

DEHYDRATION OF PRIMARY ALCOHOLS

The invention relates to a process for dehydrating primary alcohols into alpha-unsaturated hydrocarbons in the presence of a dehydration catalyst. More particularly, the invention relates to a process for dehydrating isobutanol selectively to isobutene. In addition, the invention relates to a process for preparing methyl tert-butyl ether (hereinafter MTBE) from methanol and isobutanol.

According to section 7-1 of the standard textbook, "Advanced Organic Chemistry", third ed. by J. March, dehydration of alcohols can be accomplished in several ways. According to this textbook, the Broensted acids H_2SO_4 and H_3PO_4 are common reagents, as well as a score of Lewis acids such as Al_2O_3 . Besides, also solid Broensted acids like $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ are typically used.

The ease of dehydration of alcohols increases with α -branching. It follows the sequence tertiary > secondary > primary. When protic acids catalyse alcohol dehydration, the mechanism is E_1 . It involves the conversion of ROH into the protonated alcohol ROH_2^+ and cleavage of the latter into the carbonium ion R^+ and H_2O . The dehydration rate in the presence of a protic acid is quite high. Tertiary alcohols are dehydrated easily with even a trace of acid.

However, in many cases the use of protic acids lead to rearrangement products or to ether formation. Thus, less stable carbonium ions will rearrange whenever possible to form a more stable carbonium ion. n-Butanol, for example, yields the n-butyl cation that rearranges to the sec-butyl cation. According to sections 5.19 to 5.23 of "Organic Chemistry", third ed., by Morrison and Boyd,

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this cation loses a hydrogen ion to give 2-butene, in particular the trans isomer. Only the methyl cation and, of the primary alcohols, only the ethyl cation cannot rearrange to form a more stable carbonium ion.

5 In case side reactions involving shift of the double bond or skeletal rearrangements are to be avoided, vapour-phase dehydration over Al_2O_3 is an excellent method for dehydrating volatile alcohols ("concerted, E2 mechanism"). Drawback of Al_2O_3 and similar solid Lewis acids,
10 is that the excellent selectivity to the (optionally substituted) alpha-olefin is provided at the cost of activity.

 The inventors set out to provide: (i) a catalyst for dehydration of primary alcohols, in particular isobutanol, that is as selective as but more active than the
15 aforementioned Al_2O_3 ; and (ii) a process for dehydrating primary alcohols in the presence of this catalyst.

 Surprisingly, it was found that this objective could be achieved with Group Vb metal oxide hydrates, i.e.,
20 niobic acid and tantalic acid (respectively $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$). Of these, niobic acid is preferred. Accordingly, the invention provides a process for dehydrating primary alcohols into alpha-unsaturated hydrocarbons in the presence of a dehydration catalyst, wherein the
25 dehydration catalyst is niobic acid and/or tantalic acid.

 It is to be understood, that methanol is excluded from the definition of primary alcohols, as dehydration thereof (into dimethylether) proceeds via a different mechanism. In order for the dehydration to the corresponding alpha-olefin to occur, the primary alcohol must
30 have a vicinal hydrogen atom. Methanol does not have an adjacent carbon atom, let alone a hydrogen atom thereon, and is hence not dehydrated into an alpha-unsaturated hydrocarbon.

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Suitably, the primary alcohol has at least 3 carbon atoms. Although ethanol may also be dehydrated using the present dehydration catalyst, selectivity of the catalyst is usually not a problem. The primary alcohol typically has less than 20, say less than 10 carbon atoms, to allow for gas-phase dehydration. It is, however, possible to carry out the process with larger primary alcohols, dissolved in an inert solvent.

The primary alcohol may contain further functional groups and unsaturated carbon-carbon bonds. Preferably, it is an alkanol. Use of a functionalised primary alcohol such as ethylene glycol may lead to the isomer (tautomer) of the alpha-unsaturated hydrocarbon.

Primary alcohols that may be dehydrated advantageously into the corresponding alpha-unsaturated hydrocarbons are for instance 1-propanol, 1-butanol, 2-methyl-1-propanol (isobutanol), 2-methyl-1-butanol, etc. The process of the invention is particularly suitable for the selective conversion of isobutanol into isobutene in high yields.

