

Hierarchical Zeolites and their Catalytic Performance in Selective Oxidative Processes

Manuel Ojeda,^[a] Aida Grau-Atienza,^[b] Rafael Campos,^[a] Antonio A. Romero,^[a] Elena Serrano,^[b] Jose Maria Marinas,^[a] Javier García Martínez,^{*[b]} and Rafael Luque^{*[a]}

Hierarchical ZSM-5 zeolites prepared using a simple alkali treatment and subsequent HCl washing are found to exhibit unprecedented catalytic activities in selective oxidation of benzyl alcohol under microwave irradiation. The metal-free zeolites promote the microwave-assisted oxidation of benzyl alcohol with hydrogen peroxide in yields ranging from 45–35% after 5 min of reaction under mild reaction conditions as well as the epoxidation of cyclohexene to valuable products (40–60% conversion). The hierarchically porous systems also exhibited an interesting catalytic activity in the dehydration of N,N-dimethylformamide (25–30% conversion), representing the first example of transition-metal free catalysts in this reaction.

Zeolites form an important family of microporous crystalline aluminosilicates and have been the subject of extensive studies. Owing to properties such as high crystallinity, hydrothermal stability, and acidity, they have found application in fields including adsorption and catalysis.^[1] However, the microporous crystalline frameworks impose a series of inherent limitations, mostly related to diffusional constraints.^[2–5]

Recent efforts have focused on the development of mesoporosity in zeolites, which can widen the applicability of zeolites in reactions with bulky substrates.^[6-20] Desilication by alkali treatment is a simple and extensively investigated approach to introduce mesoporosity.^[6-11,21] The procedure is generally followed by an acid wash to remove the alumina debris formed after silica extraction.^[22]

Acidity is an important property of zeolites. The presence of aluminum leads to the formation of Brønsted (Si–OH–Al) and Lewis (coordinately unsaturated aluminum) sites. These provide various possibilities in acid-catalyzed processes, particular-

[a]	Dr. M. Ojeda, R. Campos, Prof. A. A. Romero, Prof. J. Maria Marinas,
	Prof. R. Luque
	Departamento de Quimica Organica
	Universidad de Cordoba
	Campus de Rabanales, Edificio Marie Curie (C-3)
	Ctra Nnal IV-A, Km 396, 14014 Cordoba (Spain)
	Fax: (+ 34) 957212066
	E-mail: q62alsor@uco.es
[b]	A. Grau-Atienza, Dr. E. Serrano, Prof. J. García Martínez
	Laboratorio de Nanotecnología Molecular
	Departamento de Química Inorgánica
	Universidad de Alicante
	Ap. 99, 03080, Alicante (Spain)
	Fax: (+ 34) 965903454
	E-mail: j.garcia@ua.es
	Supporting Information for this article is available on the WWW under
	http://dx.doi.org/10.1002/cssc.201500124

10.1002/cssc.201500124. isc

1

ChemSusChem 0000, 00, 0-0 Wiley Online Library

These are not the final page numbers! 77

ly useful for the petrochemical industry.^[23-25] In this regard, both microporous and hierarchical (mesoporous) zeolites have been extensively employed in a range of acid-catalyzed processes, including alkylations and acylations as well as, more recently, transformations of biomass-derived compounds.^[23, 26-28]

Other microporous zeolites (e.g., ZSM-5) have also been reported in selected transition-metal-free alkane functionalizations.^[29] Interestingly, zeolites have rarely been reported in selective oxidation processes. Pescarmona and Jacobs disclosed the first and only remarkable example of good catalytic activity for zeolites beta and Y, with Si/AI ranging from 2.6 to 15, in alkene epoxidation. Under optimized conditions, a maximum cyclooctene conversion of 60% with an 82% conversion to the epoxide was achieved under mild reaction conditions (80 °C, 4 h).^[30] The authors related this unusual epoxidation activity in USY to the formation of surface hydroperoxide species (Al–OOH) from the reaction of Al–OH groups with hydrogen peroxide as previously reported for Al₂O₃.^[31]

