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Transition-metal-free microporous and mesoporous catalysts for the epoxidation of cyclooctene with hydrogen peroxide

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Abstract

Transition-metal-free microporous and mesoporous materials were studied as heterogeneous epoxidation catalysts. MCM-41-type materials and zeolites with various porous structures and aluminium or gallium content but devoid of any transition metal were prepared and tested in the epoxidation of cyclooctene with aqueous hydrogen peroxide. The most promising catalytic results were obtained with Al-MCM-41, Ga-MCM-41, and ultra-stable zeolite Y (USY) with a low Si/Al ratio. All of these catalysts have acid sites of moderate strength. With Ga-MCM-41, 95% conversion of cyclooctene with 96% selectivity toward the epoxide was reached after 24 h of reaction. The catalyst could be recycled with no loss of catalytic properties.

Keywords: Cyclooctene epoxidation; H_2O_2; Transition-metal-free heterogeneous catalysts; Ga-MCM-41; Sustainable process

1. Introduction

The catalytic epoxidation of alkenes is a reaction of great industrial interest given the numerous applications of epoxides as precursors in the production of fine chemicals [1]. The ideal catalyst for this reaction should have high activity and selectivity with a wide range of substrates, use aqueous H_2O_2 as an oxidant, be stable and easy to separate from the products, and operate in environmentally acceptable solvents. Several heterogeneous catalysts fulfilling many of these criteria have been reported to date [2–9]. In general, these catalysts contain transition-metal centres either as substituents in the framework or as adsorbed or immobilised species. However, each of these catalysts has some limitation related to the scope of alkenes that it can epoxidise or to leaching of transition metals during the epoxidation process. Therefore, the development of a transition-metal-free heterogeneous catalyst for the epoxidation of alkenes with hydrogen peroxide is a timely research subject from both an environmental and an economic standpoint.

Recently, it has been discovered that different aluminium and gallium oxides show promising catalytic performance in the epoxidation of alkenes with aqueous hydrogen peroxide [10–13]. The proposed active centre is a surface hydroperoxide (Al–OOH or Ga–OOH) obtained by reaction of surface hydroxyls (Al–OH or Ga–OH) with H_2O_2 [14]. The latter surface centres are also present in aluminosilicates and gallosilicates, which thus could display catalytic activity in epoxidation reactions. Crystalline microporous materials, such as zeolites, and ordered mesoporous materials, such as MCM-41, which can be prepared with Al or Ga partially substituting for Si in the framework, are particularly interesting candidates in this respect [15–17]. The ordered structures of these materials are expected to provide catalysts with higher stability than aluminium and gallium oxides, which deactivate on recycling [10,18]. Aluminium- and gallium-substituted MCM-41 and a number of aluminium-containing zeolites were investigated as heterogeneous catalysts for the epoxidation of *cis*-cyclooctene with aqueous H_2O_2 (Scheme 1).

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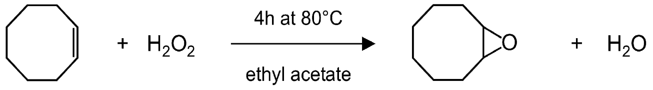

Scheme 1. Epoxidation of cyclooctene with hydrogen peroxide.

2. Experimental

2.1. Materials

Al-MCM-41 and Ga-MCM-41 were prepared according to two similar methods, derived from procedures described previously [19,20]. First, 9.85 g of a 25 wt% solution of tetramethylammonium hydroxide (TMAOH) in H_2O was added to 56.30 g of deionised H_2O. Next, 7.77 g of an aqueous solution of sodium silicate (27 wt% SiO_2, 8 wt% Na_2O) was added while stirring. Then a 25 wt% aqueous solution of cetyltrimethylammonium bromide (CTABr), prepared by dissolving 9.84 g of CTABr in 29.52 g of deionised H_2O, was slowly added while stirring, followed by the slow addition of 3.91 g of SiO_2 as Cab-O-Sil M-5 fused silica. The white diluted gel was stirred for 30 min. The solutions of the Al or Ga precursors were prepared by dissolving either 3.33 g of aluminium sulfate, $Al_2(SO_4)_3$, or 2.73 g of gallium nitrate hydrate, $Ga(NO_3)_3{\cdot}xH_2O$, in 10 g of deionised H_2O (for Al-MCM-41 and Ga-MCM-41, respectively). The aqueous solution of the Al or Ga precursor was slowly added to the diluted gel, and stirring was continued for 40 min. The molar composition of the final gel was $1SiO_2{:}0.20NaOH{:}0.27TMAOH{:}0.27CTABr{:}60H_2O{:}0.05Al_2O_3$ (or Ga_2O_3). The gel was aged for 20 h. Then aqueous H_2SO_4 (1 N) was added to the gel until a pH value of ∼11.5 was reached for the Al-sample and a pH value of 10.5–11 was reached for the Ga sample. The white gel was placed in a stainless steel autoclave and heated for 3 days in an oven at 150 °C. The white product was filtered under vacuum and washed with 1 L of deionised H_2O, dried at 100 °C for 16 h, and then calcined at 550 °C for 8 h (from 25 to 550 °C at 2 °C/min).

