Contents lists available at ScienceDirect





Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Conversion of ethanol to but adiene over mesoporous In_2O_3 -promoted MgO-SiO₂ catalysts

Check for updates

Blanka Szabó^a, Gyula Novodárszki^a, Zoltán May^a, József Valyon^a, Jenő Hancsók^b, Róbert Barthos^{a,*}

^a Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, Magyar tudósok körútja 2, Budapest 1117, Hungary
^b Institute of Chemical and Process Engineering, University of Pannonia Veszprém H-8201, Hungary

A R T I C L E I N F O A B S T R A C T Keywords: Mesoporous MgO-SiO₂ mixed oxide catalysts were prepared for the conversion of ethanol to 1,3-butadiene. Ethanol Mesoporous MgO-SiO₂ mixed oxide catalysts were prepared for the conversion of ethanol to 1,3-butadiene. Butadiene Mesoporosity was obtained by using SBA-15 material as support for magnesia or by applying one-pot synthesis MgO-SiO₂ catalysts method wherein magnesia precursor, such as, magnesium methoxide or ethoxide, was admixed to the synthesis gel of the SBA-15 material. The SBA-15 support was wet-impregnated by Mg(NO₃)₂ solution or wet-kneaded with Mg(OH)₂ precipitate. The synthesized samples were mesoporous, however, the alkoxide in the synthesis gel hindered the formation of regular SBA-15 structure. In wet-kneaded and one-pot-synthesized samples the pre

with $Mg(OH)_2$ precipitate. The synthesized samples were mesoporous, however, the alkoxide in the synthesized samples were mesoporous, however, the alkoxide in the synthesized samples the presence of Mg-O-Si bonds was confirmed by X-ray diffractometry. The acid-base properties of the preparations were characterized by the room-temperature adsorption capacity for CO₂ and NH₃. Formation of Mg-O-Si bonds were shown to be responsible for the increased acidity/basicity of the samples. The best catalysts were the wet-kneaded sample and the sample synthesized using methoxide as magnesium source. Over these catalysts the butadiene yield reached 15 % at 400 – 425 °C. To enhance the ethanol-to-butadiene activity the mixed oxides were promoted by In₂O₃. Additive In₂O₃ significantly improved dehydrogenation activity generating more acetaldehyde, and suppressed dehydration activity giving less ethylene and diethyl ether. Butadiene yields above 40% were achieved.

1. Introduction

1,3-butadiene (BD) is the most important conjugated diene. It is used as monomer in the synthesis of poly-butadiene or as a building block of different heteropolymers, such as, styrene-butadiene, nitrilebutadiene rubber, styrene-butadiene latex and acrylonitrile-butadienestyrene resin. Synthesis of monomers, like hexamethylenediamine and chloroprene, which are monomers of Nylon and Neoprene, respectively, uses also BD as reactant [1]. Currently, BD is obtained mainly as byproduct of ethylene production by steam cracking naphtha. The feedstock lightening, such as, the use of shale gas for ethylene production led to BD shortage and rise in BD prices [2]. An alternative way of getting BD can be the catalytic coupling of ethanol to butadiene (ETB reaction). 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 the ETB process were elaborated by Lebedev [4] and Ostromisslensky [5], usually distinguished as one-step and two-step process, respectively, in the first half of the previous century. In the one-step process only, ethanol is introduced into a catalytic reactor, whilst in two-step process first the ethanol is dehydrogenated to acetaldehyde separately, then the produced acetaldehyde is mixed up with ethanol and fed into the reactor. In condensation reaction two acetaldehyde molecules can give crotonaldehyde, which is then hydrogenated by another ethanol molecule to crotyl alcohol. Such transfer hydrogenation is known as heterogeneous catalytic Meerwein–Ponndorf–Verley (MPV) reduction. In the final step crotyl alcohol must to become dehydrated to get BD. The nice feature of the process is that reducing agent ethanol is not lost as sacrifice but is converted to acetaldehyde that is intermediate of the ETB process.

Among all the tested catalysts the MgO-SiO₂ materials showed the best activities in the ETB reaction [6–20]. Since ethanol dehydrogenation to acetaldehyde is the rate determining step of the consecutive reaction different metals/metal-oxides such as Zn, Zr, Cu, Au, and Ga were added to the MgO-SiO₂ catalyst to promote this step. It was pointed out that the catalytic activity depends not only on the composition but also on the structure and morphology of the catalyst that

* Corresponding author.

https://doi.org/10.1016/j.mcat.2020.110984

E-mail addresses: szabo.blanka@ttk.hu (B. Szabó), novodarszki.gyula@ttk.mta (G. Novodárszki), may.zoltan@ttk.hu (Z. May), valyon.jozsef@ttk.hu (J. Valyon), hancsokj@almos.uni-pannon.hu (J. Hancsók), barthos.robert@ttk.hu (R. Barthos).

Received 7 December 2019; Received in revised form 21 April 2020; Accepted 27 April 2020 2468-8231/ © 2020 Elsevier B.V. All rights reserved.

determines the nature and amount of available active sites. Latter properties can be directed by the method applied for catalyst preparation. The methods reported for the preparation of MgO-SiO₂ catalyst were (i) mechanical mixing, (ii) co-precipitation, or (iii) wet kneading of the components, and (iv) incipient wetness impregnation of one component, usually the SiO₂, with the precursor of the other one. All cases the preparation was finished by calcination. Nevertheless, there is no consensus about the best catalyst structure and method of catalyst preparation. It is generally accepted that the ETB reaction demands an appropriate balance of basicity and acidity. In MgO-SiO₂ 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 was also shown that the BD yield depends on the specific surface area [10], crystal size/shape [21,22] and pore diameter of the MgO-SiO₂ catalyst [23,24].

