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# Efficient catalysts for simultaneous dehydration of light alcohols in gas phase.

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We report on the simultaneous dehydration of light alcohols over rare earth phosphate catalysts. Catalytic reactions were carried out in a gas-phase fixed-bed reactor at temperatures ranging from 490 to 643 K. The catalyst samples were synthesized and characterized using various techniques, and their acid properties compared by monitoring the desorption of 2,6-dimethylpyridine by means of FTIR spectroscopy. The catalysts were found to be very efficient for the simultaneous dehydration of ethanol and 1-butanol to ethylene and 2-butene. This catalytic dehydration should involve the moderately strong Brønsted and Lewis acid sites revealed on the catalysts' surface, whose strength distribution was sufficiently broad to minimize the competition between dehydration of the two alcohols. The catalysts were also very efficient in the direct dehydration of alcohol mixtures produced by bacterial fermentation (PBE: propanol-1butanol-ethanol and ABE: acetone-1-butanol-ethanol). This outcome makes it possible to consider a metathesis-based industrial process for the production of propylene, in which the first step involves the dehydration of alcohol mixtures produced by biomass degradation. These catalysts are shown to present further advantages such as their insensitivity to the addition of water in the gas feeds, relative stability with time on stream, and straightforward regeneration.

## 1. Introduction

The drive to reconvert compounds produced by a biomass has led chemical engineers to design new processes, which must be as efficient as possible, since economic sustainability has become the major trend in the industrialization of such systems. This involves the minimization of the number of transformations, by converging sequential reaction steps into a single synthetic operation, in order to save time and avoid costly intermediate purification steps. It also calls for the development of highly selective catalysts, for reasons of atomic economy**,** the management of by-products, and the energy saving requirement of working at low temperatures. In this context, publications pertaining to new, multifunctional catalytic systems provide an illustration of what can be achieved in terms of combining successive (frequently referred to as tandem, or cascade) reactions.[1-5]

Catalytic systems are not frequently developed for tandem reactions, because this is highly challenging: both active and selective sites must be present for each reaction, and their catalytic properties and reaction condition windows must be tuned in order to maximize the final product yield of each sequential transformation. This approach, allowing several catalytic reactions to be combined in a single step, is of interest not only in the development of catalytic systems for the successive reaction steps of a given process, but also for parallel reactions leading directly to suitable charge compositions for the following reaction stage of a complex process.

New, emerging biomass reconversion processes for such applications are highly demanding, since they combine numerous reaction steps with intermediate purifications, which affect their economic viability. Among the new platform chemicals originating from renewable biomass feedstock, light alcohols are of considerable importance.[6] The dehydration of these alcohols to their corresponding alkenes is becoming a basic step in such reconversion processes, which are carried out mainly in the gas phase, and can be catalysed by various solid acid catalysts. Whereas it is relatively straightforward to achieve complete conversion of the alcohols, the challenge is to obtain the highest selectivity and the best stability with time on stream. In this context, there is a drive to develop catalysts allowing these objectives to be reached, which can be used for the simultaneous dehydration of different alcohols in a one-step reaction. In this case it would be advantageous either to use the alcohol mixture produced by fermentation, with no preliminary purification, or to obtain alkene mixtures suitable for the successive reaction step of a process such as a metathesis reaction.

A strong increase in the demand for propylene is expected in the coming years, as a consequence of growth in the markets for polypropylene and propylene oxide. On the other hand, the next generation of steam crackers will use shale gas ethane as raw material, and relatively smaller volumes of by-products will be available for propylene production.[7] In this context, bio-propylene could rapidly become a viable future option for the chemical industry, which is furthermore motivated by the drive for sustainable development. The direct dehydration of 1 or 2-propanol would in this case be the simplest chemical pathway. However, contrary to the case of ethanol and 1-butanol, large-scale industrial processes for the production of 1 or 2-propanol, which could advantageously be directly dehydrated to produce propylene, have not yet been developed. Nonetheless, propylene can be produced by a metathesis reaction from ethylene and 2-butene, according to the following reaction:

$$CH_3CH{=}CHCH_3 + CH_2{=}CH_2 \rightleftarrows 2\ CH_3CH{=}CH_2 \quad (1)$$

Cost evaluations indicate that, in response to the growing demand for propylene, its future production via the metathesis of ethylene and 2-butene could be economically attractive.[8,9] As 2-butene is needed to achieve the highest possible efficiency in the production of propylene via the metathesis reaction, it would be highly advantageous to produce 2-butene directly from the dehydration of 1-butanol, which is the predominant isomer produced by fermentation. Furthermore, if a stoichiometrically proportional mixture of 1-butanol and ethanol could be dehydrated in a single step, this would make the process even more economically efficient. These alcohols are generally obtained in a mixture with water. It would be even more advantageous if their separation from water, prior to catalytic dehydration, could be avoided. Similarly, most fermentation processes produce alcohol mixtures that would, advantageously, be simultaneously transformed, thus postponing their separation from the alkene mixtures if necessary.

