $Zn/Ti_{0.8}Zr_{0.2}O_2$  catalysts and from 1.6 to 4.5 g/day for Pd– $Zn/TiO_2$ . The selectivity to MBE also increases from 95.4 to 97.2% for Pd– $Zn/Ti_{0.8}Zr_{0.2}O_2$  and from 89.0 to 94.6% for Pd– $Zn/TiO_2$ .

The reactor productivity after 32 h of continuous flow of the MBY solution in methanol and hydrogen increases in the series  $Pd-Zn/TiO_2 < Pd-Zn/Ti_{0.8}Zr_{0.2}O_2 < Pd-Zn/Ti_{0.5}Zr_{0.5}O_2$ , and the selectivity and productivity of the catalysts are almost independent on their composition (Table 2). The weight of the catalytic coating on the inner surface of the capillary increases in the same order with increasing Zr : Ti molar ratio, which is due to the formation of a more



**Fig. 9.** Effect of time on stream on the productivity of the reactor (a) and selectivity (b) in MBY hydrogenation on (*I*) Pd–Zn/Ti<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>, (*2*) Pd–Zn/Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>, and (*3*) Pd–Zn/TiO<sub>2</sub> films. Reaction conditions:  $C_{\text{MBY}, 0} = 1.0-2.0 \text{ mol/L}$ ; gas flow rate, 6.0 mL/min;  $P_{\text{H}_2} = 1$  atm, T = 313 K.

viscous sol and thickening of the catalytic layer. Thus, the high performance of the reactor is due to the greater loading of the catalyst.

For comparison, Fig. 10 shows the kinetic dependences of the concentrations of the starting reagent and MBY hydrogenation reaction products on the contact time on Pd–Zn/TiO<sub>2</sub> and Pd–Zn/Ti<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> coatings after 32 and 20 h on stream, respectively. Under these conditions, the selectivity to MBE was maximal (Fig. 9). The contact times were calculated from the values of the liquid flow velocity using the Lockhart–Martinelli–Chisholm equation under the assumption that a circular two-phase flow was realized under the experimental conditions [29]. When adding Zr to the support matrix the rate of MBE hydrogenation reaction increases (Figs. 10c, 10d). Table 3 shows

**Table 2.** Effect of the catalyst composition and the time onstream on the reactor productivity and selectivity of 2-methyl-3-butyn-2-ol hydrogenation

Sample	$Q_t = 32,$ $g_{MBE}/day$	$A_{t=32},$ $g_{\text{MBE}} s^{-1}$ $g_{\text{Pd}}^{-1}$	$S_{x=97}, \%$
Pd–Zn/TiO <sub>2</sub>	4.5 <sup>1</sup>	1.5	96.9
$Pd-Zn/Ti_{0.8}Zr_{0.2}O_2$	8.6 <sup>2</sup>	1.9	97.2
$Pd{-}Zn/Ti_{0.5}Zr_{0.5}O_2$	11.0 <sup>2</sup>	1.6	96.5

<sup>1</sup>Reaction conditions: [MBY] = 0.8 M,  $v_{\text{liquid}} = 6.00 \text{ mL/min}$ ,  $P_{\text{H}_2} = 1 \text{ atm}$ , T = 313 K.

<sup>2</sup>Reaction conditions: [MBY] = 1.0 M,  $v_{\text{liquid}} = 6.00 \text{ mL/min}$ , 1 atm H<sub>2</sub>, T = 313 K.

the kinetic parameters of the reaction calculated from the kinetic dependencies shown in Figs. 10a, 10b, 11. To find the adsorption constant  $K_{\rm MBE}$ , the effect of the MBE concentration in the range 0.1–3.1 mol/L on the initial reaction rate was studied. The kinetic parameters were calculated using the Langmuir–Hinshelwood model according to the methodology described previously in [18]. The observed increase in the MBE hydrogenation rate for mixed oxide catalysts can be explained by a decrease in the  $K_{\rm MBA}/K_{\rm MBY}$  adsorption constant ratio and an increase in the MBE hydrogenation rate constants  $k'_2$ . The alkyne adsorption constant decreased with the addition of zirconium, but its value was 60 times higher than the alkene adsorption constant. The rate constant of direct hydrogenation of

MBY to MBA  $k'_3$  was lower for the titanium-zirconium catalyst. Low values of  $K_{\text{MBE}}/K_{\text{MBY}}$  were responsible for the high selectivity of the  $Pd-Zn/Ti_{0.8}Zr_{0.8}O_2$  coating at a conversion of 97%.