The mesoporous materials have several advantages compared to microporous or non-porous materials. Mesopores foster mass and heat transport and facilitate the high dispersion of the metal/metal oxide promoters. Two major techniques were developed for the preparation of basic catalyst that retain the favorable mesoporous structure: (i) the two-step method, wherein the mesoporous framework is synthesized first, followed by ion-exchange, impregnation, microwave irradiation or anchoring of the basic guest, and (ii) the one-pot synthesis, where the precursors of the basic guest and the mesoporous host are loaded together in a single reactor vessel.

The imperceptible acidity and basicity limits the catalytic application of ordered mesoporous silica. In order to exploit the benefits of its mesoporosity, Chae et al. [21] used silicas, such as, SBA-15, KIT-6, and MMS, as support for basic tantalum pentoxide and used the obtained Ta₂O₅/silica catalyst for the transformation of ethanol/acetaldehyde mixture to BD. The mesoporous catalysts were found to show better coke tolerance, catalytic longevity, as well as, activity than catalysts based on conventional silica. Klein and Palkovits [24] studied ZnO/ zeolite catalysts in the ETB reaction. Higher catalytic activity was attained, if the zeolite particles contained not only micropores but also mesopores. Fujita et al. [25] used Mg-incorporating MCM-41 mesoporous silica materials as catalysts for the aldol condensation of 4-nitrobenzaldehyde and acetone. It was reported that the large surface area and pore volume of the catalyst was favorable for the reaction. Catalysts, containing both zinc and tantalum as active components on different supports were compared by Pomalaza et al. [26] in the ETB reaction. The mesoporous silica TUD-1 silica was found to be much more advantageous support for magnesia than the dealuminated zeolite Beta or the fumed silica.

To our knowledge mesoporous MgO-SiO₂ materials have not been examined yet in ETB reaction. Commonly, the mesoporous silica is synthesized first and impregnated then by the precursor of MgO, such as, Mg(NO₃)₂ [27] or Mg(CH₃COO)₂ [28]. Calcination of the preparation results in silica-supported MgO catalyst. Unfortunately, the catalyst usually cannot fully retain the mesoporous structure of the support. Zukal et al. [29] elaborated a modified method to avoid destruction of silica mesopores. Magnesium acetate, impregnated on silica surface was converted by oxalic acid to magnesium oxalate. The oxalate could be converted to magnesia at relatively low temperature. According to an alternative method magnesium salt and as-prepared micelle-templated silica (MTS) were ground together at room temperature and calcined then to remove the structure directing agent (SDA) of the MTS material [30]. The basicity of the catalyst could be further enhanced by adding alkali salt, such as KNO₃ to the preparation [31]. In the so-called onepot method silica, magnesia source (magnesium nitrate or magnesium acetate), and SDA are mixed to get a synthesis mixture [31-36]. In the synthesis process silica is believed to incorporate magnesium ions in its structure. 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 was also shown that both anions and cations have an effect on the mesostructure of the SBA-15. Wang et al. [34] found that the strength of effect follows the lyotropic series $NO_3^- < Cl^- < CH_3COO^-$ of the anions. The MgO/mesoporous silica preparations were used as adsorbents for CO_2 [29,35] and curcumin [28] or as catalyst in selective oxidation [27], transesterification [30] and CO_2 reforming of methane [36].

It is well known that SBA-15 material possesses hexagonally arranged, channel-like, parallel mesopores of about uniform diameter, large specific surface area, and high silanol group concentration. Catalytically active species can be stabilized in high dispersion within the regular pore structure, providing very similar chemical environment for the active sites that is beneficial regarding the catalytic selectivity. Thanks to its thick pore walls the SBA-15 material is known to have excellent thermal, hydrothermal stability and outstanding acid resistance [37]. Considering above benefits this work deals with MgO/ SBA-15 catalysts prepared by the methods of (i) impregnation, (ii) wet kneading, and the (iii and iv) one-pot synthesis method using magnesium ethoxide or magnesium methoxide as Mg source. The MgO/SBA-15 preparations were characterized by means of Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES), X-ray Diffraction (XRD), N₂ physisorption, and Transmission Electron Microscopy (TEM). TPD curves of adsorbed carbon dioxide and ammonia were recorded to learn more about the relative basicities and acidities of the samples. The catalysts were tested in direct conversion of ethanol to butadiene. The promoting effect of In₂O₃ on the ETB reaction is also discussed.

2. Experimental

2.1. Preparation of catalysts

Basic MgO/SBA-15 catalysts were prepared by impregnation and wet kneading methods using SBA-15 material provided by Nanjing XFNANO Materials Tech Co., Ltd, China, and a magnesia precursor. Moreover, two catalysts were synthesized by the so-called one-pot method using magnesium ethoxide and methoxide as Mg source.

The impregnation was carried out by adding 200 mL 0.5 M solution of $Mg(NO_3)_2$ ·6H₂O (Sigma-Aldrich, 99%) to 10.00 g of SBA-15, dried at 120 °C for 2 h. The water was removed under continuous stirring at 70 °C. The sample was dried then at 120 °C overnight and calcined in air at 500 °C for 5 h. The sample was designated as IMP.

For the wet kneading procedure Mg(OH)₂ precipitate was made. To a sodium hydroxide solution Mg(NO₃)₂·6H₂O solution was added at pH of 12. During formation of precipitate the pH was maintained by slow addition of 2 M NaOH. The precipitate was aged in the mother-lye for 24 h, washed then to remove sodium and dried at 120 °C overnight. The wet kneading was carried out by stirring of 2.15 g Mg(OH)₂ and 5.00 g of dried SBA-15 in 100 mL of distilled water at room temperature for 5 h. The suspension was centrifuged, the solid was dried at 120 °C overnight and calcined in air at 500 °C for 5 h. The sample was designated as WK.