The dehydration catalyst may be prepared either as a bulk oxide or supported on an acidic or amphoteric carrier, like gamma-Al₂O₃ or the more neutral SiO₂ supports.

The synthesis of niobic acid and the use thereof as dehydration catalyst is known. For instance, in JP 1290636, the preparation of isobutene is disclosed, comprising gaseous phase dehydration of tert-butanol over niobic acid. In an article entitled "Acidic and Catalytic Properties of Niobium Penta-oxide" by T. Izuka et al, published in 1983 in Bull. Chem. Soc. Jpn., 56, 2927-2931, the dehydration of 2-butanol is disclosed. That this catalyst and its analogue tantalic acid could also be used for the selective preparation of isobutene from isobutanol is neither disclosed nor hinted at. Rather, the aforementioned article discloses that Nb₂O₅·nH₂O

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showed a remarkable isomerization activity.

The dehydration catalyst is suitably prepared by precipitating niobium hydroxide and/or tantalum hydroxide from e.g., a solution of the Group Vb metal oxalate, followed by washing the niobium hydroxide and/or tantalum hydroxide with water and then heat-treating the Group Vb metal oxide hydrates thus obtained at a low temperature. Expediently, the hydrates may be treated with e.g., sulphuric acid, hydrofluoric acid or phosphoric acid before the low-temperature heat treatment. Typically (cf. EP-A-0,135,145) the hydrates are pre-treated with heat at a moderate temperature in the range of 100 to 400 °C. At temperatures in excess of 400 °C the hydrates become fully dehydrated, resulting in a change of properties. Preferably, the dehydration catalyst is pre-treated at a temperature in the range of 100 to 300 °C, more preferably at about 300 °C.

The dehydration process is carried out at conditions typically found for dehydration of alcohols by heterogeneous catalysts. Thus, the dehydration catalyst is packed into a reactor to prepare a fixed catalyst bed. The catalyst is then activated at 100 to 400 °C, and the reactor is set to 150 to 350 °C, preferably 250 to 300 °C. The primary alcohol is fed to the catalyst bed at a weight hourly space velocity (WHSV) of 1 to 20 kg/kg_{cat}·hr, preferably 3 to 10 kg/kg_{cat}·hr. The reaction pressure is ordinarily in the range of 0 and 20 bar g, preferably in the range of 1 to 10 bar g.

The production of fuel oxygenates entirely from synthesis gas is one of petrochemical industries' most interesting challenges. Indeed, Air Products (sponsored by the US Department of Energy) is focusing on developing a "C₁" route to MTBE that involves three reaction steps: (1) synthesis of mixtures of methanol and isobutanol from synthesis gas, (2) dehydration of isobutanol to

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isobutene, and (3) reaction of isobutene with methanol from step (1), using known technology (OIL GAS -European Magazine 1 (1994), pp. 39-42). The selective dehydration of isobutanol to isobutene is a crucial step in this process, since the direct etherification of the intermediates isobutanol and methanol using conventional catalysts leads to methyl isobutyl ether, a lower octane isomer of MTBE.

Accordingly, the present invention also provides a process for preparing MTBE from methanol and isobutanol, comprising the dehydration of the isobutanol in the presence of a dehydration catalyst into isobutene, followed by the etherification of the isobutene with the methanol, wherein the dehydration catalyst is niobic acid and/or tantalic acid.

The first step of the C₁ route to MTBE comprises the conversion of the synthesis gas into methanol and isobutanol (e.g., using a caesium-promoted Cu/ZnO/Al₂O₃ methanol synthesis catalyst as described in the OIL GAS reference, one of the catalysts described in Uhlmann, 5th ed., A16, pp. 469-471 or according to the experiments reported by Klier and co-workers, e.g., J.G. Nunan, K. Klier and R.G. Herman, J. Catal., 139, (1993), 406-420).

