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Hydrogenation of styrene oxide in the presence of supported platinum catalysts to produce 2-phenylethanol

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Abstract

Gas-phase hydrogenation of styrene oxide was investigated using platinum catalysts deposited on magnesia, γ-alumina and activated carbon (AC), at atmospheric pressure and within a wide range of temperature (348–398 K). In order to correlate the chemical and textural properties with the catalytic activity, all catalysts were characterized by several techniques such as X-ray diffraction (XRD), temperature-programmed reduction (TPR), H_2-temperature-programmed desorption (TPD) N_2 physisorption and H_2 chemisorption. Obtained results indicate that the catalytic activity and the selectivity were affected by the nature of the support. In the presence of MgO or activated carbon, as supports, the main product was 2-phenylethanol (2-PEA). However, when the support was γ-alumina, the main product was phenylacetaldehyde (PAD). The basic character of the support led to the formation of the less substituted alcohol (2-PEA). This was obtained at high conversion (85%) with practically total selectivity (around 99%). However, more acid support such as γ-alumina led to the formation of the more substituted alcohol 1-phenylethanol (1-PEA) and phenylacetaldehyde, mainly due to the isomerisation of the epoxide. Consequently, the acid–base character of the support plays an important role in the selectivity of this reaction.

Keywords: Styrene oxide hydrogenation; 2-Phenylethanol; Platinum catalysts

1. Introduction

2-Phenylethanol (2-PEA) is a colorless liquid possessing a faint but lasting odor of rose petals, making it as a valuable article of commerce that is widely employed as a fragrance chemical and is used in perfumes, deodorants, etc. [1–8]. 2-PEA also has bacteriostatic and antifungicidal properties and is extensively used in the formulation of cosmetics, as well as in important applications in the manufacture of chemical compounds [3,4].

Nowadays, 2-phenylethanol is industrially produced by different processes, such as Friedel–Crafts alkylation of benzene with ethylene or reacting chlorobenzene with Grignard-type reactants, followed by several steps, which finally give rise to the formation of 2-phenylethanol but with a poor quality due to the presence of other by-products and causing environmental problems [5,6].

On the other hand, it is possible to obtain 2-PEA by ring opening of epoxide with reductor agents such as hydrides or alkaline metals [9–22]. The product of this reaction is a mixture of primary and secondary alcohols, whose separation becomes difficult. However, it has recently been demonstrated that by ring opening of the epoxide using borohydride of zinc supported in silica gel and aluminum phosphate, the less substituted alcohol, can be obtained as the main product [23,24]. This is an interesting result because the use of inorganic solids as supports for the reducing agent can allow the control of the selectivity in this reaction. Nevertheless, the preparation of these reducing agents introduces an additional stage in the process to obtain 2-PEA making very difficult at commercial level. Another serious disadvantage of this method is the low selectivity to the desired product; a mixture of primary and secondary alcohol and others by-products are obtained making necessary posterior separation steps.

Another method of obtaining 2-phenylethanol is from styrene oxide using acid materials such as zeolites as well as ultraviolet radiation [25,26]. However, the yield of this process is low. 2-

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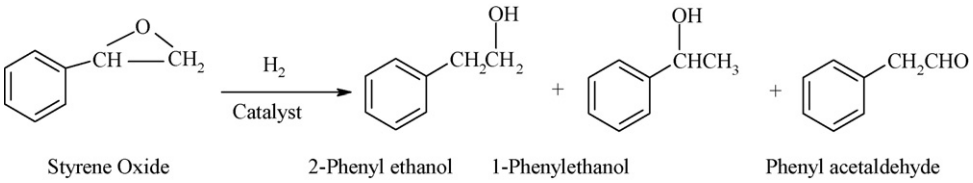

Fig. 1. Main products during the hydrogenation reaction of styrene oxide.

Phenyethanol can also be obtained as a low purity by-product in the process of styrene monomer and propylene oxide [27,28].

Therefore, better processes to produce 2-phenylethanol with high yield and selectivity, including low costs, security and simplicity in the operations and with an awareness for the effect on the environment are necessary for application at industrial scale [7,8].

One interesting proposal is the production of 2-phenylethanol by a heterogeneous catalytic process, which involves first the catalytic oxidation of styrene to styrene oxide, and then the catalytic hydrogenation of styrene oxide to 2-phenylethanol [29,30].

In this sense, the catalytic hydrogenation of styrene oxide to alcohol using heterogeneous catalysts has been studied (Fig. 1) [16–26]. It has been observed, that when alkali is used as a basic promoter, a good selectivity to 2-PEA is obtained [6,18,24]. This behavior has been explained by Mitsui et al. [31] taking into account the interaction between the styrene oxide and the active site of the catalyst.

