Conversion of ethanol to butadiene over mesoporous In$_2$O$_3$/MgO/SiO$_2$ catalysts

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Abstract

Mesoporous MgO-SiO$_2$ catalysts were prepared to investigate the one-step conversion of ethanol to 1,3-butadiene. The impregnated and wet-kneaded SBA-15 samples were compared to one-pot synthesized materials. In one-pot synthesis magnesium-methoxide and magnesium-ethoxide was introduced into the synthesis gel of SBA-15. Effect of In$_2$O$_3$ as a new dehydrogenation promoter in MgO-SiO$_2$ systems is tested. Results of TEM and N$_2$ physisorption measurements showed that in impregnated and wet-kneaded samples the original pore structure of SBA-15 is partially destructed by introducing of magnesia. The one-pot synthesized samples are mesoporous, but magnesium-alkoxides hindered the formation of the SBA-15 structure. XRD measurements confirm the formation of Mg-O-Si bonds in wet-kneaded and one-pot synthesized samples. Wet impregnation of In$_2$O$_3$ on the MgO-SiO$_2$ preparations rearranged the morphology of the samples characteristic for inorganic oxide gels with pore system made up of interconnected network of pores of different size and shape. The CO$_2$ and NH$_3$ TPD measurements show that the formation of Mg-O-Si bonds results in an increased acidity/basicity of the samples. Addition of In$_2$O$_3$ causes a further enhancement of these properties. The best catalytic results over sole MgO-SiO$_2$ catalysts were achieved over wet-kneaded and magnesium-methoxide based samples at 400-425 °C with 15 % butadiene yield. Doping of In$_2$O$_3$ significantly improved the catalytic activity of the samples by increasing of acetaldehyde

formation rate and suppression of dehydration reactions of ethanol. Over In_2O_3 containing catalysts butadiene yields above 40% were achieved.

1. Introduction

1,3-Butadiene (BD) is the most important conjugated diene. It is used as a monomer block for a synthesis of poly-butadiene or as a building block for a different heteropolymers such as styrene-butadiene-rubber, styrene-butadiene latex, acrylonitrile-butadiene-styrene resin, adiponitrile, nitrile rubber and polychloroprene [1]. Currently, BD mainly is produced from naphtha steam crackers as by-product of ethylene production. The lightening of the feedstock such as use of shale gas for ethylene production lead to butadiene shortage and rise in prices [2]¶. An alternative way for synthesis of butadiene is the catalytic coupling of ethanol to butadiene. Ethanol is one of the most abundant renewable raw materials. Its annual production rapidly grows which results in a price reduction [3]. The fundamentals of ethanol to butadiene (ETB) process were elaborated by Lebedev (one step synthesis) [4] and Ostromislenky (two step sytnhesis) [5] in first half of the previous century. In one-step process only ethanol is introduced into reactor, while in two step process first the ethanol is dehydrogenated to acetaldehyde, then the mixture of acetaldehyde and ethanol is fed into the reactor. The ETB reaction starts with dehydrogenation of ethanol to acetaldehyde, followed by condensation of two acetaldehyde molecules to yield crotonaldehyde, which is then hydrogenated by another ethanol molecule (Meerwein–Ponndorf–Verley (MPV) reduction) to form crotyl alcohol, which in final step dehydrates to butadiene. Of all the supports tested MgO-SiO$_2$ showed the best catalytic activities in ethanol to butadiene reaction [6,7,16–20,8–15]. Since ethanol dehydrogenation to

acetaldehyde is the rate determining step in consecutive reaction chain different metals/metal-oxides such as Zn, Zr, Cu, Au, and Ga were added to the MgO-SiO$_2$ support in order to promote this step. The detailed studies disclosed that the catalytic activity strongly depends on synthesis method. For the synthesis of the MgO-SiO$_2$ supports different methods are reported: (i) mechanical mixing of components (ii) coprecipitation (iii) wet kneading (iv) incipient wetness impregnation. However, there is no agreement in literature about most efficient preparation method. The ETB reaction demands an appropriate balance of basic and acidic sites. In MgO-SiO$_2$ systems the role of magnesia component is to provide basic sites, while acidic sites rise due to charge imbalance along Mg–O–Si bonds. The number and strength of basic sites depends on the dispersity of the magnesia, while the acidity of the mixed oxide is linked to the number and nature of Mg–O–Si bonds. It is also shown that the butadiene yield depends on the specific surface area [18], crystal size/shape [21,22] and pore diameter of the MgO-SiO$_2$ support [23,24].

The mesoporous materials have several advantages compared to micro or non-porous materials. Inside of mesopores the mass and heat transport is more efficient, and it facilitates the high dispersion of the metal/metal-oxide promoters. However, the lack of the acidic/basic sites on the ordered mesoporous silicas raises difficulties in their application in catalysis. Two techniques were developed for the synthesis of mesoporous basic materials: (i) in two-step method the mesoporous framework is synthesized first, followed by ion-exchange, impregnation, microwave irradiation or anchoring of the basic guest (ii) in one-pot synthesis the precursors of mesoporous host and basic guest are loaded together to synthesis gel.

In order to exploit the benefits of mesoporous supports Chae et al. [21] used Ta$_2$O$_5$ supported on different ordered mesoporous silica (SBA-15, KIT-6, MMS) in the transformation of ethanol/acetaldehyde mixture to BD. They found that the mesoporous catalysts show better

coke tolerance and catalytic longevity as well as catalytic activity than conventional silica based catalysts. Klein and Palkovits [24] investigated the catalytic effect of ZnO supported on mesoporous zeolites (BEA and LTA) in ETB reaction and observed that the by building of mesopores into the structure the catalytic activity drastically improves. Fujita et al. [25] used Mg incorporated MCM-41 catalysts for the aldol condensation reaction of 4-nitrobenzaldehyde and acetone and report the positive effect of large surface area and pore volume with regard to catalytic activity. Pomalaza et al. [26] synthesized ZnTa/TUD-1 mesoporous silica catalyst in ETB reaction and achieved significantly better yields compared to ZnTa supported on dealuminated BEA and fumed silca (69 % vs 57 and 45%, respectively).