The (indirect) etherification of isobutene and methanol is ordinarily performed in the presence of an acidic catalyst. Typically, the catalyst is a sulphonic acid substituted ion exchange resin or an acidic natural or synthetic silicate (e.g., amorphous silica-alumina or acid zeolites). Preferably, the catalyst is an ion exchange resin, e.g., produced by polymerization of aromatic vinyl compounds to which catalytically active functional groups are covalently bonded. Suitable sulphonic acid substituted ion exchange resins and their proper use are disclosed in SRI Report PEP No. 158A, in European

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patent application No. 102,840 and in International application No. 90/08758. A very suitable catalyst is a sulphonic acid substituted ion exchange resin having at least 1.2, more preferably about 1.2 to 1.8 sulphonic acid groups for each aromatic ring system. Typical examples of very suitable catalysts are sulphonic acid substituted divinylbenzene-styrene resins sold under the trademarks "DUOLITE" C20, "DUOLITE" C26, "AMBERLYST" 15, "AMBERLITE" IR-120, "AMBERLITE" 200 and "DOWEX" 50.

The source of raw material for the synthesis gas may be coal, coke, natural gas, associated gas or (fractions of) petroleum. The raw material may be converted into synthesis gas by steam reforming and/or by partial oxidation (e.g., as described in Uhlmann, 5th ed., A16, pp. 472-473).

The invention will be illustrated by the following examples.

Example 1

Niobic acid is pre-calcined at 300 °C for 2 hours. Isobutanol ("IBA") was dehydrated in a reactor operating at an isobutanol partial pressure of 1.2 bar g and a WHSV of 4,5 kg/kg_{cat}·hr. The yield of isobutene ("i-C₄" in %mol/mol IBA) was monitored as a function of the temperature as well as of residence time. It was compared at alike pressures, temperatures and conversions (the latter by varying the residence time) with that using either a commercial gamma-Al₂O₃ (ex. Engelhard) or SiO₂·Al₂O₃ ("ASA-13", i.e., amorphous alumina-silica containing 13% alumina, ex. Grace-Davison) as dehydration catalyst. Note that at these reaction conditions, the maximum yield attainable is about 75 % mol/mol.

The activity of the SiO₂·Al₂O₃, the gamma-Al₂O₃, and the niobic acid for the conversion of isobutanol is shown in Fig. 1. The activity follows the order SiO₂·Al₂O₃ > niobic acid > gamma-Al₂O₃. From Fig. 2 it is clear that

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-within the margins of experimental error- the overall selectivity towards isobutene follows the order niobic acid $\approx$ gamma- Al_2O_3 > $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$. By-products of the dehydration comprise the isomers of isobutene; 1-butene, cis-2-butene and trans-2-butene, as well as some oligomeric hydrocarbons.

C L A I M S

1. A process for dehydrating primary alcohols into alpha-unsaturated hydrocarbons in the presence of a dehydration catalyst, wherein the dehydration catalyst is niobic acid and/or tantalic acid.
- 5 2. A process as claimed in claim 1, wherein the dehydration catalyst is niobic acid.
3. A process as claimed in claim 2, wherein the dehydration catalyst is niobic acid, pre-treated at a temperature in the range of 100 to 400 °C.
- 10 4. A process as claimed in any one of claims 1 to 3, wherein the primary alcohol has at least 3 carbon atoms.
5. A process as claimed in claim 4, wherein the primary alcohol has less than 20 carbon atoms.
- 15 6. A process as claimed in claim 4, wherein the primary alcohol is selected from 1-propanol, 1-butanol, 2-methyl-1-propanol (isobutanol), 2-methyl-1-butanol.
7. A process as claimed in claim 4, wherein the primary alcohol is isobutanol.
- 20 8. A process as claimed in any one of claims 1 to 7, wherein the dehydration catalyst is packed into a reactor to prepare a fixed catalyst bed, is then activated at 100 to 400 °C, and wherein the reactor is set to 150 to 350 °C, preferably 250 to 300 °C.
- 25 9. A process as claimed in claim 8, wherein the primary alcohol is fed to the catalyst bed at a weight hourly space velocity (WHSV) of 1 to 20 kg/kg_{cat}·hr, preferably 3 to 10 kg/kg_{cat}·hr.
- 30 10. A process as claimed in claim 8 or 9, wherein the reaction pressure is between 0 and 20 bar g, preferably in the range of 1 to 6 bar g.



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- 5 11. A process for preparing methyl tert-butyl ether from methanol and isobutanol, comprising the dehydration of the isobutanol in the presence of a dehydration catalyst into isobutene, followed by the etherification of the isobutene with the methanol, wherein the dehydration catalyst is niobic acid and/or tantalic acid.