However, practically all the results have been achieved using batch reactors with the disadvantage that at the end of the reaction the catalyst must be removed from the products. Consequently, Hölderich et al. [32] and Buechele et al. [33] suggested performing this reaction in a flow reactor.

Previous studies in our group using nickel and palladium catalysts [34,35] have shown that the acid–base nature of the support have a strong influence in the selectivity to 2-phenylethanol.

Taking into account these results, in this paper we have studied the preparation of 2-PEA by catalytic hydrogenation of styrene oxide in gas phase using a continuous reactor. Platinum catalysts on different supports such as activated carbon (AC), γ-alumina and magnesia were studied in order to determine how the acid–base nature of the support affects the selectivity to the desired product (2-PEA). Our results demonstrate that the acid–base nature of the support plays an important role in the selectivity to the desired products.

2. Experimental

2.1. Catalyst preparation

Three platinum catalysts were obtained by impregnating the supports with a solution of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich) in ethanol, containing the appropriate amount of metal: 2% Pt/γ-Al_2O_3 (T1), 2% Pt/MgO (T2) and 2% Pt/AC (T3). After impregnation, the solid was dried at 383 K and calcined at 623 K (except for T3 catalyst) for 3 h. All the catalysts were then activated by reduction in H_2 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^2 for the cross-section of the nitrogen molecule. The same equipment automatically calculated 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 Kα radiation (λ = 1.54056 Å). 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-Al_2O_3 (JCPDS-ICDD 47-1308) and Pt metallic phase (JCPDS-ICDD 04-802).

Hydrogen chemisorption was measured with a Micromeritics ASAP 2010 C 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) 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. [36]. The metal surface atoms were calculated assuming a stoichiometry H/Pt = 1 at the surface.

Temperature-programmed reduction (TPR) of catalytic precursors and temperature-programmed desorption (TPD) of H_2 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 the 2% Pt/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_2 in argon with a flow of 20 ml/min).

Before the TPD of H_2, the sample (around 20 mg) was reduced to 623 K with a 5% H_2 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_2 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).

2.3. Determination of the catalytic activity

The catalytic hydrogenation of styrene oxide was carried out at steady-state conditions in the gas phase using a tubular fixed-bed flow reactor (10 mm internal diameter and 20 cm long) heated by an oven equipped with a temperature control system. The experiments were carried out over a wide range of temperature (348–398 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 H_2/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 analyzed 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 T1 (2% Pt/γ-Al_2O_3), T2 (2% Pt/MgO) and T3 (2% Pt/AC). The crystalline phases (determined by powder X-ray diffraction) of the catalyst showed only the crystalline phases of the supports [37]. The patterns corresponding to the detected phases were: MgO Periclase (JCPDS-ICDD 45-0946), Graphite C (JCPDS-ICDD 47-1308) and γ-Al_2O_3 (JCPDS-ICDD 47-1308). No signals for platinum or platinum oxide were detected for T1, T2 and T3 catalysts. This is probably due to the low amount of Pt in the samples. The specific surface areas of the catalyst are shown in Table 1. The values of BET areas for the samples were 273, 36 and 998 m^2/g for T1, T2 and T3 catalysts, respectively. The BET values obtained for T1 and T3 catalysts are very similar than those obtained for pure supports (280 and 980 m^2/g, respectively). However, T2 catalyst shows an important decrease in the BET value with respect to the pure support MgO (36 and 98 m^2/g, respectively). Metal dispersion of the T1, T2 and T3 catalysts was around 31, 22 and 45%, respectively. This fact indicates a strong dependence between the metal dispersion and the BET surface area of the support. Furthermore, the low metal dispersion obtained for Pt/MgO catalyst can be related to the decrease of the BET area of this catalyst with respect to the MgO support. This fact could be related to the acid property of platinum salt (hexachloroplatinic acid), which can react with a basic support such as MgO producing the partial dissolution of the support, blocking the pores of the support or encapsulating the Pt particles in the MgO support [38,39].

Table 1
Characterization data of platinum catalysts

Catalysts	T1	T2	T3
Crystalline phases (XRD)	γ-Al_2O_3	MgO	CA
Specific surface area[a] (m^2/g)	273	36	998
Metal dispersion[b] (%)	31.6	22.3	45

[a] BET area.
[b] By hydrogen chemisorption.