The one-pot synthesis with magnesium ethoxide was performed as follows: 16 g template for SBA-15 synthesis (Pluronic P-123, Aldrich) was dissolved in 600 mL 0.03 M HCl solution by stirring at room temperature for 2 h. A second mixture was made by mixing 37 mL TEOS (Tetraethyl orthosilicate, Aldrich, 98%) and 8.20 g magnesium ethoxide (Aldrich, 98%) in 250 mL in methanol. Thereafter, the second mixture was dropwise added to the vigorously stirred Pluronic P-123 solution at room temperature. After 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 in air. The sample was calcined by heating up at a rate of 1 °C min⁻¹ to 500 °C and keeping at this temperature overnight. The sample was designated as OPET.

For the one-pot synthesis with magnesium methoxide first a pre-

hydrolized TEOS solution was made using the same amounts of Pluronic P-123 template, HCl solution and TEOS as used for the synthesis with magnesium ethoxide (vide ultra). To this stirred solution 155 mL magnesium methoxide solution (7-8 wt.%) in methanol, Alfa Aesar) was added dropwise. The gelation of the obtained sol started immediately. 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 the OPET sample. The sample was designated as OPMET.

Catalysts, promoted by In_2O_3 were obtained by impregnating the mixed oxide catalysts using an about 33 mM/dm^3 solution of In $(NO_3)_3$ ·xH₂O (Alfa Aesar 99.99% metal purity) in an amount needed to get catalysts having In_2O_3 content of about 2.0 wt.%, 5.0 wt.%, and 10.0 wt.%. In order to get appropriate metal concentration for the aliquots the water content of the nitrate salt was determined by thermogravimetry. The number before the abbreviation of the catalysts name denotes the In_2O_3 content of the sample in weight percent, e.g., 5IMP means 5 wt.% In_2O_3 on the surface of the catalyst, made by the impregnation method.

2.2. Characterization

The composition of the samples was determined by inductively coupled plasma optical emission spectrometry (ICP OES) with axial plasma observation and capability for simultaneous and multi-element determination (Spectro Genesis).

X-ray diffraction patterns were recorded at ambient conditions by Philips PW 1810/3710 diffractometer applying monochromatized CuK_{α} ($\lambda = 0.15418$ nm) radiation (40 kV, 35 mA) and proportional counter. Data were collected between 3° and 75° 2 θ , in 0.02° steps for 0.5 s in each step. The low-angle XRD measurements were executed by Philips X'Pert MPD system using $2\theta - \omega$ scan method between 0.6–3.0 2θ , in 0.002 steps for 10 s in each step.

Nitrogen physisorption measurements were carried out at 77 K using Thermo Scientific Surfer automatic, volumetric adsorption analyzer. Before adsorption measurement, 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 from distilled water suspension onto a copper mounted holey carbon film.

Temperature-programmed desorption (TPD) measurements were carried out by CO₂ and NH₃ 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 $30 \text{ cm}^3 \text{min}^{-1}$ flow of O₂ at 500 °C for 1 h, then flushed by N₂ $(30 \text{ cm}^3 \text{ min}^{-1})$ at the same temperature for 15 min. The pre-treated sample was evacuated at 500 °C, cooled to room temperature and contacted with NH₃ or CO₂ at 13 kPa pressure. After 15 min of contact the physiosorbed molecules were removed by evacuation. Then the reactor temperature was ramped up in He flow $(20 \text{ cm}^3 \text{ min}^{-1})$ at a rate of 10 °C min⁻¹ 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 NH₃ or CO₂ is based on the peak areas. The TCD was calibrated by passing known amounts of NH₃ or CO₂ through the detector.

2.3. Catalytic activity

Catalytic reactions were carried out at atmospheric pressure in a fixed-bed, continuous flow glass tube ($\emptyset = 10 \text{ mm}$) microreactor. Prior to reaction the catalysts were activated in oxygen flow (20 mL min^{-1}) for 1 h at 450 °C. In the reaction 1 g of catalyst (particle size 0.315 - 0.65 mm) was used. By a Gilson 307 HPLC Piston Pump reactant ethanol was fed in an evaporating zone kept at 120 °C and

flushed through the catalyst bed with a helium flow. The effect of weight hourly space velocity (WHSW) on the conversion was measured by 14.7 vol.% ethanol/He feed in the flow rate range of 5-120 cm³ min⁻¹ at 350 °C temperature. The effect of reaction temperature was at the total flow rate of $30 \,\mathrm{mL}\,\mathrm{min}^{-1}$ examined (WHSV = $0.5 g_{ethanol} g_{cat}^{-1} h^{-1}$). All gas lines of the reactor system were kept at 120 °C temperature to avoid the condensation of ethanol and reaction products. The reaction products were analyzed by on-line Shimadzu GC-2010 gas chromatograph equipped with two FID detectors. A Chrompack PLOT Fused Silica column with Al₂O₃/KCl stationary phase (50 m long, 0.32 mm diameter) was used for the analysis of hydrocarbon products and a HP-PLOT-U column (30 m long, 0.32 mm diameter) was used for the analysis of oxygenates. The calibration of the GC was carried out for the reactant and each product separately. The conversion of ethanol was calculated from the ethanol concentration of the feed and the reactor effluent. The selectivity calculation was based on the carbon atom content of the products. The carbon balance accuracies were usually better than 95%.

3. Results

XRD patterns of the MgO-SiO₂ samples are shown on Fig. 1. Each sample exhibit a broad diffraction line at around $2\theta = 23^{\circ}$, which can be attributed to amorphous silica.

On the XRD patterns of one-pot-synthesized samples two additional lines can be observed at $2\theta = 35.14^{\circ}$ and 60.62° (Fig. 1a, OPET, OPMET). According to the literature these lines indicate Mg–O–Si bonds and are interpreted as magnesia-silica hydrates [20] or chrysotile [38]. However, on the diffractograms the (001) indexed lines are lacking and the observed broad lines can be attributed with great uncertainty to talc structure disordered in direction c.

