

Conversion of 2,3-Butanediol over Phosphate Catalysts

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2,3-Butanediol (BDO) is an excellent feedstock for expanding the network of bio-based chemicals through catalytic technologies. The dehydration of BDO provides an alternative green route to important chemicals such as methyl ethyl ketone (MEK) and 1,3-butadiene (BD). In this contribution, we report on the catalytic performance of boron (BP), aluminum (AIP), titanium (TiP), zirconium (ZrP), and niobium (NbP) phosphates in BDO dehydration. The kinetic study points to three reaction

Introduction

In the few last years the production of bio-based chemicals from renewable resources has received growing attention, especially as the availability of petrochemical feedstocks is diminishing. 2,3-Butanediol (BDO) can be produced by fermentation of sugars with various bacteria^[11] as well as by fermentation of syngas by using acetogenic organisms^[2] and can be considered as a potential feedstock for a number of useful chemicals. It can be used as an antifreeze agent, solvent, and precursor for plastics manufacturing. Its ester derivatives are precursors of polyurethane and can be applied in cosmetic, pharmaceutical, and other industries.^[1,3] But the most important applications are connected with BDO dehydration into butan-2-one (methyl ethyl ketone, MEK), 3-buten-2-ol (3B2OL), and 1,3-butadiene (BD).^[1b,4-6]

MEK is a widely used organic solvent as well as a precursor for MEK peroxide. Nowadays, it is mainly produced from *n*butane feedstocks by consecutive dehydrogenation-hydration-dehydrogenation steps.^[7] 3B2OL finds applications in medicine and agrochemicals production.^[8] Whereas, BD is a bulk chemical that has an enormous application scope. It is an important monomer for the production of such polymers as polybutadiene, styrene-butadiene rubber, styrene-butadiene latex, acrylonitrile-butadiene-styrene polymer, nitrile rubber, and some others.^[9] At present, about 95% of butadiene is produced by isolation from naphtha steam cracker fractions, generated during ethylene production. But the trends in the devel-

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pathways operating over phosphate catalysts, leading to MEK, 2-methyl-propanal (MP), and BD via intermediate 3-butene-2-ol (3B2OL) formation. The major reaction pathway is shown to involve pinacol rearrangement to MEK. The reactivity of phosphates is found to increase in the order: BP < TiP < ZrP = NbP < AIP. The best catalytic performance is achieved over AIP, which shows the highest selectivity towards MEK (78%) at 100% 2,3-butanediol conversion.

opment of the ethylene industry are such that ethylene producers are switching to more efficient ethylene production technologies. This leads to a lack of butadiene on the market and therefore requires the development of alternative technologies leading to butadiene. Therefore, the synthesis of MEK, BD, and 3B2OL from BDO appears to be a challenging goal.

Synthesis of MEK from BDO has been reported over strong solid catalysts such as H-Nafion,^[10] heteropoly acids,^[11] aluminosilicates,^[12] and zeolites.^[1f, 13, 14] Bucsi et al.^[10] reported high conversions of BDO into MEK over H-Nafion catalysts at temperatures as low as 150°C; the acetalization of MEK with BDO being the main side reaction. MEK and its acetals accounted for 94% of the products over these catalysts. Other strong acids such as heteropoly acids have also demonstrated high conversion into MEK in the temperature range 150-180°C.[11] The selectivity to MEK varied from 50 to 95%, the main byproducts were the corresponding dioxolanes and 2-methylpropanal (MP). Zeolites were found to be active catalysts for transforming BDO into MEK in the temperature range 230- $350\,^\circ C.^{[1f,\,13-15]}$ Different zeolite structures, including FAU, MFI, MOR, and BEA, have also been tested. Whereas medium-pore zeolites favored MEK formation, the large-pore zeolites yielded acetals and ketals.^[13]

The selective synthesis of 3B2OL and BD from BDO has been achieved over less acidic solids and at higher temperatures.^[8b,16,17] The first attempts for 3B2OL and BD synthesis go back to the 1940s. Winfield^[16] studied a large number of metal oxides and salts and found that the best catalyst for 3B2OL and BD production is ThO₂. They disclosed that over ThO₂, 3B2OL can be obtained with a yield of 70% at 350 °C, whereas 62% yield of BD can be reached at 500 °C.^[16]

Significant contribution to the synthesis of 3B2OL and BD from BDO has been made by the group of Sato et al.^[8b,17,18] during the few last years. These authors have investigated BDO dehydration over a large range of rare-earth-oxide catalysts. They disclosed that Sc_2O_3 calcined at 800 °C shows excellent catalytic activity at 325 °C with 85% selectivity to 3B2OL at

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100% BDO conversion.^[18] The highest BD yield of 88.3% was achieved over Sc₂O₃ at 411 °C under H₂ carrier gas flow.^[18] In addition, it was found that the yield of BD can be increased up to 94% at 318 °C in a double-bed reactor containing Sc₂O₃ in an upper layer and Al₂O₃ in a lower layer.

Analysis of the literature data suggests that BDO dehydration has been extensively studied over oxides, zeolites, and heteropoly acids. However, as far as we know, no information is available for phosphates, which are known to be efficient solid catalysts for a number of acid-catalyzed reactions,^[19,20] including different pinacol-type rearrangements, ketalization of ketones, isomerization of unsaturated compounds, dehydration of alcohols and sugars,^[19a,b] isoprene synthesis from formaldehyde and isobutene,^[20] and so on. For example, Maurin^[21] disclosed that phosphate catalysts (Li₃PO₄) can be used for isoprene synthesis from corresponding diol.