Zeolite NaY (FAU), ultra-stable zeolites Y (FAU) with different Si/Al ratios, and beta zeolites (BEA) were obtained from PQ Zeolites: NaY (CBV 100, Si/Al = 2.6), $USY_{(2.6)}$ (CBV 600, Si/Al = 2.6), $USY_{(6)}$ (CBV 712, Si/Al = 6), $USY_{(15)}$ (CBV 720, Si/Al = 15), NaHBeta (CP 806-B25, Si/Al = 12.5), and HBeta (CP 811-BL25, Si/Al = 12.5). Before use, the zeolites were calcined at 550 °C for 2 h (from 25 to 550 °C at 5 °C/min).

AlPO-5 (AFI) was prepared in an ice bath under continuous stirring from H_3PO_4 (85 wt%), tripropylamine (⩾98%), aluminium isopropoxide (⩾98%), and bi-distilled water. First, 4.86 g of Al-isopropoxide was slowly added to 85.67 g of water under continuous stirring. Then 2.74 g of H_3PO_4 was added to this solution. Finally, 2.04 g of template was introduced dropwise. The molar composition of the final gel was $1Al_2O_3{:}1P_2O_5{:}1.2Pr_3N{:}400H_2O$. After another 15 min of stirring, the gel was loaded into a stainless steel autoclave. The crystallisation was carried out dynamically under autogenous pressure for 14–15 h at 190 °C. Afterward, the autoclaves were quenched, and the crystals were centrifuged at 1000 rpm, washed thoroughly with bi-distilled water, and then dried at 60 °C for 24 h. To remove the template, the sample was calcined at 550 °C for 14 h (from 25 to 550 °C at 2 °C/min). The formation of the desired AFI structure was confirmed by powder XRD analysis.

VPI-5 (VFI) was prepared as described previously [21]. First, 10.92 g of pseudoboehmite was mixed with 32.40 g of bi-distilled water. Then 18.15 g of H_3PO_4 (85 wt%), diluted in 21.60 g of bi-distilled water, was added dropwise under continuous stirring. This mixture was aged at 95 °C for 25 min and then at room temperature for 165 min under gentle stirring, after which 16.67 g of tributylamine (99%) and 2.36 g of dipentylamine (99%) were added dropwise as templates. Finally, 2.25 g of Ludox AS-40 (40 wt% suspension in water) was added at once. The molar composition of the final gel was $1Al_2O_3{:}1.05P_2O_5{:}1.2but_3N{:}0.02DPTA{:}0.01SiO_2{:}40H_2O$. The hydrothermal treatment was carried out statically at 150 °C for 18 h. The solid was then centrifuged at 10,000 rpm, washed thoroughly with bi-distilled water, and dried at 40 °C. The formation of the desired VFI structure was confirmed by powder XRD analysis. Small amounts of template were present in the final material as counterions for the Si atoms partially substituting for P in the framework, as confirmed by thermogravimetric analysis (TGA) on a TA Instruments Q500 at 25–900 °C (heating rate, 10 °C/min) under flowing O_2.

2.2. Characterisation

Powder XRD patterns were measured on a STOE Stadi P instrument using $CuK\alpha_1$ radiation ($\lambda = 0.154$ nm). Data were recorded with an image plate detector in transmission mode with a resolution of 0.030° (acquisition time, 60 s). Nitrogen adsorption–desorption isotherms were measured at 77 K on a Micrometrics Tristar 3000 surface area and porosimetry analyser. The samples were treated at 250 °C under N_2 flow for 6 h before analysis. ^{27}Al MAS NMR spectra were recorded on a Bruker DSX400 spectrometer (9.4 T). The samples were packed in 2.5-mm Zirconia rotors. A total of 12,000 scans were accumulated with a recycle delay of 100 ms. The spinning frequency of the rotor was 20 kHz. A 0.1 M aqueous solution of $Al(NO_3)_3{\cdot}9H_2O$ was used as a shift reference. Elemental analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin–Elmer Optima 3000DV. Before this analysis, the samples were dried at 140 °C for 24 h.

2.3. Catalytic tests

To allow comparison of the results obtained with the different materials as a function of the number of Al or Ga centres, the same total amount of Al or Ga was used in all catalytic experiments (0.5 mmol per sample) [22] except those with low catalyst concentration (see below). This approach implies that different amounts of each catalyst were used, under the assumption that mass transfer is not strongly affected by the volume of sample.