On the XRD pattern of the IMP sample no characteristic lines can be observed. This suggests that the dispersion of MgO over the SBA-15 support is high enough to be XRD amorphous.

In contrast, the XRD lines of MgO appear on the diffractogram of the calcined WK sample at $2\theta = 42.92^{\circ}$ and 62.04° . The line, also appearing at $2\theta = 35.52^{\circ}$, and the shoulder at $2\theta = 60.62^{\circ}$ proves that during the wet kneading and calcination process Mg-O-Si bonds were formed. In the XRD patterns of indium doped samples no lines of indium oxide appeared proving the absence of crystalline indium oxide (only the pattern of 100PMET is shown in Fig. 1a). Only the IMP and WK samples give reflections characteristic for the hexagonally ordered two-dimensional pore system of SBA-15 materials (Fig. 1b).

Fig. 2a shows the N₂ adsorption-desorption isotherms of the neat basic catalyst preparations. According to the IUPAC classification [39] the isotherms of parent SBA-15 and IMP samples are of Type IV, those of the OPET and OMET samples are of Type II, while the isotherm of the WK sample is the combination of the Type II and IV isotherms. Hysteresis loops can be observed on each isotherm indicating the presence of mesoporous system wherein capillary condensation occurs. Only the isotherm of neat SBA-15 material shows adsorption and desorption branches characteristic for H1 type hysteresis loops stemming from fairly regular array of mesopores having narrow distribution of sizes. In case of IMP and WK samples the hysteresis loop is somewhat distorted compared to that of neat SBA-15 material, indicating that the introduction of magnesia mechanically and/or chemically shattered the pore system. The isotherm of WK sample presents open hysteresis loop even at relative pressure close to one. This may indicate large mesopores among agglomerated MgO nanoparticles. The hysteresis loop on the isotherm of the OPET sample resembles to H3 type loop which is characteristic for the morphology of aggregated plate like particles [40]. The OPMET sample exhibits H2 type hysteresis loop. Such loop is usually found on the isotherm of inorganic oxide gels having pore system made up of interconnected network of pores of different sizes and shapes [40]. The N2 adsorption-desorption isotherms of the indium-oxide-promoted samples are shown on Fig. 2b. The H2 type



Fig. 1. XRD patterns of MgO-SiO₂ samples in a) wide and b) small-angle 2θ region. Samples were prepared by impregnation of SBA-15 material (IMP), wet kneading of SBA-15 material and Mg(OH)₂ precipitate (WK), and by modified micelle-templated SBA-15 synthesis method using magnesium ethoxide (OPET), or magnesium methoxide (OPMET) as magnesium source. The In-promoted sample, containing 10 wt.% In₂O₃ (100PMET) was made from the OPMET sample by wet impregnation.

hysteresis loops suggest that the more or less ordered SBA-15-like materials became restructured during the In-doping procedure. The data obtained from ICP-OES analysis and N₂ adsorption measurements are summarized in Table 1. The silica to magnesia mass ratio of the samples, except that of the OPET sample, was near to one. The SSA of the one-pot synthesized samples was higher than that of the IMP and WK samples. Relative to the specific pore volume of parent SBA-15 material magnesia introduction reduced the pore volume of WK and IMP samples, indicating that impregnation partially clogged the pores. At the same time the diameter of the most frequent pores remained practically unchanged suggesting that part of the channels remained intact. The Inmodification of IMP and WK samples led to increased specific surface area (SSA, Table 1). In contrast, the SSA and pore volume of the OPET and OPMET samples decreased upon introduction of In_2O_3 (Table 1). The impregnation of the OPMET sample with indium salt resulted in a further decrease of the pore volume and the most frequent pore size. The pores, formed between aggregated $MgO-SiO_2$ nanoparticles made the mesopore structure of the OPET sample bimodal. The pore volumes and pore size data of Table 1 are relevant for this bimodal structure.

Textural properties of the samples were characterized by means of TEM images (Fig. 3). The obtained results are in harmony with the conclusions drawn above from XRD and N₂ physisorption results. The partially damaged SBA-15 structure can be observed on the images of the IMP and WK samples, whereas images of the OPMET and OPET samples are similar to those usually obtained for inorganic oxides/ mixed oxides. On the images of the In-doped samples no regular channel system is discernable. In this respect the 5IMP sample seems to be an exception. No In_2O_3 crystallites show up on any image of the In-containing samples.

Results of ETB reaction over MgO-SiO₂ preparations are shown in



Fig. 2. N_2 adsorption-desorption isotherms of the samples at -196 °C. Adsorption and desorption branches are indicated by full and open symbols, respectively. For the meaning of sample designations see the legend of Fig. 1.

Table 1Characterization of the catalysts.

Sample ID	${\rm SiO_2}^{\rm a}$	MgO ^a	$In_2O_3^a$	SSA ^b	PV ^c	PD^d
	wt%			m²/g	cm ³ /g	nm
SBA-15	100	-	-	494	1.20	8.09
IMP	57.81	42.19	-	191	0.51	7.89
WK	51.22	48.78	-	356	0.90	8.05
OPET	70.93	29,07	-	594	1.38	37.81
OPMET	48.96	51.04	-	486	0.48	3.72
20PMET	47.72	50.31	1.97	334	0.26	3.62
50PMET	49.02	46.17	4.81	326	0.31	3.56
100PMET	44.16	46.04	9.80	327	0.31	3.58
5IMP	54.41	39.71	5.88	400	0.39	3.47
5WK	48.84	46.52	4.65	402	0.50	3.73
50PET	65.91	27.03	7.01	411	0.85	25.70

^a Elemental composition determined by ICP-OES measurements.

^b Specific Surface Area.

^c Pore volume calculated by Gurvich method.

^d The most frequent pore diameter calculated from desorption branch by BJH method.