Very few studies have reported the testing of catalysts used for the dehydration of several different alcohols, and almost none have investigated the simultaneous dehydration of alcohol mixtures. The most commonly proposed industrial solid acid catalysts are alumina and silica-alumina, due to their high productivity, stability, low price, and low induced corrosion.[10,11] In several cases, zeolites catalysts such as HZSM-5 or SAPO are used for their lower reaction temperature and higher water tolerance.[12,13] However, they are more sensitive to coke formation because of their porous texture and non-uniform distribution of acid sites.[14]

Lanthanum phosphates with different P/La ratios had earlier been shown to be active and selective in the temperature range of 490-643 K.[15] The solid with the highest P/La ratio (P/La=2) has the highest ethanol conversion and ethylene selectivity. In a previous study, we have shown that a catalyst does not need to contain a large quantity of phosphorus in order to be efficient; the catalytic properties of catalysts are related to the sub-surface $(H_nPO_4)^{-3+n}$ (n=1 or 2) species, and their optimal surface distribution is a key parameter.[16]
We further extended this study to include the pure phases of rare earth phosphates (*RE*=Nd, Gd, Sm), which appear to be considerably more efficient, in particular for the dehydration of 1-butanol to 2-butene.[17] In this case, the surface P/*RE* ratio was always close to one, and the dominant parameter leading to high performance appeared to be the nature of the rare earth element, i.e. its Lewis acidity.

In the context of our ongoing research in the field of new processes for the production of light olefins, we report on the catalytic properties of rare earth phosphates, when these are tested for the dehydration of light alcohol mixtures. The designed catalysts correspond to rare earth orthophosphates (La, Nd, Gd and Sm), the detailed characterization of which has been described in previous papers. The alcohols chosen to be included in the mixtures were ethanol, 1- and 2-propanol and 1-butanol. In order to define a complete industrial process, the study of the catalytic properties of these solids was extended to include ternary PBE (propanol-butanol-ethanol) and ABE (acetone-butanol-ethanol) mixtures, produced by bacterial fermentation. A specific study was made of the stability of these catalysts, and of the influence of the addition of water on their catalytic properties, in order to demonstrate the relevance of the related processes.

## 2. Experimental

Phase-pure $REPO_4$ samples (where *RE*=Nd, Gd, or Sm) were prepared according to the method described elsewhere.[17] A slurry was first prepared by dissolving 6.6 mmol of cetyl trimethyl ammonium bromide in 100 mL of a 1:1 water: ethanol solution, and adding 12 mL of aqueous ammonia (32 wt%). 0.029 mol. of $RE(NO_3)_3$,$6H_2O$ were then added under continuous stirring. After 2 h, the resulting solid was collected by filtration, washed with distilled water, dried in air at ambient temperature, and then digested in an aqueous solution of phosphoric acid (1 mol/L, 100 mL) for 48 h. The final product was filtered, washed with distilled water, dried in air at ambient temperature, and calcined at 823 K for 6 h.

The catalysts' performances were determined at atmospheric pressure, and at temperatures between 490 and 733 K, using a fixed-bed down-flow reactor.[17] The catalyst was packed into a glass plug-flow micro-reactor and stabilized in flowing nitrogen for 1h. Whenever the reaction temperature was varied, the system was allowed to stabilise for 30 min at each temperature, prior to any measurement. Feed was introduced into the carrier gas ($N_2$) using a syringe pump. The reaction products were analysed directly online by gas chromatography, or were trapped and analysed offline. The carbon balances were always higher than 99% and testing with an empty reactor at 628 K revealed conversions lower than 3%.

The metal content of the solids was determined by atomic absorption (ICP) in Argon plasma, using a SPECTROLAME-ICP manufactured by SPECTRO. The surface area of the solids was measured using the Brunauer-Emmett-Teller (BET) method with a Micrometrics ASAP 2020 instrument, after degassing for 3 h under vacuum at 573 K. X-ray photoelectron spectroscopy measurements (XPS) were performed using a Kratos Axis Ultra DLD spectrometer. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 X-ray diffractometer (Cu Kα radiation $\lambda$ = 1.54184 Å), and by progressively increasing the 2θ diffraction angle from 5° to 80° during the measurements. To study the deactivation of the catalysts as a function of time, the carbon content of the catalyst was determined after reaction using a Thermo Scientific MAS 200R CHNS/oxygen automatic analyzer.

FTIR spectroscopy was used to characterize the acid properties of the catalysts by following the spectra of adsorbed 2,6-dimethylpyridine. The phosphates were pressed into pellets and treated at 573 K under vacuum, cooled to 373 K and exposed to 2,6-dimethylpyridine for 15 min. The spectra were recorded after evacuation, under vacuum at 298, 323, 373, 423, 473 and 523 K for 15 min, and were then normalized to a 10 mg.cm$^{-2}$ disc.

## 3. Results and discussion

### 3.1 Characterization of the catalysts

The main characteristics of the rare earth phosphate catalysts used in this study are summarized in Table 1. These are all single-phase compounds with a Rhabdophane type structure, and have relatively high specific surface areas and mesopores of uniform size with a distribution centered on 8-10 nm. The surface P/*RE* ratios calculated from XPS analyses were close to the bulk ratios and unity, with the exception of $LaPO_4$, which exhibited a slight surface excess of phosphorus.