The development of mesoporosity in hierarchical zeolites can open up the porous framework in these materials, and induce the formation of a large number of accessible terminal Al–OH groups.^[3] Liu et al.^[32] recently reported the catalytic performance of alkali-treated ZSM-5 zeolite in the selective oxidation of benzylalcohol with hydrogen peroxide, pointing out that the reaction mechanism involves the formation of Al–OH groups by direct reaction of Al–OH sites with H₂O₂. We recently reported the synthesis and characterization of iron oxide-functionalized hierarchical ZSM-5 zeolites with different Si/Al ratios. The surface acid properties of these catalysts were investigated and correlated to the catalytic activity of these materials in the microwave-assisted alkylation of toluene with benzyl chloride, preferentially catalyzed by Lewis acids.^[33]

In light of these findings, we set out to investigate the feasibility of using these hierarchical zeolites, with and without iron oxide nanoparticles, in selective oxidation processes taking advantage of terminal Al–OH groups to generate redox sites in zeolites. Mesoporous ZSM-5 materials were consequently synthesized and employed in various selective oxidation test reactions under microwave irradiation, namely the oxidation of benzyl alcohol to benzaldehyde, the epoxidation of cyclohexene, and the multistep conversion of *N*,*N*-dimethyl formamide (DMF) into products of interest.

The textural and surface acid properties of zeolite materials synthesized in this work are summarized in Table 1. All hierarchical ZSM-5 zeolites exhibited type I + IV isotherms typical of micro- and mesoporous materials, as compared to the type I isotherms observed for parent microporous zeolites (Z40c and



Table 1. Chemical composition, textural parameters, and surface properties of hierarchical zeolites used in this work. Microporous Z40c and Z15c are compared to post-treated and Fe-functionalised materials.^[33]

Sample	Si/Al ^[a]	Fe ^[a] [wt %]	$S_{BET}^{[c]}$ [m ² g ⁻¹]	$S_{meso}^{[d]}$ [m ² g ⁻¹]	$V_{ m micro}^{ m [d]}$ [cm ³ g ⁻¹]	$V_{meso}^{[e]}$ [cm ³ g ⁻¹]	Surfa [µmc	ce acidity ol g ⁻¹]	/ ^[f]
							PY	DMPY	PY-DMPY
Z40c	48.2	_	410	210	0.14	0.16	218	14	204
Z40c-H	50.0	-	610	440	0.16	1.13	264	249	15
Fe1/Z40c-H (BM)	42.3	0.7/1.8 ^[b]	425	365	0.07	0.64	322	250	72
Z15c	19.5	-	360	190	0.14	0.13	529	285	244
Z15c-H	20.0	-	690	590	0.16	0.89	367	355	12
Fe0.5/Z15c-H (BM)	22.4	0.3/0.7 ^[b]	355	330	0.06	0.68	329	294	35

[a] Surface Si/Al mole ratio and Fe contents as determined by XPS after the samples were etched. According to the manufacturer, the Si/Al molar ratios in Z40 and Z15 zeolites before calcination are 40 and 15, respectively. [b] From ICP-AES analysis (samples treated with phosphoric acid and hydrochloric acid). [c] BET surface area obtained using multipoint BET method from the adsorption data (P/P₀ range=0.05–0.30). [d] "External" surface area and micropore volume from the isotherms using the *t*-plot method. [e] Mesopore volume from the isotherms using PY and DMPY as probe molecules at 200 °C. Lewis acidity was obtained by subtracting PY and DMPY values, by assuming that PY characterizes both B and L sites while DMPY mainly for B sites.

Z15c).^[33] The surface areas of Z40c-H and Z15c-H, particularly the "external" surface area, were comparably superior to those of the parent microporous materials after the introduction of mesoporosity, Table 1 (see Ref. [33] for further details).

