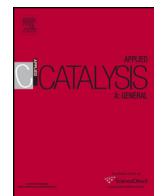




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Preparation of a raspberry ketone precursor in the presence of rare earth oxide catalysts

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This publication is devoted to the 75th birthday of Prof. Dr. Jacques Védrine, France in recognition of his tremendous work for the catalysis community.

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ABSTRACT

The raspberry precursor 4-(4-hydroxyphenyl)-but-3-ene-2-one which afterwards undergoes a catalytic hydrogenation to produce raspberry ketone was synthesized by aldol condensation of acetone and 4-hydroxybenzaldehyde over rare earth oxides as basic catalysts and supported rare earth oxides as acid–base bifunctional catalysts. Thereby, several rare earth metal oxides were tested in their neat form as well as supported on carriers with high surface areas such as alumina, titania, tetragonal zirconia and charcoal. The catalysts were characterized by XRD, BET, NH₃/CO₂-TPD and pyridine-FTIR. All experiments were carried out batch wise in 75 ml autoclaves adjusting molar ratios of acetone and 4-hydroxybenzaldehyde from 12:1 to 4:1, temperature range from 80 to 200 °C and autogeneous pressures from 1 to 25 bar. It could also be realized, that titania and alumina are no inert materials, but also highly active catalysts for this reaction. An experimental design program was used to optimize the reaction conditions as well as the conversion and selectivity. In addition the reaction was carried out in a fixed bed plug flow reactor to determine stability and robustness of the catalyst. The quality/contaminations of the starting material have a strong influence on the catalytic performance.

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1. Introduction

In normal day life, the sense of smell is considered to be less important than the sense of hearing or sight. Despite this fact, it has a major contribution to our perception and improves tremendously our living standard. Fragrances are part of the everyday life and find application in many consumer goods like household cleaners, perfumes, oils or even food [1]. To satisfy the growing demand for synthetic fragrances, key compounds like raspberry ketone are absolutely essential. In 1957, raspberry ketone was discovered by Schinz and Seidel [2,3] as primary aroma component of red raspberries as it is already indicated by the name of this compound. Raspberry ketone is a typical character impact compound with an extremely low odor threshold value. Therefore it is applied in perfumery, in cosmetics and as a food additive in products such as soft drinks and sweets to impart a fruity odor.

Since natural abundance of raspberry ketone is with 1–4 mg/kg raspberries very low, it has to be prepared synthetically [4,5]. The current production is carried out by a crossed aldol condensation of 4-hydroxybenzaldehyde (4-HBA) and acetone to form the α,β -saturated ketone, [4-(4-hydroxyphenyl)-but-3-ene-2-one] (4-HPB), which afterwards is catalytically hydrogenated to produce raspberry ketone as shown in Fig. 1. In laboratory scale, the first step is generally catalyzed by a homogeneous base such as sodium hydroxide [6], while in industrial scale, the first step is preferably enzymatically catalyzed at low temperatures and pressures, but reaction times of approximately 8 h are comparable long [7–9].

The aim of our work is to find a heterogeneously catalyzed alternative route for 4-(4-hydroxyphenyl)-but-3-ene-2-one. As known from preceding research [10,11] acid–base bifunctional rare earth metal oxides supported on carriers are suitable catalysts for transesterifications and aldol condensations, they have been tested for the reaction of 4-hydroxybenzaldehyde with acetone as illustrated in Fig. 1.

Therefore our research focused on several rare earth metal oxides in their neat form as well as supported on several materials with high surface areas such as alumina, partly tetragonal stabilized zirconia, titania and activated charcoal, because the pure

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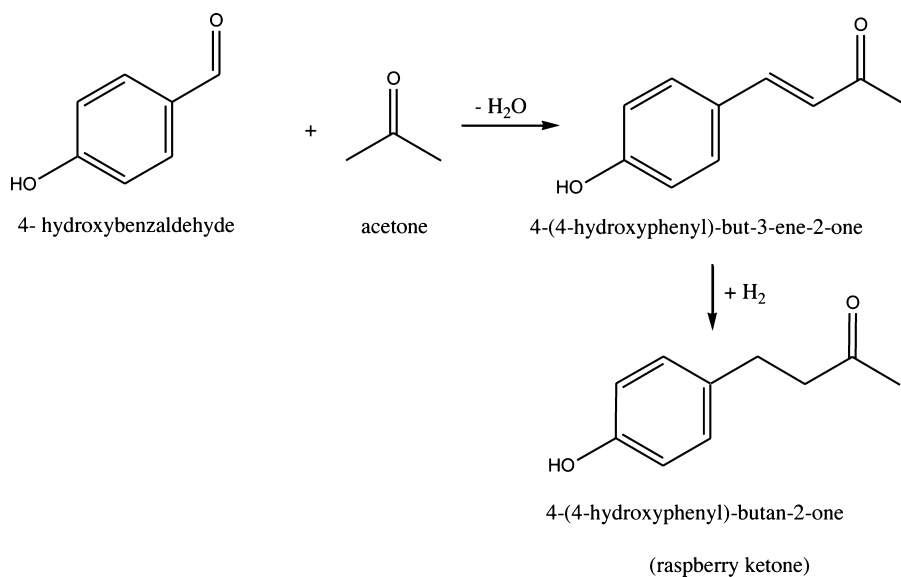