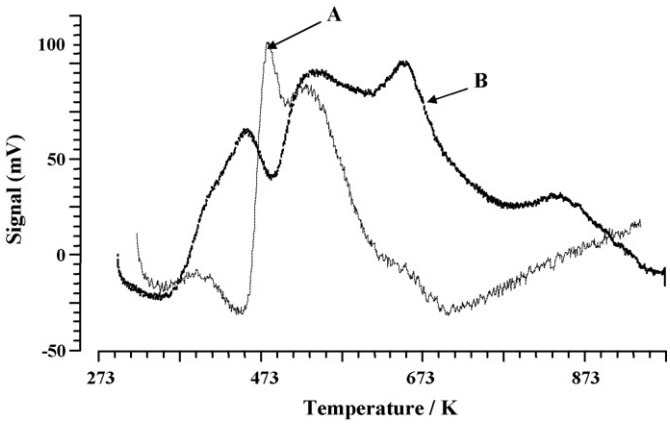

Fig. 2. TPR profile of: (A) T1 (2% Pt/γ-Al_2O_3) and (B) T2 (2% Pt/MgO) catalysts.

The reducibility of precursors of T1 and T2 catalysts was studied by TPR. Fig. 2 shows the TPR profile of T1 (A) and T2 (B) samples, respectively. The reduction temperature for T1 sample was relatively low with a large peak around 560 K and one more sharp peak at 490 K. These results show the existence of different species of platinum that are reduced at different temperatures. The first peak obtained at 490 K can be assigned to the reduction of platinum oxide dispersed on the support [40]. The second peak around 560 K can be assigned to the reduction of Pt(IV) to Pt(0) [41,42]. This second peak could be also assigned to the presence of platinum oxychlorides species (PtO_xCl_y) reported by Marceau et al. [43]. However, Hwang and Yeh [44] indicated that these species are reduced at higher temperature. Probably, the drift of the TPR base line at temperatures higher than 700 K could indicate this fact.

Fig. 2B shows the TPR profile of T2 (2% Pt/MgO) sample. The TPR process shows a wide range of temperature reductions between 373 and 900 K. These bands can be attributed to the reduction of different species of platinum with different interactions with magnesium oxide. This fact is in agreement with the results reported by other authors [39], however, it is very difficult to have an accurate explanation about the presence of different species during the reduction process.

All these features indeed show the complexity of the interaction of the Pt species with the supports.

The interaction between hydrogen and platinum catalysts was also studied by TPD of H_2. Fig. 3 shows the H_2–TPD profiles of T1 (2% Pt/γ-Al_2O_3) and T2 (2% Pt/MgO) catalysts, respectively. The T1 sample shows three bands centered at 510, 700 and 950 K, respectively. The first band represents hydrogen associated with the Pt, either chemisorbed on the Pt surface or held between the metal particle and the support surface (interfacial hydrogen) [45]. The second band results from hydrogen species on the support distant from the Pt. The third band shows hydrogen desorbed at high temperature and has been ascribed as spillover hydrogen [46]. However, Miller et al. suggest that this desorbed hydrogen results from the decomposition of a hydro-

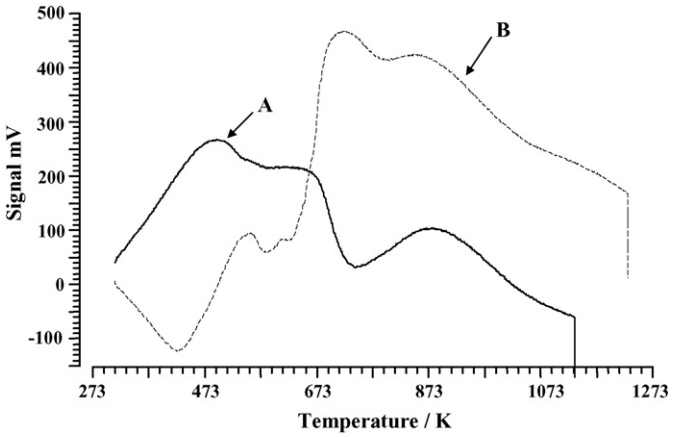

Fig. 3. TPD of H_2 of: (A) T1 (2% Pt/γ-Al_2O_3) and (B) T2 (2% Pt/MgO) catalysts.

gen containing compound, which is present prior to reduction and desorbs from the support at high temperature [46].

