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Catalytic Performance of Nanoscopic, Aluminium Trifluoride-Based Catalysts in the Synthesis of (all-*rac*)-α-Tocopherol

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Abstract: A novel nanoscopic, partly hydroxylated aluminium fluoride was prepared in a sol-gel fluorination synthesis and characterised by IR probe molecules. It was shown that this material has, in contrast to high surface area aluminium fluoride (HS-AlF_3) which is one of the strongest Lewis acids, a low amount of strong Lewis acid sites combined with weak and medium strength Brønsted sites. Both materials were tested in the synthesis of (all-*rac*)-α-tocopherol through the condensation of 2,3,6-trimethylhydroquinone (TMHQ) with isophytol (IP). The activity data indicate the partly hydroxylated aluminium fluoride to be a very efficient and highly selective catalyst for (all-*rac*)-α-tocopherol (>99.9%, for an IP conversion of 100%) whereas high surface area aluminium fluoride is a poor catalyst for this reaction.

Keywords: Brønsted acidity; heterogeneous catalysis; Lewis acidity; nanoscopic aluminium fluoride; vitamins

The industrial-scale synthesis of (all-*rac*)-α-tocopherol through the condensation of 2,3,6-trimethylhydroquinone (TMHQ) with isophytol (IP) comes up against corrosion caused by acidic media, contamination of the waste-water with acids, and the difficult purification of the main product.[1] For example, the formation of regioisomeric benzofuran derivatives as by-products, which are very difficult to separate from the main product, has been frequently reported.[2] Then, IP easily dehydrates in the presence of acids[3], forming phytadienes. Last but not least, it is known that traces of oxygen in the reaction system can lead to the formation of quinone compounds.[4] Therefore data concerning the use of active and selective heterogeneous[5] or homogeneous (e.g., rare earth metal triflates) catalysts – in biphasic green type systems[2] have been published. These new catalysts have the advantage of simple separation from the reaction mass, the absence of wash-water containing the dead catalyst and a high purity of (all-*rac*)-α-tocopherol. On the other hand, it was recently shown that the unwanted benzofuran regioisomers can be successfully avoided either by using tailored catalysts in which the active site units are bonded to bulkier polymeric anions[5e] or by using catalysts in which one of the functions is to modulate the phytyl carbocation equilibrium.[5c]

However, in many cases the high purity of the main product is not only due to the merits of the catalyst itself but also of the experimental approach, which unfortunately sometimes becomes complicated, and therefore less attractive for practical applications.[2,6]

The development of a more effective and practical catalytic system for an industrial process, that is able to fulfil all the features needed to avoid the formation of the by-products but that does not affect the catalyst performances, is still much sought after. In this respect we recently discovered the unexpected catalytic perfomances of nanoscopic hydroxylated aluminium fluoride prepared by a novel sol-gel fluorination synthesis.[7] Here we report on this new catalyst, its catalytic performances in the synthesis of (all-*rac*)-α-tocopherol, and the comparison to pure but highly Lewis acidic aluminium fluoride.

Applying the non-aqueous sol-gel route for inorganic fluorides results in the formation of very strong Lewis acid sites on high surface area aluminium fluoride (HS-AlF_3), comparable to those of SbF_5.[8] The HS-AlF_3 synthesis consists of two consecutive steps: i) the sol-gel reaction of aluminium isopropoxide and non-aqueous HF in dry isopropanol, and ii) the post-fluorination of the resulting xerogel with $CHClF_2$ or HF.[9] By adding a stoichiometric amount of HF in the form of its aqueous solution not only Lewis but also Brønsted acid sites can be introduced in the solid cat-

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alyst because of partial hydrolysis of the M–OR bond resulting in M–OH bond formation [Eq. (1)]. The reaction of the metal alkoxides with HF results in an M–F bond formation (fluorolysis) and consequently generates Lewis acidity (under coordinated M^{n+} sites). Schematically, the particular synthesis of the partly hydroxylated aluminium fluoride using this approach can be depicted as in Eq. (1).

$$Al(O\text{-}i\text{-}Pr)_3 + 3\text{–}x\ HF + x\ H_2O \longrightarrow AlF_{3-x}(OH)x + 3\ i\text{-}PrOH \quad (1)$$

$x << 3$

By using different molar ratios of HF to H_2O during the sol-gel synthesis different partly hydroxylated aluminium fluorides were obtained and tested in the synthesis of (all-*rac*)-α-tocopherol. Noteworthy results are shown in Table 1.