The catalysts were tested for their activity in the epoxidation of cyclooctene with hydrogen peroxide using similar conditions to those reported previously for testing aluminium and gallium oxides [10,12]. 1.25 mmol of *cis*-cyclooctene (95%), 0.625 mmol of di-*n*-butyl ether, 2.73 g of ethyl acetate, and either 2.50 or 12.50 mmol of hydrogen peroxide as a 50 wt% aqueous solution were added to each sample. For the experiments with low catalyst concentration, 0.625 mmol of *cis*-cyclooctene (95%), 0.313 mmol of di-*n*-butyl ether, 1.36 g of ethyl acetate, and 6.25 mmol of 50 wt% aqueous hydrogen peroxide were added to an amount of catalyst containing 0.05 mmol of Al or Ga [22]. First, a solution of cyclooctene and di-*n*-butyl ether in ethyl acetate was added to the solid catalysts while stirring, followed by addition of the aqueous solution of hydrogen peroxide. Both solutions were dispensed using an automated HTE workstation [10]. The samples with lower H_2O_2 concentration are biphasic (the solid catalyst and a liquid solution); those with higher H_2O_2 concentration, triphasic (the solid catalyst and a biphasic liquid system). The samples were stirred for 4 h at 500 rpm and 80 °C in capped vials placed in a parallel HTE reaction block [10]. The rubber septa of the caps were pierced with a sharp needle to prevent formation of overpressure inside the reactors.

Cyclooctene conversion (X, %), epoxycyclooctane and byproducts yield (Y, %) and selectivity (S, %) were determined by gas chromatography (GC) analysis using an Interscience Finnigan Trace GC Ultra equipped with a RTX-5 fused silica column (10 m, 0.1 mm). The analysis time for each sample was of 2.25 min. The temperature profile during the analysis was 45 s at 70 °C, 70 to 250 °C at 180 °C/min, and 30 s at 250 °C. Before GC analysis, the samples were centrifuged for 5 min at 3000 rpm. An aliquot of the reaction mixture (~0.3 ml) was added to an equal volume of decane; any H_2O that might be present in the sample would separate in a phase at the bottom of the GC flask and be removed before injecting the sample into the chromatograph. The conversions and yields were calculated by normalising the areas of the GC peaks by means of the area of the internal standard peak (di-*n*-butyl ether).

Gas chromatography–mass spectrometry analysis (GC–MS) on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer was used to identify the byproducts of the epoxidation reaction. The GC was equipped with a WCOT fused silica column (30 m, 0.25 mm) coated with a 0.25-µm-thick HP-5 MS film. The temperature program was analogous to that employed for the GC analysis.

For the recycling of the catalysts, first the reaction solution was removed from each sample, then 7 ml of ethanol was added to each vial, and the samples were stirred for 5 min. The samples were then centrifuged for 5 min at 3500 rpm to deposit the solid catalyst. The supernatant ethanol solution was removed. The washing procedure was repeated 3 times. Finally, the samples were dried in an oven at 90 °C for 16 h.

The amount of H_2O_2 decomposed in H_2O and O_2 during the catalytic test was determined by titration of the reaction solution (after 4 h at 80 °C) with a 0.1 M solution of $Ce(SO_4)_2$. The 0.1 M solution of $Ce(SO_4)_2$ was prepared by dissolving $Ce(SO_4)_2 \cdot 4H_2O$ (50.0 mmol) in H_2SO_4 (28 ml) and bi-distilled H_2O (28 ml), followed by dilution with H_2O to a total volume of 500 ml. The reaction solution was separated from the solid catalyst by centrifugation. Then 10 vol% of the reaction solution was diluted with H_2O (18 ml) and a 7 vol% aqueous solution of H_2SO_4 (2 ml). The colourless solution thus obtained was titrated with the 0.1 M Ce^{IV} solution until it turned yellow ($2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2$).

Some of the catalytic tests were performed in duplicate or in triplicate. In such cases, the average values for conversion, yield, and selectivity are reported.

3. Results and discussion

3.1. Characterisation of Al-MCM-41 and Ga-MCM-41

The powder XRD patterns of both Al-MCM-41 and Ga-MCM-41 present a dominant (100) peak typical of MCM-41 materials at $2\theta = 2.05°$ ($d_{100} = 4.31$ nm) and at $2\theta = 1.72°$ ($d_{100} = 5.14$ nm), respectively [19,20]. The textural properties of the two materials were investigated by N_2 adsorption–desorption isotherms (Fig. 1). Both Al-MCM-41 and Ga-MCM-41 exhibited type IV isotherms, typical of mesoporous MCM-41 materials, with a H_3 hysteresis loop [20,23]. The pore size distributions were calculated from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. Both materials display a narrow pore size distribution, centred at 2.6 nm for Al-MCM-41 and at 2.7 nm for Ga-MCM-41. The t-plot of both solids indicates the absence of micropores. The