**Table 1**: Main characteristics of the rare earth phosphate catalysts.

| Catalyst | Composition [a] |  | SSA [b] | Pore Vol. | Pore size |
|---|---|---|---|---|---|
|  | bulk P/*RE* | surf. P/*RE* | ($m^2.g^{-1}$) | ($cm^3.g^{-1}$) | (nm) |
| $LaPO_4$ | 1.1 | 1.32 | 124 | 0.2 | 8 |
| NdPO4 | 1.1 | 0.96 | 117 | 0.3 | 8 |
| $SmPO_4$ | 1.1 | 1.10 | 82 | 0.2 | 10 |
| $GdPO_4$ | 1.1 | 1.06 | 95 | 0.3 | 11 |

[a] Bulk P/*RE* ratios determined from chemical analyses, and surface ratios computed from X-ray photoelectron spectroscopy data. [b] SSA specific surface area measured using the BET method.

The acid properties of the rare earth phosphates were first characterized using thermal desorption of pyridine monitored using FTIR spectroscopy.[17,18] The results showed that both Brønsted and Lewis acidities of phosphates were lower than those of conventional catalysts but comparable for the different compounds except for $LaPO_4$, which exhibited a lower number of acid sites at high and low temperature. In order to better characterize the acidity of the compounds the adsorption of 2,6-lutidine, which exhibits a higher $pK_{BH+}$ and is better adapted to the detection of weak acid sites, has been studied.[19] This has been done despite the fact that all Lewis acid sites might not be detected because of steric hindrance of methyl groups. [20-22]

The adsorption of 2,6-dimethylpyridine on rare earth phosphates produces several spectroscopic bands, which are attributed to adsorption on Brønsted and Lewis acid sites.[23] The progressive desorption of DMP at increasingly high temperatures leads to a decrease in the intensity of all bands, and a shift towards higher wavenumbers. The variation in intensity of the peaks at 1608 and 1649 cm$^{-1}$, corresponding to 2,6-dimethylpyridine adsorbed on Lewis and Brønsted sites, respectively, were monitored as a function of temperature (Fig. 1). The number of weak Brønsted acid sites varied at low temperatures in the following order: Sm > Gd > Nd > La, whereas at high temperatures the numbers of Sm, Gd and Nd sites were comparable, but lower in the case of La. Concerning the number of Lewis sites, the order at low temperatures was: Gd > Nd > La > Sm, whereas at high temperatures the numbers were again comparable for Sm, Gd and Nd, but lower for La.

These features were confirmed by thermal programmed desorption of ammonia and were in agreement with earlier studies.[16,17]

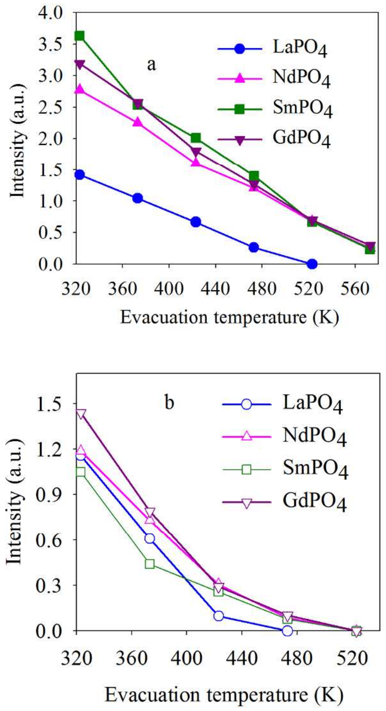


**Fig. 1**: Normalized adsorption peak intensities at 1649 cm$^{-1}$ (a) and at 1608 cm$^{-1}$ (b), for the different phosphates as a function of temperature.

### 3.2 Separate dehydration of ethanol, propanol and 1-butanol

The dehydration of ethanol, 1-propanol and 1-butanol on the rare earth phosphates was first studied separately. The variations of the conversion efficiency and selectivity of these alcohols to their corresponding alkenes, on the different rare earth phosphate catalysts, are shown in Fig 2 as a function of reaction temperature. These results show that the catalysts were very active and selective for the dehydration of these three alcohols, which were totally converted on all catalysts at temperatures below 733 K.

For the dehydration of ethanol, $GdPO_4$ was the most active and selective catalyst with 100% selectivity to ethylene at 673 K. This temperature is at least 30 K higher than on conventional alumina based catalysts, which are more active but the rare earth phopshates are more selective with selectivity reaching almost 100%.[18]

At low temperatures, diethyl ether was the only by-product formed, whereas at higher temperatures only traces of acetaldehyde and diethyl ether were detected.

For propanol dehydration, the study has been focused on 1-propanol. Dehydration of 2-propanol has been studied for a long time since it is used as a model reaction to characterize the acid properties of oxides.[24,25] Many catalysts exhibited a very high selectivity to propylene at low temperatures. It appeared more informative to focus on the dehydration of 1-propanol, which is more difficult to achieve. Furthermore, very few studies have been carried out on this reaction, and 1-propanol is produced with higher yields by fermentation. The $LaPO_4$ and $NdPO_4$ catalysts were tested for this reaction, and were found to be very active and selective for 1-propanol dehydration. The characterization of these catalysts has revealed that $LaPO_4$ has an excess of phosphorus at its surface, which may have been believed to be the reason for its lower efficiency as catalyst.