The temperature-programmed desorption of hydrogen of T2 (2% Pt/MgO) catalyst, is shown in Fig. 3B. The obtained results show a small band at low temperature (around 533 K), together with two bands broad and intense centered at 700 and 853 K. The first band (533 K) can be ascribed, in the same way as for T1 catalyst, to the hydrogen associated with the Pt. This band is smaller for catalyst T2 than for catalyst T1, this is in agreement with the results obtained by hydrogen chemisorption indicating that catalyst T1 shows a higher dispersion than catalyst T2 (31.6 and 22.3%, respectively). The second band (at 700 K) represents the hydrogen species on the support distant from the Pt and is more intense than that for T1 catalyst. The third band centered at 853 K, which is also more intense than for the T1 catalyst, could correspond to hydrogen desorbed from the decomposition of some hydrogen containing compound formed during the preparation of the catalyst, as is suggested by Miller et al. [46]. This is in agreement with the platinum salt used in the preparation of catalysts (H_2PtCl_6). Due to the acid character of this salt, the reaction with a basic support such as MgO is easier than for an acid support such as γ-Al_2O_3.

3.2. Catalytic activity

The reaction was performed at atmospheric pressure and between 348 and 398 K, with a H_2/SO molar ratio of 20 and a space velocity of 10,000 and 30,000 h^{-1}. The catalytic results show that 2-phenylethanol, 1-phenylethanol (1-PEA) and phenylacetaldehyde (PAD) were the main products. Tables 2–4 show the catalytic results for the 2% Pt/γ-Al_2O_3 (T1), 2% Pt/MgO (T2) and 2% Pt/AC (T3), respectively.

Table 2 shows the catalytic results obtained in the presence of 2% Pt/γ-Al_2O_3 (T1) catalyst. Styrene oxide conversion increased from 95.0 to 99.6% when the reaction temperature increased from 348 to 398 K at a space velocity of 10,000 h^{-1}. Phenylacetaldehyde was the main product (between 56.1 and 90.3%). At 348 K the selectivity to 1-phenylethanol was 36.2%. When the reaction temperature increased, the selectivity to 1-PEA decreased favoring the formation of PAD and 2-phenylethanol. However, the selectivity to 2-PEA was always lower than 10% at these reaction conditions. Other by-products such as ethylbenzene, styrene and oligomerisation products were also obtained. A slight increase in selectivity to 2-PEA was observed when the space velocity increased from 10,000 to 30,000 h^{-1}. Our results show that when the 2% Pt/γ-Al_2O_3 (T1) catalyst was used in the hydrogenation reaction of styrene oxide, a competitive reaction between hydrogenation (to give the alcohol) and isomerisation (to give phenylacetaldehyde) was observed. An increase in the temperature reaction favors the isomerisation reaction giving the aldehyde.

The formation of phenylacetaldehyde as main product is due to the acid character of alumina support. The formation of phenylacetaldehyde by the isomerisation of styrene oxide has been studied by several authors, indicating that the acid–base prop-

Table 2
Catalytic activity of 2% Pt/γ-Al_2O_3

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)			
		2-PEA	1-PEA	PAD	Others
348[a]	95.0	3.9	36.2	56.1	3.8
373[a]	97.5	3.8	5.0	90.3	0.9
398[a]	99.6	10.0	2.0	87.1	0.9
348[b]	60.0	10.8	35.2	54.0	–
373[b]	68.0	16.5	25.3	68.0	0.2
398[b]	75.0	20.5	9.6	69.4	0.5

[a] Space velocity was 10,000 h^{-1}.
[b] Space velocity was 30,000 h^{-1}.

Table 3
Catalytic activity of 2% Pt/MgO

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)			
		2-PEA	1-PEA	PAD	Others
348[a]	99.8	94.6	–	5.4	–
373[a]	99.9	87.8	–	3.4	8.8
398[a]	99.9	25.2	34.5	39.6	0.7
348[b]	70.0	99.1	–	0.9	–
373[b]	85.0	99.0	–	1.0	–
398[b]	93.0	92.1	3.5	4.2	0.2

[a] Space velocity was 10,000 h^{-1}.
[b] Space velocity was 30,000 h^{-1}.

Table 4
Catalytic activity of 2% Pt/AC

Temperature (K)	Styrene oxide conversion (%)	Selectivity (%)			
		2-PEA	1-PEA	PAD	Others
348[a]	99.7	78.3	2.8	18.9	–
373[a]	99.6	42.7	10.5	38.9	7.9
398[a]	99.9	42.3	5.2	24.3	28.2
348[b]	68.0	98.0	–	2.0	–
373[b]	77.3	66.5	2.4	29.1	2.0
398[b]	89.2	58.6	3.5	24.9	13.0

[a] Space velocity was 10,000 h^{-1}.
[b] Space velocity was 30,000 h^{-1}.

