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Mesoporous carbon as an efficient catalyst for alcoholysis and aminolysis of epoxides

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ABSTRACT

The ring opening reaction of epoxides by alcohols and amines using mesoporous activated carbon as efficient and environmentally friendly heterogeneous catalyst is reported. Carbon xerogels were synthesized by polymerization of resorcinol and formaldehyde. The surface of the activated carbon was oxidized in liquid phase with HNO₃ and then functionalized with H_2SO_4 .

Chemical and textural characterization by elemental analysis, pH_{PZC} , TPD, BET and XPS indicates that oxidation in liquid phase is effective in the introduction of strong acid groups in the carbon surface. The functionalization with H_2SO_4 led to more acid functional groups, as expected. The activated carbons were tested in alcoholysis and aminolysis of epoxides, having been obtained excellent results of conversion and selectivity, both over 95%.

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1. Introduction

For the sustainability of our ever evolving modern world it is necessary to keep looking for new and diverse ways to optimize the available resources. In this sense the development of new and less expensive heterogeneous catalysts and their application in reactions with synthetic interest such as the ring opening of epoxides is an important challenge with industrial repercussions.

Epoxides are versatile and valuable intermediates in organic synthesis. These oxygen heterocycles are significantly more reactive than other ethers due to the strain induced by the presence of the three-membered ring; thus, epoxides undergo ring-opening reactions with alcohols to give β -alkoxy alcohols [1,2], which may result in valuable organic solvents or be used as a synthetic route for the synthesis of relevant compounds such as antitumorals or immunosuppressives [3].

It is also possible to synthesize amino alcohols by the amination of epoxides, where the cleavage of the C–O bond occurs in the presence of an amine. β -Amino alcohols are of growing importance for the pharmaceutical industry for their role as treatment agents of several human disorders [4–6].

Among the possible synthetic approaches yielding these products, the ring opening reaction appears as a very attractive method due to its simplicity leading to the corresponding β -substituted alcohols in high yields.

Suitable epoxide ring opening catalysts include Lewis acids and bases, Brönsted acids, porphyrin complexes [1], triflates [7] and perchlorates [8] in homogeneous phase. Heterogeneous catalysts have also been reported among them polymer supported ferric chloride [9], aluminumdodecatungstophosphate [10] and AlKIT-5 [11].

Other methods used include electrochemical reaction with triorganylborane [12] and microwave assisted synthesis [13–15].

All these catalysts used in the alcoholysis or aminolysis of epoxides show some disadvantages such as high reaction temperature, prolonged reaction time, non-catalytic nature of the reagent, low conversion and low regioselectivity. Furthermore, some of them may become explosive, are expensive, need special conditions for their preparation and, in homogenous phase, have some problems for the separation, isolation and purification of the product. Thus, the development of new catalytic methods for the reaction under study is highly desirable.

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In recent years, heterogeneous catalysts [16,17] and among them activated carbon [18,19], have attracted much attention as catalysts for various organic transformations as well as process related to fine-chemical synthesis in the scope of green chemistry.

Activated carbons with microporous structure have been employed successfully in several catalytic reactions [20–24].

However, mesoporous carbon has the advantage of presenting meso and macro porous [25] which may result in more efficient selectivity toward products.

Otherwise, carbon gels are inexpensive materials and have relatively simple synthesis, so these porous materials are important heterogeneous catalysts that display very interesting features about their structural characteristics because they are very sensitive to the conditions used during gel synthesis and processing [26,27].

Even though carbon gels are obtained through different procedures, the preparation has to account for 3 phases: gel synthesis, with the formation of a three-dimensional polymer in a solvent; gel drying, for removing the solvent; and pyrolysis under an inert atmosphere to form the porous carbon material. Resorcinol-formaldehyde (RF) aqueous gels are among the most studied systems [28]. Several thermal and chemical processes can be used to tailor the porous structure and the type and concentration of specific oxygen surface groups.

In this context we report here the ring opening reaction of epoxides by alcohols and amines using mesoporous activated carbon functionalizated with sulfonic acids as efficient and environmentally friendly heterogeneous catalyst.

2. Experimental

2.1. Preparation of the catalysts

All reagents and solvents used in the preparation of RF aqueous gels and surface functionalization of the carbon xerogels were purchase from Aldrich and used as received.