As Table 1 shows, all partly hydroxylated aluminium fluorides samples are very active catalysts, the conversion of IP being 100% in 1 h of reaction. At the same time the distribution of the reaction products is different as a function of the aqueous HF solution concentration used during the catalyst preparation or, in other words – as a function of the Lewis/Brønsted acid site ratio. Therefore, for a ratio of THMQ/IP = 1/1 the yield to tocopherol decreases in the order: AlF_3-70 > AlF_3-60 > AlF_3-50 > AlF_3-40 > > > HS-AlF_3 (Y = 0%). Accordingly with these results, it seems that the synthesis needs a certain Lewis/Brønsted acid site distribution, with certain strengths. However, in the case of the AlF_3-40 sample (Table 1, entry 8), the number of the Brønsted acid sites is too high and responsible for the decreased selectivity to tocopherol. The main by-product of the reaction is phytadiene and, when using an active catalyst like AlF_3-40, formation of considerable amounts of this by-product is favoured.

Table 1. The influence of the different aluminium fluorides samples on the yield to (all-*rac*)-α-tocopherol.[a]

Catalyst	Al:HF:H_2O molar ratio	TMHQ/IP molar ratio	Yield to tocopherol [%]
HS-AlF_3[b]	1:3:0	1/1	0
AlF_3-70	1:3:1.3	1/1	90.1
AlF_3-70	1:3:1.3	2/1	94.3
AlF_3-60	1:3:2	1/1	89.3
AlF_3-60	1:3:2	2/1	91.7
AlF_3-50	1:3:3.6	1/1	84.7
AlF_3-50	1:3:3.6	2/1	**> 99.9**
AlF_3-40	1:3:5	1/1	71.4
AlF_3-40	1:3:5	2/1	93.5

[a] *Reaction conditions:* 152 mg or 304 mg TMHQ + 0.4 mL IP (1/1 or 2/1 molar ratio), 6 mL solvent [propylene carbonate/heptane = 50/50 (v/v)], 50 mg of catalyst, 100 °C, reaction time = 1 h, C = 100%.

[b] C = 70%.

For each catalyst, increasing the TMHQ/IP molar ratio from 1/1 to 2/1 leads to a higher yield to tocopherol by decreasing the formed by-product amounts. This effect was accompanied by a shift of the maximum yield from the AlF_3-70 sample (in the case of TMHQ/IP = 1/1) to the AlF_3-50 sample. Therefore, it is possible that the excess of TMHQ not only blocks the dehydration of IP to phytadienes but also regulates the Lewis/Brønsted acid sites ratio on the catalysts surface, by a competitive chemisorption of its Brønsted sites.

Since the best catalytic results in the (all-*rac*)-α-tocopherol synthesis were obtained for the sample prepared with 50% wt aqueous HF (AlF_3-50), this sample was further characterised and compared with the pure Lewis HS-AlF_3 sample.

HS-AlF_3 and AlF_3-50 are X-ray amorphous and exhibit high surface areas connected with mesoporous pores: 190 $m^2 g$ (D_p = 65 Å) for AlF_3-50 and 250 $m^2 g$ (D_p = 68 Å) for HS-AlF_3. Nevertheless, the acidic properties, for example, the nature, the strengths and the densities of the acidic sites, are quite different depending on the preparation method.

Recently, using CO-IR spectroscopy, we showed that pure Lewis acid HS-AlF_3 displays a large number of very strong Lewis acidic centres and just a few weak Lewis centres at the surface.[8b] Furthermore, water exposed to this material at room temperature has been found to adsorp non-dissociatively at the surface forming layers with strong hydrogen bonds to other water molecules. In this way the very strong Lewis acid sites become blocked by water, and some Brønsted acid sites with moderate strength are generated. The CO experiments clearly show that these OH groups are situated at the surface of the solid and do not destroy the bulk structure at ambient temperature. However, heating of HS-AlF_3 up to 573 K under a certain partial pressure of water results in partial hydrolysis.