In this contribution, we report on the catalytic performance of metal (III–V) phosphate catalysts in the BDO dehydration. Boron (BP), aluminum (AIP), titanium (TiP), zirconium (ZrP), and niobium (NbP) phosphates with high surface areas of 80 m²g⁻¹ were prepared and characterized by elemental analysis, X-ray diffraction, low-temperature nitrogen adsorption, temperature-programmed desorption (TPD) of ammonia, and FTIR of adsorbed pyridine. The catalytic activity was investigated at a wide range of temperatures (250–400 °C) and weight hourly space velocities (WHSV) of 1.5–500 h⁻¹. The results point to the high activity of phosphates in the BDO conversion to MEK.

Results and discussion

Catalysts preparation and characterization

The literature data contains a lot of information on different amorphous and crystalline phosphate materials and the methods of their preparation.^[19a,22-26] Crystalline phosphates with α , γ , ζ structures are usually not thermally stable and convert into other crystalline forms during calcination over 300 °C. Thermal treatment of such materials is accompanied by the decrease of their acidity and specific surface area.^[19,27] Therefore, in this study we have concentrated on amorphous solids with high surface areas and acid site availability. Metal (III, IV, V) phosphates, namely, BP, AIP, TiP, ZrP, and NbP were selected owing to their high acidity and wide scope of their application as catalysts.^[19b,20-22,28]

Synthesis of the ZrP, AIP, and NbP materials was carried out according to the standard procedures based on the treatment of the corresponding salts or oxides with orthophosphoric acid, which leads to amorphous phosphates with high acidity and surface areas.^[24-27] The M/P ratio was adjusted to have a range of catalysts with similar specific surface areas (Table 1). The highest content of phosphorus was required for ZrP and TiP. Attempts to decrease the phosphorous content resulted in a significant decrease in the specific surface area and the amount of acid sites. Quite the opposite situation was observed in the case of AIP and NbP materials, which have the highest metal content in the series of samples synthesized. In these materials, the M/P ratio reaches 1.5 and 2.5, respectively,

Table 1. Characteristics of the phosphate catalysts.						
Symbol	M precursor	M/P [mol/mol]	S_{BET} [m ² g ⁻¹]	V_{pore} [cm ³ g ⁻¹]	d _{pore} [nm]	a₀ [μmol g ⁻¹]
BP	B(<i>i</i> PrO) ₃	1	73	0.5	10-80	430
AIP	AICI₃	1.5	88	0.6	20-90	930
TiP	Ti(OBu) ₄	0.5	87	0.3	20-100	410
ZrP	ZrOCl ₂ •8H ₂ O	0.6	85	0.1	5-100	840
NbP	$Nb_2O_5 \cdot nH_2O$	2.5	88	0.4	20-80	640

which points to some contribution from the corresponding metal oxide phases.

To obtain TiP and BP catalysts with similar specific surface areas, organic precursors were used. Boron phosphate is usually synthesized through interaction of boron acid with the aqueous solution of H_3PO_4 .^[24,29] However, this method leads to the formation of a crystalline material with a specific surface area of $\approx 7 \text{ m}^2 \text{ g}^{-1}$ and very low content of acidic sites. The application of the organic precursor tri-*iso*-propylborate allowed us to increase the specific surface area up to $\approx 73 \text{ m}^2 \text{ g}^{-1}$ (Table 1), but also yielded crystalline material after calcination.^[26] Attempts to obtain amorphous BP found no success. Conversely, in the case of TiP, the use of titanium butoxide as the precursor resulted in the formation of amorphous phosphate with high surface area (Table 1).

The main characteristics of the phosphate catalysts prepared are shown in Table 1 and Figures 1–4. According to the XRD data, all samples except boron phosphate are amorphous materials (Figure 1). The BP catalyst shows a XRD pattern typical for crystalline phosphate with a cristobalite structure.^[30]



Figure 1. XRD patterns of the metal phosphates.

Nitrogen adsorption-desorption measurements show that all the samples studied have comparable specific surface areas in the range 73–88 m²g⁻¹. According to Barrett-Joyner-Halenda (BJH) analysis, the pore size distribution is very broad (Table 1), which is typical for amorphous materials.

The FTIR spectra of the calcined samples are shown in Figure 2. A broad band at \approx 3400 cm⁻¹ and bands in the range 1635–1945 cm⁻¹ correspond to hydroxyl groups and to adsorbed water molecules.^[31] The bands in the region 850–1160 cm⁻¹ are due to asymmetric and symmetric stretching vibrations of the P=O and P–OH groups.^[31b, 32] Additionally, the small bands in the range 1300–1400 cm⁻¹ and 700–900 cm⁻¹



Figure 2. FTIR spectra of the metal phosphate materials.

can be attributed to free ${\rm PO_4^{3-}}$ and the P–O–P link, respective-ly. $^{\rm [31b,33]}$

The spectrum of boron phosphate shows significant differences with respect to the other spectra owing to the crystalline structure of this sample. The bands at approximately 555, 620, and 929 cm⁻¹, observed only in the case of BP, can be assigned to bending vibrations in the $[PO_4]^{3-}$ tetrahedron and to pseudo-lattice translations of B–O, respectively.^[34]

In the case the NbP and AIP samples, a broad band in the range 500–700 cm⁻¹ is observed along with the bands attributed to the phosphates. This band corresponds to the stretching vibrations of bridging M–O–M bonds in the oxide phases^[35] and indicates that these samples are a mixture of metal oxide and phosphate phases.^[35a] The possibility of metal oxide phase formation depends on the elemental composition of the materials. In the case of AIP and NbP samples, the metal content is the highest (Table 1), which is in line with the formation of the corresponding oxide phases.