Fig. 4. Similar conversion curves were obtained for all four catalysts. The main reaction products were formed in ethanol dehydration reactions. The exothermic reaction of diethyl ether (DEE) formation dominated at lower temperatures, whereas the endothermic ethylene (EE) formation reaction prevailed at higher temperatures. The highest BD selectivity was achieved using the WK catalyst. It was about 20%-30% in the applied 250 - 425 °C temperature range. Over other catalysts, not regarding the selectivity at low conversion, the BD selectivity was around 10%. Small amounts of acetaldehyde (AA) and butene isomers (BUE, 1%-5% selectivity) were also identified in the product mixture. Crotyl alcohol and crotonaldehyde was present only in traces.

The addition of $5 \text{ wt.}\% \text{ In}_2\text{O}_3$ to the MgO-SiO₂ catalysts remarkably enhanced ethanol conversion and improved BD selectivity (Fig. 5). The activity improvement is more pronounced below about 350 °C reaction temperature than at higher temperatures. The higher BD selectivities and yields are paralleled with reduced yields of DEE and EE. The conversion to EE rapidly increases on the expense of conversion to BD as we increase the reaction temperature. The In₂O₃ in the catalysts also increases the selectivities for AA, BUE, and butanol (BOL), relative to the corresponding selectivities of the In-free catalysts.

The ETB activity of OPMET catalysts containing 2 wt.%, 5 wt.% and 10 wt.% In₂O₃ was compared. Over the catalyst, containing 5% In₂O₃ the EE selectivity was only 20% even at the highest applied reaction temperature and the BD selectivities remained above about 45% on all the applied reaction temperatures (Fig. 6b). At lower and higher In contents the EE selectivity was higher and lower, respectively. It has to be also noticed that not only the BD but also the AA yields are higher than that over the In-free catalysts. The AA selectivity changes parallel with the In content of the catalysts. Its increase occurs on the expense of butadiene yields. The stability test over 50PMET catalyst at 375 °C shows that after 10 h time on stream the conversion falls from the initial 52% to 39%. After 25 h it stabilizes at 30%. We observed continuous fall and increase of BD and AA selectivities, respectively (Fig. 6d). In view of formation rates the highest values were achieved over WK and 50PMET samples at 425 °C, by reaching the values of 0.9 and $1.7 \text{ mmol}_{BD^*}g_{cat^*}^{-1} h^{-1}$, respectively. These values are in the same range as it is reported by Da Ros et al. [19] for ZrZn-MgO/SiO₂ catalysts $(0.6-3 \text{ mmol}_{\text{BD}*} g_{\text{cat}*}^{-1} h^{-1})$ and a somewhat lower than earned by Sekiguchi et al. [41] for the zinc containing talc catalysts $(8-19 \text{ mmol}_{\text{BD}^*} g_{\text{cat}^*}^{-1} \text{ h}^{-1}).$

For better understanding the role of MgO and In₂O₃ the catalytic activity of neat MgO and In₂O₃/SBA-15 was compared. Fig. 7a shows that in studied temperature range BOL (~30%), AA, BD and CA (~20% – 20%) were formed with almost constant selectivity at low conversion level (~0.5%–10%) over MgO catalyst. It is also worth noting that only EE was identified among the dehydration products with a selectivity of 2%–10%, whereas over pure MgO-SiO₂ catalysts (cf. Fig. 4) DEE and EE were obtained with a selectivity of 70%–90% in the temperature range applied. AA was formed over the In₂O₃/SBA-15 catalyst (Fig. 7b) with high selectivity (~95%), whereas DEE, EE and ethyl acetate could be detected as other products. It can also be seen in the figure that ethanol conversion was significantly higher over In₂O₃/SBA-15 catalyst than over neat MgO, however, the conversion over the In₂O₃/SBA-15 catalyst was lower in the whole temperature range than over any of the MgO-SiO₂ catalysts (Fig. 4).

The acidity and basicity of the catalysts were characterized by their room-temperature adsorption capacity for NH₃ and CO₂, respectively (Table 2). Fig. 8 shows the acidity and basicity of the neat and In₂O₃-modified catalysts and their activity in the ETB reaction at the same conversion. Identical conversions were achieved over the different



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



Fig. 4. Catalytic conversion of ethanol/He mixture at atmospheric pressure as function of reaction temperature over MgO-SiO₂ catalysts using flow-through microreactor. The WHSV and the partial pressure of ethanol were $0.5 g_{ethanol}g_{cat}^{-1} h^{-1}$ and about 15 kPa, respectively. The conversion curve is labelled by letter C. Selectivity curves are given for butadiene (BD), diethyl ether (DEE), ethylene (EE), acetaldehyde (AA), and butenes (BUE). For the meaning of sample designations see the legend of Fig. 1.

catalysts by selecting the suitable WHSV of ethanol. The WHSV was set by adjusting the feed-rate of the 14.7 vol.% ethanol/He reactant mixture at 350 °C temperature. From the neat MgO-SiO₂ preparations at 25% conversion level the WK catalyst showed the highest BD selectivity (Fig. 8a). The other In-free samples possess similar or higher concentration of acid sites, as indicated by the NH₃ adsorption capacity, and lower concentration of basic sites, suggested by the adsorption capacity for CO_2 . Low concentration of basic sites combined with high concentration of acidic sites results in a high dehydration activity, thus higher ethylene-plus-diethyl-ether selectivities in the ETB reaction on the expense of BD formation.

Addition of 5 wt.% In₂O₃ to the MgO-SiO₂ preparations brings to the



Fig. 5. Catalytic conversion of ethanol/He mixture over In-modified MgO-SiO₂ catalysts. For reaction conditions, catalyst and curve identifications see the legends of Fig. 1 and 4. In the designation 50PET the prefix number 5 indicates that the catalyst contains 5 wt.% In₂O₃.



