

Liquid phase aldol condensation of cyclopentanone with valeraldehyde catalysed by oxynitrides possessing tuneable acid–base properties

Moez Hasni^a, Gwenola Prado^a, Jean Rouchaud^a, Paul Grange^{a,1},
Michel Devillers^b, Stéphanie Delsarte^{a,*}

^a *Unité de Catalyse et Chimie des Matériaux Divisés, Université catholique de Louvain, Croixdu Sud 2/17, 1348 Louvain-la-Neuve, Belgium*

^b *Unité de Chimie des Matériaux Inorganiques et Organiques, Université Catholique, de Louvain, Place Louis Pasteur 1/3, 1348 Louvain-la-Neuve, Belgium*

Received 27 June 2005; received in revised form 16 November 2005; accepted 16 November 2005

Available online 28 December 2005

Abstract

The aldol condensation reaction between valeraldehyde and cyclopentanone was carried out in a batch reactor, at atmospheric pressure and 130 °C over “AlPON” and “ZrPON” catalysts. Those catalysts were obtained by heating AlPO_4 and $\text{Zr}_{0.9}\text{PO}_{4.3}$ phosphates in a flow of gaseous ammonia at 750 and 700 °C, respectively. The nitridation treatment allows to substitute framework oxygen atoms by nitrogen atoms, consequently reducing the number of solid acid sites and increasing the number of basic sites. Nitridation has a positive effect on valeraldehyde conversion which increases from 33 to 57% after 2 h of reaction for the “AlPO” system and from 80 to 94% after 2 h for the “ZrPO” system. The influence of the acid–base properties of catalysts for this particular reaction is discussed by measuring the activity and selectivity of basic (MgO), and amphoteric (Al_2O_3) catalysts. The zirconophosphate precursor “ZrPO” and its nitrated samples are the most active for the reaction.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Oxynitrides; Acid–base catalysis; Aldol condensation reaction

1. Introduction

Aldol condensation reactions are used in the synthesis of numerous large-volume chemicals such as mesityl oxide, diacetone alcohol, isophorone, and 2-ethylhexenal, which are frequently hydrogenated to yield valuable solvents and plasticizers. In addition, the aldol condensations are also used for the synthesis of fine chemicals such as fragrances, pharmaceuticals, and flavours (jasminaldehyde, pseudoionone, etc.) [1].

The present work deals with the aldol condensation of cyclopentanone (**1**) (Scheme 1) with valeraldehyde (**2**) to produce 2-pentylidene-cyclopentanone (**3**) which is a precursor of perfume ingredients. Compound (**3**) is used in the synthesis of methyl dihydrojasmonate (2% incorporated in “Eau Sauvage” (Dior, 1966)) [2] and 2-pentylcyclopentanone (used in

low-cost fragrances for use in laundry powders and household cleaners) [3].

The homogeneous aldol condensation reaction of valeraldehyde with cyclopentanone has already been studied by several authors, using either catalytic amounts of KOH [4–7], or neutral solubilized catalysts. For instance, the solvent-free condensation of cyclopentanone with valeraldehyde catalysed by zirconocene complexes cp_2ZrH_2 or $\text{cp}_2\text{Zr}(\text{O}-i\text{-Pr})_2$ in an autoclave at 130 °C under argon for 8 h gave (**3**) with a yield of 47% [8]. The same reaction run with $\text{Ti}(\text{O}-t\text{-Bu})_4$ as catalyst in toluene refluxed for 2 h gave (**3**) with a yield of 74% [9].

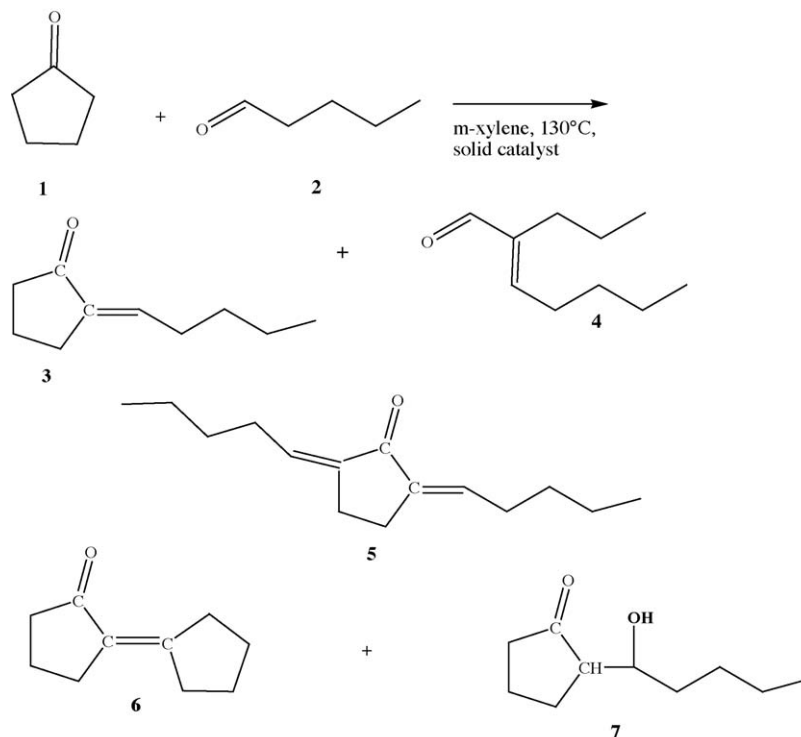
2-Pentylidene-cyclopentanone (**3**) was also synthesized in a two-step procedure by the successive transformation of cyclopentanone into an ene-amine, which thereafter was condensed with valeraldehyde. Refluxing cyclopentanone with morpholine in the presence of *p*-toluenesulfonic acid gave 1-morpholino-1-cyclopentene, which was refluxed with valeraldehyde; when heated in water the condensation product gave compound (**3**) [10].