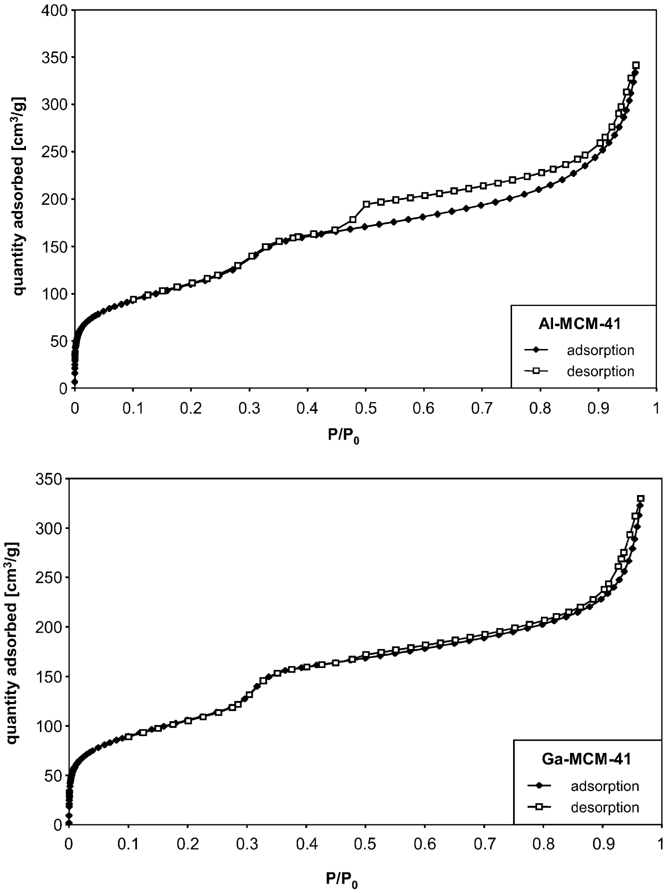

Fig. 1. N_2 adsorption–desoprtion isotherms of Al-MCM-41 (top) and Ga-MCM-41 (bottom).

BET surface area of Al-MCM-41 is 416 m^2/g, while that of Ga-MCM-41 is 390 m^2/g.

3.2. Catalytic results

The microporous and mesoporous materials selected as catalysts for the epoxidation of cyclooctene with hydrogen peroxide are reported in Table 1. These materials were chosen in order to gain insight into and rationalise the effect of various parameters on the catalytic properties. To compare the effect of the type of group 13 element, Al-MCM-41 and Ga-MCM-41 samples were prepared following similar synthesis methods. To investigate the effect of the nature and of the strength of the acid sites, zeolites with the same type of framework (FAU) but different Si/Al ratios were used ($USY_{(2.6)}$, $USY_{(6)}$, and $USY_{(15)}$). To study the influence of Brønsted acidity, zeolites with the same framework

Table 1

Catalytic epoxidation of *cis*-cyclooctene with 50 wt% aqueous H_2O_2 after 4 h at 80 °C with different microporous and mesoporous materials [X = cyclooctene conversion, $Y_{epoxide}$ = epoxide yield, $S_{epoxide}$ = epoxide selectivity]

	Catalyst	Si/Al or Si/Ga	H_2O_2/cyclooctene	X (%)	$Y_{epoxide}$ (%)	$S_{epoxide}$ (%)	*Cis*:*trans* epoxide	Mass balance (%)
1	Al-MCM-41	9.2	2	5.5	5.2	97	1:0	100
2			10	10	10	96	1:0	100
3	Ga-MCM-41	15	2	11	11	98	1:0	100
4			10	20	20	97	1:0	100
5	NaY	2.6	2	0.9	0.2	27	1:0	100
6			10	5.1	4.6	91	1:0	100
7	$USY_{(2.6)}$	2.6	2	10	8.4	88	0.9:0.1	100
8			10	17	15	90	1:0	100
9	$USY_{(6)}$	6	2	24	4.7	46	0.3:0.7	87
10			10	51	10	47	0.6:0.4	70
11	$USY_{(15)}$	15	2	80	7.2	28	0:1	46
12			10	100	0.1	1.0	0:1	11
13	NaHBeta	12.5	2	17	1.9	44	0:1	87
14			10	68	4.6	43	0:1	42
15	HBeta	12.5	2	24	2.3	33	0:1	83
16			10	66	8.8	45	0:1	53
17	AlPO-5	–	2	2.0	1.5	73	1:0	100
18			10	4.2	3.6	86	1:0	100
19	VPI-5	–	2	5.5	4.6	83	1:0	100
20			10	3.9	3.5	89	1:0	100
21	Blank	–	2	0.0	0.0	–	1:0	100
22			10	3.3	3.3	100	1:0	100

