Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Influence of structural parameters on the conversion of ethanol into 1,3-butadiene using mesoporous zeolites

CrossMark

Alexander Klein, Regina Palkovits *

Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, D-52074 Aachen, Germany

ARTICLE INFO

ABSTRACT

In this contribution, the influence of structural parameters of zeolites in the transformation of ethanol into 1,3-butadiene has been investigated. Therefore, two material series were synthesized. First, a zeolite-β has been desilicated to achieve a hierarchical structure. This zeolite turned out being too unstable. Nevertheless conducted reactions confirmed, that there is a connection between crystallinity, microporous structure and conversion. The second series comprised conventional and mesoporous LTAs. We synthesized similar materials with mean pore widths of 5.9 and 7.0 nm, respectively. Using those in the considered reaction led to a significant increase of the conversion with the pore size.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

After the latest oil price peak at the end of last century, industry reinforced their efforts finding new ways to produce important bulk chemicals. One example in this context is 1,3-butadiene. Conventionally it is obtained as a by-product in the steam cracker process [1]. Since the so called "shale-gas boom" in the USA the cracking feedstock is shifting from naphtha to shorter chained carbon sources, such as ethane. In turn the production volume of 1,3-butadiene decreased [2]. This got two alternative processes back into focus, the Lebedev and the Ostromislensky process. Both utilise ethanol as feed; however, while the Lebedev process is a one-step route [3], the Ostromislensky process proceeds via dehydrogenation of ethanol to acetaldehyde followed by a second step converting acetaldehyde with co-fed ethanol to 1,3-butadiene [4]. Several publications pointed out that the addition of intermediates, mostly acetaldehyde, increases catalyst performance minimizing the differences of the two processes [5–8].

After the first comprehensive catalyst study by Corson et al. 1950 [9], several investigations focused on catalyst design for an efficient and selective 1,3-butadiene production. Except few exotic representatives, the main studied systems present alumina and silica based catalysts [10,11]. The by far most intensively considered catalysts are supported on silica, with either ordered or non-ordered structures [10,11]. A lot of different metals were used as dopants including alkali and earth alkali metals [8,12], transition metals [5,8,9,13–25] and major emphasis on magnesium oxide [10,15,22,26–28]. Recent publications focused on zirconia

[15–18], tantalum [23], silver [18,25] and gold, respectively [22]. Especially the crucial role of catalyst's acid and base properties has been pointed out. In a recent contribution, we could clearly correlate the catalyst's acidity with the catalytic performance. Using a tailored material series based on zeolite-β, a MgO-doped silicon rich H-β280 enabled high 1,3-butadiene selectivity of up to 72% [29]. Unfortunately, a distinct trade-off between catalyst acidity, catalytic activity and 1,3-butadiene selectivity became evident hindering further catalyst optimization (Fig. S1).

This study is built on these results. To enhance the catalytic activity while keeping 1,3-butadiene selectivity high, we aimed at introducing an additional mesoporous system into the present zeolite. Considering recent literature, there are only two publications dealing with the impact of different pore sizes on catalytic performance. 2011 Jones et al. observed a positive effect of larger pores on 1,3-butadiene selectivity while the conversion was hardly affected [8]. They explained this with a lower proportion of acidic Q^2 and Q^3 sites. Chae et al. used SBA-15 with different pore sizes [19]. Interestingly, they observed increasing conversion for larger pore sizes, which they explained by facilitated mass transfer. Obviously, further studies are required to clarify the impact of active site accessibility in the transformation of ethanol to 1,3-butadiene.

Therefore, our contribution focuses on the influence of varying pore size for selected zeolites. We focused on two different synthesis concepts, the top-down and the bottom-up strategies. Both have been investigated and developed in the last 15 years [30–32]. The top-down strategy, a post-synthetic method etches silicon or aluminium atoms out of the zeolite framework. Especially desilication has been investigated and optimized intensively. A massive dissolution of the structure,

Table 1
Desilification experiments: Synthesis parameters and substrate concentrations.

Entry	Material	t/min	T/K	[NaOH]/mol/L	[Al(NO₃)₃]/mol/L	[Al(NO₃)₃]/mol/L	[TPAOH]/mol/L	[TMAOH/mol/L
1	mesoH-β280-A	30	313	0.2	0.003	–	0.1	–
2	mesoH-β280-B	10	313	0.2	0.003	0.003	–	0.02
3	mesoH-β280-C	10	313	0.1	–	–	–	–
4	mesoH-β280-D	30	313	0.1	–	0.003	0.01	0.02
5	mesoH-β280-E	30	338	0.1	0.003	–	–	0.02
6	mesoH-β280-F	30	313	–	0.003	–	0.1	–

mainly for high module zeolites and non-connected pore systems are the biggest challenges [30–33]. The research group of Pérez-Ramírez investigated possibilities to overcome these challenges by using *pore directing agents* (PDA), e.g. aluminium hydroxide [33]. The bottom-up method in turn is a pre-synthetic templating synthesis. In literature, there is a countless number of different synthesis methods and templates. We refer at this point to one of the present reviews [30,31] and focus on the method of Choi et al. published in 2006 [34,35]. With the use of organo silanes, such as [3-(trimethoxysilyl)propyl]tetradecyldimethylammonium chloride (TPHAC) and their structural analogues, they reached, dependent on the chain length, LTA and MFI type zeolites with defined, very narrow sized mesopores.

