

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), γ -alumina and magnesia. We performed several characterization techniques, such as powder XRD, TPD of H₂, NH₃ and styrene oxide, TPR, N₂ physisorption and H₂ 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), γ -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)₂ in toluene, containing the appropriate amount of metal: 0.2% Pd/MgO (C1), 2% Pd/MgO (C2), 2% Pd/ γ -Al₂O₃ (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 H₂ 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 nm² 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 α radiation ($\lambda = 1.54056 \text{ \AA}$). The patterns were recorded over a range of 2θ 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), γ -Al₂O₃ (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 turbomolecular 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⁻¹) 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 H₂, NH₃ 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% H₂ in argon with a flow of 20 ml/min).

Before the TPD of H₂, the sample (around 20 mg) was reduced to 623 K with a 5% H₂ 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% H₂ 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 NH₃ TPD. After catalyst reduction and at room temperature, a flow of 3% NH₃ 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 NH₃ and the NH₃ 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⁻¹ and the H₂/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

line in a SHIMADZU GC-17 gas chromatograph equipped with a capillary column ULTRA 2 and FID detector.

3. Results and discussion

3.1. Characterization of the catalyst

Table 1 shows some characterizations data of the catalysts C1, C2, C3 and C4. The crystalline phases (determined by powder X-ray diffraction) of the catalyst showed only the crystalline phases of the supports. The patterns corresponding to the detected phases were: MgO Periclase (JCPDS-ICDD 45-0946), Graphite C (JCPDS-ICDD 47-1308) and γ -Al₂O₃ (JCPDS-ICDD 47-1308). No signals for Pd or PdO were detected for C1, C2, C3 and C4 catalysts (see Table 1). This indicates the high palladium dispersion of these catalysts (particle size less than 4 nm).

The specific surface areas of the catalyst are shown in Table 1. The values of BET areas for the samples were 118, 90, 250 and 990 m²g⁻¹ for C1, C2, C3 and C4 catalysts, respectively. When the amount of palladium increased from 0.2 to 2.0 wt.%, the BET surface area decreased from 118 to 90 m²g⁻¹, which indicates that palladium particles can block some pores of the MgO support.

Metal dispersion of the catalysts, which depended on the BET surface area of the support and the amount of Pd in the sample, was in the 10.3–41.8 (%) range. For catalysts C2, C3 and C4 that have the same Pd amount (2 wt.%), the C4 catalyst, which had the highest BET surface area, also had the highest metal dispersion (around 41.8%). When the amount of palladium increased, for MgO support, the metal dispersion also increased (see C1 and C2 catalysts).

The reducibility of the precursors of C1, C2 and C3 catalysts was studied by TPR. Fig. 1 shows the TPR profiles of the three samples. In the TPR plots, the reduction temperatures were relatively low (<500 K) for all samples. However, the reduction temperature of the Pd/ γ -Al₂O₃ sample shifted to lower temperatures than for the Pd/MgO samples. The hydrogen consumption was determined during TPR experiments. The 2% Pd/ γ -Al₂O₃ sample showed an hydrogen consumption peak of 174.7 μ mol g⁻¹ cat, that corresponds to a reduction degree of around 93%. This fact could indicate that probably part of the palladium is in its reduced form before TPR experiment. In this sense, Padmasri et al. [28], have detected by XPS the presence of Palladium in metallic form for 6% Pd/MgO, that was formed during the

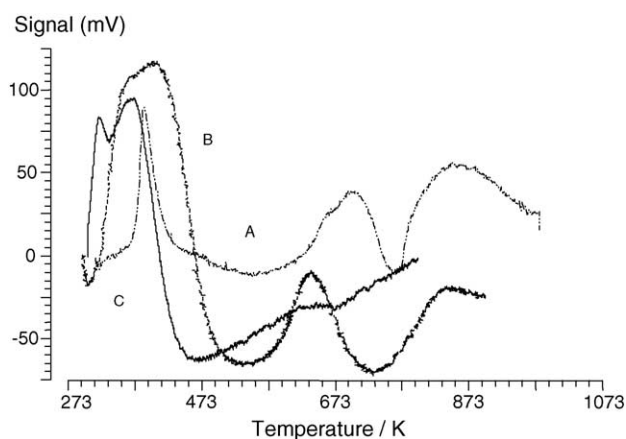


Fig. 1. TPR of 0.2% Pd/MgO (A), 2% Pd/MgO (B) and 2% Pd/ γ -Al₂O₃ (C) samples.