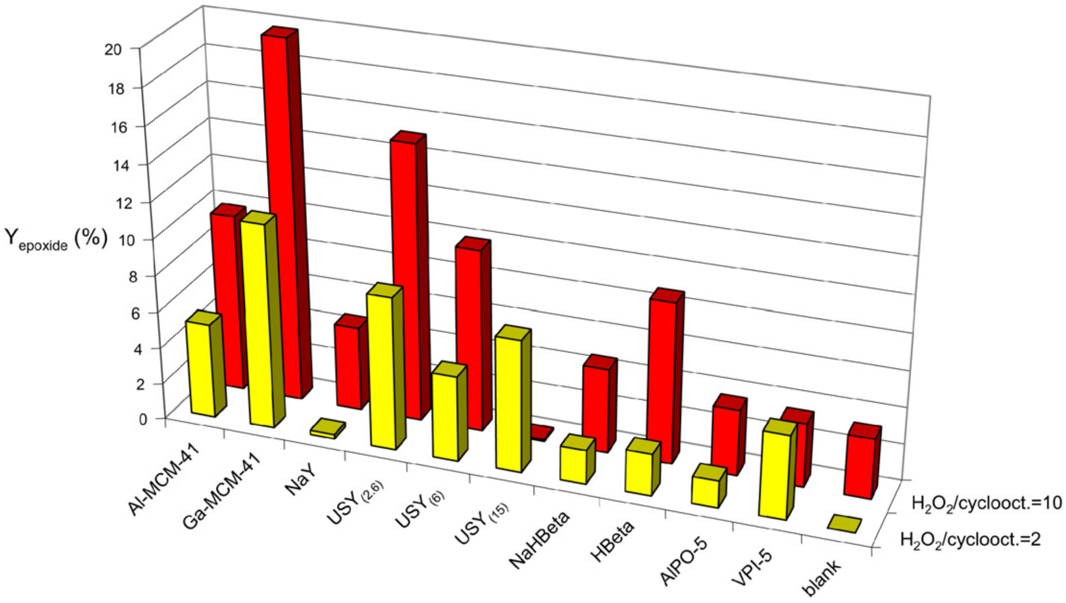

Fig. 2. Epoxidation of cyclooctene with 50 wt% aqueous H_2O_2 catalysed by different Al- and Ga-containing microporous and mesoporous materials [$Y_{epoxide}$ = epoxide yield after 4 h at 80 °C].

type and equal Si/Al ratio but with a different counterion (i.e., Na or H) were used (NaY and USY$_{(2.6)}$, NaHBeta and HBeta). To gain information on the effect of the porous structure, zeolites with similar Si/Al ratios but different framework types were used (USY$_{(15)}$, HBeta). Finally, two crystalline microporous aluminophosphates (AlPO-5 and VPI-5) were selected to explore the catalytic behaviour of this class of frameworks characterised by alternating AlO_4 and PO_4 units and large micropores [24]. All of the chosen materials have pores of sufficiently large size to allow fast diffusion of the reagents and of the epoxide.

The epoxidation activity of the catalysts was tested using two molar ratios of hydrogen peroxide and cyclooctene (2 and 10). The conversion of cyclooctene was higher when a higher oxidant/substrate ratio was used with all of the catalysts except VPI-5, which showed constant low activity in both cases (Table 1). The yields of epoxycyclooctane also improved with the higher oxidant/substrate ratio, with the exception of USY$_{(15)}$ and VPI-5 (Fig. 2 and Table 1). The highest yields in the epoxide were found with the ordered mesoporous materials, Ga-MCM-41 and Al-MCM-41, and with zeolite USY$_{(2.6)}$ (Table 1, entries **2**, **4**, and **8**). The better catalytic results obtained with Ga-MCM-41 compared with Al-MCM-41 are in agreement with those found for the respective oxides [10]. Remarkably, these catalysts are not those that give the highest conversion of cyclooctene, but rather those that convert cyclooctene to epoxycyclooctane with high selectivity. This result can be explained in terms of the acid strength of the Al and Ga centres. Zeolite USY$_{(2.6)}$ has milder acid sites compared with other zeolites with higher Si/Al ratios [25–27]. Mesoporous aluminosilicate MCM-41 has fewer and weaker Brønsted acid sites compared with zeolites with the same Si/Al ratio [19,28,29]. Consequently, it can be concluded that acid sites with moderate strength are needed for the efficient epoxidation of cyclooctene. These sites are suitable for the formation of surface hydroperoxides and are of sufficiently mild acidity to prevent further reaction of the epoxide, which would cause a decrease in the selectivity of the process [14,18]. In principle, the epoxidation activity of USY$_{(2.6)}$ could be related also to extra-framework octahedral aluminium species present in varying amounts in USY zeolites [27]. However, Al-MCM-41 has only a very small amount of octahedral aluminium compared with USY$_{(2.6)}$, as shown by ^{27}Al MAS NMR analysis (Fig. 3) [27,30]. Because these two catalysts are both active in the epoxidation of cyclooctene with H_2O_2, we can infer that the active sites are tetrahedral aluminium species and that extra-framework aluminium plays a minor role, if any, in the catalytic behaviour of zeolite USY$_{(2.6)}$.