CO-IR spectra of the novel AlF_3-50 sample (Figure 1) show two bands: an intensive band at 2172 cm^{-1} (assigned to Brønsted acid sites) and a band at 2207 cm^{-1} (assigned to the Lewis acid sites) that only developed as a small feature. Therefore, the Lewis/Brønsted ratio is quite small. On the other hand, the lutidine-IR spectra of the AlF_3-50 (Figure 2) display three bands at 1581 cm^{-1} (physisorbed species), 1595 cm^{-1} (assigned to the ν_{8a} mode) and 1604 cm^{-1} (assigned to the ν_{8b} mode), corresponding to weakly coordinated species. In addition, the spectra display another two bands at 1655 cm^{-1} and 1631 cm^{-1} (assigned to the ν_{8a} mode and ν_{8b} mode, respectively) corresponding to protonated species, which are only

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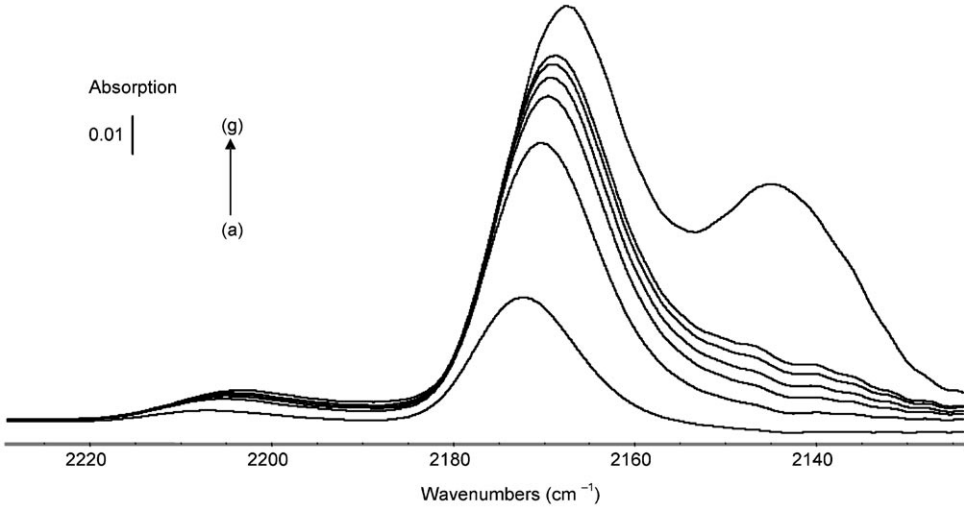


Figure 1. IR spectra of AlF_3-50 recorded at 100 K after the adsorption of increasing CO doses (a→g).

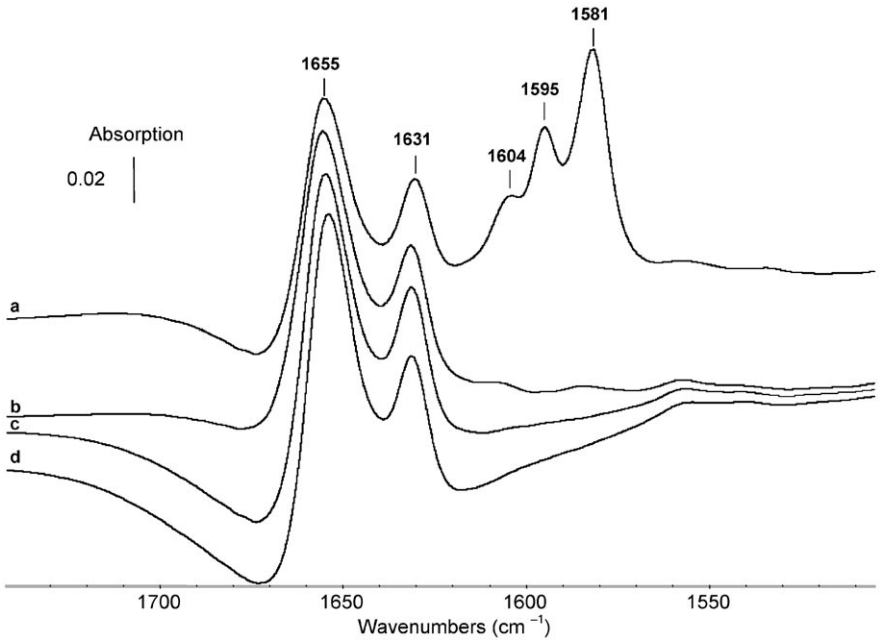
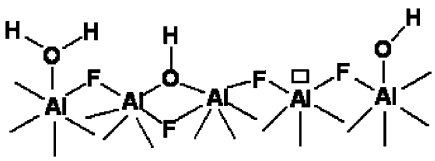