The catalysts samples were prepared according Lin and Ritter [29] by sol-gel technique. In more detail, solution containing 5% (w/v) solids was prepared, in which the R/F mole ratio was fixed at 1:2 and the R/C (resorcinol/sodium carbonate) mole ratio was fixed at 50:1. The initial pH of the solution was adjusted to 6.10-6.20 with diluted HNO₃. After curing for one week in an oven at $85 \,^{\circ}$ C the washed gel was dried under N₂ atmosphere using a heating rate of 0.5°C/min until 65°C and then held there for 5h. Subsequently, it was heated to 110°C and then held there for another 5 h. Finally, the carbon xerogel was formed by pyrolysis of the dried gel at 800 °C for 3 h in a N₂ atmosphere with both heating and cooling rates set at 0.5 °C/min (CM). The carbon xerogel (CM) was refluxed with a nitric acid solution (13 M) for $6 h (1 g/20 cm^3)$ then washed with deionized water in soxhlet until pH 7 and then dried in oven at 110°C (carbon CMN).

The oxidized carbon (**CMN**) was heated at $150 \degree$ C with concentrated sulfuric acid solution (1 g Carbon/20 cm³ sulfuric acid solution) for 13 h under N₂ atmosphere, washed with deionized water in soxhlet until pH 7 and then dried in oven at 110 °C (carbon **CMNS**).

2.2. Characterization of the catalyst

 N_2 adsorption. Textural characterization was performed by N_2 adsorption at 77 K on an ASAP 2010 V1.01 B Micromeritics. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions were obtained from desorption branch of the nitrogen

isotherms by Barrett–Joyner–Halenda (BJH) method. The mesoporous volume was obtained by DFT method using a micromeritics software DataMaster version 4. Microporous volume and mesoporous surface area were determined by the *t*-method, using a standard isotherm proposed by Greeg and Sing [30].

Temperature-programmed desorption analyses (TPD-MS) were carried out using a Micromeritics TPD/TPR 2900 instrument, with the evolution of CO (m/z 28) and CO₂ (m/z 44) being monitored by mass spectrometry using a Fisons MD800 (Leicestershire, UK) instrument. Prior to analysis, the sample (ca. 50 mg) was placed in a fixed bed U-shaped quartz tubular micro-reactor and dried at 383 K in flowing He, overnight. The temperature was then increased at a rate of 10 K/min to 1273 K, under a flow of helium (25 cm³/min, 0.1 MPa).

Chemical composition. Elemental analysis of the carbons was carried out in a CHNS Analyser (Thermofinnigan Flash, EA, 1112 series). Oxygen content was obtained by the difference between the total percentage (100 wt%) and the sum of percentages (wt%) of nitrogen, carbon, hydrogen and sulfur.

Carbon acidity. The pH at the point of zero charge (pH_{PZC}) was determined by reverse mass titration, following the method proposed by Noh and Schwarz [31].

XPS measurements. The XPS instrument used was an XSAM800 (Kratos) X-ray spectrometer operated in the fixed analyzer transmission mode, with a pass energy of 20 eV, and the non monochromated Mg K α X-radiation ($h\nu$ = 1253.7 eV). Power was 130 W (13 V × 10 mA). Details about data acquisition and treatment can be found elsewhere [32]. For quantitative purposes, the following sensitivity factors, provided by Kratos, were used: C 1s: 0.25; O 1s: 0.66.

2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor with reflux, at different temperatures. In a typical experiment, the reactor was loaded with 3 cm³ of alcohol, 1.5 mmol of styrene oxide and 0.1 g of catalyst.

Particle sizes of the catalysts were maintained between 25 and 20 mesh, since preliminary tests with smaller particle sizes revealed no change in conversion. Stirring rate was kept at high values (>1000 rpm) to minimize external mass transfer limitations.

Samples were taken periodically and analyzed by GC, using a KONIC HRGC-3000C instrument equipped with a $30 \, m \times 0.25 \, mm$ DB-1 column.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the textural characterization of the carbon samples. The synthesized carbons present a nitrogen adsorption-desorption isotherm type IV (according to IUPAC nomenclature) with a type H3 hysteresis loop typical of materials with mesoporosity. However they can also be considered as a combination of type I and type IV isotherms [26,33].