We selected H-β280 and LTA zeolites as model systems. First we desilicated H-β280 under different synthesis conditions and used the resultant mesoH-β280 as a support for magnesium oxide. Due to the fact, that we explicitly remove silicon atoms, the acidic behaviour is affected. For a better understanding of the pore width effect, we additionally used templated mesoporous LTA type zeolites with different pore widths but comparable structural and chemical parameters.

2. Experimental

First stage catalysts have been synthesized by *incipient wetness impregnation* on SiO₂ and can be found elsewhere [29].

For the desilication experiments, the zeolite-β structure H-β280, provided by Clariant AG (referred to as HCZB650), were used as a starting material. Six experiments were conducted by using different amounts of NaOH (98.8%, Chemsolute), Al(NO₃)₃ (99%, Sigma-Aldrich), Ga(NO₃)₃ (99.9%, Chempur), TPAOH (40% in water, Chempur) and TMAOH (25% in water, Sigma-Aldrich), respectively. The synthesis parameters are summarized in Table 1. The resultant materials were analysed by powder *X-ray diffraction* (XRD) patterns. Furthermore nitrogen sorption isotherms were recorded. The acidic behaviour was observed by conducting *temperature programmed desorption* of ammonia (NH₃-TPD). To finally prepare the catalysts, each material was impregnated with Mg(NO₃)₂·6H₂O (99%, Sigma-Aldrich). The actual magnesium content was checked by inductively coupled plasma (ICP). The catalysts are labelled as MgO(10)\mesoH-β280-X (with X as a consecutive letter A–F).

Mesoporous LTA catalysts were synthesized using a method of Choi et al. [34] As templates, [3-(trimethoxysilyl)propyl]tetradecyldimethylammonium chloride (TPTAC, 50% in MeOH, FluoroChem) and its structural C18 analogue (TPOAC, 50% in MeOH, FluoroChem) were applied. The structures, labelled as LTA, mesoLTA-C14 and mesoLTA-C18, respectively, were analysed by ICP-AES, XRD, nitrogen sorption, SEM-EDX and NH₃-TPD. The resultant materials were used as supports adding 10 wt.% MgO by *wet impregnation*.

Catalytic investigations were carried out in a continuous two-step gas phase setup. The procedure is described in detail in the ESI.

3. Results and discussion

As described earlier, the introduction of mesopores into zeolite structures was carried out to examine the possibility of increasing the low activity of the previously described highly selective H-β280 based catalysts [29]. Therefore H-β280 was desilicated to change the textural properties of this material. Since it is known that silicon rich β-structures are rather unstable [30,33], reaction parameters have been
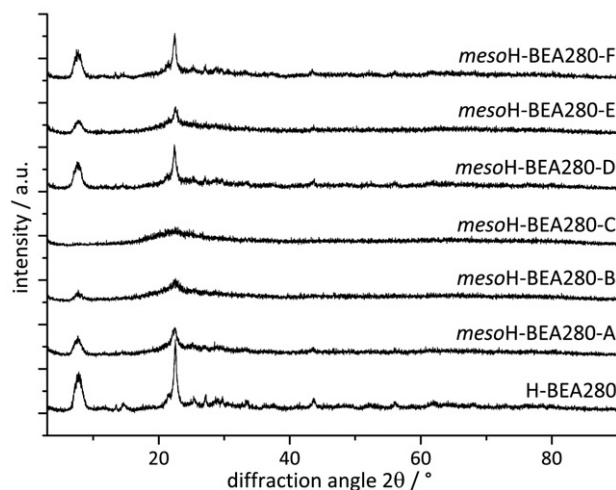

Fig. 1. X-ray diffraction patterns of the desilicated H-β280 and the unmodified materials.

Table 2
Material parameters: Specific surface area, pore volume and number of acidic sites.

Entry	Material	SiAl-ratio/	S_micro/m²/g	S_BET/m²/g	V_micro/cm³/g	V_total/cm³/g	n_A/mmol/g
1	H-β280	280	273	467	0.12	0.50	0.065
2	mesoH-β280-A	n.d.	149	414	0.07	0.71	0.048
3	mesoH-β280-B	n.d.	86	189	0.04	0.44	0.043
4	mesoH-β280-C	n.d.	15	125	0.01	0.47	0.047
5	mesoH-β280-D	n.d.	235	469	0.11	0.67	0.081
6	mesoH-β280-E	n.d.	159	318	0.07	0.60	0.075
7	mesoH-β280-F	n.d.	257	448	0.12	0.54	0.060
8	LTA	1.3	n.d.	n.d.	n.d.	n.d.	0.110
9	mesoLTA-C14	1.2	n.d.	108	n.d.	0.19	0.120
10	mesoLTA-C18	1.2	n.d.	88	n.d.	0.16	0.110

n.d. not determined.