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An FT-IR study on Diels–Alder reactions catalysed by heteropoly acid containing sol–gel silica

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Abstract

Following the general trend of using heterogeneous catalysts whenever possible, the replacement of traditional homogeneous Lewis acid catalysts for the Diels–Alder reaction is currently considered in the literature. In this contribution, we report the successful application of sol–gel derived tungstophosphoric acid–silica composites as catalysts in the reaction of 1,3-cyclo-hexadiene and 2-propenal. The reaction was monitored by in situ FT-IR spectroscopy following the changes in the fine structure of the ν (C=O) band. The catalytic activity of the sol–gel immobilised heteropoly acids seems to be comparable with that of more conventional sol–gel silica–aluminas and their selectivity is even better because Broensted acid sites are destroyed upon calcination of the dry gel. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Diels–Alder type (4,2) cycloaddition reaction is a very useful tool of synthetic organic chemistry [1] because it makes it possible to prepare complex, optically active molecules in one simple reaction step, traditionally performed using homogeneous Lewis acid catalysts [2]. However, following the general trend of replacing homogeneous acidic catalysts by their heterogeneous counterparts, quite a number of studies are currently focused on Diels–Alder reactions catalysed by solid organic networks [3], clays [4], zeolites [5] and immobilised heteropoly acids [6].

We have recently performed a detailed investigation [7] on the acidity of silica-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbrev.: HPWA) composites prepared by the sol-gel method and are currently

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developing a membrane reactor for heterogeneous Diels–Alder reactions. In this paper, we present FT-IR spectroscopic evidence for the applicability of HPWA–SiO₂ catalysts in the reaction of 1,3-cyclohexadiene and 2-propenal with results comparable to those achieved on conventional silica–alumina systems. The key differences between our studies and a similar work by Meuzelaar et al. [6] are that: (i) our catalysts are prepared in one-step sol–gel incorporation instead of impregnation; (ii) we attempt to utilise FT-IR spectroscopy for reaction monitoring instead of capillary GC and (iii) we have followed the reaction in the adsorbed phase, not in the gas phase.

2. Experimental

Silica–HPWA composites containing 0, 5 and 20 wt% tungstophosphoric acid were prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) in

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aqueous HPWA solution. The resulting gels were dried, calcined at 873 K and labelled PW(0), PW(5) and PW(20), respectively. Details of the synthetic procedure are given elsewhere [7]. A silica–alumina composite with Si/Al ratio of 20 was prepared by the co-hydrolysis of TEOS and $Al(i-OC_3H_7)_3$ in the presence of a non-ionic detergent dried, calcined at 673 K and labelled Al(20).

Catalytic measurements were performed by placing a self-supported catalyst wafer (ca. 10 mg/cm²) into a heatable cell allowing in situ IR measurements. The catalyst was outgassed for 1 h at 673 K and then the 2:1 mixture of 1,3-cyclohexadiene and 2-propenal was introduced into the cell at room temperature. Both the gas phase and the catalyst surface was monitored at regular intervals by recording their IR spectrum (32 scans, 2 cm⁻¹ resolution) on a Mattson Genesis FT-IR 1 instrument.

3. Results and discussion

The acidity of the samples was determined in a previous study [7] using the pyridine adsorption technique. It is enough to note here that sample PW(0) has a practically neutral surface, samples PW(5) and PW(20) possess considerable Lewis but no Broensted acidity and sample Al(20) has both Lewis and Broensted acidic centres in commensurable amounts. Note that the PW composites were deliberately deprived of their Broensted acidity by using a high calcination temperature. In the literature, it is accepted [8] that at the applied 873 K temperature phosphotungstenic acid suffers partial decomposition and therefore, the active catalytic centres are likely to be various oxide species and not Keggin-type acid molecules.

Examination of the gas phase spectra revealed no changes in either series, as only the additive spectrum of 1,3-cyclohexadiene and 2-propenal was visible. This phenomenon is most likely caused by the strong adsorption of both the reactants and the products on the catalyst surface. Although these species are probably removable by elevating the temperature of the cell, such experiments were not performed to avoid the oligomerisation of 2-propenal. For this reason, only adsorbed phase spectra will be discussed further herein. All presented spectra were derived by subtracting the spectrum of the clean, activated catalyst wafer from the actual measurement.

In order to be able to use vibrational spectroscopy for monitoring catalytic reactions, one first has to find molecular parts that make the spectra of the reactants and products different from each other. It is visible in Scheme 1 (Diels–Alder type reaction between 1,3-cyclohexadiene and 2propenal. I: 1,3-cyclohexadiene, II: 2-propenal, III.a: *endo* bicyclo(2.2.2)-5-octene-2-carboxyaldehide, III.b: *exo* bicyclo(2.2.2)-5-octene-2-carboxyaldehide) that in our Diels–Alder reaction this is no easy task, as the reactants and the products possess very similar bonds and groups. Our experimental conditions and instrumentation are clearly inadequate to distinguish between *endo* and *exo* products, therefore no attempt shall be made to do so.