To our knowledge the mesoporous $MgO-SiO_2$ materials have not been tested yet in ETB reaction. In literature different methods are described for synthesis of Mg-containing mesoporous silicas. Commonly, the mesoporous silica is synthesized first, followed by impregnation of $Mg(NO_3)_2$ [27] or $Mg(CH_3COO)_2$ [28]. Zukal et al. [29] elaborated a modified impregnation method to avoid the destruction of silica support. In this method first step is the precipitation of magnesium acetate on the silica surface followed by in situ chemical conversion of magnesium acetate with oxalic acid to magnesium oxalate, while final magnesium oxide was formed by calcination. Another technique rests on the manual grinding of the magnesium salt with as-prepared mesoporous silica at room temperature, followed by calcination to remove structure directing agent (SDA) [30]. The basicity of the magnesia (catalyst) can be further enhanced by alkali salts, such as KNO_3 [31]. In one-pot methods the magnesia is in-situ coated into the mesoporous silica network, i. e. the silica and magnesia sources (magnesium nitrate or magnesium acetate) and SDA are added simultaneously to the synthesis mixture [31–36]. In that way the magnesia can be built into the silica frame in high dispersion. However, Kónya et al.

[33] demonstrated that during the synthesis of SBA-15 in presence of different metal salts the fully washed samples were white and free of metal ions. It is also shown that both anions and cations have an effect on the mesostructure of the SBA-15. Wang et al. [34] found that effect of anion follows the lyotropic series $NO_3^- < Cl^- < CH_3COO^-$. The MgO/mesoporous silica preparations were used as adsorbents for CO_2 [29,35] and curcumin [28] or as catalyst in a selective oxidation [27], transesterification [30] and CO_2 reforming of methane [36].

This work deals with the synthesis of different MgO/SBA-15 catalysts: (i) impregnated, (ii) wet kneaded, one-pot synthesized with magnesium-ethoxide (iii) or magnesium-methoxide (iv). The MgO/SBA-15 preparations were characterized by means of Inductively coupled plasma - optical emission spectrometry (ICP-OES), X-ray Diffraction (XRD), N_2 physisorption, Transmission Electron Microscopy (TEM). The basicity and acidity of the samples was determined by CO_2 and NH_3 TPD measurements, respectively. The catalysts were tested in direct conversion of ethanol to butadiene. The promoting effect of In_2O_3 in ETB reaction is also discussed.

2. Experimental section

2.1. Preparation of catalysts

For the synthesis of the impregnated (IMP) and wet-kneaded (WK) MgO/SBA-15 samples the SBA-15 provided be Nanjing XFNANO Materials Tech Co., Ltd, China was used. The impregnation was executed by adding of $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich, 99 %) solution (27.27 g / 200 ml distilled water) to 10.00 g of dried SBA-15 (120 °C, 2h). The water was

removed under continuous stirring at 70 °C, and then the sample was dried at 120 °C overnight and calcined in air at 500 °C for 5h. In the first step of the wet kneading process Mg(OH)$_2$ was precipitated by adding of Mg(NO$_3$)$_2$·6H$_2$O solution to NaOH solution at pH=12 maintained with 2 M NaOH. The precipitation was aged in mother-lye for 24 h, followed by washing to remove sodium and drying at 120 °C overnight. The wet kneading was carried out by mixing of 2.15 g of Mg(OH)$_2$ and 5.00 g of dried SBA-15 in 100 ml of distilled water for 5 h at room temperature. The suspension was centrifuged, dried at 120 °C overnight and calcined in air at 500 °C for 5h. The one-pot synthesis with magnesium ethoxide (OPET) was performed as follows: 16 g of the template for SBA-15 synthesis (Pluronic P-123, Aldrich) was dissolved in 600 ml of 0.03 M HCl soulution with stirring at room temperature for 2 h. The second mixture was produced by mixing of 37 ml TEOS (Tetraethyl orthosilicate, Aldrich, 98%) 8.20 g of magnesium ethoxide (Aldrich, 98%) in 250 ml of methanol. Thereafter, the second mixture was dropwise added to vigorously stirred Pluronic P-123 solution at room temperature. After the stirring for further 24 h at 40 °C the mixture was transferred into a Teflon lined autoclave and treated for a 24 h at 100 °C. The solid sample was washed with distilled water until the supernatant was free of chloride. The product was dried overnight at 120 °C, and the template was removed by calcination step in air at heating rate of 1 °C/min to 500 °C and keeping at this temperature overnight. The one-pot synthesis with magnesium-methoxide (OPMET) was executed according to the following procedure: 16 g of Pluronic P-123 was dissolved in 600 ml of 0.03 M HCl soulution with stirring at room temperature for 2 h. Then 37 ml of TEOS was added to solution and the mixture was stirred for 24 h at room temperature. In next step 155 ml of magnesium-methoxide solution (7-8% in methanol, Alfa Aesar) dropwise is added to the pre-hydrolyzed TEOS solution. The gelation of the sol immediately started. The viscous gel was stirred for further 30 min and after

was transferred into a Teflon lined autoclave. The procedure was finished as described above for OPET sample. The In_2O_3 doped catalysts were prepared by impregnating the supports applying ~ 33 mM/dm^3 solution $In(NO_3)_3 \cdot xH_2O$ (Alfa Aesar 99.99 %, metals basis) in an amount needed to get catalysts of about 2, 5 or 10 wt% metal-oxide content. In order to get an appropriate metal concentration for the aliquots the crystal water content of the nitrate salt was determined by thermogravimetric measurements. The number before the abbreviation of the catalysts name denotes the In_2O_3 content of the sample in wt-%, i. e. 5IMP means 5 wt% In_2O_3 impregnated on the surface of the impregnated sample.