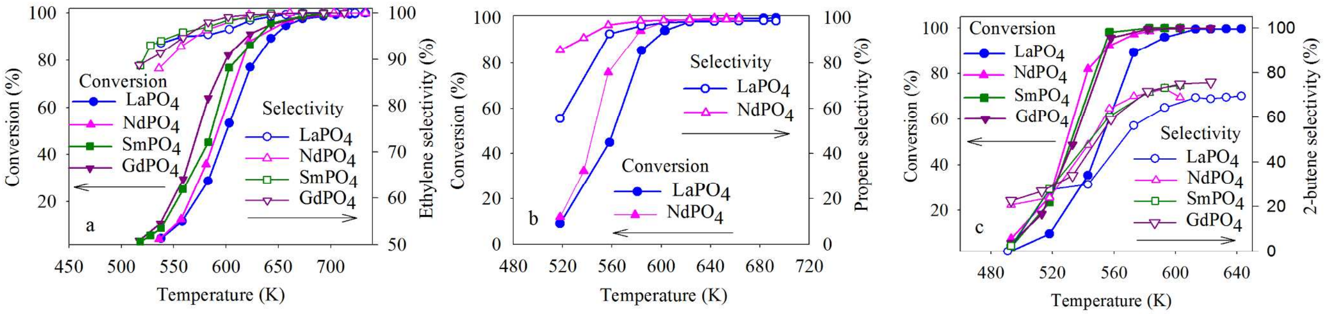


**Fig.2**: Catalytic properties of the tested rare earth phosphates for the dehydration of (a) ethanol, (b) 1-propanol, and (c) 1-butanol. Test conditions: $m_{cata}$: 101 mg, W/F=28.1 $g_{cata}$.h.mol$^{-1}$, $N_2$: 100 mL.min$^{-1}$

Their efficiency was as good as that of many previously studied catalysts[26,27], with the exception of microporous niobium silicate AM-11 which has a 100% selectivity to propylene, and total conversion, at only 523 K.[28] $NdPO_4$ appeared to be slightly more active than $LaPO_4$. Both phases were very selective to propylene, with dipropyl ether being the only by-product formed at low temperatures. The catalytic properties of Gd and $SmPO_4$, which were similar to those of $NdPO_4$ at 560 and 580 K, are not reported in the figure.

In the dehydration of 1-butanol, the formation of 1-butene was favoured at low temperatures, and that of 2-butene at high temperatures. No other alkenes were detected. The measured cis/trans ratio was approximately 0.9. The rare earth phosphates were found to have the same activity ranking for the dehydration of 1-butanol as for ethanol. At total conversion, the selectivity to 2-butene reached 76 % on $GdPO_4$. It was almost comparable for Nd and Sm, but lower for $LaPO_4$. Traces of dibutyl ether (<0.1%) were observed at low temperatures (< 553 K). The catalysts, which were tested between 12 and 34 h, appeared to be stable on stream in all cases.

Activity ranking showed that the catalytic activity was correlated to the number of strongest Brønsted and Lewis acid sites. However, we consider that these sites cannot be very strong, since it was found that the phosphates were not able to crack cumene.[29] A previous study has shown that a good correlation is obtained between the Lewis acid strength of the phosphates and the initial rate of ethanol conversion at 558 K.[17] However, during the course of another study focusing on the preparation techniques used for similar phosphates, a $LaPO_4$ phase was prepared with no excess phosphorous (P/La=1.07), and the catalysts appeared to be even less active and selective (to ethylene and 2-butene) than the catalyst tested in the present study.[17]

### 3.3. Simultaneous dehydrations of ethanol and 1-butanol

The simultaneous dehydration of ethanol and 1-butanol mixtures has been tested over the Nd, Gd and Sm phosphates. The variation of ethanol and 1-butanol conversion, as well as their selectivity to ethylene and 2-butene, are shown in Fig. 3 as a function of reaction temperature. All three catalysts were very active for the dehydration of both alcohols, and total conversions were obtained above 600 K. The ethanol dehydration activity of these catalysts was ranked in the following order: Gd>Sm>Nd. However, the reverse ranking was found for the catalysts' activity with 1-butanol, and for their selectivity to 2-butene. Almost no difference was found between their selectivities to ethylene and 2-butene.

The conversions of both alcohols were compared over the $GdPO_4$ catalyst when tested pure or in a mixture, but were tested with the same WHSV with respect to 1-butanol and ethanol (W/F = 50.9 $g_{cata}.h.mol^{-1}$).

