

# Preparation of 2-phenylethanol by catalytic selective hydrogenation of styrene oxide using palladium catalysts

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## Abstract

We have studied the gas-phase hydrogenation of styrene oxide to obtain 2-phenylethanol (2-PEA) using palladium catalysts on supports such as activated carbon (AC),  $\gamma$ -alumina and magnesia. We performed several characterization techniques, such as powder XRD, TPD of H<sub>2</sub>, NH<sub>3</sub> and styrene oxide, TPR, N<sub>2</sub> physisorption and H<sub>2</sub> chemisorption, in order to correlate the chemical and textural properties with catalytic activity. The acid–base nature of the support played an important role in the selectivity to the products. An acid support, such as alumina or activated carbon, favoured the formation of phenyl acetaldehyde and 1-phenylethanol. On the other hand, when a basic support such as MgO was used, the main product was 2-PEA. Selectivity to 2-PEA was above 98% even at practically total conversion of styrene oxide.  
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## 1. Introduction

2-Phenylethanol (2-PEA), commonly known as phenethyl alcohol, is widely used to enhance the aroma of chemical perfumes, colognes, other perfumed articles and in the soap and detergent industry [1,2]. It is the main component of rose oils obtained from rose blossoms [3]. It is also used to prepare important chemical intermediates, such as phenyl acetaldehyde, phenylacetic acid and benzoic acid [2].

In practice, 2-PEA can be obtained by various chemical reactions. One example is Friedel-Crafts alkylation of benzene using ethylene oxide and molar quantities of aluminium chloride [1]. A major disadvantage of this process, however, is the fact that Friedel-Crafts catalysts are corrosive. This means that expensive corrosion resistance equipment is needed, causes environmental problems and makes it difficult to separate the catalyst from the product.

2-PEA can be obtained as a minor impurity in the production of styrene monomer and propylene oxide, but this

process is expensive because 2-PEA is at trace levels in the product mixture and separation costs are high. Conventionally, 2-phenylethanol is prepared by Grignard synthesis, starting from chlorobenzene, which is converted to phenylmagnesium chloride, which reacts with ethylene oxide to give phenylethoxy magnesium chloride. This is then decomposed with sulphuric acid to give 2-PEA. The drawbacks with this process are the use, in situ, of dangerous diethyl magnesium chloride and the poor quality of the 2-phenylethanol intended for use in perfumery [3].

On the other hand, the reductive cleavage of epoxides to alcohols is one of the most useful reactions in organic synthesis [4,5]. The alcohol can be obtained by the ring opening of the epoxide with a reducing agent such as hydride or alkaline metals [6–13]. In general, the formation of the more substituted alcohol is favoured. So, it is difficult to obtain the less substituted alcohol with high selectivity [14–16].

The catalytic hydrogenation of styrene oxide to alcohol using heterogeneous catalysts has been studied [14–26]. However, practically all the results have been achieved using batch reactors. It has also been observed that when alkali is used as a basic promoter, the selectivity to 2-PEA increases

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[14,15,22]. Here, the disadvantage in the liquid phase is the need to remove the suspension catalyst at the end of the reaction or to use readily flammable reagents [23]. Holderich et al. [23] and Buechle et al. [24] suggested performing this reaction in a flow reactor, the former using metal catalysts supported on zeolites and/or phosphates, and the latter using a monolithic metal supported catalyst.

In this paper, we have studied the preparation of 2-PEA by catalytic hydrogenation of styrene oxide in gas phase using a continuous reactor. Palladium catalysts on supports such as activated carbon (AC),  $\gamma$ -alumina and magnesia were studied in order to determine how the acid–base nature of the support affected the selectivity to the desired product (2-PEA). We demonstrate that the acid–base nature of the support plays an important role in selectivity to the products. An acid support, such as alumina or activated carbon, favoured the formation of phenyl acetaldehyde and 1-phenylethanol. On the other hand, with a basic support such as MgO, the main product was 2-PEA and selectivity was over 98%, even at practically total conversion of styrene oxide.

## 2. Experimental

### 2.1. Catalyst preparation

Four Pd catalysts were obtained by impregnating the supports with different solutions of Pd(acac)<sub>2</sub> in toluene, containing the appropriate amount of metal: 0.2% Pd/MgO (C1), 2% Pd/MgO (C2), 2% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (C3) and 2% Pd/AC (C4). After impregnation, the solid was dried at 383 K and calcined at 623 K (except for C4 catalysts) for 3 h. All the catalysts were then activated by reduction in H<sub>2</sub> flow at 623 K for 3 h.