Acidic properties

The acidic properties of the prepared catalysts were studied by using TPD NH_3 measurements and IR spectroscopy of adsorbed pyridine. Whereas the former was used for the determination of the amount and strength of the acid sites, the latter was applied for the investigation of their nature.

The FTIR spectra of adsorbed pyridine are presented in Figure 3. Four main bands are observed in the region of pyridine vibrations. In accordance with ref. [36], the bands at approximately 1592 and 1490 cm⁻¹ are assigned to hydrogenbonded pyridine; the band at 1544 cm⁻¹ is attributed to pyridine protonated on Brønsted acid sites; whereas the band in the region 1449–1461 cm⁻¹ is assigned to pyridine adsorbed on Lewis acid sites.

The results suggest that all the catalysts studied contain both Brønsted and Lewis sites. The origin of the Brønsted acidity of the samples is due to the terminal P–OH groups along with some contribution from M–OH groups. The Lewis acidity can be attributed to the coordinatively unsaturated M^{n+} sites.^[36a] The amount of Lewis and Brønsted sites in metal phosphate catalysts usually depends on the amount of chemi-



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Figure 3. FTIR spectra of pyridine adsorbed on the phosphate catalysts.

sorbed water. Water molecules interact with unsaturated metal sites (Lewis sites), leading to the formation of OH groups.^[20] Dehydroxylation of the samples leads to the transformation of Brønsted sites into Lewis sites and, vice versa, the addition of water may restore the content of Brønsted sites. The intensity of the band assigned to pyridine adsorbed on Brønsted acid sites increases in the order: AIP < ZrP < TiP < BP < NbP, whereas the intensity of the band related to Lewis sites increases in the order: ZrP < AIP < TiP < NbP < BP (Figure 3).

Comparison of the spectra in the region 1445–1465 cm⁻¹ reveals a significant difference for the boron phosphate sample. Whereas for most of the samples, the band attributed to pyridine adsorbed on Lewis sites is observed at \approx 1449 cm⁻¹, in the case of BP catalyst it is shifted to 1461 cm⁻¹. A similar shift was observed by Travert et al.^[36b] in a series of metal oxide materials. In particular, the band of pyridine adsorbed on Lewis sites was shifting from 1449 to 1462 cm⁻¹ in the following range of materials: MgO/ZrO₂/Al₂O₃/SiO₂/B₂O₃. The authors ascribed their observation to the increase in polarizing power of the cation in the above range of oxides. We can speculate that a similar effect can be observed for phosphate materials. Indeed, a small shift to 1454 cm⁻¹ is also seen in the case of the AIP sample. Another explanation could be related to the crystalline structure of the BP sample, which results in stronger Lewis acidity for this sample.

The TPD NH₃ profiles obtained for the phosphate materials are presented in Figure 4. All the samples show only one peak in the TPD profiles, which is typical for amorphous materials.^[37] However, the acid site distribution is very different. AlP and TiP contain only weak and medium sites desorbing NH₃ in the range 100–450 °C. Conversely, ZrP and NbP show very broad TPD profiles (100–600 °C) with a high contribution of strong acid sites, whereas boron phosphate demonstrates intermediate behavior. It should be mentioned that the AlP sample shows the narrowest acid site distribution and the highest content of sites, which is typical for AlPO₄ zeotypes.^[38] However, the XRD data do not show any reflections corresponding to the crystalline structure of AlPO₄ materials (Figure 1). The total amount of acid sites calculated from TPD NH₃ data increases in the order: TiP < BP < NbP < ZrP < AlP.



Figure 4. TPD NH₃ curves for the metal phosphates materials.

Dehydration of 2,3-butanediol

The dehydration reaction was studied at 200–400 °C in the WHSV range 1.5–500 g g⁻¹ h⁻¹. All the catalysts showed stable catalytic performance with time on stream: the decrease in conversion was less than 0.5% over 5 h of the experiment. It should be mentioned that the high stability of the catalytic activity demonstrated by phosphate catalysts is a significant advantage with respect to other solid catalysts, such as zeolites, which show 15–20% decline in diol conversion within 3–4 h on stream.

Reaction products and reaction network

The main reaction products observed over the phosphate catalysts studied included MEK, MP, and BD. In addition, small amounts of 3B2OL and C_8-C_{12} heavy products including mainly dioxolanes were observed. To determine the primary and secondary reaction products and to establish the reaction network, a kinetic study was performed over the ZrP catalyst at 250 °C in the WHSV range 1–400 h⁻¹. The yields of different products are plotted versus the conversion of BDO in Figure 5. The kinetic analysis of these curves was performed on the basis of the models calculated in ref. [39] for primary or secondary, stable or unstable reaction products.

The results show that MEK and MP appear at very low conversion levels and can be attributed to primary unstable prod-



Figure 5. Yields of reaction products versus BDO conversion with the ZrP catalyst at 250 °C.

ucts. Further transformations of these products may include their condensation with BDO, leading to formation of cyclic ethers, mainly dioxolane. Indeed, the kinetic curves of cyclic ethers are typical for primary + secondary products formed as a result of the interaction of the reactant with primary products (Figure 5).^[39] Similar products were observed by Török et al.^[11] during BDO dehydration over heteropoly acids. The authors suggested that MEK and MP are the intermediates in the formation cyclic ethers.

The precise analysis of the kinetic curves at low conversion levels allows the third primary product to be identified— 3B2OL, which shows a maximum at \approx 40% conversion. The origin of this maximum is most probably due to further transformation of 3B2OL into BD, which behaves as a secondary stable product (see inset in Figure 5). Similar conclusions about the intermediate product in BD formation were reached by Duan et al.,^[18] who have investigated transformations of 3B2OL and MEK over oxide catalysts and pointed out that the only product of 3B2OL conversion is BD, whereas MEK does lead to BD and gives mainly butene isomers, propylene, and ethylene.