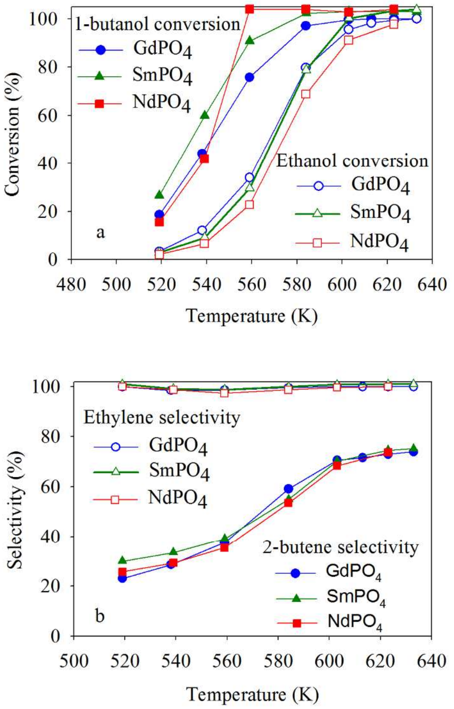


**Fig.3**: Variation of ethanol and 1-butanol conversion (a), and selectivity to ethylene and 2-butene (b), as a function of temperature. Test conditions: ethanol and 1-butanol in 1:1 molar ratio, $m_{cata}$: 101 mg, W/F=25 $g_{cata}.h.mol^{-1}$, $N_2$: 100 mL.min$^{-1}$

Fig. 4 shows that the dehydration of pure 1-butanol took place at a lower temperature, and more selectively, to 2-butene, than in the case of the dehydration of a 1-butanol + ethanol mixture. A much smaller decrease in the conversion of ethanol is observed when it is present in a mixture, and this is associated with no difference in selectivity to ethylene. These results can be explained by the fact that during dehydration of the mixture, the strong acid sites, which should be the most selective to 2-butene, were used by ethanol rather than by 1-butanol. However, at high temperatures it is possible to have a comparable selectivity to both alkenes, with total conversion of the alcohols.

### 3.4. Effect of added water, stability with time on stream and regenerability of the catalysts

The fermentation of a biomass always leads to the production of alcohol mixtures containing large quantities of water. The separation of alcohol from water consumes large quantities of energy and is expensive, whatever the technique selected (extraction with solvents, distillation, azeotropic distillation). Furthermore, as it would be inefficient to implement a dehydration step prior to a reaction step producing water, which would later have to be removed, it could be advantageous to run the dehydration reaction in the presence of water.

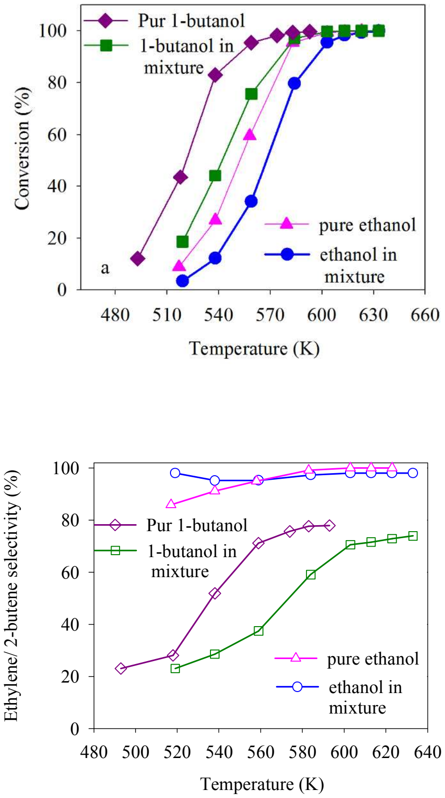


**Fig. 4:** Dehydration of ethanol and 1-butanol in a mixture, compared with dehydration of both alcohols alone, over a $GdPO_4$ catalyst under the same conditions. Test conditions: $m_{cata}$: 101 mg, W/F=50 $g_{cata}.h.mol^{-1}$, $N_2$: 100 mL.min$^{-1}$

The water could then be separated from the alkenes produced by this reaction, more easily and economically than if it were to be removed from the alcohols. For this reason, we tested the catalysts while adding water to the gas feeds, in order to determine whether they are deactivated by the water, and thus require it to be totally removed before the alcohols can be fed into the catalytic reactor.

The influence of water was studied by adding it to the mixture (12.5 mol %), whilst maintaining the same ethanol to 1-

butanol ratio and the same reaction conditions. Water was found to have almost no influence on the ethanol, nor on the 1-butanol conversion (Table 2). These results were confirmed, under the aforementioned conditions, over the temperature range between 583 and 633 K.

Another important parameter to be evaluated, when planning the industrial use of a dehydration catalyst, is its stability with time on stream. As shown in Fig. 5, this stability was studied for the case of the $GdPO_4$ catalyst, which appears to remain relatively stable with time on stream. No deactivation of the 1-butanol conversion was observed, even after 60 h on stream. However, over the same period of time a small but limited decrease (-1.5%) in ethanol conversion was observed. In parallel, no change in the catalyst's selectivity to ethylene was observed, whereas its selectivity to 2-butene decreased slightly (-3%), leading to an increase in its selectivity to 1-butene.

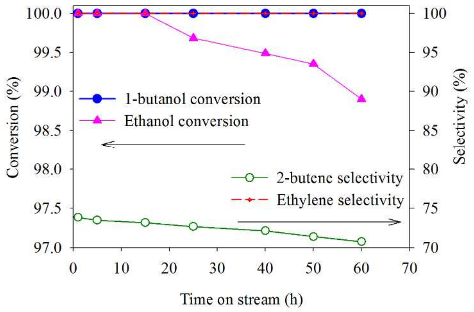


**Fig. 5**: Variations in the catalytic properties of $GdPO_4$ for the dehydration of a 1:1 mixture of ethanol and 1-butanol, as a function of time; test conditions: T=633 K, $m_{cata:}$ 101mg, W/F=25 $g_{cata}.h.mol^{-1}$, $N_2$: 100 $mL.min^{-1}$.