Fig. 6. Activity and selectivity of In_2O_3 -modified MgO-SiO₂ catalysts in the ETB reaction between 250 and 425 °C temperatures. The catalyst was modified by a) 2 wt. % (20PMET), b) 5 wt.% (50PMET), and c) 10 wt.% (100PMET) In_2O_3 . Section d) shows the stability of the 50PMET catalyst at 350 °C. The ethanol WHSV and partial pressure were 0.5 $g_{ethanol} g_{cat}^{-1} h^{-1}$ and about 15 kPa, respectively.



Fig. 7. Ethanol conversion activity and selectivity of a) MgO and b) $5 \text{ wt.} \% \text{ In}_2 \text{O}_3 / \text{SBA-15}$ catalysts. The WHSV and the partial pressure of ethanol were $0.5 \text{ g}_{\text{ethanol}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ and about 15 kPa, respectively.

Table 2

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

Catalyst	Support		5% In ₂ O ₃		
	C _{basic} ^a C _{acidic} ^b μmol/g (μmol/m ²)		C _{basic} ^a μmol/g (μmol/n	C _{acidic} ^b n ²)	
IMP	3.16 (0.017)	343.60 (1.796)	26.51 (0.066)	1070.17 (2.676)	
WK	64.25 (0.180)	429.94 (1.207)	47.42 (0.118)	922.66 (2.297)	
OPET OPMET	25.44 (0.043) 19.14 (0.039)	948.19 (1.598) 523.24 (1.077)	36.74 (0.113) 42.09 (0.102)	934.66 (2.271) 905.96 (2.776)	

 a Adsorption of CO₂ at 13 kPa and room temperature, flushed for 15 min, evacuated, then ramped up in He flow at a rate of 10 °C min $^{-1}$ to 500 °C and held at this temperature for 1 h.

^b Same procedure by using 13 kPa NH₃.

same level NH_3 and CO_2 adsorption capacity of the samples (Fig. 8b and c). Sample 5IMP is an exception. The somewhat higher acidity and lower basicity of the 5IMP sample led to lower BD and higher ethyleneplus-diethyl-ether selectivities. It can be also noticed that the best BD selectivities were achieved over the In_2O_3 promoted one-pot synthesized samples. As the In_2O_3 promotes the dehydrogenation of ethanol, the AA selectivities are also higher over the promoted samples. This is more significant at lower conversion level (i.e., at lower space time), when the lower concentrations favor less AA consuming side reactions. Nevertheless, the enhanced AA formation facilitates the aldol addition step and, thereby, increases the yield of butenes and C_4 -oxygenates.

4. Discussion

The heterogeneity/homogeneity of MgO/SiO₂ systems has a decisive role on the butadiene yields in the ETB reaction. There is a contradiction in the literature about the incorporation of magnesium from its salt (nitrate, acetate) 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 was omitted [32,36]. It was also observed that the synthesis product contains chloride ions in nonnegligible amount that can come from the hydrochloric acid component of the synthesis mixture [32]. The obtained MgO/SBA-15 material shows the same features as the pure silica SBA-15, i.e., sharp XRD reflection at low-angle and hexagonally ordered cylindrical mesopores, appearing on the TEM images. Wu et al. [31] claim that by using onepot synthesis method the surface of the SBA-15 pores becomes decorated by magnesium species. This species is believed to get converted to smooth MgO_x layer on the pore walls during calcination. Formation of some Mg-O-Si bonds is also possible in reaction of the magnesium species and the silanol groups of SBA-15 material. The upper limit of MgO content by using this method is around 30 wt% [32].

We carried out one-pot sol-gel synthesis using TEOS as silica source and magnesium alkoxide as magnesium source. The difficulty of synthesis lies in the different hydrolysis rates of the TEOS and magnesium alkoxide. Moreover, the magnesium ethoxide is not soluble in TEOS, so it must be dissolved in methanol before adding to the synthesis gel. The XRD patterns in Fig. 1 show that the faster hydrolysis of magnesium alkoxide did not result in the formation of separate MgO phase. Crystalline magnesium silicates could be observed besides amorphous silica. Another advantage of the sol-gel synthesis besides of good homogeneity of the mixed oxide is that it is possible to achieve high SSA. The SSA of OPMET and OPET samples are 486 and 594 m^2/g . respectively (Table 1). These values are close to those reported for onepot preparations obtained using inorganic salts as magnesium source $(400-600 \text{ m}^2/\text{g})$. On the basis of nitrogen adsorption isotherms and TEM images it can be concluded that our OPMET and OPET samples are mesoporous but does not have SBA-15 structure. It may be supposed that the SDA promoted the formation of mesopores, but the diversity of the chemical properties of TEOS and magnesium alkoxide prevent arrangement to a regular array having narrow pore size distribution that is characteristic of the SBA-15 material. 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 $356 \text{ m}^2/\text{g}$ for IMP and WK samples, respectively) despite the considerably high MgO content of the samples (~50 wt.%). Impregnation by In(NO₃)₃ solution caused structural rearrangement of the OPET and OPMET preparations. The IMP and WK preparations suffered total loss of their mesoporous structure.

According to the generally accepted mechanism, the ETB reaction takes place in the following consecutive reaction steps with the involvement of specific catalytic sites. [42] In the first and second reaction steps ethanol undergoes dehydrogenation over basic sites to form AA, which undergoes then through aldol addition reaction also over basic sites. Taifan et al. [43] studied the ETB reaction over wet-kneaded MgO-SiO₂ catalyst by in-situ DRIFTS and DFT studies, and concluded that the conversion of ethanol to AA takes place through the surface ethoxy groups formed on MgO, followed by hydrogen loss from its alpha carbon. The results shown in Fig. 7a support this theory, as the reaction gives AA as well as C_4 products.