2.2. Characterization

The elemental composition of the samples was determined by means of ICP-OES measurements performed with a simultaneous plasma emission spectrometer with axial plasma observation (Spectro Genesis).

X-ray patterns were recorded by Philips PW 1810/3710 diffractometer applying monochromatized CuKα (λ=0.15418 nm) radiation (40 kV, 35 mA) and proportional counter. The patterns recorded at ambient and data were collected between 3° and 75° 2Θ, by 0.02° steps for 0.5 s. The low-angle XRD measurements were executed on Philips X'Pert MPD system by using 2Θ-ω scan method between 0.6-3 2Θ, by 0.002 steps for 10 s.

Nitrogen physisorption measurements were carried out at 77 K using Thermo Scienctific Surfer automatic, volumetric adsorption analyzer. Before adsorption analysis, samples were outgassed under vacuum for 2 h at 523 K.

Sample morphology was studied by an FEI Tecnai G2 20 X Twin transmission electron microscope (TEM) at a 200 kV accelerating voltage. Samples were drop-cast onto a copper mounted holey carbon film from distilled water suspension.

Temperature-programmed desorption measurements were carried out by CO_2 and NH_3 using a flow-through microreactor (I.D. 4 mm) made of quartz. About 100 mg of catalyst sample (particle size: 0.315–0.65 mm) was placed into the microreactor and was pre-treated in a 30 cm^3/min flow of O_2 at 500 °C for 1 h, then flushed by N_2 (30 cm^3/min) at same temperature for 15 minutes. The pre-treated sample was evacuated at 500 °C, cooled to room temperature and contacted with ~13 kPa of NH_3 or CO_2. After 15 minutes the physisorbed molecules were removed by evacuation. Then the reactor temperature was ramped up in He flow (20 cm^3/min) at a rate of 10 °C/min to 500 °C and held at this temperature for 1 h, while the effluent gas was passed through a dry ice/acetone trap and a thermal conductivity detector (TCD). Data were collected and processed by computer. Calculation of the adsorbed amount of NH_3 or CO_2 is based on the peak areas. The calibration values were determined with the passing of the known amount of NH_3 or CO_2 through the TCD detector.

2.3 Catalytic activity measurements

Catalytic test reactions were carried out at atmospheric pressure in a fixed-bed, continuous flow glass tube (∅=10 mm) microreactor. Prior to the reaction the catalysts were activated in oxygen flow (20 ml/min) for 1 h at 450 °C. In the reaction 1 g of sample (particle size 0.315-0.65 mm) was tested. The ethanol was transferred to evaporating zone heated to 120°C by using Gilson 307 HPLC Piston Pump and flushed into reactor with helium. The molar

composition of the feed was 14.7 % ethanol/He. The effect of reaction temperature was examined at total flow rate of 30 ml/min (0.5 $g_{ethanol} \cdot g_{cat}^{-1} \cdot h^{-1}$). The effect of weight hourly space velocity (WHSW) was measured by using 14.7 % ethanol/He feed in range of 5-120 cm^3 min^{-1} at 350 °C. All gas lines of the apparatus were heated to 120 °C in order to avoid the condensation of ethanol and reaction products. The reaction products were analyzed by on-line Shimadzu GC-2010 gas chromatograph equipped with a two FID detectors. A Chrompack PLOT Fused Silica column with Al_2O_3/KCl stationary phase (50 m long, 0.32 mm diameter) was used for an analysis of hydrocarbon products and a HP-PLOT-U column (30 m long, 0.32 mm diameter) was used for an analysis of oxygenates. The calibration of the GC for a reactant and each product was carried out separately. The conversion of ethanol was calculated from the ethanol concentration of the feed and the reactor effluent. The selectivities were calculated from the carbon atom content of the products. The carbon balance accuracies were usually better than 95%.

3. Results

The XRD patterns of the MgO-SiO_2 samples are shown on Fig 1. All the samples exhibit a broad diffraction line around $2\Theta = 23°$ which can be attribute to the amorphous silica network of the samples. On the XRD pattern of the IMP sample no additional lines can be observed. This suggests that the dispersion of the MgO over SBA-15 support is high and cause that the magnesia particles are XRD amorphous. On the XRD patterns of one-pot synthesized samples two additional lines can be observed at $2\Theta = 35.14°$ and $60.62°$ positions. According to literature these lines prove the formation of Mg-O-Si bonds and are interpreted as magnesia-silica hydrates [15] or chrysotile [37]. However, on the diffractograms the (00l) indexed lines are lacking and

the observed broad lines with great uncertainty can be attributed to talc structure disordered in direction c. As the WK sample was prepared by the mechanical mixing of SBA-15 and $Mg(OH)_2$ the XRD lines of MgO appear on the diffractogram of the calcined sample at $2\Theta = 42.92°$ and $62.04°$ positions. At the same time the line at $2\Theta = 35.52°$ and shoulder at $2\Theta = 60.62°$ proves that during the wet kneading and calcination process the Mg-O-Si bonds are formed in this sample, too. On XRD pattern of the 10OPMET no lines of the In_2O_3 can be observed. At lower In_2O_3 contents the same results were found (not shown) proving that no crystalline india was formed on the samples. Fig 1B shows the small-angle XRD patterns of the neat $MgO-SiO_2$ samples. Only the IMP and WK samples show XRD diffraction patterns characteristic to the two-dimensional hexagonal pore ordering of SBA-15 materials. On the XRD patterns of OPET, OPMET and In_2O_3-impregnated samples (not shown) no diffraction lines can be detected in low-angle region.