Fig. 1. Reaction scheme of the crossed aldol condensation of 4-hydroxybenzaldehyde and acetone to form the α,β -saturated ketone, [4-(4-hydroxyphenyl)-but-3-ene-2-one], followed by catalytic hydrogenation to raspberry.

rare earth oxides itself exhibit only low surface areas with almost no porosity. The experiments were carried out in autoclaves at a temperature range from 80 to 200 °C, autogeneous pressures from 1 to 25 bar and reaction times of 1–3 h using molar ratios of acetone and 4-hydroxybenzaldehyde from 12:1 to 4:1. In addition the reaction was carried out in a fixed bed plug flow reactor to get information about stability and robustness of the catalyst.

2. Experimental

2.1. Used chemicals

Acetone was used in reagent grade and 4-hydroxybenzaldehyde was obtained from Merck, Germany in p.s. grade 98% and Alfa Aesar. All rare earth oxides were purchased from ABCR, Germany in p.a. grade (99.9%). As catalyst supports activated charcoal was obtained from Fluka in analytical grade made out of wood, $\gamma\text{-Al}_2\text{O}_3$ and titania P25 were kindly provided by Evonik GmbH, Germany as well as $\text{Zr}(\text{OH})_4$ by Mel Chemicals, United Kingdom.

An experimental design program (Design Expert 5 from Stat-Ease) was used to optimize the reaction conditions as well as the conversion and selectivity.

2.2. Analytics

2.2.1. Gas chromatography

In order to identify and quantify the starting materials, products and side products as well as to calculate conversions and selectivities the sample mixtures were separated and analyzed by means of a HP 6890 Series Plus gas-phase chromatograph, a FS-SE 54; 60 m; CS 25288-6 column and a flame ionization detector (FID). Ethyl benzoate was added to the samples as internal standard to calculate the correction factors.

The calculation of conversion and selectivity occurs via the determination of the peak area in the GC diagram. First methyl benzoate was added as standard to the product mixture. In relation to that standard correction factors have been determined for the silylated and not silylated samples. The correction factors are 1.56 for acetone, 0.71 for the silylated 4-HBA and 1.42 for the non silylated 4-HBA, respectively, as well as 0.79 for the silylated 4-HPB and 1.42 for the non silylated 4-HPB, respectively. The correction

factor KF for the unknown compounds was adjusted at 1. The area of the 4-HBA peak was determined

$$KF_{4\text{-HBA}} \cdot A_{4\text{-HBA prior}} = KF_{\text{HBA}} \cdot A_{\text{HBA after}} + KF_{\text{HPB}} \cdot A_{\text{HPB}} \cdot \frac{M_{\text{HBA}}}{M_{\text{HPB}}} + KF_{\text{NP}} \cdot A_{\text{NP}} \quad (1)$$

where A , peak area; KF, correction factor; HBA, 4-hydroxybenzaldehyde; HPB, 4-(4-hydroxyphenyl)-but-3-ene-2-one; NP, by products.

The conversion is calculated

$$\text{Conversion} = 1 - \frac{A_{\text{HBA after}}}{A_{\text{HBA prior}}}$$

The selectivity is calculated out of the ratio of the peak areas of 4-HPB and the converted 4-HBA.

$$\text{Selectivity} = \frac{KF_{\text{HPB}} \cdot A_{\text{HPB}}}{KF_{\text{HBA}} \cdot A_{\text{HBA prior}} \cdot \text{Conversion}} \cdot \frac{M_{\text{HBA}}}{M_{\text{HPB}}}$$

2.2.2. XRD investigations

The X-ray powder diffraction patterns were recorded on a Siemens D-5000 of 217.5 mm goniometer radius. The anode consisted of copper with the characteristic X-rays $\text{Cu K}\alpha_1$ (154.0598 pm) as well as $\text{Cu K}\alpha_2$ (154.4426) and nickel was used as filter. Measurements were carried out in the 2θ range 3–90° using a 0.02° step size and a 1 s step time. The recorded X-ray patterns were assigned to the appropriate solids by comparison with the Joint Committee on Powder Diffraction Standards JCPDS-database.

2.2.3. BET measurements

The nitrogen adsorption isotherms were determined on a Micromeritics ASAP 2010 at 77 K. The BET surface area was calculated for the partial pressure range p/p_0 of 0.05–0.25, the micropores for 0.2–2 nm diameter and the mesopores for 2–100 nm diameter with the help of the BJH method.

2.2.4. NH_3 - and CO_2 -TPD measurements

The NH_3 - and CO_2 -TPD measurements have been carried out on a TPD 110 from Thermodefinition in order to determine the acid sites and basic sites, respectively, as well as the strengths of those sites.

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