The sharp increase in external surface area and mesopore volume in hierarchical ZSM-5 zeolites is directly related to the increase in the surface acidity, measured using 2,6-dimethylpyridine (DMPY) as probe molecule, thus leading to a sharp decrease in the Lewis acidity of these samples, which only slightly increased in iron-containing material (Table 1). Pyridine (PY) is considered to characterize both Brønsted (B) and Lewis (L) acid sites, while DMPY mainly titrates B acid sites. Moreover these two bases, with differing molecular dimensions, may detect acid sites located in different pore spaces, that is, PY reaches all acid sites either in micropores or in mesopores/on the surface, while DMPY is only applicable the quantification of acid sites in mesopores or on the surface.^[24,33,34] Therefore, the development of mesoporosity in Z40c-H and Z15c-H samples is related to the higher accessibility of DMPY, giving rise to a materials with essentially B acid sites, as shown in Table 1.^[33]

Base titration experiments correlated well with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of PY adsorbed on zeolites (Figure 1 and Supporting Information). Z15c-H and Z40c-H generally exhibited a much lower concentration of accessible Lewis acid sites as compared to their parent microporous counterparts, both systems having a large concentration of Brønsted acid sites developed upon HCI treatment (particularly Z15 materials, Figure 1). This is also the trend observed upon incorporation of iron (Supporting Information).

Upon porous and acidic characterization, the prepared zeolites were next investigated in various selective oxidation processes under microwave irradiation. Given the experience of our group in the selective oxidation of benzyl alcohol to benzaldehyde, this reaction was firstly attempted under microwave irradiation and similar previously optimized conditions.^[35] Microwaves were selected as reaction tool due to their inherent advantages in providing a fast and homogeneous heating of the reaction mixture, as opposed to the slow and bulk heating achieved under conventional heating. Results for the different investigated catalysts are summarized in Table 2. These results prove the remarkable catalytic activities of mesoporous Z40c-H and Z15c-H, even after several catalytic cycles, as compared to their parent microporous zeolites. Benzaldehyde was selectively obtained (90-99%) with conversions between 35% to 45% of benzyl alcohol under mild reaction conditions and very short reaction times (typically 3-5 min). A further increase in reaction time did not signifi-



Figure 1. DRIFT spectra of pyridine (PY) for surface acidity comparison of Z15c-H (left) and Z15c (right) at different temperatures (from bottom to top: 100, 150, 200, and 300 °C). *B* and *L* refer to Brønsted and Lewis acid sites, respectively.

cantly improve conversion in these systems, which remained in the 40-50% range. Results were also comparable to designed supported iron oxide nanoparticles previously reported in the literature (Table 2).^[23] The enhanced catalytic activity of hierarchical zeolites over their parent zeolites could be related to (i) their higher accessibility (as evidenced by their larger pore volume),^[7] and (ii) a higher amount of terminal and highly accessible Al-OH groups (high DMPY/PY ratios) created by alkalitreatment.^[34] For comparison purposes the catalytic results obtained with three alumina-silica catalysts with Si/Al ratio ca. 40 are included in Table 2.^[35] They all show excellent textural properties (Brunauer-Emmett-Teller (BET) areas of ca. 700 m²g⁻¹). However, their surface acidy, measured by DMPY adsorption, is lower than the one determined for hierarchical Z15c-H and Z40c-H zeolites, which could explain their inferior catalytic activity.