dried and calcined processes of the sample. While the 2% Pd/ γ -Al₂O₃ sample showed only one hydrogen consumption peak, the Pd/MgO samples presented other hydrogen consumption peaks at higher temperatures. For 2% Pd/MgO three hydrogen consumption peaks were detected around 373, 633 and 833 K, respectively. For 0.2% Pd/MgO sample, the peaks were detected at around 373, 693 and 853 K, respectively. The amount of hydrogen consumed for 2% Pd/MgO in each reduction peak was 159.7, 28.1 and 15.0 μ mol g⁻¹ cat, respectively. These values represent around 85, 15 and 8% of the reduction degree of Pd²⁺. For 0.2% Pd/MgO the amount of hydrogen consumed was 9.9, 7.9 and 6.2 μ mol g⁻¹ cat, respectively, that represent around 53, 42 and 62% of Pd²⁺ reduction degree in the sample. In order to see if the hydrogen consumptions detected at higher temperatures for Pd/MgO catalysts are due to the presence of CH_x species in the calcined samples, the evolution of CH₄ by mass spectrometry was performed during TPR experiments. Negative signals were found for all the samples. This fact is in agreement with the results reported by Lomot et al. [29], that indicate that a calcination temperature of 523 K is sufficient to remove all the carbon species in Pd(acac)₂/SiO₂ catalysts, even with 1% O₂ in He atmosphere. So, the high temperature of hydrogen consumption could be attributed to the reduction of some Pd species which have a strong interaction with the MgO [30], as well as due to spill over of the hydrogen activated on metallic Pd on the MgO support [31]. Lopez and Illas [32], investigated the nature of the interaction of Pd with the acidic and basic sites of the MgO (1 0 0) surface by means of ab initio wave functions and DFT techniques. They predicted a fairly strong interaction of Pd over basic sites but a rather weak interaction of the metal over acidic sites. A quantum chemical study by Ferrari and Pacchioni [33], also predicts good interaction between Pd and MgO.

It is important to note that no negative peak, corresponding to β -PdH_x decomposition, was observed for these catalysts during TPR experiments, probably because of the high metal dispersion and the small crystallite size of Pd (not detected

Table 1
Characterization data of palladium catalysts

Catalysts	C1	C2	C3	C4
Crystalline phases (XRD)	MgO	MgO	γ -Al ₂ O ₃	Graphite
Specific surface area (m ² g ⁻¹) ^a	118	90	250	990
Metal dispersion (%) ^b	10.3	24.8	35.5	41.8

^a BET area.

^b By hydrogen chemisorption.

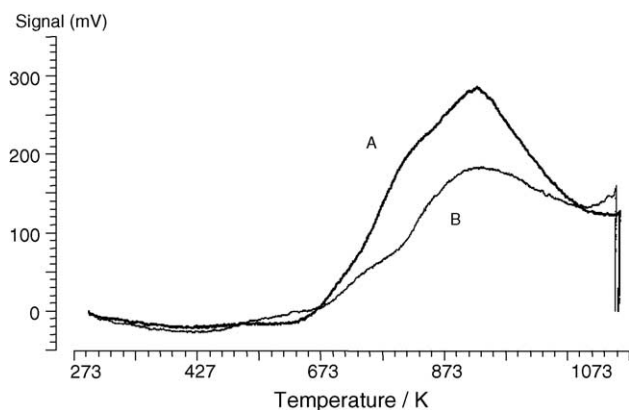


Fig. 2. TPD of H₂ of 2% Pd/γ-Al₂O₃ (A) and 2% Pd/MgO (B) samples.

by XRD) in the samples. An increase in the dispersion of Pd in the Pd/SiO₂ system or a decrease in the Pd crystallite size is reported to lead to a decrease in the intensity of the β-PdHx decomposition peak [28,34].

Fig. 2 shows the H₂-TPD profiles of C2 and C3 catalysts, both with a main peak at around 950 K. Catalyst C3 shows a more intense signal, which indicates that the dispersion of the 2% Pd/γ-Al₂O₃ sample (35.5%) was higher than for the 2% Pd/MgO sample (24.8%). This could be due to the higher BET surface area of this catalyst (250 m²g⁻¹ for 2% Pd/γ-Al₂O₃ compared to 90 m²g⁻¹ for 2% Pd/MgO).