Fig. 2A shows the N_2 adsorption-desorption isotherms of the neat samples. According to the IUPAC classification [38] the isotherms of parent SBA-15 and IMP samples are of Type IV, the OPET and OMET are of Type II, while the isotherm of WK is the combination of the Type II and IV isotherms. Hysteresis loops can be observed on each isotherm indicating the capillary condensation in mesopore structures. Only the parent SBA-15 show steep condensation step on both adsorption and desorption branches characteristic for H1 type hysteresis loops stem from fairly regular array and narrow pore distribution of the mesopores. In case of IMP and WK samples the hysteresis loop is somewhat distorted compared to that of on pure SBA-15, indicating that the introduction of magnesia mechanically and/or chemically shatter the initial pore system. On the isotherm of WK sample the hysteresis loop does not close above p/po>0.9 due to the mesopores formed by agglomeration of MgO particles. The hysteresis loop on

isotherm of OPET sample is most similar to H3 type which is often given by the aggregates of platy particles [39]. OPMET sample exhibits H2 type hysteresis loop which is characteristic for inorganic oxide gels with pore system made up of interconnected network of pores of different size and shape [39]. The N_2 adsorption-desorption isotherms of the india impregnated samples are shown on Fig. 2B. It can be observed that the mesopore structures of IMP and WK samples are altered to H2 type indicating that during the evaporation of indium-nitrate solution the well-ordered SBA-15 structure suffered the further destruction. The formation of the new structure in case of IMP and WK samples led to increased surface area (Table 1). The data evaluated from ICP-OES and N_2 adsorption measurements are collected in Table 1. Except of OPET sample the m/m ratio of the samples is ~1/1. It can be noticed that the SSA of IMP and WK samples decreased compared to parent SBA-15. However, after the wet-impregnation with $In(NO_3)_3$ solution the SSA of the samples increased cause the structure rearrangement of the samples. The SSA of the one-pot synthesized samples are higher than that of the WK samples, and it decreases with about 25-30 % after the In_2O_3 impregnation step. The pore volume of parent SBA-15 material drops from 1.20 cm^3/g to 0.90 and 051 in case of WK and IMP samples respectively, indicating that impregnation partially clogs the pores of the SBA-15. At the same time the maximum of pore diameters is practically unchanged suggesting that part of the channels remain intact. The impregnation with indium salt results in a further decrease in pore volumes and pore diameters, too. The high pore volume and pore diameter data for OPET and 5OPET are derived from the volume formed between the $MgO-SiO_2$ particles

Textural properties of the samples were determined by means of TEM measurements (Fig. 3). The obtained results are in harmony with the above described XRD and N_2 physisorption results. The partially damaged SBA-15 structure can be observed on the images of

IMP and WK samples, while OPMET and OPET samples show an image characteristic for inorganic oxides/mixed oxides. On the images of the india doped samples except of 5IMP sample no regular channels are present. Furthermore, In_2O_3 crystallites cannot be observed on the images of the india containing samples. (The images of parent SBA-15 and of the catalysts samples in different magnifications are shown in Supporting Information, F1.)

Results of ETB reaction over pure MgO-SiO_2 preparations are shown on Fig. 4. The conversion curves run almost identical in case of each catalyst. The main reaction products are formed in dehydration reactions, namely diethyl ether (DEE) at lower (exothermic reaction) and ethylene (EE) at higher temperatures (endothermic reaction). The best BD selectivities were achieved over WK sample (20-30 %) throughout the whole investigated temperature range. Over other catalysts except of at low temperatures (and low conversions) the BD selectivity was around 10%. Small amounts of acetaldehyde and butene isomers (1-5% selectivity level) were also identified amongst the product molecules, while the crotyl alcohol and crotonaldehyde was present only in traces. As Fig. 5. shows the addition of 5wt% of In_2O_3 remarkably enhances the BD selectivities and ethanol conversions over all of the MgO-SiO_2 supports. It can be observed that at low temperatures the enhanced BD selectivities are linked with the suppression of the diethyl ether and ethylene formation. However, at higher temperatures the BD selectivities decrease induced by enhanced ethylene formation. The addition of In_2O_3 also increases the selectivities of acetaldehyde, butanol and butenes compared to sole MgO-SiO_2 supports. The effect of the In_2O_3 loading on the ETB reaction over OPMET support is shown on Fig. 6. It should be emphasized that over 5% In_2O_3/OPMET catalyst the ethylene selectivity reach only 20% even at the higher examined reaction temperature and the higher BD yields are achieved over this preparation. Besides enhanced BD selectivities it can be also noticed that the

acetaldehyde yields are the highest amongst investigated catalysts. At highest In_2O_3 loading the further increase of the acetaldehyde selectivities in expense of butadiene yields can be observed. The stability test at 375 °C over 5OPMET catalyst (Fig 6D) shows that after 10 hours the conversion falls from the starting 52 to 39 % , and after 25 h stabilizes at 30%, while the BD selectivity drops from 56 to 47 % followed by increasing of acetaldehyde selectivity from starting 17 to 25 %.

The acidity and basicity of the samples were characterized by the NH_3 and CO_2 adsorption capacity of the samples. Results of the NH_3 and CO_2 TPD measurements are collected in Table 2. Fig. 7 shows the effect of acidic and basic properties of the neat and In_2O_3 impregnated samples on the catalytic activity of the samples in ETB reaction at the same conversion levels. The identical conversions were achieved by varying of space velocity at 350°C and 14.7 % ethanol/He concentration. In case of neat samples the highest BD selectivity at 25 % conversion level was achieved over WK sample (Fig. 7A). The other samples possess higher or almost equal concentration of the acidic sites, indicated by higher NH_3 adsorption capacity. However, the basicity of other three samples is significantly lower compared to WK sample. The low concentration of basic sites combined with high concentration of acidic sites results in a high dehydration activity, thus higher ethylene + diethyl ether selectivities at the expense of BD formation. Addition of 5 wt% In_2O_3 to the MgO-SiO_2 preparations except of 5IMP sample complanate the NH_3 and CO_2 adsorption capacity of the samples (Fig. 7 B and C, 30 and 65 % conversion of ethanol, respectively). A somewhat higher acidity and lower basicity of the 5IMP sample led to lower BD and higher ethylene + diethyl ether selectivities. It can be also noticed that after india doping the best BD selectivities were achieved over one-pot synthesized samples. As the In_2O_3 promotes the dehydrogenation of ethanol, the acetaldehyde

selectivities are also higher over doped samples, especially at lower conversion level (i.e. at lower residence time), when the contact time of formed acetaldehyde was not enough to take part in condensation reactions. However, the enhanced acetaldehyde formation facilitates the coupling step (and suppresses dehydration reactions) and thus the yield of butenes and C_4 oxygenates also increases over india doped samples.