A plausible mechanism is shown in Scheme 1. Terminal and highly accessible Al–OH groups can react with H_2O_2 to generate highly reactive aluminum hydroperoxide surface species, which can then oxidize benzyl alcohol to benzaldehyde.^[32,36]



Sample	Reaction time [min]	Conversion [mol %]	Selectivity to benzaldehyde [mol%]	Max. temp. [°C]
blank (no catalyst)	30	< 10	100	-
Z40c	5	<15	100	101
Fe1/Z40c (BM)	5	26	100	131
Z15c	5	< 15	100	86
Fe0.5/Z15c (BM)	5	20	100	132
Z40c-H	3	34	91	166
Z40c-H	5	41	90	170
Z15c-H	3	34	99	150
Z15c-H	5	44	93	170
Z15c-H, 2 nd use	5	32	99	160
Z15c-H, 3 rd use	5	26	99	162
Fe0.5/Z15c-H (BM)	5	46	97	111
AI-SBA-15 ^[b]	60	<15	99	130
Fe/Al-SBA-15 or Al-MCM-41 ^[b]	1.5	53–54	92	150

[a] Reaction conditions: 0.2 mL benzyl alcohol, 0.3 mL H_2O_2 , 2 mL acetonitrile, 0.05 g cat., 300 W, 3-5 min reaction time. [b] Optimized activity and selectivity of previously reported iron-containing catalysts (0.63 wt% Fe).^[35]



Scheme 1. Proposed peroxide species from AI–OH terminal groups involved in selective benzyl alcohol oxidation.

Indeed, H₂O₂ efficiency (obtained from the ratio between the moles of product per consumed $H_2O_2 \times 100$) was found to be >75% in all cases, supporting the proposed mechanism. This mechanism has already been proposed for homogeneous^[36a] and heterogeneous alumina-based catalysts^[36b-d] as well as for alkali-treated ZSM-5 zeolites.[32] Importantly, the proposed mechanism involves subsequent dehydration steps, which can be favored in acidic zeolite-type materials.^[36] These dehydration steps seem to be effectively promoted in both Z40c-H and Z15c-H systems. To the best of our knowledge, this is the first report of selective oxidation of alcohols catalyzed by hierarchical zeolites and illustrates the potential of using Al-OH sites, which are generally not relevant in acid-catalyzed processes by turning them into highly active and accessible Al-OOH sites for various chemistries. As expected, the incorporation of iron oxide nanoparticles slightly increases conversion values, probably due to a synergetic Fe/Al effect.^[33,35b] This in turn may be due to the combination of the Fenton process $(Fe^{^{3}+}+H_2O_2{\rightarrow}Fe^{^2+}+H^++HOO\cdot)^{^{[37]}}$ and the generation of highly reactive Al–OOH surface species.[32,37]

Zeolites beta and Y were previously reported as active catalysts in the selective oxidation of alkanes^[38] and alkenes, such as cyclooctene conversion.^[30a] Therefore, the catalytic activity of hierarchical zeolites has been also tested on the microwaveassisted cyclohexene oxidation and compared to that of microporous Z40c and Z15c zeolites (Figure 2). Cyclohexene was converted in moderate to good yields (35–50%) over Z40c-H and Z15-c with varying selectivity to products including minor concentrations of epoxycyclohexane (< 20%). 1,2-Cyclohexanediol and 2-cyclohexen-1-one were obtained as major reaction products. While the production 2-cyclohexen-1-one seems of plausibly favored via hydroxylation from AI-OOH groups (subsequent oxidation of the hydroxyl to ketone leads to the observed product), the diol was obtained upon ring opening of the epoxide on Brønsted acid sites of the zeolites.[39] These results are in good agreement with previous reported work on the oxidation of alkenes using Al₂O₃



Figure 2. (left) Microwave-assisted conversion and selectivity to diol (mol%, *x*-axis) of cyclohexene oxidation catalyzed by different zeolite materials. (right) Selectivity (mol%) to products for Z15c-H sample. Reaction conditions: 1 mL cyclohexene, 0.4 mL H₂O₂, 2 mL acetonitrile, 0.05 g cat., 300 W, 30 min reaction time.

systems, in which the formation of Al–OOH groups was reported by direct reaction of Al–OH sites with H_2O_2 .^[31] H_2O_2 efficiencies of ca. 75–90% confirmed the formation of those Al–OOH groups in hierarchical zeolites.