**Table 2**: Comparison of the catalytic properties of $GdPO_4$ in the dehydration of a 1:1 mixture of ethanol (Et) and 1-butanol (Bt), in the presence or absence of added water, after 1 h and 60 h of testing, Test conditions: 663 K $m_{cata:}$ 101 mg, W/F=25 $g_{cata}.h.mol^{-1}$, $N_2$: 100 $mL.min^{-1}$.

| Temp. (K) | Without added water | | | | With 12.5 mol% of added water | | | |
|---|---|---|---|---|---|---|---|---|
| | Conv. (%) | | Selec. (%) | | Conv. (%) | | Selec. (%) | |
| | 1-BtOH | EtOH | $2-C_4^{=}$ | $C_2^{=}$ | 1-BtOH | EtOH | $2-C_4^{=}$ | $C_2^{=}$ |
| 583 | 97.1 | 81.8 | 53.3 | 99.6 | 97.8 | 81.6 | 54.9 | 99.7 |
| 603 | 99.5 | 92.0 | 65.5 | 100.0 | 99.8 | 95.2 | 67.0 | 100.0 |
| 623 | 100.0 | 99.4 | 72.7 | 100.0 | 100.0 | 99.6 | 73.9 | 100.0 |
| 633 | 100.0 | 100.0 | 74.0 | 100.0 | 100.0 | 100.0 | 74.4 | 100.0 |

This result can be explained by the fact that when coke is formed on the catalyst, the strongest acid sites are the first to be neutralized. Since these sites are more active for ethanol dehydration, this reaction is the first to be affected. Furthermore, these acid sites should be the most selective to 2-butene, thus explaining the observed decrease in selectivity to this alkene. It is also possible that, independently of the dehydration reaction, 1-butene is isomerized to 2-butene on the strongest acid sites. However the selectivity to 2-butene was slightly affected by the deactivation, which tend to show that this reaction was not favored.

The relative weight carbon content of the catalyst has been measured after 60 h and corresponded to only 0.3%, which confirm the high resistance to coking.

Although the tested catalysts were found to be rather stable, a suitable regeneration technique is needed for their successful use in an industrial process. Deactivation of these catalysts results from surface coke deposition. It was found that it is possible to regenerate both of the catalysts tested in the present study by passing air through the catalyst bed, in order to burn the coke formed on their surface. After 60 h on stream, the reaction flow was switched to a flow of air (75 mL $min^{-1}$), and the temperature was increased to 723 K, which was shown to be optimum for coke formed in this type of reaction and maintained at this temperature for 1 h.[30] The $GdPO_4$ catalyst was then cooled to the catalytic reaction temperature, and the initial catalytic reaction flow re-introduced. Table 3 shows that the catalyst recovered its initial properties with no significant loss in selectivity, and only a slight decrease in activity.

Table 3: Comparison of the catalytic properties of a $GdPO_4$ catalyst, fresh and after regeneration (Reg.) in air at 723 K for 4 h, in the dehydration of a 1:1 mixture of ethanol and 1-butanol, after 1 or 60 h of testing. Test conditions: 633 K, $m_{cata}$: 101 mg, W/F=25 $g_{cata}.h.mol^{-1}$, $N_2$: 100 mL.min-1.

| Catalyst | after 1h | | | | after 60 h | | | |
|---|---|---|---|---|---|---|---|---|
| | Conv. (%) | | Selec. (%) | | Conv. (%) | | Selec. (%) | |
| | 1-BtOH | EtOH | $2-C_4^{=}$ | $C_2^{=}$ | 1-BtOH | EtOH | $2-C_4^{=}$ | $C_2^{=}$ |
| Fresh | 100.0 | 100.4 | 74.0 | 100.0 | 100.0 | 98.9 | 70.8 | 100.0 |
| Reg. | 100.0 | 99.6 | 74.0 | 100.0 | 100.0 | 98.7 | 71.9 | 100.0 |

### 3.5. Dehydration of alcohol mixtures produced by the ABE and PBE processes

1-butanol and ethanol can be produced simultaneously by the ABE fermentation process (Acetone-Butanol-Ethanol). This is one of the oldest known industrial fermentation processes, and involves the anaerobic bacterial fermentation of starch, to produce acetone, 1-butanol and ethanol in a 3-6-1 ratio.[31]

The results reported in this section were obtained with $SmPO_4$ and $NdPO_4$ catalysts. The catalysts' conversion of acetone, 1-butanol and ethanol, as well as their selectivity to 2-butene and ethylene, are shown in Fig. 6 as a function of reaction temperature.