4. Discussion

The heterogeneity/homogeneity of MgO/SiO_2 systems has a decisive role on the butadiene yields in ETB reaction. There is a contradiction in literature whether the inorganic magnesium salts (nitrate, acetate) are incorporated into the silica framework of the SBA-15 during one-pot synthesis. In publications which claim that the incorporation of the magnesium is possible the washing step is neglected [32,36]. At the same time the product contains chloride ions in non-negligible amount originating from hydrochloric acid used for synthesis [32]. The produced MgO/SBA-15 show the features like pure SBA-15 i.e. sharp peaks on low-angle XRD pattern and highly ordered mesoporous structure on TEM images. Wu et al. [31] state that by using this synthesis method the magnesium species are decorated on the surface of SBA-15 and this species convert to smooth MgO_x layer during the calcination step. Formation of small amount of Mg-O-Si bonds is also possible by interaction of magnesium species with silanol groups of SBA-15. The threshold of MgO dispersion with this method is around 30 wt.-% [32]. In present article the one-pot sol-gel synthesis was executed by using magnesium-alkoxides. The difficulty of this synthesis method lies in the different hydrolysis rates of the TEOS and magnesium-alkoxides. Moreover the magnesium-ethoxide is not soluble in TEOS, so it must be dissolved in methanol before to adding to synthesis gel. The XRD patterns on Fig 1. show that

the faster hydrolysis of magnesium-alkoxides did not result in the formation of separate MgO particles, besides amorphous silica the presence of magnesium-silicates can be observed. Another advantage of sol-gel synthesis besides of great homogeneity is the possibility to achieve high SSA. As Table 1. shows the SSA of OPMET and OPET samples are 486 and 594 m^2/g, respectively, and are in the same range as it is published for samples prepared by using inorganic magnesium salts (400-600 m^2/g). On the basis of nitrogen adsorption isotherms and TEM images it can be concluded that the OPMET and OPET samples are mesoporous but have no SBA-15 structure. It may be supposed that the SDA promoted the formation of the mesoporous structure, but the differences between chemical properties of TEOS and magnesium-alkoxides hindered the formation of the regular array and narrow pore distribution characteristic to SBA-15. Based on nitrogen adsorption isotherms and TEM images (Figs 2A and 3), it can be concluded that the impregnation and wet kneading steps have only partially damaged the original SBA-15 structure and the SSA of the samples remain considerably high (191 and 356 m^2/g for IMP and WK samples, respecitively) despite to the considerably high MgO content of the samples (~50 wt.-%). Impregnation of parent MgO-SBA-15 preparations with $In(NO_3)_3$ solution resulted in a structure loss of IMP and WK samples and with structure rearrangement of OPET and OPMET samples.

Over non-doped $MgO-SiO_2$ catalysts the higher butadiene selectivities were achieved over WK sample. The XRD pattern of the sample (Fig 1.) show that the wet kneading results in material consisting of MgO and SiO_2 islands linked by Mg-O-Si bonds. On the other samples the magnesium is well dispersed in SiO_2 framework or is a part of Mg-O-Si linkages. The data in Table 2 and lines on Fig, 7A prove that the separated MgO phase enhances the CO_2 adsorption

capacity of the catalysts, while on the other hand the Mg-O-Si bonds (which are not present in IMP sample) are responsible for higher NH_3 adsorption capacity, i.e. higher acidity.

As it is discussed in Introduction Section addition of metals/metal-oxides to catalyst enhances conversion as well as selectivity for butadiene by promoting dehydrogenation of ethanol to acetaldehyde. The results presented on Figs 5 and 6 fully support this theory. It also can be concluded from the results that by directing of reaction to the dehydrogenation pathway the dehydration step is suppressed and besides of BD the selectivity of other C4 products (mainly butenes and butanol) also increases slightly. This phenomenon was investigated in details on best performing catalyst (OPMET, Fig 6.). The results show that by increasing the amount of india, the selectivity of the products formed in dehydration reactions is gradually reduced. However, it is also observed that the selectivity of butadiene over a given indium content (5 wt%) does not increase further, but instead the selectivity of the acetaldehyde formed during the ethanol dehydrogenation is growing. The stability study on 5OPMET catalysts (Fig 6D) also showed that as the activity of the catalyst decreases, the selectivity of butadiene decreases, while of the acetaldehyde increases and the other products remain unchanged during 30h.

Angelici et al. [7] stated that "Studies on these dehydrogenation promoters typically report limited characterization data on both the acid−base and structural properties, making the explanations for the observed beneficial or detrimental catalytic effects often somewhat speculative." In present study the structure of the catalysts were characterized by XRD and TEM measurements, while acidic/basic properties of the catalysts were determined by NH_3 and CO_2 adsorption capacity of the samples. Results presented on Fig. 7 suggests that there is a correlation between acidic/basic properties and catalytic activity of the samples. However, in a complex reaction network of ETB reaction, it is not only acidity/basicity that affects the

selectivity of the formation of different products. Fig 7A shows that the selectivity of BD (and of other C4 products) is the highest over WK sample on which the CO_2 adsorption capacity is the highest and the amount of adsorbed NH_3 is almost the same or lower than in the other samples. The lower basicity and higher acidity of samples results in a low BD and high dehydration (i.e. ethylene and diethyl ether formation) activity. The Fig 2. shows that the structure of the samples changed significantly after impregnation of indium oxide. The hysteresis loops on the N_2 adsorption/desorption isotherms suggest that the pore structure of the samples became very similar after the impregnation and their structure is most similar to inorganic oxide gels with pore system made up of interconnected network of pores of different size and shape. The impregnation of the In_2O_3 increased both NH_3 and CO_2 adsorption capacity of the samples. It can be also noticed that over best performing catalysts (5WK, 5OPET, 5OPMET) the NH_3 and CO_2 adsorption capacities are very similar, while the 5IMP sample possess higher acidity and lower basicity what resulted in a lower BD and higher dehydration activity.