Among the non-doped MgO-SiO₂ catalysts the WK sample showed the highest butadiene selectivity. The XRD pattern of the sample (Fig. 1) shows that wet kneading-generated MgO and SiO₂ islands are linked by Mg-O-Si bonds. In the other samples the magnesium is well dispersed in the SiO₂ framework and is a part of Mg-O-Si linkages. The presence of separated MgO phase increases the CO₂ adsorption capacity of the catalysts and the basicity of the sample, whereas the



Fig. 8. Bar and line chart of product selectivities and acid-base properties, respectively. Selectivities of a) neat, and b), c) 5 wt.% $In_2O_3/MgO-SiO_2$ catalysts are shown at conversion level a) 25%, b) 30%, and c) 65%. The identical conversions with the different catalysts were achieved by adjusting the ethanol WHSV. The lines and the values on the secondary axis give the room-temperature NH_3 and CO_2 adsorption capacities of the catalysts determined by TPD measurements.

Mg–O–Si bonds are responsible for the enhanced acidity and dehydration activity of the sample (Table 2 and Fig. 8a).

As it is discussed in the Introduction Section addition of transition metals/metal oxides to the MgO-SiO2 catalysts enhances conversion as well as selectivity for BD by promoting dehydrogenation of ethanol to AA. As it can be clearly seen in Fig. 7b, In₂O₃ promotes the dehydrogenation of ethanol to AA with high efficiency. It is also worth to note that, although In₂O₃ is a strong Lewis acid (increased the ammonia uptake of the samples by two to three times, see Table 2), no significant amounts of dehydration products were formed in its presence. The results presented on Fig. 5 and 6 fully support the promoting effect of In_2O_3 additive. It also can be concluded from the results that by steering reaction toward the dehydrogenation pathway the dehydration step is suppressed and besides the selectivity of BD the selectivity of other C4 products (mainly BUE and BOL) also increases to some extent. This phenomenon was investigated in details on the best performing OPMET catalyst (Fig. 6). The results show that by increasing the added amount of indium oxide, the selectivity of products formed by dehydration was gradually reduced. However, it was also observed that upon increasing the indium oxide content over 5 wt.% the BD selectivity did not show further increase but instead the acetaldehyde selectivity was growing. The stability study of the 5OPMET catalysts (Fig. 6d) also showed that during the 30 h time on stream the activity of the catalyst and the BD selectivity decreased, while the acetaldehyde selectivity increased. The selectivity of the other products remained virtually unchanged.

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 structures of the catalysts were characterized by XRD and TEM measurements, while the acid-basic properties of the catalysts were characterized by their NH₃ and CO₂ adsorption capacity. Results presented on Fig. 8 suggested that there is a correlation between acid-base properties and catalytic activity of the samples. However, in a complex reaction network of ETB reaction, it is not only the acidity/basicity that affects the selectivity of the formation of different products. Fig. 8a shows that the selectivity of BD (and of other C₄ products) is the highest over the WK sample on which the CO₂ adsorption capacity is the highest and the amount of adsorbed NH₃ is almost the same or lower than on 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. Fig. 2 shows that the structure of the samples changed significantly upon promotion by indium oxide. The hysteresis loops on the N2 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 sizes and shapes. It can be also noticed that over the best performing catalysts (5WK, 5OPET, 5OPMET) the NH₃ and CO₂ 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.

As it can be seen from the data in Table 2 and Fig. 5 and 6, after the addition of In_2O_3 , the acidity of the samples (i.e., the NH₃ uptake) as well as the conversion and butadiene selectivity also increased significantly for all catalysts. It is worth considering whether these positive changes can be explained by the increased "acidity"? Independent measurements showed well the role of the catalyst components in the reaction. Dehydrogenation of ethanol and aldol condensation take place over MgO, whereas In_2O_3 significantly increases the acetaldehyde concentration in the system, while Mg–O–Si bonds promote the dehydration step. A good catalyst for butadiene selectivity is formed when these three functions work together. However, it is questionable whether the appropriate ratio of the three functions can be characterized by acidity/basicity measurements only? In heterogeneous catalytic reactions, the rate of the reaction is determined also by the number of active

sites and the surface concentration of the reactant and intermediates. Comparing the NH₃ adsorption data collected in Table 2 and the measured conversion values, it can be seen that catalysts with higher NH₃ uptake convert ethanol with higher conversion. Results suggest that the selectivities of the different MgO-SiO₂ catalysts, promoted by the same amount of In₂O₃, is determined by the properties of the support. However, an exception to this rule is the OPMET catalyst that suggests that results can be improved by applying innovative synthesis methods.

5. Conclusions

Four methods were applied to prepare MgO-SiO₂ catalysts for conversion of ethanol to butadiene. Besides common impregnation and wet kneading methods the one-pot synthesis method was employed adding magnesium methoxide or ethoxide as magnesium source to the synthesis gel of SBA-15 material. The XRD results showed that all the methods, except the impregnation method resulted in formation of Mg-O-Si linkages. Separate MgO phase was detected in the wetkneaded sample only. All the preparations are mesoporous with rather high specific surface area $(190-590 \text{ m}^2/\text{g})$. The magnesium alkoxides in the gel of micelle-templated synthesis hindered the formation of SBA-15 structure. Over neat MgO-SiO₂ 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.% In₂O₃ to the MgO-SiO₂ preparations significantly increased the butadiene selectivity. For instance, the In-promoted magnesium-containing silica catalyst, obtained by micelle-templated synthesis method showed 45%-60% butadiene selectivity in the temperature range of 250-425 °C. The ethylene/diethyl ether selectivity could be suppressed below 10% by increasing the indium oxide loading to 10 wt.%. However, the selectivity for butadiene was also reduced because the rate of acetaldehyde coupling was not high enough to consume all the acetaldehyde formed at an increased rate. At 25% conversion the best performing neat MgO-SiO₂ preparation was the wet-kneaded sample. This sample has the highest basicity and about the same or lower acidity than the rest of the catalyst preparations. Introduction of In₂O₃ changes both the structure and the acid-base properties of the neat MgO-SiO₂ samples. The pore structure of the samples becomes quite similar. The samples of similar acid-base properties show similar catalytic activity. The catalyst having relatively high CO2 and low NH3 adsorption capacity showed high butadiene selectivity. The highest dehydration activity and lowest butadiene selectivity was observed using the catalyst made from MgO-impregnated SBA-15 silica by indium oxide introduction. This catalyst was the most acidic and the less basic.