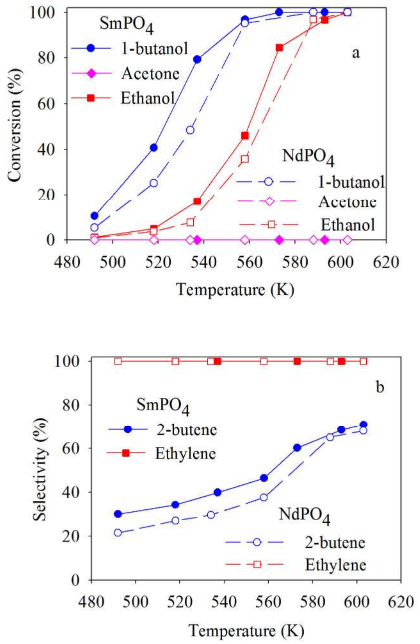


**Fig. 6**: Catalytic properties of Nd and $SmPO_4$ catalysts in the dehydration of an ABE mixture (acetone, 1-butanol and ethanol in 3:6:1molar ratio): (a) alcohol conversion and (b) selectivity to ethylene and 2-butene as a function of temperature. Test conditions: $m_{cata}$: 101 mg, W/F=28.3 $g_{cata}$.h.mol$^{-1}$, $N_2$: 100 mL.min$^{-1}$

Both of the tested catalysts appeared to be very active for the conversion of the two alcohols, but totally inactive for the transformation of acetone in the ABE mixture. Although $SmPO_4$ appeared to be more active and selective to 2-butene than $NdPO_4$, there was almost no difference in their selectivities to ethylene. 1-butene was the only other alkene formed, in addition to 2-butene, by the dehydration of the 1-butanol in the ABE mixture.

It has recently been shown that the metabolic engineering of Escherichia coli can be used to produce mixtures of light alcohols (ethanol, 1-propanol and 1-butanol), with considerable efficiency.[32] It was thus of interest to determine whether such mixtures could be dehydrated as efficiently as in the case of an ABE mixture. Although mixtures with richer 1-propanol and poorer ethanol contents could be obtained, the composition of the ABE mixture was maintained simply by replacing the acetone with propanol. The $SmPO_4$ and $NdPO_4$ catalysts were thus tested with this mixture. A 50:50 mixture of 1- and 2-propanol was used.

The propanol, 1-butanol and ethanol conversion efficiencies, and the catalysts' selectivity to propylene, 2-butene and ethylene, are shown in Fig. 7 as a function of reaction temperature. Although both catalysts were found to be efficient for the dehydration of a PBE mixture, as in the case of an ABE mixture, $SmPO_4$ appeared to be more active and selective to 2-butene than $NdPO_4$. As for the case of the ABE mixture, 1-butene was formed in addition to 2-butene, when 1-butanol was dehydrated. The only difference in the results was a slightly higher selectivity to 2-butene from 1-butanol, presumably because some of the most selective sites to 2-butene were occupied by acetone.

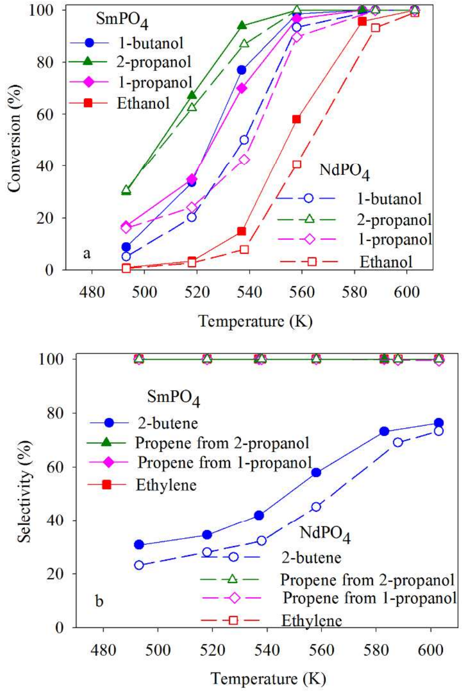


**Fig. 7**: Catalytic properties of Nd and $SmPO_4$ catalysts for the dehydration of a PBE mixture: (a) alcohol conversion and (b) selectivity to ethylene, propylene and 2-butene as a function of temperature. Test conditions: $m_{cata}$: 101 mg, W/F=28.3 $g_{cata}$.h.mol$^{-1}$, $N_2$: 100 mL.min$^{-1}$

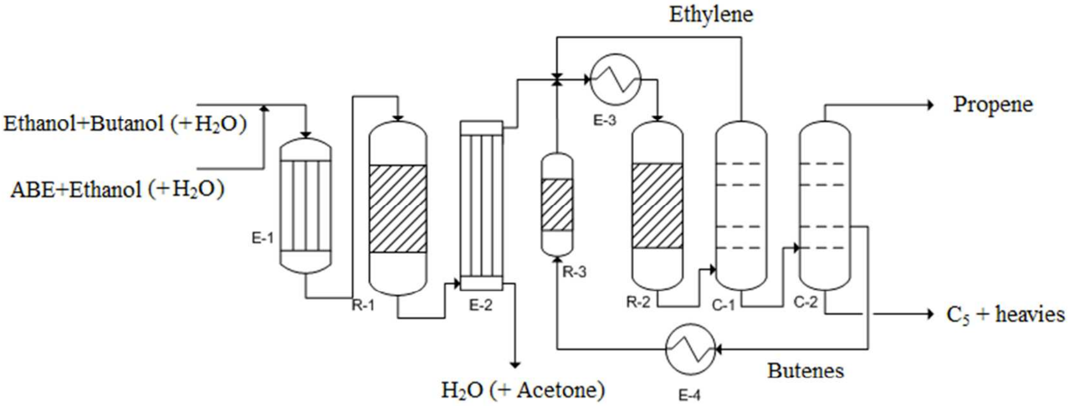
Although there is almost no difference between the two catalysts in terms of their selectivity to ethylene and propylene, $SmPO_4$ is more selective to 2-butene than $NdPO_4$. In the case of $SmPO_4$, both its greater activity in the dehydration of ethanol and 1-propanol and its higher selectivity to 2-butene can be explained by the presence of more strongly acid sites on its surface. Nevertheless, it is still unclear why $NdPO_4$ is more active for the dehydration of 1-butanol alone, than for the dehydration of 1-butanol in the presence of ethanol and propanol. It may be hypothesized that in the case of $SmPO_4$ a slightly greater number of sites of moderate acid strength was involved, than in the case of $NdPO_4$ (Fig. 1).