5. Conclusions

Four preparation methods were applied to prepare MgO-SiO_2 catalysts for one-step conversion of ethanol to butadiene. Besides common impregnation and wet-kneading the one-pot synthesis method was used when magnesium-ethoxide or magnesium-ethoxide was introduced into synthesis gel of SBA-15. The XRD results showed that except of impregnation all the preparation methods resulted in a formation of Mg-O-Si linkages. The separated MgO phase was observed only in case of WK sample. All the preparations are mesoporous with rather high specific surface area (190-590 m^2/g), but the presence of magnesium-alkoxides in synthesis gel

hindered the formation of SBA-15 structure. Over neat MgO-SiO$_2$ catalysts 10-30 % butadiene selectivities were achieved. The main reaction products were diethyl ether at lower and ethylene at higher temperatures. The addition of 5 wt% In$_2$O$_3$ significantly increased the selectivity of butadiene in all catalysts tested. The one-pot synthesized catalyst by using magnesium-methoxide showed 45-60% butadiene selectivity in temperature range of 250-425 °C. The india loading tests showed that by increasing of india content to 10 wt% the ethylene/diethyl ether formation can be suppressed below 10% selectivity level. However, the selectivities for butadiene are also reduced because the increased amount of acetaldehyde formed in the dehydrogenation reaction is no longer able to completely participate in the coupling reaction to form C4 products. The comparison of catalytic activity pure MgO-SiO$_2$ catalysts at same conversion level (25%) showed that the best performing WK sample possesses the higher CO$_2$ adsorption capacity (highest basicity) while the NH$_3$ adsorption capacity (acidity) of this sample is almost the same or lower than in the other samples. The impregnation of the samples with In$_2$O$_3$ causes further changes in the structure of the samples. The N$_2$ adsorption/desorption isotherms suggest that the pore structure of the samples becomes very similar after the impregnation. The samples with the similar CO$_2$/NH$_3$ adsorption capacities show the almost same catalytic activity and relatively high CO$_2$ and low NH$_3$ adsorption capacity led to the high butadiene selectivities. Over india-containing samples the higher dehydration activity and lowest butadiene selectivity was observed on impregnated sample which is more acidic and less basic.

[1]   H.N. Sun, J.P. Wristers, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 2000. doi:10.1002/ 0471238961.02212001192114.a01.

[2]   P.C.A. Bruijnincx, B.M. Weckhuysen, Shale Gas Revolution: An Opportunity for the Production of Biobased Chemicals?, Angew. Chemie Int. Ed. 52 (2013) 11980–11987. doi:10.1002/anie.201305058.

[3]   J. Sun, Y. Wang, Recent advances in catalytic conversion of ethanol to chemicals, ACS Catal. 4 (2014) 1078–1090. doi:10.1021/cs4011343.

[4]   S. V. Lebedev, No Title, J. Gen. Chim. 3 (1933) 698–708.

[5]   J. Ostromisslenski, No Title, J. Russ. Phys. Chem. Soc. 47 (1915) 1472–1506.

[6]   M. Lewandowski, G.S. Babu, M. Vezzoli, M.D. Jones, R.E. Owen, D. Mattia, P. Plucinski, E. Mikolajska, A. Ochenduszko, D.C. Apperley, Investigations into the conversion of ethanol to 1,3-butadiene using MgO:SiO2 supported catalysts, Catal. Commun. 49 (2014) 25–28. doi:10.1016/j.catcom.2014.02.003.

[7]   C. Angelici, F. Meirer, A.M.J. Van Der Eerden, H.L. Schaink, A. Goryachev, J.P. Hofmann, E.J.M. Hensen, B.M. Weckhuysen, P.C.A. Bruijnincx, Ex Situ and Operando Studies on the Role of Copper in Cu-Promoted SiO2-MgO Catalysts for the Lebedev Ethanol-to-Butadiene Process, ACS Catal. 5 (2015) 6005–6015. doi:10.1021/acscatal.5b00755.

[8]   Y. Sekiguchi, S. Akiyama, W. Urakawa, T.R. Koyama, A. Miyaji, K. Motokura, T. Baba, One-step catalytic conversion of ethanol into 1,3-butadiene using zinc-containing talc, Catal. Commun. 68 (2015) 20–24. doi:10.1016/j.catcom.2015.04.023.

[9]   O. V. Larina, P.I. Kyriienko, S.O. Soloviev, Ethanol Conversion to 1,3-Butadiene on ZnO/MgO-SiO2 Catalysts: Effect of ZnO Content and MgO:SiO2 Ratio, Catal. Letters. 145 (2015) 1162–1168. doi:10.1007/s10562-015-1509-4.

[10]   C. Angelici, M.E.Z. Velthoen, B.M. Weckhuysen, P.C.A. Bruijnincx, Influence of acid-base properties on the Lebedev ethanol-to-butadiene process catalyzed by SiO<inf>2</inf>-MgO materials, Catal. Sci. Technol. 5 (2015) 2869–2879. doi:10.1039/c5cy00200a.

[11]   M. Zhang, M. Gao, J. Chen, Y. Yu, Study on key step of 1,3-butadiene formation from ethanol on MgO/SiO2, RSC Adv. 5 (2015) 25959–25966. doi:10.1039/c4ra17070a.