The two catalysts were prepared in consecutive batches, starting from the same initial carbon followed by the treatment with nitric acid and then sulfuric acid.

The textural properties of the different samples were not modified significantly by the two treatments. The oxidation of the carbon with nitric acid had no meaningful effect on the BET area, but some decrease of the mesoporous volume is observed. This may be due to the presence of functional groups in the entrance of the pores blocking the accessibility. In any case Fig. 1 shows that the oxidation step does not change the size of the mesoporous [34]. The

Table I	
Textural	properties

Catalyst	S _{BET} (m ² g ⁻¹) BET	$V_{ m micro} (m cm^3 g^{-1})$ t method	V _{meso} (cm ³ g ⁻¹) DFT Method	V _{macro} (cm ³ g ⁻¹) V _{total} – V _{micro} – V _{meso}	V _T (cm ³ g ⁻¹) Gurvitsh	D _p (Å) BJH method
СМ	771	0.18	0.5	0.08	0.76	65.4
CMN	760	0.19	0.32	0.08	0.59	51.6
CMNS	797	0.20	0.51	0.08	0.79	74.5



Fig. 1. Pore size distribution by BJH method desorption branch.

posterior treatment with concentrated sulfuric acid may have caused the formation of new pores and the widening of existing pores which explains the difference in the pore size distribution obtained for catalyst CMNS.

The surface chemistry was characterized by TPD-MS, elemental analysis, XPS and pH_{PZC} . The results summarized in Table 2 show that there is an increase of the total amount of oxygen in the sample treated with the HNO₃ meaning that the surface oxidation was successful. When treated with sulfuric acid the value of pH_{PZC} of the resulting catalyst is smaller indicating an increase in acidity. This effect is probably not due to the increase of oxygen but to the presence of sulfonic groups at the surface which were detected using XPS (BE = 168.5 eV).

The O/C ratio detected by XPS is just slightly smaller than the value obtained by elemental analysis. This means that it was possible to obtain material presenting a homogeneous distribution of the oxygen groups throughout the carbon, although some oxygen may be located inside the pores and was not accessible for detection by XPS. After peak fitting of the XPS C 1s peak, it was possible to establish the presence of different carbon containing groups, Fig. 2. The major contribution is from the peak at binding energy 284.8 eV which can be assigned to a mixture of C–C bonds of the graphite-like structure of the carbon ($BE \cong 284.3 \text{ eV}$) [35], and the C–C and C–H groups involving sp³ carbon atoms ($BE \cong 285.0 \text{ eV}$) [36]. The other 4 peaks can be assigned to different oxygen containing functional groups present in the surface of the catalysts. The peak centered at $286.6 \pm 0.2 \text{ eV}$, has the second largest contribution and is attributed to the C–O bond in alcohols and/or ethers. The other components can be associated to C=O and/or O-C-O at $288.4 \pm 0.2 \text{ eV}$ to more oxidize species such as OC=O in carboxylic acids and/or esters and, finally, at 291.9 \pm 0.2 eV, the $\pi \rightarrow \pi^*$ excitation associated to the graphitic carbon.

Table 2

Surface chemistry characterization.

Sample	O/C XPS (atomic ratio)	O/C EA (atomic ratio)	Total oxygen EA (at.%)	pH _{PZC}
СМ	0.06	0.075	6.3	9.7
CMN	0.20	0.25	16.0	3.2
CMNS	0.19	0.29	20.2	2.4

The TPD analysis of the samples is presented in Fig. 3. From the deconvolution of TPD curves presented in Fig. 3a and b into the various contributions from the different surface groups following the method presented in previous reports [37,38], it is possible to obtain the summarized conclusions (Fig. 3c). The results obtained with TPD are in guite accordance with the XPS and AE analysis. There is a great difference in the chemical surface characteristics between the original carbon and the modified ones. A pronounced increase in the functional group content of the samples after oxidation with HNO₃ was observed. Phenols and carboxylic groups are the most abundant species in the surface of the oxidized carbons and are responsible for the acidity of the sample [39]. However the carbon functionalized with sulfonic groups (CMNS) exhibits smaller amount of carboxylic acids which confirms that the increase in acidity is due to the presence of sulfonic anchored groups. The decomposition of the sulfonic groups was detected as SO_2 (*m*/*z* 64) above 530 K.