Zeolite NaY showed much lower activity compared with the corresponding zeolite in the H form, USY$_{(2.6)}$ (Fig. 2). The catalytic results of NaHBeta and HBeta followed the same trend, although the difference is less marked, probably due to the presence of both Na^+ and H^+ counterions in the NaHBeta zeolite. These results confirm the role of Brønsted acid sites as catalytic active centres in the epoxidation of alkenes with hydrogen peroxide, in agreement with the mechanism proposed for the epoxidation catalysed by aluminium oxide [10]. In view of these considerations, the poor activity of the microporous aluminophosphates AlPO-5 and VPI-5 can be ascribed to their negligible Brønsted acidity.

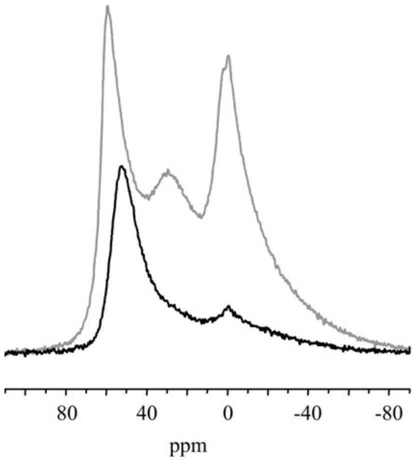

Fig. 3. ^{27}Al MAS NMR spectra of Al-MCM-41 (black) and USY$_{(2.6)}$ (grey). The peak around 60 ppm originates from tetrahedral aluminium located in the framework of the aluminosilicates. The peak around 0 ppm belongs to octahedral aluminium species, which in the case of aluminosilicates are identified as extra-framework species. The peak around 30 ppm, present only in the spectrum of USY$_{(2.6)}$, is assigned either to pentacoordinated or to distorted tetrahedral species [27,30].

When zeolites with Si/Al $\geqslant 6$ (i.e., with stronger acid sites) were used, high conversions of cyclooctene but low yields in epoxycyclooctane, and thus low selectivities, were observed (Table 1, entries **9**–**16**). Along with the epoxide, the main products were 1,2-cyclooctanediol, 1,2-cyclooctanediol diacetate, and 5-hydroxy epoxycyclooctane, that is, products of the further reaction of epoxycyclooctane, which is catalysed by strong acid sites. This behaviour is particularly evident when comparing the results obtained with the USY zeolites with different Si/Al ratios (Table 1, entries **8**, **10**, and **12**); the cyclooctene conversion increased with the value of Si/Al, whereas the selectivity toward the epoxide decreased dramatically. The higher reactivity observed with zeolites with higher Si/Al ratios also explains the decreased yield in the epoxide measured with USY$_{(15)}$ when the oxidant/substrate ratio is increased from 2 to 10. For the catalytic tests performed using zeolites with Si/Al $\geqslant 6$, it was not possible to obtain a good mass balance, in contrast with the total mass balance found with all of the other catalysts used in this work (Table 1). This effect was more pronounced for the catalysts that showed the highest cyclooctene conversion (e.g., **12**), suggesting that in the presence of strong acid sites, polymeric species are produced, which might cause blocking of the zeolite pores [31]. This is in agreement with the GC–MS analysis of the reaction products of catalysts **9**–**16**, which, along with the byproducts mentioned above, showed the formation of dimeric species.

Cis-cyclooctene was used as substrate in all of the catalytic tests reported here [10,12]. Generally, the epoxidation of cyclooctene is a stereoselective reaction even when using the strained *trans*-cyclooctene as substrate [32,33]. Nevertheless, when the epoxidation was performed in the presence of zeolite beta or USY, a product assigned to *trans*-epoxycyclooctane on the basis of the GC–MS analysis was observed. Whereas this compound is present in minor amounts with $USY_{(2.6)}$ as the catalyst, its relative amount increases with $USY_{(6)}$ and it becomes the only epoxide product with $USY_{(15)}$ and with both beta zeolites (Table 1). The formation of the *trans*-isomer can be explained assuming a carbonation intermediate that allows rotation around the C_1–C_2 bond of the substrate [33] and a geometrically constrained configuration on the active site inside the zeolite framework that would favour such rotation.