The reaction network presented in Scheme 1 rationalizes further the above observations. The elimination of the first water molecule leads to the 3-butenium-2-ol ion, which can further evolve by three possible routes:

- 1) a hydride shift results in the formation of MEK;
- 2) a methyl shift leads to MP;
- the elimination of a proton gives 3B2OL, which is further converted into BD through elimination of a second water molecule.



Scheme 1. Reaction network



Condensation of the primary products further leads to the formation of heavy byproducts, including different cyclic ethers.

The reaction network presented in Scheme 1 is in line with the results obtained over other types of catalysts: oxides,^[8b, 17, 18] zeolites,^[13-15] and heteropoly acids.^[11]

Effect of catalyst type

To compare the activity of different phosphate catalysts in the BDO dehydration, the initial rates of BDO conversion have been calculated from the initials slopes of the kinetic curves obtained for each catalyst at 250 °C. The WHSV values were adjusted for each catalyst to go down to conversions below 10%.

The initial rates obtained can be compared in Table 2. The results show that the activity of the phosphate catalysts increases in the order: BP < TiP < ZrP = NbP < AIP. The highest initial rate of 1.9×10^{-4} mol (g s)⁻¹ is observed for AIP, whereas the BP sample shows the lowest initial rate of 1.0×10^{-4} mol (g s)⁻¹.

The comparison of the catalytic properties of metal phosphates with other solid acids suggests that their activity in the BDO dehydration is higher than in the case of oxides^[8b] and comparable with those of zeolites^[14] and heteropoly acids.^[11] Indeed, high conversions of 90–100% can be reached over phosphates already at 250 °C, whereas rare-earth oxides require 325–375 °C to reach 100% conversion.^[8b] In the case of zeolites catalysts,^[14] high BDO conversions can be achieved at 250 °C, whereas heteropoly acids, such as H₃[PW₁₂O₄₀], show high conversions already at 200 °C.

The product distribution observed over various phosphate catalysts is shown in Table 3 for the conversion level of 11–12%. The same products, namely, MEK, MP, 3B2OL, BD, and cyclic ethers are observed. The product selectivity is rather similar for all the catalysts studied. The major reaction pathways are pinacol-type rearrangements yielding MEK through a hydride shift and MP through a methyl shift. Such product distribution is typical for strong solid acids, such as zeolites and heteropoly acids, which catalyze dehydration at moderate temperatures.^[11,14]

The content of MEK is between 60-67 wt % for all the phosphates, whereas the contribution of MP differs significantly for the catalysts studied (Table 3). The highest selectivity of

Table 2. Initial and (250 °C).	regional	rates o	of BDO	conversion	over	phosphate catalysts
	AIP	ZrP	NbP	TiP	BP	
Initial reaction rate [10 ⁻⁴ mol (g s) ⁻¹]	1.9	1.4	1.4	1.1	1.0	
E ₁ -E ₂ [kJ mol ⁻¹]	Regional amount of acid sites $[\mu mol g^{-1}]$				Regional rates [10 ⁻¹ mol (mol s) ⁻¹]	
80–120 120–155 155–220	755 164 12	221 417 203	229 316 117	200 171 41	170 209 59	$\begin{array}{c} 1.2 \pm 0.2 \\ 6.6 \pm 0.9 \\ -8.0 \pm 1.8 \end{array}$

Table 3. Product distri	ibution at t	he same co	onversion le	evel (250 °C	.).
	ZrP	BP	NbP	TiP	AIP
BDO conversion [%] WHSV [h ⁻¹]	11.2 400	11.3 300	11.2 400	12.1 300	12.1 500
	Product s	selectivity [wt %]		
MEK	65.8	60.0	60.4	67.4	64.7
2MP	23.5	14.0	30.8	23.8	21.7
3B2OL	3.1	6.4	3.8	6.0	3.8
BD	3.5	5.4	1.5	1.6	1.4
CC	4.1	14.2	3.5	16	8.3

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 \approx 30 wt % is observed for the NbP sample, whereas the lowest selectivity of \approx 14 wt % is found in the case of BP.

11.8

6.6

5.3

7.6

5.2

The reaction pathway leading to BD (Scheme 1) gives only a marginal contribution to the overall reaction products for phosphate catalysts. The highest selectivity to 3B2OL and BD combined reaches 12 wt% for the BP catalyst. Duan, Sato et al.^[8b,17,18] have reported that highly crystalline materials are required to achieve high yields of BD with rare-earth-oxide catalysts. We can speculate that similar requirements hold for the phosphate catalysts as the BP sample is the only crystalline material in the series of phosphates studied.

In addition to the typical dehydration products, a rather high contribution of heavy byproducts resulting from the condensation of dehydration products with BDO (Scheme 1) is observed with the phosphate catalysts. Boron and aluminum phosphate samples show the highest selectivity to these products and, at the same time, these two samples give the lowest contribution of MP. Conversely, NbP shows the highest selectivity to MP and the lowest content of C_8-C_{12} heavy products. One can suppose that C_8-C_{12} heavy products result mainly form the condensation of MP with BDO over phosphate catalysts. This supposition is in agreement with Török et al.^[11] who have demonstrated that MP mainly contributes to dioxolane formation with heteropoly acids.

Effect of reaction temperature

BD+3B2OL

The effect of temperature has been studied with AIP, which is found to be the most active among the phosphate catalysts.

The temperature was varied between 200-400 °C, with WHSV being equal to 1.5 h⁻¹ (Table 4). The results point to the fact that increasing the temperature from 200 to 250 °C has a dramatic effect on BDO conversion. Whereas at 200 °C the conversion is only 20.7 %, at 250 °C it reaches 100 %.