[12]   Z. Han, X. Li, M. Zhang, Z. Liu, M. Gao, Sol-gel synthesis of ZrO2-SiO2 catalysts for the transformation of bioethanol and acetaldehyde into 1,3-butadiene, RSC Adv. 5 (2015) 103982–103988. doi:10.1039/c5ra22623f.

[13]   S.H. Chung, C. Angelici, S.O.M. Hinterding, M. Weingarth, M. Baldus, K. Houben, B.M. Weckhuysen, P.C.A. Bruijnincx, Role of magnesium silicates in wet-kneaded silica-magnesia catalysts for the Lebedev ethanol-to-butadiene process, ACS Catal. 6 (2016) 4034–4045. doi:10.1021/acscatal.5b02972.

[14]   S. Da Ros, M.D. Jones, D. Mattia, J.C. Pinto, M. Schwaab, F.B. Noronha, S.A. Kondrat, T.C. Clarke, S.H. Taylor, Ethanol to 1,3-Butadiene Conversion by using ZrZn-Containing MgO/SiO2Systems Prepared by Co-precipitation and Effect of Catalyst Acidity Modification, ChemCatChem. 8 (2016) 2376–2386. doi:10.1002/cctc.201600331.

[15]   S. Shylesh, A.A. Gokhale, C.D. Scown, D. Kim, C.R. Ho, A.T. Bell, From Sugars to Wheels: The Conversion of Ethanol to 1,3-Butadiene over Metal-Promoted Magnesia-Silicate Catalysts, ChemSusChem. 9 (2016) 1462–1472. doi:10.1002/cssc.201600195.

[16]   J.V. Ochoa, C. Bandinelli, O. Vozniuk, A. Chieregato, A. Malmusi, C. Recchi, F. Cavani, An analysis of the chemical, physical and reactivity features of MgO-SiO2catalysts for butadiene synthesis with the Lebedev process, Green Chem. 18 (2016) 1653–1663. doi:10.1039/c5gc02194d.

[17]   Y. Hayashi, S. Akiyama, A. Miyaji, Y. Sekiguchi, Y. Sakamoto, A. Shiga, T.R. Koyama, K. Motokura, T. Baba, Experimental and computational studies of the roles of MgO and Zn in talc for the selective formation of 1,3-butadiene in the conversion of ethanol, Phys. Chem. Chem. Phys. 18 (2016) 25191–25209. doi:10.1039/c6cp04171j.

[18]   X. Huang, Y. Men, J. Wang, W. An, Y. Wang, Highly active and selective binary MgO-SiO 2 catalysts for the production of 1,3-butadiene from ethanol, Catal. Sci. Technol. 7 (2017) 168–180. doi:10.1039/c6cy02091g.

[19]   J.V. Ochoa, A. Malmusi, C. Recchi, F. Cavani, Understanding the Role of Gallium as a Promoter of Magnesium Silicate Catalysts for the Conversion of Ethanol into Butadiene, ChemCatChem. 9 (2017) 2128–2135. doi:10.1002/cctc.201601630.

[20]   Y. Xu, Z. Liu, Z. Han, M. Zhang, Ethanol/acetaldehyde conversion into butadiene over sol-gel ZrO2-SiO2catalysts doped with ZnO, RSC Adv. 7 (2017) 7140–7149. doi:10.1039/c6ra25139k.

[21]   H.J. Chae, T.W. Kim, Y.K. Moon, H.K. Kim, K.E. Jeong, C.U. Kim, S.Y. Jeong, Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts, Appl. Catal. B Environ. 150–151 (2014) 596–604.

doi:10.1016/j.apcatb.2013.12.023.

[22] S. Li, Y. Men, J. Wang, S. Liu, X. Wang, F. Ji, S. Chai, Q. Song, Morphological Control of Inverted MgO-SiO2 Composite Catalysts for Efficient Conversion of Ethanol to 1,3-Butadiene, Appl. Catal. A Gen. (2019). doi:10.1016/j.apcata.2019.03.007.

[23] M.D. Jones, C.G. Keir, C. Di Iulio, R.A.M. Robertson, C. V. Williams, D.C. Apperley, Investigations into the conversion of ethanol into 1,3-butadiene, Catal. Sci. Technol. 1 (2011) 267–272. doi:10.1039/c0cy00081g.

[24] A. Klein, R. Palkovits, Influence of structural parameters on the conversion of ethanol into 1,3-butadiene using mesoporous zeolites, Catal. Commun. 91 (2017) 72–75. doi:10.1016/j.catcom.2016.12.009.

[25] S.I. Fujita, S. Segawa, K. Kawashima, X. Nie, T. Erata, M. Arai, One-Pot Room-Temperature Synthesis of Mg Containing MCM-41 Mesoporous Silica for Aldol Reactions, J. Mater. Sci. Technol. 34 (2018) 2521–2528. doi:10.1016/j.jmst.2016.08.025.

[26] G. Pomalaza, G. Vofo, M. Capron, F. Dumeignil, ZnTa-TUD-1 as an easily prepared, highly efficient catalyst for the selective conversion of ethanol to 1,3-butadiene, Green Chem. 20 (2018) 3203–3209. doi:10.1039/c8gc01211c.

[27] J. Scholz, A. Walter, A.H.P. Hahn, T. Ressler, Molybdenum oxide supported on nanostructured MgO: Influence of the alkaline support properties on MoOx structure and catalytic behavior in selective oxidation, Microporous Mesoporous Mater. 180 (2013) 130–140. doi:10.1016/j.micromeso.2013.05.032.

[28] I.M. El-Nahhal, J.K. Salem, N.S. Tabasi, Uptake of curcumin by supported metal oxides (CaO and MgO) mesoporous silica materials, J. Sol-Gel Sci. Technol. (2018) 647–656. doi:10.1007/s10971-018-4763-2.