Chen et al. reported the desorption profiles for Pd/MgO and Pd supported on calcined hydrotalcites detecting a broad desorption peak between 473 and 873 K depending on the interaction between palladium and the support [35]. Besides, Frusteri et al. have detected hydrogen desorption around 773 K during H₂-TPD experiments on Pd/MgO catalysts [36]. Furthermore, Padmasri et al. [28], have detected hydrogen desorption on Pd/MgO at higher temperatures (>700 K) which may attributed to the partial desorption of hydrogen that is chemisorbed on both palladium and magnesia.

The temperature-programmed desorption of styrene oxide, performed for C2 and C3, is shown in Fig. 3. The C3 catalyst shows a desorption peak at higher temperature (around 800 K), which was not observed for C2 catalyst. This indicates that the adsorption of styrene oxide in 2% Pd/γ-Al₂O₃ was stronger than in 2% Pd/MgO catalysts, probably because of the greater acid character of γ-Al₂O₃ compared to MgO. To study the acid character of the catalysts, we performed the temperature-programmed desorption of NH₃. Fig. 4 shows the results for the C2, C3 and C4 catalysts. The C3 catalyst has a main peak at around a temperature desorption of 520 K and C4 catalyst has a main peak at around

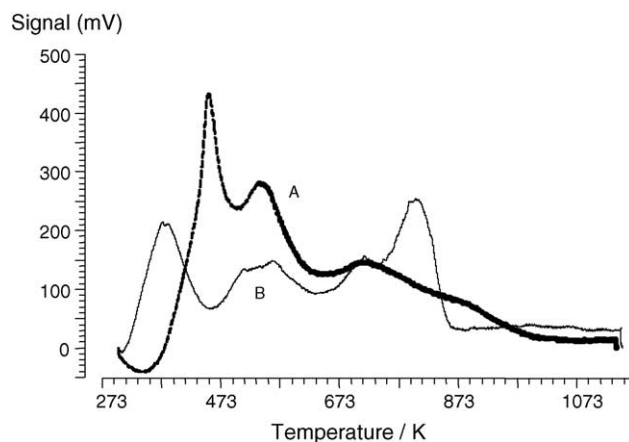


Fig. 3. Styrene oxide TPD of 2% Pd/MgO (A) and 2% Pd/γ-Al₂O₃ (B) samples.

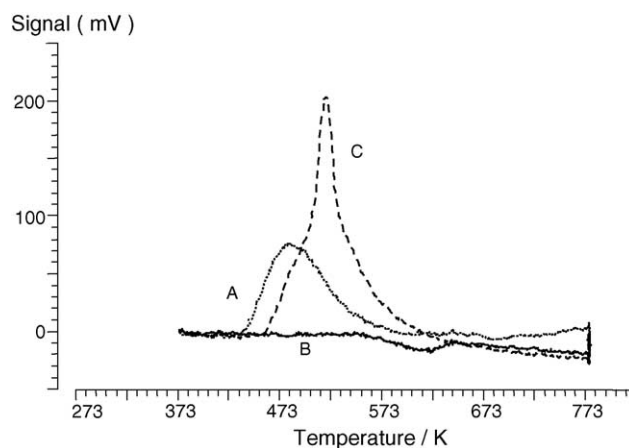
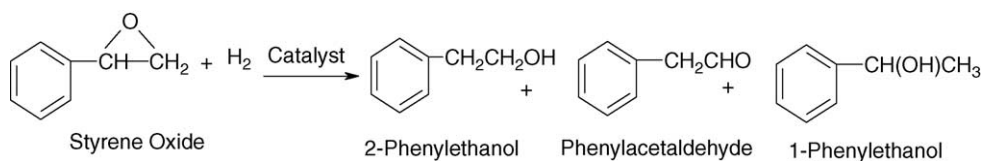


Fig. 4. TPD of NH₃ of 2% Pd/CA (A), 2% Pd/MgO (B) and 2% Pd/γ-Al₂O₃ (C) samples.