Figure 2. IR difference spectra after adsorbtion of lutidine on AlF_3-50 sample which was before activated at 373 K (**a**) equilibrium pressure, and evacuated (**b**) at room temperature, (c) 323 K and (**d**) 373 K.

observed for medium and/or strong Brønsted acid sites.[10]

The strength of these sites also becomes evident during evacuation of the sample at different temperatures and the persistency of the protonated species in comparison with the coordinated species (Figure 2). Although it cannot be clearly proven, these sites are probably due to surface OH groups which are formed during the synthesis. It is worth mentioning that such surface hydroxy groups are observed and are well established for aluminas.[11–13]

Based on the CO- and lutidine-IR spectroscopic results, the acidic species on the surface of the AlF_3-50 sample can be represented schematically and in a very simplified manner as shown in Scheme 1.



Scheme 1. Here, the symbol (□) indicates a vacancy (Lewis) site – Al undercoordinated and accessible site for a nucleophilic reactant.

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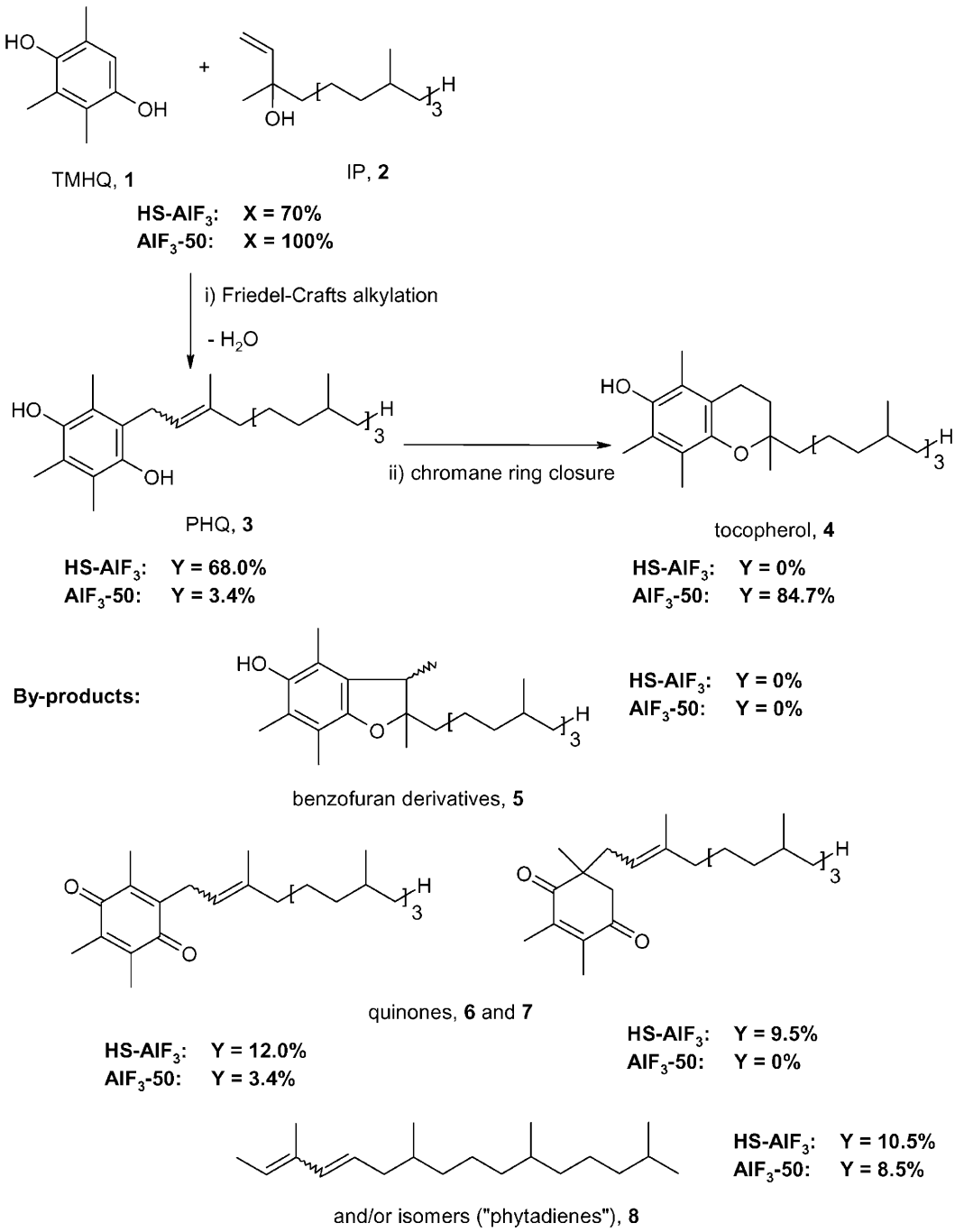