Nowadays, because of growing environmental concerns, the substitution of homogeneous catalysts by heterogeneous cata-

* Corresponding author. Tel.: +32 10 47 36 50; fax: +32 10 47 36 49.

E-mail address: delsarte@cata.ucl.ac.be (S. Delsarte).

¹ Deceased on July 2003.



Scheme 1. Aldol condensation reaction between cyclopentanone and valeraldehyde.

lysts in industrial production processes is however highly desirable.

The replacement of liquid bases by solid heterogeneous base catalysts enables the easy separation and recycling of the catalyst from the reaction mixture. In this way the generation of noxious substances and wastes (which consist primarily of inorganic salts formed in the reaction or in subsequent neutralization steps) is avoided. Moreover, it is frequently possible to prepare solid base catalysts with a different nature of active sites (Brønsted, Lewis, chiral), with a wide range of basic strengths, or even acid–base bi-functional catalysts.

The substitution of oxygen by nitrogen in “AlPON”, “ZrPON” and “AlGaPON” oxynitrides during nitridation of metallophosphates leads to compounds with specific catalytic properties [11,12]. As their acidity decreases while their basicity increases with their nitrogen content, they are particularly interesting in the field of acid–base catalysis. Previous IR, microcalorimetry and chemisorption studies have highlighted the evolution of the number, nature and strength of the acid and basic sites with the nitrogen content, leading to the full mastering of the acid–base properties of phosphates through nitridation. We are now at the stage of exploring the possibility to use those new families of catalysts for the production of fine chemicals through aldol condensation reactions. For those reactions, the balance between acid and basic sites has a significant impact on selectivities.

The amorphous, mesoporous and high surface area solid AlPO (aluminium phosphate) and its oxynitride derivatives (AlPON) give – for the cross-condensation of benzaldehyde with heptanal to α -amylcinnamaldehyde (jasminaldehyde) – much higher rates and selectivities than conventional solid acid

amorphous or crystalline aluminosilicates, or base catalysts ($\text{MgO}, \text{Al}_2\text{O}_3$) [13]. AlGaPO (aluminium-gallium phosphate) and ZrPO (zirconium phosphate) and their oxynitride derivatives (AlGaPON and ZrPON) give for this condensation still higher rates and selectivities for the cross aldolization product [14]. At our knowledge, the catalysis of the liquid phase condensation of cyclopentanone with valeraldehyde by high surface area oxides or by ion exchangers has not been reported in the literature so far. In the present work, the catalysis of this condensation by AlPO and ZrPO, and by their oxynitrides has been studied, in comparison with the catalysis by solid acid (amorphous $\text{SiO}_2\text{--Al}_2\text{O}_3$), amphoteric (amorphous Al_2O_3) or base catalysts (crystalline MgO).

2. Experimental

2.1. Materials

The first step of the AlPON and ZrPON synthesis involves the preparation of reactive phosphate precursors. The sol–gel process developed by Kearby was used for the synthesis of AlPO_4 [15] and zirconophosphate precursor $\text{Zr}_{0.9}\text{PO}_{4.3}$ was obtained according to the citrate method [16]. Those soft chemistry routes allow obtaining highly divided oxides with specific surface areas of 297 and 226 m^2/g for AlPO_4 and $\text{Zr}_{0.9}\text{PO}_{4.3}$, respectively. The high specific surface area of the oxide is one of the most important criteria for further activation to high surface area oxynitrides. The second step of the preparation of the oxynitrides is the activation of the precursors under ammonia flow. During the nitridation process, nitrogen atoms progressively replace the oxygen atoms of the framework. Nitridation

Download English Version:

<https://daneshyari.com/en/article/69267>

Download Persian Version:

<https://daneshyari.com/article/69267>

[Daneshyari.com](https://daneshyari.com)