The mesoporous Ga-MCM-41 and Al-MCM-41 and zeolite $USY_{(2.6)}$ (i.e., the three most promising catalysts identified in this work) were tested again in the epoxidation reaction after washing them with ethanol and drying them at 90 °C to check their stability and reusability (Table 2). All three materials displayed similar activity and selectivity in three successive runs, proving that these catalysts can be successfully recycled. This is a relevant improvement compared to the transition-metal-free aluminium and gallium oxide catalysts, which were reported to undergo deactivation on recycling [10,18]. Surprisingly, the epoxidation activity of the mesoporous catalysts slowly increased on recycling. This effect was clearly observed by performing the catalytic tests with low concentration of catalyst (Table 3). With both Al-MCM-41 and Ga-MCM-41, the cyclooctene conversion after 4 h of reaction with the catalysts recycled three times was considerably higher than with the starting materials, while retaining the high epoxide selectivity. This effect can be explained by the gradual exchange of the Na^+ ions present in the two mesoporous catalysts with H^+ (*vide supra*), as evidenced by ICP-OES elemental analysis of these materials (Table 4). The elemental analysis also shows that neither aluminium nor gallium leached during the catalytic reaction. Small amounts of iron were present at the impurity level in both samples; however, the larger amount of iron present in Al-MCM-41 compared with that in the more catalytically active Ga-MCM-41 indicates that this metal does not contribute significantly to the catalytic activity.

Table 2
Recycling test of Al-MCM-41, Ga-MCM-41, and $USY_{(2.6)}$ as catalysts for the epoxidation of *cis*-cyclooctene with 50 wt% aqueous H_2O_2 [X = cyclooctene conversion; Y_{epoxide} = epoxide yield, S_{epoxide} = epoxide selectivity; conditions: 4 h at 80 °C; H_2O_2/cyclooctene = 10; solvent: ethyl acetate]

Catalyst	Run	X (%)	Y_{epoxide} (%)	S_{epoxide} (%)
Al-MCM-41	1	10	10	96
	2	11	10	94
	3	12	11	95
Ga-MCM-41	1	20	20	97
	2	23	23	99
	3	23	22	98
$USY_{(2.6)}$	1	17	15	90
	2	17	15	90
	3	16	14	89

Table 3
Recycling test of Al-MCM-41 and Ga-MCM-41 as catalysts for the epoxidation of *cis*-cyclooctene with 50 wt% aqueous H_2O_2, using low concentration of catalyst [X = cyclooctene conversion, Y_{epoxide} = epoxide yield, S_{epoxide} = epoxide selectivity; conditions: 4 h at 80 °C; H_2O_2/cyclooctene = 10, solvent: ethyl acetate]

Catalyst	Run	X (%)	Y_{epoxide} (%)	S_{epoxide} (%)
Al-MCM-41	1	6	6	100
	4	8	8	100
Ga-MCM-41	1	7	7	100
	4	11	11	100

Catalysts active in the epoxidation of alkenes with H_2O_2 also may be active in the unwanted disproportionation reaction of H_2O_2 to O_2 and H_2O. The fraction of H_2O_2 decomposed during the epoxidation of cyclooctene with Ga-MCM-41 using a H_2O_2/cyclooctene ratio of 10 was 21%, as determined by titration with Ce^{4+}. This corresponds to a 13% epoxide selectivity on a peroxide basis. The relatively low values found for H_2O_2 decomposition and selectivity toward the epoxide with Ga-MCM-41 compared with other transition-metal-free catalysts [10,11,18] can be explained by the higher oxidant-to-substrate ratio used here.

Finally, the epoxidation reactions catalysed by Ga-MCM-41 and by zeolite $USY_{(2.6)}$ were monitored at different times to gain some insight into the kinetics. With Ga-MCM-41, an almost constant reaction rate was observed, leading to 95% conversion of cyclooctene after 24 h of reaction, while preserving the very high selectivity toward the epoxide (Fig. 4). With the $USY_{(2.6)}$ zeolite, the reaction rate decreased over time, accompanied by a drop in epoxide selectivity (Fig. 5). The main byproducts were the same as those found at shorter reaction times with zeolites with stronger acid sites (*vide supra*). This suggests that as the reaction proceeds, the formed epoxide competes with cyclooctene for the catalytic sites of the $USY_{(2.6)}$ zeolite and partially reacts further. The kinetic behaviour of Ga-MCM-41 and $USY_{(2.6)}$ zeolite demonstrates the differing nature of the two catalysts. $USY_{(2.6)}$ zeolite is expected to have more and stronger acid sites than Ga-MCM-41, which explains its lower epoxide selectivity. On the other hand, the assets of Ga-MCM-41 include the presence of gallium rather than aluminium as active centre and the larger size of the pores in MCM-41 compared with those in zeolites, which can favour diffusion of reagents and products and formation of sterically demanding intermediates.

Table 4
Elemental analysis of Al-MCM-41 and Ga-MCM-41, before the first catalytic test and after the catalysts have been recycled three times

Catalyst	Run	Al (mmol/g)	Ga (mmol/g)	Na (mmol/g)	Fe (mmol/g)	H (mmol/g)[a]	Si/Al or Si/Ga
Al-MCM-41	1	1.61		0.44	0.01	1.17	9.2
	4	1.59		0.31	0.01	1.29	
Ga-MCM-41	1		0.99	0.25	<0.01	0.75	15.0
	4		0.97	0.13	<0.01	0.84	

[a] Difference between the Al (Ga) and Na concentration.