Scheme 2. The synthesis product distribution by the condensation of TMHQ **1** and IP **2** with HS-AlF_3 and AlF_3-50 (X = conversion, Y = yield). *Reaction conditions:* 152 mg TMHQ + 0.4 mL IP (1/1 molar ratio), 6 mL solvent [propylene carbonate/heptane = 50/50 (v/v)], 100 °C, reaction time = 1 h.

As we have shown, when employing HS-AlF_3 and AlF_3-50 as catalysts in the synthesis of (all-*rac*)-α-tocopherol through the condensation of 2,3,6-trimethylhydroquinone (TMHQ, **1**) with isophytol (IP, **2**), the conversion of IP and the product distribution are completely different depending on the nature of the catalyst (Scheme 2). Therefore, in comparison with the very active AlF_3-50 sample (conversion of IP was 100% in less than 1 h), the activity of the pure but strong Lewis acidic HS-AlF_3 sample was rather low (70% conversion of IP after 1 h). Moreover, while the AlF_3-50 sample was very selective to (all-*rac*)-α-tocopherol, in the presence of the HS-AlF_3 sample the synthesis stops at the phytylhydroquinone intermediate (PHQ, **3**). On the other hand, even though only in small amounts, by-products were also identified in the

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reaction product. Some of the observed intermediates and by-products, which are also known from literature,[14] are presented in Scheme 2. To the best of our knowledge, the quinone **7** was not claimed until now in the literature for this synthesis. To elucidate its structure, after the product separation, the compound was characterised by 2D-NMR spectroscopy (^{1}H-^{1}H COSY NMR and ^{1}H-^{13}C HSQC NMR techniques). Both spectra are depicted in Figure 3.

The fact that the AlF_3-50 sample catalyses the conversion of IP faster than HS-AlF_3 is a clear indication that the pure strong Lewis acid sites are not essential in the first step. It is well known that, in Friedel–Crafts alkylations using alcohols as alkylating reagent, pure Lewis acids show only low or no activity if they are not activated by the inadvertent presence or addition of small concentrations of co-catalysts or promoters, such as water. These co-catalysts interact with the Lewis acids to generate Brønsted sites.[15] Focusing on the HS-AlF_3 sample, if exposed to moisture, this material was found to adsorb water non-dissociatively at room temperature and to form some Brønsted sites with moderate strength.[8b] The material was handled in an air atmosphere for a short time, therefore, it is very probable that some water had already been adsorbed from the atmosphere and generated some Brønsted acidity. Additionally, each molecule of phytylhydroquinone (PHQ, **3**) formed generates one molecule of water, and this may also be adsorbed non-dissociatively on the Lewis sites provoking supplementary Brønsted acid sites. Therefore moisture from air and the generated water may act as a co-catalyst in the first step of the condensation process.