The key difference between reactants and products is that the carbonyl group is conjugated with the vinyl CH₂=CH- in 2-propenal, and this conjugation no longer exists in the product molecules. On this basis, we can expect a 20–30 cm⁻¹ increase in the frequency of ν (C=O) as the reaction propagates. It should be noted that the conjugation of the C=C double bonds in 1,3-cyclohexadiene also disappears in the product. However, the frequency shifts of the ν (C=C) and ν (H-C=) bands corresponding to this structural change are smaller and, especially in the adsorbed state, hard to identify, therefore in this paper the shift of the ν (C=O) band shall be used as a measure of the propagation of the reaction.

To make sure that this shift really measures a bimolecular catalytic reaction, let us first examine Parts I and II of Fig. 1 describing two critical blank tests. It is easily noticeable that without a reaction partner 2propenal is not transformed even on an acidic surface and that even if both partners are present they are not able to react on a neutral surface.



Scheme 1.



Fig. 1. Time dependence of the fine structure of the ν (C=O) band. Part I: 2-propenal adsorbed on Al(20), Part II: reaction mixture adsorbed on non-acidic PW(0), Part III: 1,3-cyclohexadiene added to 2-pronenal preadsorbed on Al(20), Part IV: 2-propenal added to 1,3 cyclohexadiene preadsorbed on Al(20), Part V: reaction taking place on PW(5), Part VI: reaction taking place on PW(20). On all six parts, "a", "b" and "c" denote the spectrum after 2, 10 and 40 min, respectively. On Part III and Part IV "p" denotes the spectrum of the preadsorbed species.

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In Parts III and IV of Fig. 1, we check if the spectral changes are really due to the reaction between our chosen reactants and not some surface decomposition product, for instance. Sample Al(20) is covered by 2propenal on Part III and by 1,3-cyclohexadiene on Part IV, and the reaction partner is added to this preadsorbed system. The reaction can be analysed on the basis of Part III as follows. The very intense band at 1693 cm⁻¹ is instantaneously reduced to a small shoulder. This process is matched by the appearance of an intense band at 1715 cm^{-1} , and is followed by the slower development of the band at 1725 cm^{-1} . Our interpretation of this phenomenon is that the strongly adsorbed 2-propenal molecules react nearly instantaneously with 1,3-cyclohexadiene and because of this the original 1693 cm^{-1} band disappears and in the Diels-Alder reaction unconjugated C=O bonds absorbing at 1715 cm^{-1} are formed. Since the temperature is not high enough for desorption (see above), the active sites of the catalyst are gradually poisoned by the products and this reaction stops. The gradual increase of the 1725 cm^{-1} band is then explained by unwanted oligomerisation reactions taking place on the Broensted acid sites of the Al(20) catalyst. A very similar picture appears if we add 2-propenal to preadsorbed 1,3-cyclohexadiene as shown in Part IV of Fig. 1. On the basis of these findings, we may conclude that: (i) a bimolecular heterogeneous catalytic Diels-Alder reaction occurs on the acidic Al(20) surface and (ii) the reacting partners of this reaction are indeed 2-propenal and 1,3-cyclohexadiene, otherwise the "c" spectra in Parts III and IV should be different.

In Parts V and VI of Fig. 1 the propagation of the reaction over PW(5) and PW(20) catalysts is depicted, respectively. Since in these experiments the reaction mixture was let onto a clean, activated surface, the band corresponding to adsorbed 2-propenal appears at 1693 cm^{-1} . Once again we witness the quick formation of the 1715 cm^{-1} band indicating that the reaction is progressing. The Diels–Alder reaction seems to go faster on PW(20) than on PW(5) as

indicated by the larger unconjugated:conjugated ratio on spectrum "b" in Part VI. This finding agrees well with the larger number of Lewis acid sites in PW(20) as found by pyridine adsorption. The band at 1725 cm^{-1} corresponding to unwanted side reactions is a mere shoulder in both series, which can be explained by the absence of Broensted acid sites in the PW composites.

4. Conclusions

In this paper we suggested an identification scheme that can be used for the monitoring of Diels–Alder type reactions by FT-IR spectroscopy. Sol–gel derived silica–alumina and silica–heteropoly acid composites were both found to be active catalysts in the reaction of 2-propenal and 1,3-cyclohexadiene. Catalysts lacking Broensted acidity seem to be a more favourable choice for future experiments because no side reactions take place over them.

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