3.2. Catalytic study

3.2.1. Alcoholysis of epoxides

Mesoporous carbons CMN and CMNS were tested as catalysts in the ring opening reaction of epoxides. The effect of different reaction conditions on conversion and selectivity was evaluated. In general, when epoxides react with an alcohol, two different reaction products can be obtained (Scheme 1). Traditionally these are considered to be $S_N 2$ type reactions, where the alcohol attacks the most substituted carbon in the case of the split of the epoxide catalyzed by acid or attacks the less substituted carbon in the case of the split catalyzed by base, resulting in two different products.

In order to compare our results with those reported in the literature it was carried out an experiment at room temperature using styrene oxide and ethanol. For both catalysts, CMN and CMNS, high conversions and good selectivity are observed, being 2-ethoxy-2-phenylethanol (1b) the major product. For catalyst CMNS only 30 min of reaction time at room temperature attained almost 100% conversion, selectivity to **1b** being 97%. Duran-Valle et al. [40] reported that for microporous carbon treated with a sulfonitric acid mixture, the total conversion for the compound 1b was obtained only after 1 h of reaction time. These results reflect the catalytic enhancement due to the changes in the textural characteristics of the catalyst such as pore size, suggesting that they play an important role on promoting the accessibility to the active centers of the catalyst. On the other hand the value of selectivity remained very high meaning that it was possible to favor conversion with no lost in selectivity. It is important to note that the mesoporous carbon with no surface oxidation treatment revealed no activity in this reaction.

When comparing the two catalysts developed, although both of them are active in the ring opening reaction, the functionalized carbon with sulfonic groups, CMNS, presents higher reactivity. While the reaction between styrene oxide and butanol at 80 °C catalyzed by CMN presents 99% of conversion and 83% of selectivity to compound **1b** during 180 min of reaction time, when using CMNS the corresponding product was isolated with analogous conversion and selectivity in only 15 min (Table 3). These results seem to indicate a direct influence of the active sites present in the catalyst. According to TPD results, the main difference in the oxidized groups between



Fig. 2. XPS spectrum of the samples CMN and CMNS displaying the C 1s peak after peak fitting (BE = $284.8 \pm 0.2 \text{ eV}$, BE = $286.6 \pm 0.2 \text{ eV}$, BE = $288.4 \pm 0.2 \text{ eV}$, BE = $290.0 \pm 0.2 \text{ eV}$ and BE = $291.9 \pm 0.2 \text{ eV}$).



Fig. 3. TPD study of the 3 mesoporous carbon. (a) CO TPD spectra of CM, CMN and CMNS; (b) CO₂ TPD spectra of CM, CMN and CMNS; (c) amount of oxygen containing surface groups determined by integration of the TPD deconvoluted curves.



Scheme 1. Reaction of epoxides with alcohols.

Table 3

Ring opening of substituted epoxide with different alcohols. Effect of the alcohol chain.

Epoxide	Alcohol	<i>T</i> (°C)	Time (min)	Conversion (%)	Selectivity to b (%)
°	EtOH	r.t. 50 80	30 15 5	99 99 99	97 96 94
°	1-PrOH	r.t. 50 80	60 30 15	99 99 99	97 99 91
	1-BuOH	r.t. 50 80	60 30 15	99 99 97	92 95 84
	i-PrOH	50	30/60	70/97	95/84
∩ [°]	Ciclohexanol	r.t. 50 80	24 h 180 45	78 99 94	100 100 83
₩	EtOH	r.t. 80	120 30	89 99	100 100
СН3	EtOH	r.t. 80	24 h 4 h	38 97	57 52

Conditions: catalyst CMNS 0.1 g, 3 ml of alcohol, and 1.5 mmol of epoxide.

CMN and CMNS, apart from the presence of sulfonic groups, is the amount of carboxylic groups. The carbon modified with sulfonic groups presents a lower value of carboxylic groups then CMN and all the other functional groups are present in a comparable value. As so, a decrease in activity should be expected, but on the contrary, the observed increase in activity must be due to the new sulfonic groups (strong acids) introduced in the structure, even if present in only small amount.