In contrast, AlF_3-50 already contains surface OH groups representing medium Brønsted acid sites which obviously catalyse the first step of the synthesis of (all-*rac*)-α-tocopherol.

In the case of HS-AlF_3, the reaction stops at a low degree of conversion but provides a high selectivity to PHQ, **3**, the Lewis and the created Brønsted acid sites of this material are unable to transform PHQ into (all-*rac*)-α-tocopherol. Furthermore, the very strong acidic centres of HS-AlF_3 obviously adsorb some atmospheric oxygen on the surface if the material is handled in air resulting in the formation of quinones **6** and **7**.

Surprisingly, irrespective of the nature of the catalyst, the synthesis took place with a total regioselectivity as long as no benzofuran derivatives, **5** were detected in the reaction products. Generally speaking, the regioselectivity of a catalytic reaction depends on the structure of the molecule, on the structure of the catalyst, and on the reaction conditions, these factors being highly interdependent. In other words, a comprehensive interpretation of regioselectivity requires that the substrate-catalyst couple should be considered as a supramolecular system. Particularly in the condensation of TMHQ with IP, the availability and proportion of the different carbocations, for example, *i*-phytil, *n*-phytil, formed by the interaction of IP with the catalyst, seems to be the key step for the high regioselectivity to the desired (all-*rac*)-α-tocopherol.

The AlF_3-50 sample is highly selective towards the formation of (all-*rac*)-α-tocopherol which is a result of the medium Brønsted acids sites formed already during the synthesis of the catalyst. Moreover, the catalytic leaching tests did not show any solubility, meaning it behaves as a real heterogeneous catalyst under these reaction conditions. Drying the used catalysts in N_2 flow, at 100 °C for 12 h made possible the full restoration of its initial activity and selectivity.

As we showed, further optimisation of the reaction conditions in presence of the AlF_3-50 sample improved the yield to (all-*rac*)-α-tocopherol. Therefore, with an excess of TMHQ (TMHQ/IP = 2/1, molar ratio) it was possible to obtain (all-*rac*)-α-tocopherol with $>99.9\%$ yield after only 1 h of reaction (Table 1). In order to check the reproducibility of these results on a larger scale, the synthesis was performed in a glass vial with a capacity of 500 mL instead of 8 mL and using 62,5 mmol of TMHQ and IP. This experiment yielded almost identical results.

In summary, we can conclude that the novel fluorination sol-gel method has been successfully applied to create reproducible a 'bi-acidic' Lewis/Brønsted nanoscopic aluminium fluoride, by altering the structure of conventional pure Lewis acid aluminium fluoride (HS-AlF_3) to a partly hydroxylated one. The comparison of both materials in the condensation of 2,3,6-trimethylhydroquinone (TMHQ) with isophytol (IP) showed crucial differences in the reaction mixture which are the result of the different acid sites (Lewis *vs.* Brønsted) of these materials. Although the surface structure/morphology of these catalytically active systems have not been resolved with IR experiments so far, it can be stated that the difference in the catalytic properties can either be due to the different origin of Brønsted sites (coordinated water *vs.* Al–OH species) or to the strength of the Brønsted sites present on the samples. In order to be more certain about these points, a deeper investigation of both the solids and the reaction itself are required.

At this stage, it is evident that the high activity in combination with an exciting high selectivity is obviously the synergistic effect of the presence of both Brønsted and Lewis sites. However, there are several points which still need a more comprehensive investigation. Thus, it might be speculated what additional impact orginate from these surface Brønsted and Lewis sites: i) phytil carbocations may be formed at Brønsted sites in the first reaction step, (ii) reaction water may be boundd at Lewis sites, thus acting as dehydrating sites, and (iii) not only the presence of surface Brønsted sites of optimum medium strength