The dehydration of a PBE mixture over a $NdPO_4$ catalyst was also studied for shorter contact times. Fig. 7 shows the variation of propanol, 1-butanol and ethanol conversions and selectivities to propylene, 2-butene and ethylene, versus reaction temperature. It was found that a decrease in contact time led to an increase in the reaction temperature at which total conversion was obtained. More specifically, by decreasing the contact time from 28.34 $g_{cata}$.h.mol$^{-1}$ to 14.17 $g_{cata}$.h.mol$^{-1}$, the temperature required for total conversion rose from 593 K to 633 K. The propensity of rare earth phosphates to efficiently and simultaneously dehydrate $C_2$, $C_3$ and $C_4$ alcohol mixtures could be due to the presence of moderately strong Brønsted and Lewis acid sites at their surface, having a distribution in strength allowing competition between different alcohols to be minimized. Ethanol appeared to require stronger acid sites, and to be less sensitive to the presence of the other alcohols. Conversely, 1-butanol conversion was slightly less selective to 2-butane, as a consequence of competition on the strongest acid sites, which are the most selective to 2-butene.

### 3.6. Possible use of a co-dehydration step in a propylene production process

Fig. 8 provides a schematic representation of a configuration that could be used in a propylene production process, with the first step involving the co-dehydration of an ethanol/1-butanol or ABE feedstock. This is quite different to the commonly proposed processes involving the use of a metathesis reactor, since no isobutylene or other $C_4$ molecules similar to isobutene or butadiene would be present in the gas mixture. The gas mixture would however contain 1-$C_4$ in a relatively large proportion (1-$C_4$/(1-$C_4$ + 2-$C_4$)=0.22), and the metathesis reaction would have to be run under specific conditions (high ethylene-to-butene ratio), and with a catalyst selected to minimize the 1-$C_4$ reaction.

**Fig: 8**: Schema diagram of a propylene production process via alcohol dehydration and metathesis. E-1: heater, E-2: condenser, R-1: dehydration reactor, R-2: metathesis reactor, R-3 isomerization reactor, C-1: De-ehtylenizer column, C-2: De-propylenizer column



The dehydration of such a 1:1 mixture would lead to a mixture richer in ethylene than alkenes, which is the type of mixture generally used to minimize side reactions in metathesis reactions.[33] There are various new metathesis catalysts that are stable and highly selective to propylene, even at stochiometric or substoichiometric ethylene ratios.[34] For the present application, it would be straightforward to use such a catalyst and to modulate the alcohol ratios, with no consequence on its catalytic properties.

Following metathesis, the effluent is delivered to a fractionation section, where ethylene is removed in a de-ethyleniser and recycled. The bottom product is delivered to a de-propyleniser to recover the propylene.

This propylene would exceed polymer-grade propylene specifications, since it would not be polluted by the alkanes that are normally present in the feedstock when olefins are produced by cracking technologies. The bottom stream of the de-propyleniser would contain butenes and a small amount of C5+ material formed during the reaction. The gas mixture could be recycled either to a steam cracker or after separation of the C5+ fraction to the metathesis reactor, via an isomerization reactor, in order to catalytically convert 1-$C_4$ to 2-$C_4$.

## 4. Conclusions

The general conclusion from this study is that rare earth orthophosphates can dehydrate mixtures of alcohols very selectively, even in the presence of water. Light alcohol mixtures or ABE mixtures produced by industrial fermentation processes can be directly dehydrated to alkene mixtures over these catalysts, which are simultaneously very selective for all of the tested alcohols, and relatively stable with time on stream. 1-butanol is always preferentially dehydrated to 2-butene on these catalysts, which can be advantageously used to transform ethanol-1-butanol mixtures, and in direct metathesis reactions, to produce propylene in a consecutive step.

Phosphate catalysts have moderately strong Brønsted and Lewis acid sites, but more importantly have a sufficiently broad acid strength distribution to allow competition between the dehydration of different alcohols to be minimised. The properties of these catalysts allow them to be used for efficient, simultaneous dehydration reactions.

They also have the advantage of being very stable on stream, and of being easily regenerable by means of simple heat treatment in air at 723 K. In conclusion, the appropriate use of rare earth catalysts could pave the way to the development of industrial processes that minimize the generally high energy cost of the purification, separation and regeneration steps required in alcohol dehydration.

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## Notes and references

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