CRediT authorship contribution statement

József Valyon: Supervision. Jenő Hancsók: Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge the financial support of the project of the Economic Development and Innovation Operative Program of Hungary, GINOP-2.3.2-15-2016-00053: Development of liquid fuels having high hydrogen content in the molecule (contribution to sustainable mobility). The Project is supported by the European Union. Thanks is due to the support provided by the European Union and the State of Hungary,

co-financed by the European Regional Development Fund in the framework of the project No. VEKOP-2.3.2-16-2017-00013.

References

- H.N. Sun, J.P. Wristers, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 2000, https://doi.org/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, https://doi.org/10.1002/anie.201305058.
- [3] J. Sun, Y. Wang, Recent advances in catalytic conversion of ethanol to chemicals, ACS Catal. 4 (2014) 1078–1090, https://doi.org/10.1021/cs4011343.
- [4] S.V. Lebedev, J. Gen. Chim. 3 (1933) 698-708.
- [5] J. Ostromisslenski, 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, https://doi.org/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, https://doi. org/10.1021/acscatal.5b00755.
- [8] 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-SiO₂ catalysts for butadiene synthesis with the Lebedev process, Green Chem. 18 (2016) 1653–1663, https://doi.org/10.1039/c5gc02194d.
- [9] 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, https:// doi.org/10.1039/c6cp04171j.
- [10] X. Huang, Y. Men, J. Wang, W. An, Y. Wang, Highly active and selective binary MgO-SiO₂ catalysts for the production of 1,3-butadiene from ethanol, Catal. Sci. Technol. 7 (2017) 168–180, https://doi.org/10.1039/c6cy02091g.
- [11] 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, https://doi.org/10.1002/cctc. 201601630.
- [12] Y. Xu, Z. Liu, Z. Han, M. Zhang, Ethanol/acetaldehyde conversion into butadiene over sol-gel ZrO2-SiO² catalysts doped with ZnO, RSC Adv. 7 (2017) 7140–7149, https://doi.org/10.1039/c6ra25139k.
- [13] 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 zinccontaining talc, Catal. Commun. 68 (2015) 20–24, https://doi.org/10.1016/j. catcom.2015.04.023.
- [14] 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, https://doi.org/10.1007/s10562-015-1509-4.
- [15] 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, https://doi.org/10.1039/c5cy00200a.
- [16] 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, https://doi.org/10. 1039/c4ra17070a.
- [17] 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, https://doi.org/10.1039/c5ra22623f.
- [18] 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, https://doi.org/10.1021/acscatal.5b02972.
- [19] 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/SiO₂ systems prepared by Co-precipitation and effect of catalyst acidity modification, ChemCatChem 8 (2016) 2376–2386, https://doi.org/ 10.1002/cctc.201600331.
- [20] 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 magnesiasilicate catalysts, ChemSusChem 9 (2016) 1462–1472, https://doi.org/10.1002/ cssc.201600195.
- [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, https://doi.org/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. 577 (2019) 1–9, https://doi.org/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, https://doi.org/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, https://doi.org/10.1016/j.catcom.2016.12.009.
- [25] S.I. Fujita, S. Segawa, K. Kawashima, X. Nie, T. Erata, M. Arai, One-pot roomtemperature synthesis of Mg containing MCM-41 mesoporous silica for aldol reactions, J. Mater. Sci. Technol. 34 (2018) 2521–2528, https://doi.org/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, https://doi.org/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, https://doi.org/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, https://doi.org/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, https://doi.org/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, https:// doi.org/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, https://doi.org/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, https://doi.org/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 nonionic surfactant in, Chem. Commun. (Camb.) (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, https://doi. org/10.1016/j.micromeso.2005.05.024.
- [35] K.K. Han, Y. Zhou, Y. Chun, J.H. Zhu, Efficient MgO-based mesoporous CO₂ trapper and its performance at high temperature, J. Hazard. Mater. 203–204 (2012) 341–347, https://doi.org/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 CO₂ reforming of methane to syngas, Chem. Eng. Technol. 36 (2013) 1701–1707, https://doi.org/10.1002/ceat. 201300006.
- [37] R. Barthos, A. Hegyessy, S. Kl?bert, J. Valyon, Vanadium dispersion and catalytic activity of Pd/VO < inf > x < /inf > /SBA-15 catalysts in the Wacker oxidation of ethylene, Microporous Mesoporous Mater. 207 (2015), https://doi.org/10.1016/j. micromeso.2014.12.038.
- [38] 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, https:// doi.org/10.1016/j.jcis.2005.08.055.
- [39] 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.
- [40] K.S.W. Sing, F. Rouquerol, J. Rouquerol, P. Llewellyn, Assessment of mesoporosity, Adsorption by Powders Porous Solids, 2nd ed., Elsevier Ltd, 2014, pp. 269–302.
- [41] 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 zinccontaining talc, Catal. Commun. 68 (2015) 20–24, https://doi.org/10.1016/j. catcom.2015.04.023.
- [42] H. Hattori, Solid base catalysts: fundamentals and their applications in organic reactions, Appl. Catal. A Gen. 504 (2015) 103–109, https://doi.org/10.1016/j. apcata.2014.10.060.
- [43] W.E. Taifan, G.X. Yan, J. Baltrusaitis, Surface chemistry of MgO/SiO₂ catalyst during the ethanol catalytic conversion to 1,3-butadiene: In-situ DRIFTS and DFT study, Catal. Sci. Technol. 7 (2017) 4648–4668, https://doi.org/10.1039/ c7cy01556a.