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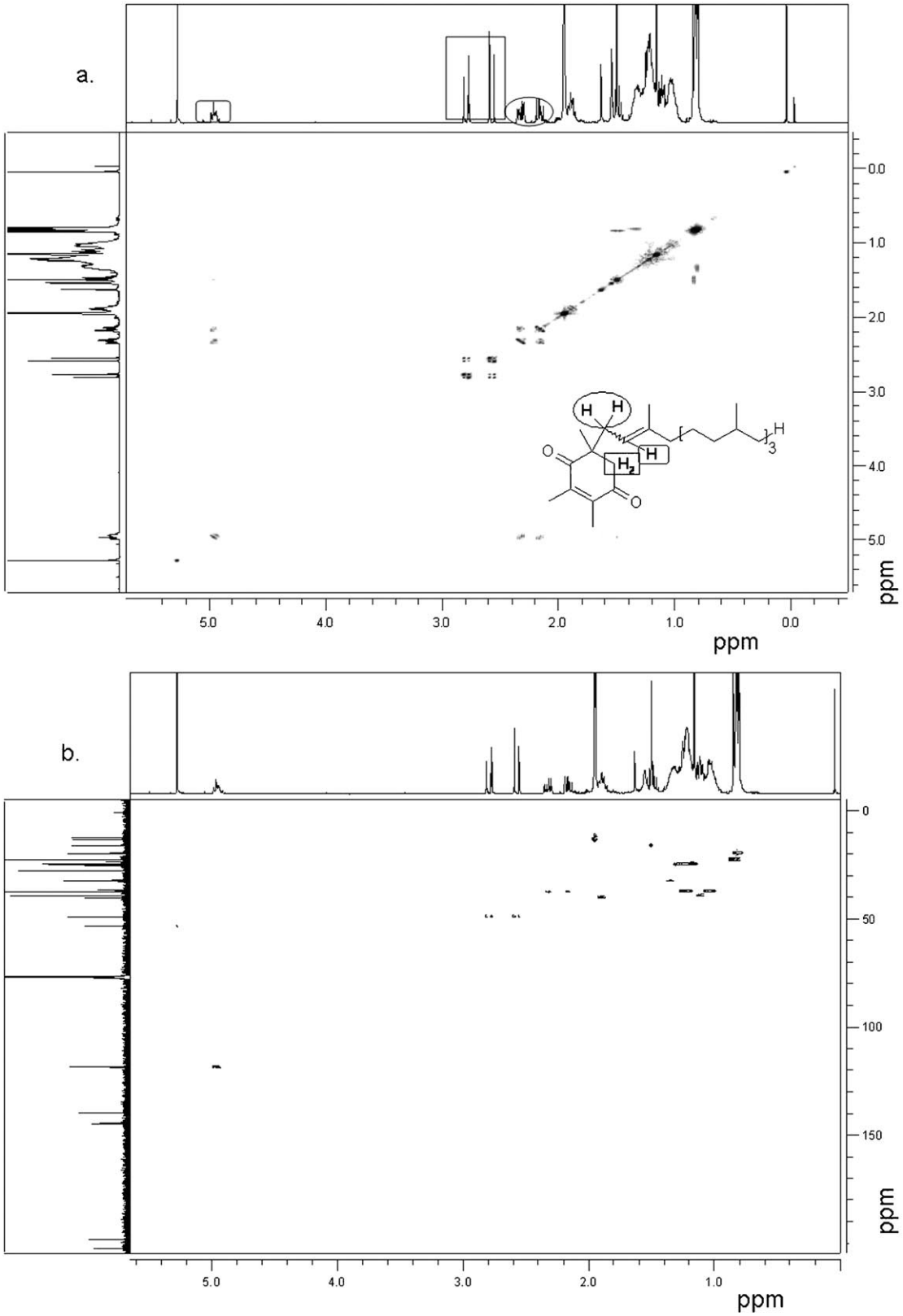

Figure 3. The 2D-NMR spectra (**a.** ^{1}H-^{1}H COSY NMR; **b.** ^{1}H-^{13}C HSQC NMR) for quinone **7** [eluent: CH_2Cl_2 ^{1}H NMR: $\delta =$ 5.27 ppm (s, 2H)].

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might be beneficial but also a certain topological arrangement at these catalysts may provide a high selectivity towards formation of the desired phytyl carbocations resulting in high regioselectivity to the desired (all-*rac*)-α-tocopherol. All these are topics of ongoing investigations.