## CONCLUSIONS

In this work, it was shown that ordered mesoporous titanium-zirconium composites using titanium isopropoxide and zirconium oxychloride as precursors of titania and zirconia and F127 triblock copolymer as a template can be obtained by self-assembly. In most cases, the EISA process in the synthesis of mesoporous oxide materials requires the addition of acid to slow down the hydrolysis-condensation of metal precursors. In our case, no acid is added to control the rate of hydrolysis, which is important in the production of catalytic coatings for microreactors. A series of titanium-zirconium nanocomposites with controlled properties was prepared by varying the TiO<sub>2</sub> content in the mixture of oxides from 15 to 80 mol %. The composites have an ordered mesoporous structure, a high specific surface area (up to  $185 \text{ m}^2/\text{g}$ ), a large pore volume  $(0.08-0.21 \text{ cm}^3/\text{g})$  and their uniform size distribution (3.6-3.8 nm). Catalytic coatings 1 wt % Pd- $Zn/Ti_xZr_{1-x}O_2$  (x = 1.0, 0.8, 0.5) were synthesized on the inner surface of a capillary reactor with a diameter of 0.53 mm and a length of 10 m. Coatings have been tested in the selective hydrogenation of 2-methyl-3butyn-2-ol at 333 K and 1 atm H<sub>2</sub>. The productivity of the reactor after 32 h of continuous flow of the MBY solution in methanol and hydrogen increases in the series  $Pd-Zn/TiO_2 \leq Pd-Zn/Ti_{0.8}Zr_{0.2}O_2 \leq Pd Zn/Ti_{0.5}Zr_{0.5}O_2$  due to increasing the catalyst loading, and the high selectivity (>96%) and the performance of the catalysts are almost independent of the coating composition.

Table 3. Kinetic parameters of the MBY hydrogenation on  $Pd-Zn/Ti_xZr_{1-x}O_2$  coatings

Parameter	Pd–Zn/TiO <sub>2</sub> <sup>1</sup>	$Pd-Zn/Ti_{0.8}Zr_{0.2}O_2^2$
$\overline{k'_{1}, \text{ mol } g_{Pd}^{-1}}$	714	750
$k_2$ , mol $g_{Pd}^{-1}$	132	230
$k'_{3}$ , mol $g_{Pd}^{-1}$	20	10
$K_{\rm MBY}$ , L/mol	61	38
$K_{\rm MBE}^{3}$	$0.8^{4}$	$0.6^{2}$
K <sub>MBA</sub>	8	0.5
$K_{\rm MBE}/K_{\rm MBY}$	0.013	0.016
$K_{\rm MBA}/K_{\rm MBE}$	10	0.8
$K_{\rm MBA}/K_{\rm MBY}$	0.13	$1.3 \times 10^{-2}$
Maximum deviation, %	20	14

<sup>1</sup> Reaction conditions:  $v_{\text{liquid}} = 6.0 \text{ mL/min}$ ,  $P_{\text{H}_2} = 1 \text{ atm}$ , T = 313 K, Pd–Zn/TiO<sub>2</sub> after 32 h of time on stream.

<sup>2</sup> Reaction conditions:  $v_{\text{liquid}} = 6.0 \text{ mL/min}$ ,  $P_{\text{H}_2} = 1 \text{ atm}$ , T = 313 K,  $\text{Pd} - \text{Zn/Ti}_{0.8}\text{Zr}_{0.2}\text{O}_2$  after 20 h of time on stream.

<sup>3</sup> Fixed value.

<sup>4</sup> Calculated from the dependence of Pd–Zn/Ti<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> activity on the MBE concentration.



**Fig. 10.** Dependences of  $(1, \blacksquare)$  MBY,  $(2, \bullet)$  MBE, and  $(3, \blacktriangle)$  MBA concentrations on the contact time on Pd–Zn/TiO<sub>2</sub> films after 32 h time on stream (a) and on Pd–Zn/TiO<sub>2</sub> after 20 h time on stream (c); dependences of the reaction rate on the contact time on Pd–Zn/TiO<sub>2</sub> film after 32 h time on stream (b) and Pd–Zn/TiO<sub>2</sub> film after 32 h time on stream (c); dependences of the reaction rate on the contact time on Pd–Zn/TiO<sub>2</sub> film after 32 h time on stream (b) and Pd–Zn/TiO<sub>2</sub> film after 20 h time on stream (d). Reaction conditions:  $v_{\text{liquid}} = 6.0 \text{ mL/min}$ ,  $P_{\text{H}_2} = 1 \text{ atm}$ , T = 313 K.



**Fig. 11.** Effect of the initial concentration of 2-methyl-3-buten-2-ol on the reaction rate on (1)  $Pd_{50}Zn_{50}/TiO_2$  and (2)  $Pd_{50}Zn_{50}/Ti_{0.8}Zr_{0.2}O_2$  films. Reaction conditions:  $C_{MBE,0} = 0.1-3.1 \text{ mol/L}$ ;  $v_{liquid} = 6.0 \text{ mL/min}$ ,  $P_{H_2} = 1 \text{ atm}$ ; 313 K.

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