In order to study the influence of the alcohol hydrocarbon chain in the ring opening reaction different alcohols were tested. Table 3 shows the results obtained for linear or branch alcohols at different temperatures using CMNS as the most efficient catalyst for this transformation. Then, the three linear alcohols lead to quantitative conversions, selectivity to compounds 1b-3b being in a range of 84-99%. Comparing the results obtained at the same temperature, as the alkyl group of the alcohol becomes bulkier, the time of reaction increases probably because of the lower diffusion rate of the corresponding reagents and products. This reactive behavior is much more pronounced when starting from branched alcohols such as *i*-propanol or cyclohexanol. Thus, the reaction of styrene oxide and *i*-propanol at 50 °C affords the corresponding alkoxy alcohol 4b in 70% of conversion and high selectivity (95%) after 30 min of reaction time. Remarkably an increment of the reaction time, additionally 30 min, produces an increase of conversion, as expected, but also decreases the selectivity. Due to the six member ring present in the cyclohexyl alcohol, this substrate exhibits the lowest reactivity; in all studied cases at different temperatures, it was necessary the use of longer reaction times to give conversions higher than 78% and also high selectivities. It suggests that alcohols with larger molecular sizes exhibit higher steric hindrance to access to the active sites present in the porous structure of the carbon. Nevertheless, there were no significant changes in the selectivity between all 5 alcohols.

The effect of temperature on the conversion and selectivity for the reaction under study was also evaluated. For the same alcohol, an increase of the temperature reaction generally reduced the time necessary to achieve the same conversion values, but a negative effect on the selectivity was observed. This effect can be explained considering a S_N2 borderline mechanism for the ring opening reaction as shown in Scheme 2. First step consisting of the protonation of oxygen atom of the epoxide leading to the intermediate specie (I); nucleophilic attack on (I) occurs through the best carbon accommodating the positive charge, in this particular case the carbon supporting the phenyl group, promoting the ring opening of the epoxide giving compounds 1b-5b at lowest temperatures. Delocalization of positive charge on the aromatic group, Ph, supposes the additional stabilization of the intermediate specie. However, at the highest temperature, 80°C, it is possible the formation of the compounds a due to additional energetic requirements (Scheme 2). Thus, optimum reaction conditions may represent a compromise between reaction time, selectivity and temperature, so that the desired products **b** can be obtained in as mild conditions as possible.



1a-5a

Scheme 2. S_N2 mechanism on ring opening reaction of styrene oxide.

Table 4	
Effect of catalyst amount in the reaction of styrene oxide and <i>n</i> -butanol.	
	_

Entry	Amount of catalyst (mg)	Conversion (%)	Selectivity to 3b (%
1	25	4	74
2	50	6	74
3	100	97	84

Conditions: catalyst CMNS in the reaction of styrene oxide with *n*-BuOH at 80 $^\circ$ C, during 15 min.

In order to widen the scope of the study, the ring opening reactions of other two epoxides with ethanol were evaluated. For cyclohexene oxide the reaction proceeds with high conversion and rather small reaction times even at room temperature affording compound **6b** with total selectivity. However, when 1,2-epoxihexane was used, the reaction requires higher reaction temperature and the selectivity drops drastically.

As mentioned above, in both cases the lower reactivity observed for both epoxides, cyclohexene oxide and 1,2-epoxihexane, is probably due to the diffusion problem of the reagents and products. The lowest selectivity to product **7b** in the case of using 1,2epoxihexane, it is probably related with small differences of the activation barrier for both pathways. Thus, substitution over the three member ring is an important limiting factor influencing both the conversion and selectivity to products for the reaction. In this sense, while Ph group stabilizes the intermediate specie **(I)** affording preferentially compounds **1b–5b** regardless the alcohol used, the substitution by a alkyl chain affects the conversion and selectivity of the reaction leading to mixtures of compound **7a** and **7b** and therefore observing a decrease of the selectivity (approximately 50%).

The optimum catalyst amount was studied in the reaction of styrene oxide with *n*-BuOH, using different amounts of catalyst, CMNS, at 80 °C (Table 4). The 3 different amounts of catalyst used did not modify notably the selectivity but have a significant impact on the conversion. Using 25 or 50 mg (entries 1 and 2) results were in very low yields, however an increase for 100 mg shows a total conversion of 99% with the highest selectivity to compound **3b**. In view of these results, the amount of catalyst used in this study was fixed at 100 mg.