### 2.2. Characterization methods

BET surface area was calculated from the nitrogen adsorption isotherms at 77 K with a Micromeritics ASAP 2000 surface analyzer and a value of 0.164 nm<sup>2</sup> for the cross-section of the nitrogen molecule. The same equipment automatically calculates the pore size distribution by the BJH method.

Powder X-ray diffraction (XRD) patterns of the samples were obtained with a Siemens diffractometer D5000 by nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The patterns were recorded over a range of  $2\theta$  angles from 5° to 85° and compared to X-ray powder references to confirm phase identities using the files of the Joint Committee on Powder Diffraction Standards (JCPDS). The patterns for the expected phases are: MgO Periclase (JCPDS-ICDD 45-0946), graphite C (JCPDS-ICDD 47-1308),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS-ICDD 47-1308), PdO Palladium oxide JCPDS-ICDD 41-1107) and Pd metallic phase (JCPDS-ICDD 87-0645).

Hydrogen chemisorption was measured with a Micromeritics ASAP 2010C instrument equipped with a turbo-molecular pump. Samples had been previously reduced under

the same conditions as for preparing the catalysts. After reduction, hydrogen was removed from the metal surface with a flow (15 ml min<sup>-1</sup>) of He for 30 min at 623 K. The sample was subsequently cooled under the same He stream. The chemisorbed hydrogen was analyzed at 343 K using the adsorption-backsorption isotherm method proposed by Benson et al. [27]. The metal surface atoms were calculated assuming a stoichiometry H/Pd = 1 at the surface.

Temperature programmed reduction (TPR) of catalytic precursors, temperature programmed desorption (TPD) of H<sub>2</sub>, NH<sub>3</sub> and styrene oxide of catalysts were studied using a TPD/R/O 1100 (ThermoFinnigan) equipped with a thermal conductivity detector (TCD) and coupled to a mass spectrometer QMS 422 Omnistar. Before the TPR, the sample (around 20 mg) was calcined under flowing air (20 ml/min) from room temperature rising to 623 K at a heating rate of 10 K/min and maintaining this final temperature for 3 h. For 2% Pd/AC sample, helium was used as the flowing gas in order to avoid carbon combustion. The reduction process was then carried out between 313 and 973 K at a heating rate of 5 K/min for 3 h flowing the reducing gas mixture (5% H<sub>2</sub> in argon with a flow of 20 ml/min).

Before the TPD of H<sub>2</sub>, the sample (around 20 mg) was reduced to 623 K with a 5% H<sub>2</sub> in argon flow (20 ml/min) at a heating rate of 10 K/min, and then holding the sample at this temperature for 3 h. The sample was then cooled to room temperature under this 5% H<sub>2</sub> in argon flow. Then, at room temperature, an argon flow (20 ml/min) was introduced through the sample for 3 h in order to evacuate the physisorbed hydrogen. Hydrogen TPD was then carried out between 313 and 1173 K at 20 K/min in Ar flow (20 ml/min). A similar procedure was carried out to perform the NH<sub>3</sub> TPD. After catalyst reduction and at room temperature, a flow of 3% NH<sub>3</sub> in helium (20 ml/min) was introduced through the sample for 3 h. A flow of helium (20 ml/min) was then introduced to evacuate the physisorbed NH<sub>3</sub> and the NH<sub>3</sub> TPD was obtained by heating at a rate of 20 K/min up to 1173 K in He flow (20 ml/min).

For the TPD of styrene oxide, the sample was treated at 333 K for 3 h with a He flow saturated with styrene oxide at 298 K. A flow of helium (20 ml/min) was then passed through the sample at 333 K for 3 h and the sample was heated at a rate of 20 K/min from 313 to 1173 K flowing He (20 ml/min).

### 2.3. Determination of the catalytic activity

The gas-phase hydrogenation of styrene oxide was studied in a tubular fixed-bed flow reactor heated by an oven equipped with a temperature control system. The experiments were carried out over a wide range of temperature (348–453 K) at atmospheric pressure and using 0.1 g of catalyst. The space velocity was between 10,000 and 30,000 h<sup>-1</sup> and the H<sub>2</sub>/SO molar ratio of 20. The flow rate of gases was controlled by Bronhorst Hi-Tec digital mass flow controllers and SO was introduced into the reactor by a Gilson 350 micro pump. The products were rapidly collected in cold traps and analysed off

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