MEK is the main reaction product in the temperature range 250–400 °C. At lower temperatures its content decreases owing to the significant contribution of dioxolanes. A similar tendency is observed for MP, the content of which is decreased by a factor of four with a temperature drop from 250 to 200 °C. These observations point to a high contribution of conden-

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Table 4. Effect of temperature on BDO conversion over AIP catalyst (WHSV = 1.5 $h^{-1}).$							
<i>T</i> [°C]	200	250	280	400			
BDO conversion [%]	20.7	100	100	100			
Product selectivity [wt%]							
MEK	45.1	78.1	72.0	69.2			
2MP	3.0	13.4	16.9	13.8			
3B2OL	3.7	0.0	0.0	0.0			
BD	1.6	6.9	9.4	13.3			
C ₈ -C ₁₂	46.6	1.5	1.7	1.8			
BD+3B2OL	5.3	6.9	9.4	13.3			

sation reactions at low reaction temperatures, which results in the transformation of MEK and MP into dioxolanes. It should be mentioned that high yields of dioxolanes in the temperature range of $150-200^{\circ}$ C were observed previously by Török et al.^[11] with heteropoly acids.

The increase in reaction temperature results in persistent growth in BD selectivity, which is accompanied by a decrease in MEK content. This result is in line with thermodynamic calculations performed by Makshina et al.^[5] and shows that the probability of BD formation increases with temperature. The highest BD selectivity of 13 wt% is reached at 400 °C, whereas the highest selectivity to MEK (78 wt%) is achieved at 250 °C.

3B2OL is observed only at 200 $^{\circ}$ C, when the conversion was only 20%. At higher conversion levels, 3B2OL is most probably converted into BD. The same tendency was observed by Duan et al.^[18] over rare-earth metal oxides.

Correlation with acidity

Comparison of the catalytic activity of the various phosphate catalysts (Table 2) with their acidic properties (Figures 3 and 4, and Table 1) does not show any direct correlation, neither with the amount of Brønsted and Lewis sites (Figure 3), nor with the total amount of sites determined by TPD NH₃ (Table 1). Indeed, the ZrP and NbP catalysts show the same initial reaction rates (Table 2), whereas the number of acid sites is quite different for these catalysts (Table 1). Likewise, the BP and TiP samples contain the same amount of sites (Table 1), whereas the initial rates found for these catalysts are quite different (Table 2).

Analysis of the literature data suggests that both Brønsted and Lewis acid sites can participate in BDO dehydration.^[5,15] Furthermore, it appears from the literature survey that the nature of the acid sites is not as important as their strength.^[5,11,14] To verify the effect of acid sites with different strengths on the BDO dehydration with phosphate catalysts, the method of "regional analysis" proposed by Yoneda^[40] has been used. This method is based on the assumption that the reaction rate over an acidic site of a catalyst is determined solely by the acid strength of this site. The main requirements for the application of this method involve i) similar types of acid sites in the selected series of catalysts; ii) a sufficient number of catalysts; and iii) different acid site distribution for the catalysts in the selected series. The phosphate catalysts used in this study satisfy all the above requirements.

According to the method of "regional analysis",^[40] the acidic spectrum of a catalyst can be subdivided into several regions with similar acidic strengths and, therefore, with the same catalytic activity. With that in mind, the experimentally determined reaction rate for the i-th catalyst (v) can be described by Equation (1):

$$v_{i} = \sum {\binom{p_{j=1}}{v_{0j}}} v_{0j} * s_{ij}$$
(1)

where s_{ij} is the number of acid sites in the j-th region of the ith catalyst, v_{0j} is the regional rate of the acid site in the j-th region, and p is the number of regions.^[40] As v_i and s_{ij} can be experimentally determined for a set of catalysts, the regional rates can be easily estimated by means of the method of least squares, when the number of catalysts employed is greater than the number of regions, p. The regional rates determined in such a way will give information about the activity of the acid sites with different strengths.

To apply this approach to the phosphate catalysts, their TPD NH₃ spectra were subdivided into three regions, as shown in Figure 4. The first region corresponds to weak acid sites with activation energies for NH₃ desorption of 80–120 kJ mol⁻¹, the second one includes acid sites of medium strength (120-155 kJ mol⁻¹), whereas the third one corresponds to strong acid sites (155–220 kJ mol⁻¹). The activation energies of NH_3 desorption were calculated as proposed in ref. [41]. The regional contents of the acid sites determined for each catalyst are presented in Table 2 along with the initial rates of BDO dehydration over these catalysts. By using the method of least squares of the difference between the calculated (v_i^c) and experimental (v_i^e) initial rates, the set of regional rates was calculated. The results are shown in Table 2. To estimate the statistical significance of analysis, a Fisher test was conducted; it showed that the results are significant at the 5% level. The correlation coefficient between v_i^c and v_i^e was found to be 0.97, which suggests that the model sufficiently describes the experimental data.

The analysis of the calculated regional rates suggest that weak $(80-120 \text{ kJ} \text{ mol}^{-1})$ and medium $(120-155 \text{ kJ} \text{ mol}^{-1})$ acid sites are preferable for 2,3-butanediol dehydration, the latter being more active than the former by a factor of five. Surprisingly, the strongest acid sites show a negative value of regional rate. One of the possible reasons for this observation could be due to fast deactivation of these sites and, therefore, the negative influence on the overall catalytic activity.