According to the mechanism presented in Scheme 2 it is necessary to occur the adsorption of styrene oxide on the active sites, similarly to an Eley–Rideal mechanism. Due to the hydrophilicity of the catalyst surface, the alcohol in excess adsorbs on the active sites and will act as a weak acid. This may explain the lower values of conversion observed with lower amounts of catalyst. When the catalyst loading increases, there are more active sites available and the styrene oxide adsorption is favored leading to higher conversion.

Considering that one of the most important features of heterogeneous catalyst is easy recover and possible reutilization, it is very important to assess this characteristics. Reutilization studies were performed with both catalysts where CMNS and CMN stability and reusability were evaluated. For this purpose, 3 different catalytic runs were carried out reacting ethanol and styrene oxide at room temperature, using the same catalyst sample. A drop in conversion was observed, and both catalysts lost 60% of its activity probably because of the esterification reaction of the acidic groups over the catalyst with ethanol. In the second and third consecutive runs the activity presented by catalyst CMNS remained higher than the one for catalyst CMN, indicating that probably the most affected groups by deactivation are the carboxylic groups present in both catalysts as mentioned earlier in the TPD analysis.

In the third reutilization of sample CMNS the drop in activity was not very pronounced, suggesting that there are still active sites in the catalyst. XPS studies of the CMNS sample after the three reutilization runs showed that the sulfonic groups remain present in the

al	ble	5	

Aminolysis of epoxides. Ring opening of styrene oxide with aniline.

Catalyst	<i>T</i> (°C)	Time (h)	Conversion (%)
CMN	r.t.	24	49
	80	24	91
CMNS	r.t.	24	46
	80	24	96

Conditions: catalyst 0.1 g, 3 ml of ciclohexane, 1.5 mmol of epoxide, and 1.5 mmol of aniline.



Scheme 3. Reaction of styrene oxide with aniline.

carbon surface even after 3 consecutive runs, indicating that no significant leaching of the sulfonic groups is observed. TPD studies of the catalyst sample CMNS confirmed this result, since it was possible to detect sulfonic groups in the sample. On the other hand, TPD of both catalysts samples after reaction showed a decrease in the amount of carboxylic groups.

Concerning the textural properties, the samples analyzed after reaction revealed a slight increase of the average pore size diameter (91 Å) and a reduction of the microporosity probably due to some blockage of the microporous.

A different approach is to consider the regeneration of the carbon catalyst. When the carbon CMN recovered from the reaction was re-oxidized with nitric acid, the catalyst regained its initial activity and selectivity. Although it seems not profitable to reuse the catalyst directly from the reaction media, the oxidation of the used catalyst proved to be an efficient method for reusability.

3.2.2. Aminolysis of epoxides

The ring opening of styrene oxide with aromatic amines was also studied in the presence of both catalysts, CMN and CMNS. The reaction was carried out in ciclohexane at two different temperatures, room temperature and $80 \degree C$ (Table 5; Scheme 3).

For all these reactions only one product was found. Both catalysts were able to catalyze the amination reaction yielding selectively β -amino alcohol **8c**. Even though the conversion is not very high at room temperature, at 80 °C almost quantitative conversions were obtained after 24 h. For this reaction it seems that the presence of the sulfonic groups is not so important for the aminolysis reaction as for the alcoholysis since no significative difference was observed between the two catalysts.

4. Conclusions

Mesoporous activated carbon proved to be effective catalysts for the ring opening reaction of epoxides affording the corresponding β -substituted alcohols with high conversion values and very good selectivity. The mesoporosity of these materials seems to have a significant role on the performance. The introduction of sulfonic groups attached to the surface of the carbon resulted in better catalysts with enhanced activity than the oxidized with nitric acid. Also the application of the catalysts reported here simplifies the experimental procedure, and allows the use of mild conditions for ring opening reactions from epoxides. It was possible to regenerate the catalyst CMN and thus restore the original activity. The ring opening reaction with amines, although not so effective, was also catalyzed by the mesoporous carbon catalysts.

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