In any case, the catalytic efficiency combined with practical advantages (e.g., no external inert atmosphere and no azeotropic removal of water) of the catalytic experimental set-up make this catalyst system appealing even in the commercial stage.

Experimental Section

Catalyst Preparation

Nanoscopic partly hydroxylated aluminium fluoride was prepared from aluminium isopropoxide using a one-pot sol-gel fluorination method as follows: 9.73 g (48 mmol) of commercially available aluminium isopropoxide (Aldrich, 98+ %) were dissolved in 300 mL isopropyl alcohol and reacted with a stoichiometric amount of approximately 40%, 50%, 60% or 70% hydrofluoric acid and the products are named in Table 1 as AlF_3-40, AlF_3-50, AlF_3-60 and AlF_3-70. After aging for 12 h, the resulting gel was dried under vacuum at room temperature. The formed solid product was then dried further under vacuum at 70 °C, for 5 h and used as obtained in this way.

Catalyst Characterisation

The XRD pattern was recorded with an XRD-7 Seiffert-FPM diffractometer equipped with a Cu-Kα radiation source. Textural properties were determined using N_2 at 77 K for adsorption by means of a Micromeritics ASAP 2020 instrument. IR spectra were recorded on a Nicolet Magna 550 spectrometer equipped with a liquid nitrogen cooled MCT detector in transmission mode and purged by a dry nitrogen flow. The resolution was 4 cm^{-1} and 128 scans were co-added for each spectrum. The cell for IR analysis consisted of vitreous silica and was equipped with CaF_2 windows. The cell was connected to a vacuum line and a glass injection loop with a known volume (2.15 cm^3). CO (> 99.997% pure; supplied by Air Liquide, France) was provided from a gas balloon, dried with liquid N_2, and dosed stepwise on the sample. The detailed procedures of NH3-TPD are given elsewere.[7]

Synthesis of (all-*rac*)-α-Tocopherol

In a typical procedure, 152 mg (1 mmol) TMHQ, 304 mg (2 mmol) TMHQ or 9.5 g (62.5 mmol) TMHQ was dissolved in 6 mL or 375 mL of solvent [heptane:propylene carbonate (50:50)] in a glass vial (standard capacity of 8 mL or 500 mL) equipped with a magnetic stirrer. To this mixture 0.4 mL (1 mmol) or 25 mL (62.5 mmol) of IP and 50 mg (20.1×10^{17} acid centres/m^2 – AlF_3-H; 18.4×10^{17} acid centres/m^2 – HS- AlF_3 calculated from NH_3-TPD) or 3.1 g of AlF_3-H of catalyst were added. After this, the vial was closed, immersed in an oil bath with a temperature of 100 °C, and the charged mixture was stirred (1250 rpm) for 30–1200 min. After the reaction, the catalyst was separated from the two-phase solvent mixture, the heptane phase (containing the tocopherol) was separated from the propylene carbonate phase and the solvent was removed under vacuum to give a crude product.

The crude product was analysed by HPLC (column – EC 125/4.6 Nucleosil 120–5 C18; eluent: acetonitrile; flow rate: 0.8 mL min^{-1}; wavelength: 280 nm; volume of sample: 15 μL) chromatography and ^1H, ^{13}C NMR (Bruker AV 400 spectrometer, in $CDCl_3$ solvent and Me_4Si as internal standard) spectroscopy. (all-*rac*)-α-Tocopherol: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 12 H, CH_3), 1.0–1.9 (m, 26 H, CH_3, CH_2, CH), 2.10 and 2.17 (both s, 9 H, CH_3-Ar), 2.60 (t, 2 H, C^4H_2, J (H, H) = 6.7 Hz), 4.3 (s, 1 H, OH).

For compound characterisation the crude product was separated by column chromatography on silica gel (eluent: CH_2Cl_2) and analysed by ^1H-^1H COSY NMR and ^1H-^{13}C HSQC NMR (400 MHz, $CDCl_3$).

For comparison, similar tests were done in the presence of HS-AlF_3 prepared through a two-step fluorination method. The preparation of the sample is described in detail elsewhere.[7]

Trimethylhydroquinone (97 wt%) and isophytol (95 wt%) were purchased from Acros Organics. The other reagents (analytical grade) were obtained from Merck.

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