Conclusions

Zirconium, niobium, aluminum, boron, and titanium phosphates are shown to be active catalysts for 2,3-butanediol dehydration in the temperature range 200-400 °C. The initial rates of butane formation are found to be within 1.0×10^{-4} - 1.9×10^{-4} mol(gs)⁻¹ at 250 °C, aluminum phosphate being the most active catalyst. The activity of phosphates is found to be

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comparable with those of zeolite catalysts. However, in terms of the stability of catalytic activity with time on stream, these catalytic systems are shown to be superior with respect to other solid catalysts.

The kinetic study pointed to three main reaction pathways operating over the phosphate catalysts: 1) pinacol rearrangement through a hydride shift, yielding methyl ethyl ketone; 2) pinacol rearrangement through a methyl shift, resulting in 2-methyl-propanal; 3) 1,2-elimination, leading to 3-butene-2-ol, which is further dehydrated into 1,3-butadiene by elimination of a second water molecule. Methyl ethyl ketone and 2-methyl-propanal may further interact with 2,3-butanediol, resulting in the formation of heavy byproducts, including different cyclic ethers.

The major reaction pathway with the phosphates involves pinacol rearrangement to methyl ethyl ketone, the selectivity for which being 60–78 wt% with the catalysts studied. The highest yield of 78 wt% methyl ethyl ketone is obtained with AIP at 250 °C and WHSV= $1.5 h^{-1}$. The 1,2-elimination gives a minor contribution to the overall reaction pathway. The maximum selectivity to 3-butene-2-ol and 1,3-butadiene at 250 °C reaches 11 wt% with boron phosphate, which is the only crystalline material among the catalysts studied.

The correlation obtained between the catalytic activity for the dehydration of 2,3-butanediol and the acid strength distribution over the phosphate catalysts points to the fact that acid sites with medium strength ($120-155 \text{ kJ} \text{ mol}^{-1}$) are the most active for dehydration; weaker sites ($80-120 \text{ kJ} \text{ mol}^{-1}$) show lower activity; whereas very strong sites (155-220 kJ mol⁻¹) have a negative effect on the activity.

Experimental Section

Catalyst preparation

Metal phosphate catalysts were prepared through the interaction of different metal-containing precursors with phosphoric acid, following the procedures described in the literature.^[22-26]

ZrP: Zirconium phosphate was prepared by the treatment of ZrOCl₂·8 H₂O aqueous solution (1 M) with 0.5 M solution of H₃PO₄. The Zr/P molar ratio was equal to 0.5. The mixture was stirred for 30 min and the resultant gel was filtered and washed with distilled water. Afterwards, the sample was dried at 110 °C and calcined at 400 °C in a flow of dry air for 3 h.

NbP: Niobium phosphate was synthesized from niobium oxide Nb₂O₅·*n* H₂O (5 g), which was treated with diluted orthophosphoric acid (0.5 m) at 80 °C. The resultant mixture was stirred for 7 h. Afterwards, it was cooled down to ambient temperature, filtered, and washed with distilled water until a pH value of 5 was obtained. The product was dried and calcined at 400 °C in a flow of dry air for 3 h.^[23]

AIP: Aluminum phosphate was prepared by the addition of aqueous ammonia (25 wt%) under continuous stirring to an aqueous solution containing equimolar quantities of aluminum chloride and orthophosphoric acid (1 M).^[24] The ammonia was added until pH = 7.0 was obtained. The resultant precipitate was aged (18 h, 25 °C), filtered, washed with distilled water several times, and dried for

24 h at 110 $^\circ\text{C}.$ The product was calcined in a flow of dry air at 500 $^\circ\text{C}$ for 3 h.

TiP: Titanium phosphate was synthesized according to the procedure described in ref. [25]. Unlike the other samples, an organic compound, Ti(OBu)₄, was used as the Ti precursor. Ti(OBu)₄ (5 g) was diluted with anhydrous EtOH (99%) to prevent TiO₂ formation. The resultant mixture was added to a H_3PO_4 solution (300 mL, 0.1 m, at 25 °C, under stirring). The mixture was stirred at ambient temperature for 1 h and at 80 °C for 24 h. The white precipitate was filtered and washed with distilled water. The product was dried at 110 °C and calcined in a flow of dry air at 500 °C for 3 h.

BP: Boron phosphate was synthesized by using an organic precursor, tri-*iso*-propylborate (B(*i*PrO)₃). B(*i*PrO)₃ was mixed with orthophosphoric acid (85%). The B/P molar ratio was equal to 1. The resultant mixture was heated to 120°C until the complete evaporation of water and *i*PrOH was achieved. The white solid was dried under vacuum at 110°C for 3 h and calcined in a flow of dry air at 500°C for 3 h.

Catalysts characterization

X-ray fluorescence analysis was used to determine the chemical composition of the samples. Measurements were performed with the X-ray fluorescence scanning crystal diffraction spectrometer "Spectroscan MaksGF2E" "Spectron". The spectrometer was equipped with a sharply focused X-ray tube with a copper anode.

The structure and phase compositions of the samples were determined by X-ray analysis. XRD patterns were recorded with a diffractometer "Bruker D2 Phaser" with CuK_{α} in the 2 θ range 5–50° with steps of 0.1°.

Low-temperature N_2 adsorption-desorption measurements were performed with an automated porosimeter Micrometrics ASAP 2000. Before the measurements, all samples were degassed at 200 °C for 2 h. Isotherms were measured at 77 K.

IR spectra were recorded with a Nicolet Protégé 380 FTIR spectrometer in transmission mode at 4 cm⁻¹ optical resolution. Prior to the measurements, the catalysts (20 mg) were pressed in self-supporting discs and activated in the IR cell attached to a vacuum line at 400 °C for 4 h. The adsorption of pyridine (Py) was performed at 150 °C for 40 min. The excess pyridine was further evacuated at 150 °C for 40 min.