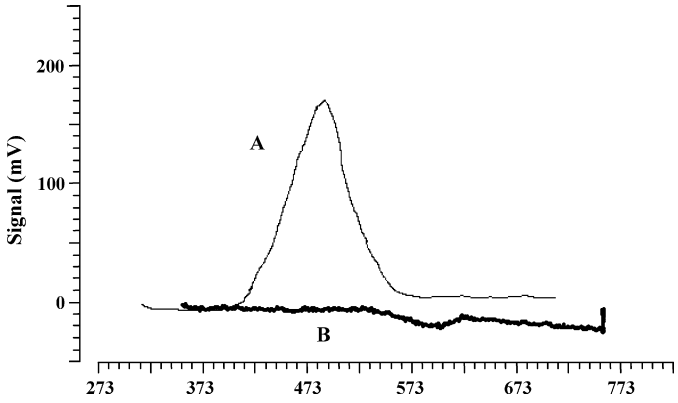

Fig. 4. TPD of NH_3 of: (A) T1 (2% Pt/γ-Al_2O_3) and (B) T2 (2% Pt/MgO) catalysts.

erties of the support play an important role in both activity and selectivity [47–50]. Similar results have been reported for the isomerisation reaction of propylene oxide giving propanaldehyde [51,52].

In this sense, the acid–base character of T1 and T2 catalysts was studied by temperature-programmed desorption of NH_3. Fig. 4 shows the obtained results. The T1 catalyst has a main desorption peak at around 490 K. However, no desorption peak was observed for T2 catalyst. These results show the more acid character of alumina support with respect to MgO support.

To study the effect of the support, the 2% Pt/MgO (T2) and 2% Pt/AC (T3) catalysts were tested at the same reaction conditions as for the T1 catalyst.

Table 3 shows the results for T2 catalyst. At reaction temperatures of 348 and 373 K and a space velocity of 10,000 h^{-1}, the styrene oxide conversion was practically total and selectivity to 2-PEA was over 87%. Increasing the space velocity led to a decrease in conversion but selectivity to 2-PEA was practically total (around 99%). However, when the reaction temperature was 398 K and a space velocity of 10,000 h^{-1}, a strong decrease in the selectivity to 2-PEA was observed favoring the formation of 1-PEA and PAD. This fact was also observed, but more attenuated, for a space velocity of 30,000 h^{-1}.

Table 4 shows the catalytic activity of platinum catalyst supported in activated carbon 2% Pt/AC (T3) working at a range of reaction temperatures between 348 and 398 K. In the presence of this catalyst the main products were 2-phenylethanol with a high selectivity (between 20 and 98%), phenylacetaldehyde (2 and 39%) and 1-phenylethanol (2 and 10%). The presence of other by-products was also observed. When the space velocity increased, the selectivity to 2-PEA increased, mainly at the expense of PAD.

These results therefore show that the acid–base character of the support plays an important role in selectivity in the hydrogenation reaction of styrene oxide. Mitsui et al. have reported that the hydrogenation of asymmetric epoxides using metal catalysts is controlled by the ring opening of the epoxides [31]. During the hydrogenation reaction of styrene oxide two routes are possible. The hydrogenation route gives 2-PEA and 1-PEA, while the isomerisation route gives the aldehyde (PAD) [53]. An acid support, such as alumina favors the formation of 1-PEA and PAD. The presence of acid sites in the catalyst led to the formation of phenyl acetaldehyde or the acetophenone, which is assisted by hydrogen giving the secondary alcohol as the major product [31,50,54]. However, more neutral or basic supports such as activated carbon or MgO increase the selectivity to 2-PEA. The selectivity to the obtained products for these catalysts could be related with the mechanism for the C–O cleavage that occurs in the metal sites and the isomerisation reactions of the obtained products. Basic supports can increase the electron density of the metal [55]. This fact favors the formation of π-benzyl complex in accordance with the mechanism proposed by Mitsui et al. [31]. This complex reacts with hydrogen giving 2-PEA. Consequently, the reductive cleavage of epoxides, that usually gives the more substituted alcohol, can be redirected to the less substituted alcohol with high selectivity using basic supports.

4. Conclusion

The selective hydrogenation of styrene oxide in gas phase using a continuous flow reactor in the presence of platinum catalysts has been studied. In addition, the effect of the acid–base character of the support on the selectivity has been studied for several supports such as γ-alumina, magnesium oxide and activated carbon. The basic character of the support led to the formation of the less substituted alcohol (2-PEA), that can be obtained at high conversion (85%) with practically total selectivity (around 99%). More acid support such as γ-alumina led to the formation of the more substituted alcohol (1-PEA) and phenylacetaldehyde, mainly due to the isomerisation of the epoxide. Consequently, the acid–base character of the support plays an important role in the selectivity for the hydrogenation reaction of styrene oxide in gas phase.

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