[29] A. Zukal, J. Pastva, J. Čejka, MgO-modified mesoporous silicas impregnated by potassium carbonate for carbon dioxide adsorption, Microporous Mesoporous Mater. 167 (2013) 44–50. doi:10.1016/j.micromeso.2012.05.026.

[30] Y. Chen, J. Han, H. Zhang, Facile synthesis and characterization of acid-base bifunctionalized mesoporous silica, Appl. Surf. Sci. 254 (2008) 5967–5974. doi:10.1016/j.apsusc.2008.03.169.

[31] Z.Y. Wu, Q. Jiang, Y.M. Wang, H.J. Wang, L.B. Sun, L.Y. Shi, J.H. Xu, Y. Wang, Y. Chun, J.H. Zhu, Generating superbasic sites on mesoporous silica SBA-15, Chem. Mater.

18 (2006) 4600–4608. doi:10.1021/cm0608138.

[32]   Y.L. Wei, Y.M. Wang, J.H. Zhu, Z.Y. Wu, In-Situ Coating of SBA-15 with MgO: Direct Synthesis of Mesoporous Solid Bases from Strong Acidic Systems, Adv. Mater. 15 (2003) 1943–1945. doi:10.1002/adma.200305803.

[33]   Z. Kónya, J. Zhu, A. Szegedi, I. Kiricsi, G.A. Somorjai, Synthesis and characterization of hyperbranched mesoporous silica prepared in a simple process using non-ionic surfactant in, Chem. Commun. (2003) 314–315.

[34]   Y.M. Wang, Z.Y. Wu, Y.L. Wei, J.H. Zhu, In situ coating metal oxide on SBA-15 in one-pot synthesis, Microporous Mesoporous Mater. 84 (2005) 127–136. doi:10.1016/j.micromeso.2005.05.024.

[35]   K.K. Han, Y. Zhou, Y. Chun, J.H. Zhu, Efficient MgO-based mesoporous CO_2 trapper and its performance at high temperature, J. Hazard. Mater. 203–204 (2012) 341–347. doi:10.1016/j.jhazmat.2011.12.036.

[36]   H. Zhang, M. Li, P. Xiao, D. Liu, C.J. Zou, Structure and Catalytic Performance of Mg-SBA-15-Supported Nickel Catalysts for CO_2 Reforming of Methane to Syngas, Chem. Eng. Technol. 36 (2013) 1701–1707. doi:10.1002/ceat.201300006.

[37]   L. Wang, A. Lu, C. Wang, X. Zheng, D. Zhao, R. Liu, Nano-fibriform production of silica from natural chrysotile, J. Colloid Interface Sci. 295 (2006) 436–439. doi:10.1016/j.jcis.2005.08.055.

[38]   K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, F. Rouquerol, Reporting physisorption data for gas/solid systems, Pure Appl. Chem. 57 (1985) 603–619.

[39]   K.S.W. Sing, F. Rouquerol, J. Rouquerol, P. Llewellyn, Assessment of Mesoporosity, in: Adsorpt. by Powders Porous Solids, Second Edi, Elsevier Ltd, 2014: pp. 269–302.

Figure legends

Figure 1. XRD patterns of MgO-SiO_2 samples in normal (A) and small (B) 2Ө region. Samples were prepared by impregnation (IMP), wet-kneading (WK), were synthesized using magnesium ethoxide (OPET), or magnesium methoxide (OPMET) and by impregnation with 10% In_2O_3 (10OPMET)

Figure 2. N_2 adsorption-desorption isotherms of the samples. Adsorption and desorption branches are indicated by full and open symbols, respectively. For the meaning of the sample designations see the legend of Fig 1.

Figure 3. TEM images of the samples. For the meaning of the sample designations see the legend of Fig 1.

Figure 4. Catalytic conversion of ethanol over samples prepared by impregnation (IMP), wet-kneading (WK), and synthesized by using magnesium ethoxide (OPET), or magnesium methoxide (OPMET). Reaction conditions: T=250-425 °C, WHSW= 0.5 $g_{ethanol} \cdot g_{cat}^{-1}$ h^{-1}, Q_{tot}=30 cm^3 min^{-1}, $p_{ethanol}$= ~15 kPa, m_{cat}=1.00 g.

Figure 5. Effect of 5 wt% In_2O_3 doping on the conversion of ethanol to butadiene over impregnated (IMP), wet-kneaded (WK) and synthesized by using magnesium ethoxide (OPET). Reaction conditions: T=250-425 °C, WHSW= 0.5 $g_{ethanol} \cdot g_{cat}^{-1}$ h^{-1}, Q_{tot}=30 cm^3 min^{-1}, $p_{ethanol}$= ~15 kPa, m_{cat}=1.00 g.

Figure 6. Effect of 2 (A), 5(B) 10 (C) wt% In_2O_3 over MgO-SiO_2 catalyst synthesized by magnesium methoxide on the activity and selectivity in ethanol to butadiene reaction between 250-425 °C. Stability test on 5OPMET catalyst at 350°C for 30 h (D). Reaction conditions: WHSW= 0.5 $g_{ethanol} \cdot g_{cat}^{-1} h^{-1}$, Q_{tot}=30 $cm^3 min^{-1}$, $p_{ethanol}$= ~15 kPa, m_{cat}=1.00 g.

Figure 7. Comparison of the product selectivities of neat (A conv =25%) and 5 wt% In_2O_3-doped (B conv=30%, C conv=65%) samples at identical conversion levels. The identical conversions were achieved by varying of space velocity. T=350 °C, $p_{ethanol}$= ~15 kPa, m_{cat}=1.00 g, Q_{tot}=5-120 cm^3 min^{-1}. The corresponding NH_3 and CO_2 adsorption capacities of the samples determined by TPD measurements are indicated on right Y axes.

Table 1. Characterization of the catalysts

Table 2. Results of CO_2 and NH_3 Temperature Programmed Desorption (TPD) measurements