Temperature-programmed desorption (TPD) of NH₃ was performed with a USGA-101 ("UNISIT"). Prior to NH₃ adsorption, the samples were calcined in a flow of dry air at 400 °C for 1 h and subsequently in a flow of dry nitrogen for 1 h and cooled to ambient temperature. The adsorption was carried out for 30 min in a flow of NH₃ diluted with N₂ (1:1). The physisorbed ammonia was removed in a flow of dry He at 100 °C for 1 h. Typical TPD experiments were carried out in the temperature range 50–800 °C in a flow of dry He (30 mL min⁻¹). The rate of heating was 7 °C min⁻¹.

Catalyst evaluation

The dehydration of BDO was carried out in a quartz fixed-bed continuous-flow reactor. The catalysts were preheated at 250 °C in a flow of nitrogen before the reaction. The reaction was carried out under atmospheric pressure in the temperature range 200– 400 °C in a flow of nitrogen as a carrier gas. The WHSV of BDO was varied from 1.5 to 500 g g⁻¹h. The products were analyzed by gas chromatography with a 40 m FFAP capillary column. Methane and



dioxane were used as internal standards for the analysis of the gas and liquid products, respectively. The products were identified by using a GC-mass spectrometer "Thermo" equipped with quadrupole mass detector "DSQ II" and gas chromatograph "Trace GC" with capillary column "HP-5 ms". The data were collected after the reaction reached a steady state.

Selectivity was defined as weight fraction of product in all products (not including water). Initial reaction rates were determined from the initial slopes of the kinetic curves (BDO conversion versus contact time) and defined as the number of moles of BDO converted into products per hour and per gram of the catalyst.

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Keywords: 1,3-butadiene · 2,3-butanediol dehydration methyl ethyl ketone · phosphate catalysts

- a) M. Köpke, C. Mihalcea, F. Liew, B. Al-Sinawi, S. D. Simpson, J. H. Tizard, M. S. Ali, J. J. Conolly, *Appl. Environ. Microbiol.* **2011**, *77*, 5467–5475; b) M. Voloch, N. B. Jansen, M. R. Ladisch, G. T. Tsao, R. Narayan, V. W. Rodwell in *Comprehensive Biotechnology, Vol. 45* (Eds.: M. Moo-Young, H. W. Blanch, S. Drew, D. I. C. Wang), Pergamon Press, Oxford, **1985**, pp. 933–947; c) C.-F. Huang, Y.-F. Jiang, G.-L. Guo, W.-S. Hwang, *Bioresour. Technol.* **2013**, *135*, 446–453; d) M. Motwani, R. Seth, H. F. Daginawala, R. Khanna, *Bioresour. Technol.* **1993**, *44*, 187–195; e) L.-Q. Jiang, Z. Fang, F. Guo, L. Yang, *Bioresour. Technol.* **2012**, *107*, 405–410; f) A. Multer, N. McGraw, K. Hohn, P. Vadlani, *Ind. Eng. Chem. Res.* **2013**, *52*, 56–60.
- [2] J. Daniell, M. Köpke, S. D. Simpson, Energies 2012, 5, 5372-5417.
- [3] M. Anvari, M. R. S. Motlagh, J. Biomed. Biotechnol. 2011, 2011, 1-7.
- [4] J. van Haveren, E. L. Scott, J. Sanders, Biofuels Bioprod. Biorefin 2008, 2, 41–57.
- [5] E. V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P. A. Jacobs, B. F. Sels, *Chem. Soc. Rev.* 2014, *43*, 7917–7953.
- [6] P. Lanzafame, G. Centi, S. Perathoner, Chem. Soc. Rev. 2014, 43, 7562-7580.
- [7] a) Z. Liu, W. Huo, H. Ma, K. Qiao, *Chin. J. Chem. Eng.* 2006, *14*, 676–684;
 b) L. H. Slaugh, G. W. Schoenthal, J. D. Richardson (Shell Oil Company Houston, TX) US Patent 4453015, **1984**; c) J. R. Black, J. Yang, J. L. Buechele (Shell Oil Company, HoustonTX), US patent 7282613 B2, 2007;
 d) S. M. Aldoshin, P. E. Matkovsky, Z. P. Pai, V. N. Parmon, L. N. Russiyan, V. N. Troitsky, WO 2007/055608A2, 2007.
- [8] a) M. Magnin-Lachaux, Z. Tan, B. Liang, E. Negishi, Org. Lett. 2004, 6, 1425–1427; b) H. Duan, D. Sun, Y. Yamada, S. Sato, Catal. Commun. 2014, 48, 1–4.
- [9] a) P. K. Frolich, C. E. Morrell, Chem. Eng. News 1943, 21, 1138-1145;
 b) N. L. Morrow, Environ. Health Perspect. 1990, 86, 7-8; c) Wm. C. White, Chem.-Biol. Interact. 2007, 166, 10-14; d) M. Arakawa, H. Yoshioka, K. Nakazawa (Japan Synthetic Rubber Co.Ltd, Tokyo) US Patent 4504692, 1985.
- [10] I. Bucsi, A. Molnar, M. Bartok, Tetrahedron 1994, 50, 8195-8202.
- [11] B. Török, I. Bucsi, T. Beregszaszi, I. Kapocsi, A. Molnar, J. Mol. Catal. A 1996, 107, 305–311.
- [12] K. Ohara, S. Furuhashi, Nippon Nogei Kagaku Kaishi 1942, 18, 143-150.