485 K. Also, the amount of NH₃ desorbed for the C3 catalyst was higher than for the C4 catalyst. No desorption peak was detected for Pd/MgO catalysts, which indicates the basic character of this sample. The NH₃ TPD results show that the acid character of the catalysts was in the order: Pd/γ-Al₂O₃>Pd/AC>Pd/MgO. Similar results have been reported by Mahata et al. [37].

3.2. Catalytic activity

Our catalytic results show that 2-phenylethanol (2-PEA), 1-phenylethanol (1-PEA) and phenylacetaldehyde (PAD) were the main products (see Scheme 1).



Scheme 1. Main products during the hydrogenation reaction of styrene oxide.

Table 2
Catalytic activity of 0.2% Pd/MgO

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)		
		2-PEA	1-PEA	PAD
348 ^a	96	99	0	1
373 ^a	99.5	98	0	2
398 ^a	99.8	70	0	30
453 ^a	99.9	40	0	60
348 ^b	32	99	0	1
373 ^b	68	98	0	2
398 ^b	88	90	0	10

^a The space velocity was 10,000 h⁻¹.

^b The space velocity was 30,000 h⁻¹.

Table 3
Catalytic activity of 2% Pd/MgO

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)		
		2-PEA	1-PEA	PAD
348 ^a	98	99.5	0	0.5
373 ^a	99.5	98.4	0	1.6
398 ^a	99.5	99.2	0	0.8
348 ^b	39	99.4	0	0.6
373 ^b	75	99.1	0	0.9
398 ^b	91	98.9	0	1.1

^a The space velocity was 10,000 h⁻¹.

^b The space velocity was 30,000 h⁻¹.

Table 4
Catalytic activity of 2% Pd/ γ -Al₂O₃

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)		
		2-PEA	1-PEA	PAD
348 ^a	99.5	8.5	56	35.5
373 ^a	99.8	16	57	27
398 ^a	99.9	14	57	29
348 ^b	55	12	60	28
373 ^b	90	19	59	22
398 ^b	99.5	16	61	23

^a The space velocity was 10,000 h⁻¹.

^b The space velocity was 30,000 h⁻¹.

Tables 2–5 show the catalytic results for the 0.2% Pd/MgO (C1), 2% Pd/MgO (C2), 2% Pd/ γ -Al₂O₃ (C3) and 2% Pd/AC (C4) catalysts, respectively.

Table 2 shows the catalytic results obtained in the presence of the C1 catalyst. The reaction was performed at

Table 5
Catalytic activity of 2% Pd/AC

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)		
		2-PEA	1-PEA	PAD
348 ^a	99.8	32	3	65
373 ^a	99.9	32	5	63
398 ^a	99.9	30	10	60
348 ^b	44	40	2	38
373 ^b	80	52	8	40
398 ^b	98	46	11	43

^a The space velocity was 10,000 h⁻¹.

^b The space velocity was 30,000 h⁻¹.

atmospheric pressure and between 348 and 453 K, with a H₂/SO molar ratio of 20 and a space velocity of 10,000 and 30,000 h⁻¹. Styrene oxide conversion increased from 96 to 99.9% when the reaction temperature increased from 348 to 453 K. 2-Phenylethanol (2-PEA) and phenyl acetaldehyde (PAD) were the main products. 1-Phenylethanol (1-PEA) was not obtained at these reaction conditions. When the reaction temperature increased, the selectivity to PAD increased at the expense of 2-PEA formation. At the lowest reaction temperature (348 K), the selectivity to 2-PEA and PAD was 99 and 1%, respectively, while at 453 K the selectivity to 2-PEA and PAD was 40 and 60%, respectively. Our results show that when the 0.2% Pd/MgO catalyst was used in the hydrogenation reaction of styrene oxide, a competitive reaction between hydrogenation (to give 2-phenylethanol) and isomerization (to give phenylacetaldehyde) was observed. Also, increasing the reaction temperature favoured the isomerization reaction, giving PAD instead of the hydrogenation giving 2-PEA. On the other hand, increasing the space velocity led to an increase in selectivity to 2-PEA and a decrease in selectivity to PAD.

The formation of phenylacetaldehyde by the isomerization of styrene oxide has been studied by several authors, who indicate that the acid–base properties of the catalyst play an important role in both activity and selectivity [38–41].