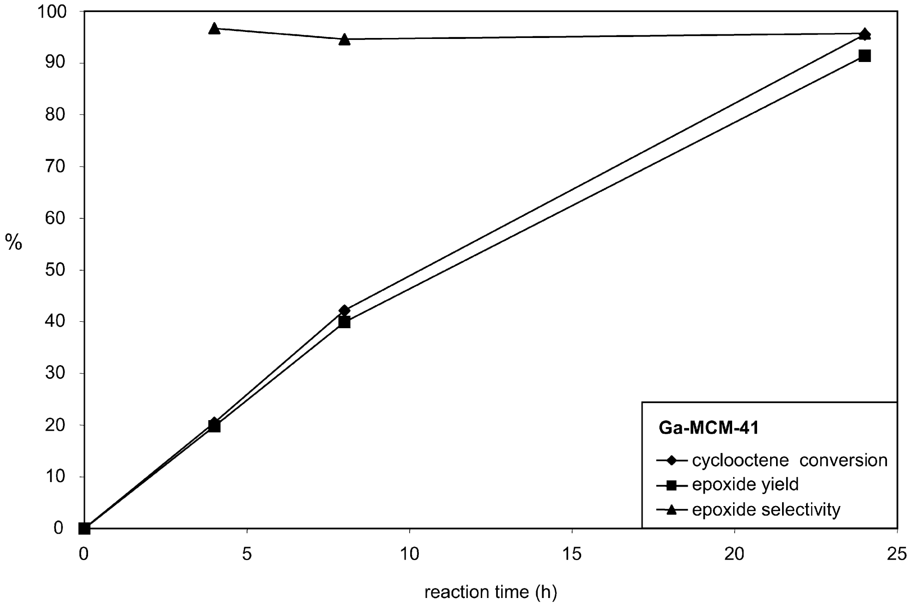

Fig. 4. Cyclooctene conversion, epoxide yield, and selectivity in time with Ga-MCM-41 as catalyst [H_2O_2/cyclooctene = 10].

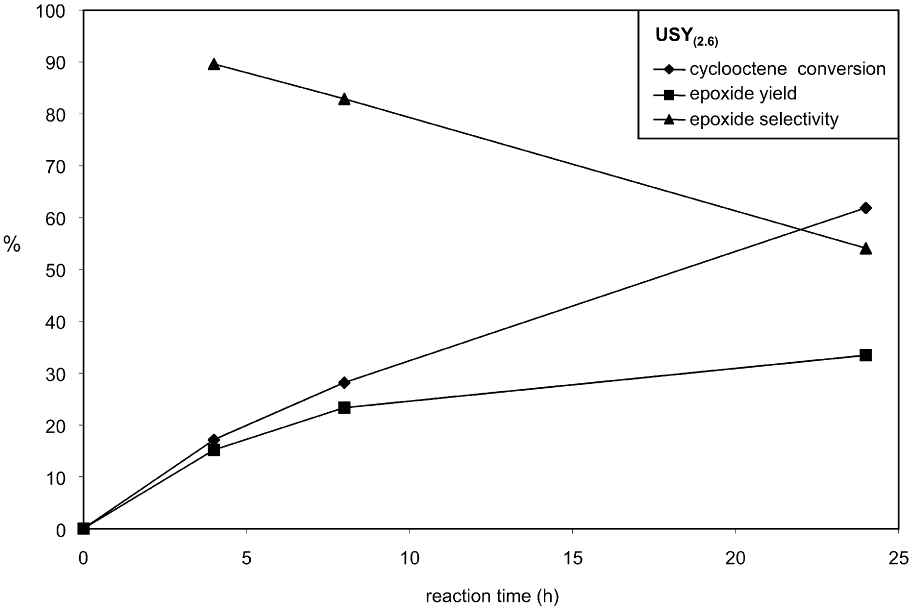

Fig. 5. Cyclooctene conversion, epoxide yield, and selectivity in time with $USY_{(2.6)}$ as catalyst [H_2O_2/cyclooctene = 10].

4. Conclusion

The study of transition-metal-free microporous and mesoporous materials as heterogeneous catalysts for the epoxidation of cyclooctene with hydrogen peroxide led to the identification of Al-MCM-41, Ga-MCM-41, and zeolite USY with a low Si/Al ratio as promising candidates. The best catalytic results were obtained with Ga-MCM-41, which displayed a 91% epoxide yield with 96% selectivity after 24 h of reaction. This material shows good potential for a sustainable epoxidation process, because it does not contain transition metals as catalytic sites, is active with H_2O_2, and is reusable. Its activity is similar to that of aluminium oxides [10] but lower than that of the most active heterogeneous catalysts [2]. However, better catalytic performances can be expected by optimising the reaction conditions during the epoxidation and by exploring other types of microporous and mesoporous materials. Future work will extend the substrate scope of the best catalysts reported here.

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