CHEMCATCHEM Full Papers

- [13] J. Lee, J. B. Grutzner, W. E. Walters, W. N. Delgass, Stud. Surf. Sci. Catal. 2000, 130, 2603–2608.
- [14] W. Zhang, D. Yu, X. Jia, H. Huang, Green Chem. 2012, 14, 3441-3450.
- [15] A. Molnár, I. Bucsi, M. Bartok, Stud. Surf. Sci. Catal. 1988, 41, 203-210.
- [16] a) M. E. Winfield, J. C. S. I. R. (Aust.) 1945, 18, 412–423; b) M. Winfield, Aust. J. Chem. 1950, 3, 290–305.
- [17] a) S. Sato, F. Sato, H. Gotoh, Y. Yamada, ACS Catal. 2013, 3, 721-734;
 b) S. Sato, R. Takahashi, T. Sodesawa, N. Honda, H. Shimizu, Catal. Commun. 2003, 4, 77-81.
- [18] H. Duan, Y. Yamada, S. Sato, Appl. Catal. A 2015, 491, 163–169.
- [19] a) A. Clearfield, D. S. Thakur, *Appl. Catal.* 1986, *26*, 1–26; b) S. Sebtia, M. Zahouily, H. B. Lazrek, J. A. Mayoral, D. J. Macquarrie, *Curr. Org. Chem.* 2008, *12*, 203–232; c) A. Tada, *Phosphorus Res. Bull.* 2004, *15*, 100–109; d) G. Aguilar-Armenta, M. E. Patino-Iglesias, J. Jimenez-Jimenez, E. Rodriguez-Castellon, A. Jimenez-Lopez, *Langmuir* 2006, *22*, 1260–1267.
- [20] V. L. Sushkevich, V. V. Ordomsky, I. I. Ivanova, Appl. Catal. A 2012, 441– 442, 21–29.
- [21] J. Maurin (Compagnie Francaise de Raffinage) US Patent 3758612, 1973.
- [22] V. F. D. Álvaro, R. A. W. Johnstone, J. Mol. Catal. A 2008, 280, 131-141.
- [23] S. Okazaki, A. Kurosaki, Catal. Today 1990, 8, 113-122.
- [24] G. J. Hutchings, I. D. Hudson, D. Bethell, D. G. Timms, J. Catal. 1999, 188, 291–299.
- [25] H. Fei, X. Zhou, H. Zhou, Z. Shen, P. Sun, Z. Yuan, T. Chen, *Microporous Mesoporous Mater.* 2007, 100, 139–145.
- [26] J. B. Moffat, J. F. Neeleman, J. Catal. 1973, 31, 274-277.
- [27] K. Segawa, Mater. Chem. Phys. 1987, 17, 181-200.
- [28] A. La Ginestra, Mater. Chem. Phys. 1987, 17, 161-179.
- [29] a) R. Vetrivel, B. Viswanathan, *Surf. Technol.* **1984**, *22*, 1–8; b) N. N. Gonchakova, N. G. Ivanova, L. Y. Kitaev, L. A. Novikova, A. A. Kubasov, V. Z. Sharf, K. V. Topchieva, *Petrol. Chem. USSR* **1981**, *21*, 133–142.
- [30] International Centre for Diffraction Data, ICDD PDF2 03-0332.
- [31] a) L. Liang, Y. Xu, L. Zhang, Y. Sheng, J. Opt. Soc. Am. B 2007, 24, 1066–1074; b) M. R. Ahsan, M. A. Uddin, M. G. Mortuza, Indian J. Pure Appl. Phys. 2005, 43, 89–99; c) S. W. Lee, R. A. Condrate Sr., J. Mater. Sci. 1988, 23, 2951–2959.
- [32] C. Dayanand, G. Bhikshamaiah, V. J. Tyagaraju, M. Salagram, A. S. R. Krishna Murthy, J. Mater. Sci. 1996, 31, 1945 – 1967.
- [33] J. C. Yu, L. Zhang, Z. Zheng, J. Zhao, Chem. Mater. 2003, 15, 2280–2286.
- [34] a) S. Chen, M. Ye, H. Chen, X. Yang, J. Zhao, *J. Inorg. Organomet. Polym.* 2009, *19*, 139–142; b) A. Baykal, M. Kizilyalli, M. Toprak, R. Kniep, *Turk. J. Chem.* 2001, *25*, 425–432.
- [35] a) T. Armaroli, G. Busc, C. Carlini, M. Giuttari, A. M. Raspolli Galletti, G. Sbrana, J. Mol. Catal. A 2000, 151, 233–243; b) Z. Ghezelbash, D. Ashouri, S. Mousavian, A. H. Ghandi, Y. Rahnama, Bull. Mater. Sci. 2012, 35, 925–931.
- [36] a) G. Busca, Phys. Chem. Chem. Phys. 1999, 1, 723-736; b) A. Travert, A. Vimont, A. Sahibed-Dine, M. Daturi, J. Lavalley, Appl. Catal. A 2006, 307, 98-107; c) C. A. Emeis, J. Catal. 1993, 141, 347-354.
- [37] a) G. Bagnasco, P. Ciambelli, A. La Ginestra, M. Turco, *Thermochim. Acta* **1990**, *162*, 91–97; b) M. Turco, P. Ciambelli, G. Bagnasco, A. La Ginestra, *J. Catal.* **1989**, *117*, 355–361.
- [38] S. G. Hedge, P. Ratnasamy, L. M. Kustov, V. B. Kazansky, Zeolites 1988, 8, 137–141.
- [39] A. N. Ko, B. W. Wojciechowski, Prog. React. Kinet. 1983, 12, 201-262.
- [40] Y. Yoneda, J. Catal. 1967, 9, 51-56.
- [41] V. V. Yushchenko, Zh. Fiz. Khim. 1997, 71 (4), 628-632.

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