To promote the hydrogenation reaction instead of isomerization, the Pd load was increased to 2%. Table 3 shows the activity and selectivity of the 2% Pd/MgO catalyst in the hydrogenation reaction of styrene oxide. Conversion was practically total and selectivity to 2-PEA was over 98% at the reaction temperatures tested. Increasing the space velocity led to a decrease in conversion but selectivity to 2-PEA remained practically constant. Note that 1-phenylethanol was not obtained in the presence of MgO as support.

To study the effect of the support, the 2% Pd/ γ -Al₂O₃ (C3) and 2% Pd/AC (C4) catalysts were tested at the same reaction conditions as for the C1 and C2 catalysts. The results are shown in Tables 4 and 5, respectively. For the C3 catalyst at a reaction temperature between 348 and 398 K and a space velocity of 10,000 h⁻¹, conversion was practically total and selectivity to 1-phenylethanol was around 55%. Selectivity to PAD was in the 29–35% range. Note that 2-PEA was also obtained but always as a minor product (<20%). A slight increase in selectivity to 2-PEA was observed when the space velocity increased from 10,000 to 30,000 h⁻¹.

Table 5 shows the catalytic behaviour for C4. In the range of reaction temperatures tested (between 348 and 398 K), selectivity to phenyl acetaldehyde, 2-phenylethanol and 1-phenylethanol was 60–65%, 30–32% and 3–10%, respectively. When the space velocity increased, the selectivity to 2-PEA increased, mainly at the expense of PAD, and selectivity to 1-PEA remained practically constant. These results therefore show that the acid–base nature of the support plays an important role in selectivity in the hydrogenation reaction of styrene oxide.

It has been reported that the hydrogenation of asymmetric epoxides using metal catalysts is controlled by the ring open-

ing of the epoxides [22]. There are two routes for styrene oxide. The first is hydrogenation to give 2-PEA and 1-PEA, and the second is the isomerization reaction to give aldehydes or ketones [4]. An acid support, such as alumina and activated carbon, favours the formation of Phenyl acetaldehyde and 1-phenylethanol. The formation of these products can be related to the presence of acid sites that can produce phenyl acetaldehyde or the acetophenone, which is assisted by hydrogen giving secondary alcohol as the major product [21,22,41–43]. For basic catalysts, however (using MgO as support), the main product is 2-PEA. This is in agreement with the results of experiments in liquid phase and batch reactor, which indicate that the presence of an inorganic base such as NaOH is needed to obtain a high selectivity to 2-PEA [21,22].

The high amount of 1-PEA formed in Pd/Al₂O₃ catalysts with respect to the Pd/MgO catalyst could be related with the mechanism for the C–O cleavage that occurs at the Pd sites and the isomerization reactions of the obtained products. The electron density of Pd supported on MgO is higher than for Pd supported on Al₂O₃ [44]. This fact favours the formation of π -benzyl complex according with the mechanism proposed by Mitsui et al. [22], that assisted by hydrogen leads to the formation of 2-PEA. Besides, the basic character of the support inhibit the isomerization reaction which is responsible of the formation of 1-PEA [16]. Consequently, the selective formation of 2-phenylethanol and phenylacetaldehyde without 1-phenylethanol or acetophenone in the presence of 2% Pd/MgO implies that the abnormal cleavage of the inner carbon–oxygen bond was selectively accelerated by the catalyst [4].

4. Conclusion

We have studied the selective hydrogenation of styrene oxide using a continuous flow reactor in the presence of Pd catalysts on different supports such as MgO, γ -Al₂O₃ and activated carbon. Our results show that the 2% Pd/MgO sample can be a useful catalyst for the selective hydrogenation reaction of styrene oxide, obtaining a high selectivity to 2-phenylethanol (>98%) even at total conversion. 1-phenylethanol (1-PEA) and Phenyl acetaldehyde (PAD) were the main products in the presence of 2% Pd/ γ -Al₂O₃, whereas with 2% Pd/AC, the main products were 2-phenylethanol and phenyl acetaldehyde. We should mention that the acid–base nature of the support plays an important role in the selectivity to the products. An acid support such as alumina and activated carbon favours the formation of Phenyl acetaldehyde and 1-phenylethanol, while a basic support (MgO) favours the formation of 2-PEA.

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