In view of the oxidative dehydration activities of hierarchically porous ZSM-5 materials, the catalytic activity of Z40c-H was also tested in a challenging oxidative dehydration reaction, using DMF as substrate (Table 3). The reaction profile is depicted in Figure 3.

Hydrogen peroxide was also employed to generate Al–OOH sites on the zeolites. Interestingly, acetonitrile was observed as exclusive product of DMF conversion. An almost negligible acetonitrile conversion was obtained with parent microporous ZSM-5 materials, as compared to a significantly improved activity observed for the analogous reaction using hierarchical ZSM-5 zeolites under identical conditions (20–25%) after 0.5 to 2 h of microwave irradiation (Table 3). Due to the small molec-



CHEMSUSCHEM
Communications

Table 3. Conversion of DMF to acetonitrile using zeolites under microwave irradiation.						
Sample	Reaction time [min]	Conversion [mol %]	Selectivity to acetonitrile [mol %]	Max. temp. [°C]		
blank (no catalyst)	120	-	-	105		
Z40c	30	< 5	-	120		
Z40c-H	30	20	>99	127		
Z40c-H	120	25	>99	130		
[a] Reaction conditions: 2 mL <i>N</i> , <i>N</i> -dimethylformamide, 0.3 mL H_2O_2 50% (v/ v), 0.05 g catalyst, 300 W, 120–130 °C, MW irradiation.						



Scheme 2. Proposed reaction mechanism for the production of methyl cyanide (acetonitrile) from *N*,*N*-dimethylformamide via subsequent demethylation, oxidative dehydration, and isomerization reactions over hierarchical ZSM-5 zeolites (CBV3024L stands for Z15c-H sample).



Figure 3. Microwave-assisted conversion (mol%, *x*-axis) of cyclohexene catalyzed by different zeolite materials. Inset corresponds to selectivity (mol%) to products for Z15c-H. Reaction conditions: 1 mL cyclohexene, 0.4 mL $H_2O_{2\nu}$ 2 mL acetonitrile, 0.05 g cat., 300 W, 30 min reaction time.

ular sizes of DMF and acetonitrile, the observed improvement in activity cannot be correlated to better reactant and/or product diffusion in the mesoporous zeolites but to the larger concentration of accessible Al–OH (upon generation of porosity via desilication + washing) and subsequent generation of Al– OOH sites through reaction with hydrogen peroxide.

This particular reaction followed a significantly different pathway as proposed in Scheme 2, starting with a demethylation of DMF to *N*-methylformamide followed by a plausible oxidative dehydration to methyl isocyanide (Scheme 2). Demethylation (dealkylation) reactions are common zeolite-catalyzed processes taking place on the strong acid sites of the zeolites and/or under base-catalyzed conditions.^[40] Furthermore, the oxidative dehydration of *N*-methylformamide has been previously reported using supported metals.^[41] Methyl isocyanide undergoes isomerization to methyl cyanide (acetonitrile) in the last step, a reaction that has been previously promoted under heat^[42] or catalyzed by metal complexes.^[43]

The generation of mesoporosity in zeolites has been generally at to improving accessibility and/or diffusional constraints inherent in microporous zeolites. In this work, we have shown that opening-up the porous framework of zeolites can render potentially interesting terminal groups (e.g., Al–OH), upon functionalization, into ones that can successfully be utilized in a number of different processes, including selective oxidations. An unprecedented versatility of hierarchical zeolites in oxidative processes has been reported in this work, in which moderate to good activities are achieved in alcohol and alkene oxidation as well as in tandem acid/redox processes for the conversion of DMF into acetonitrile. We believe these remarkable findings can pave the way to a more extended utilization of functionalized hierarchical zeolites in oxidation reactions.

Experimental Section

Synthesis of hierarchical zeolites: Commercial MFI zeolites CBV8014 (Zeolyst International, Si/Al molar ratio = 40, denoted as Z40c) and CBV3024E (Zeolyst International, Si/Al molar ratio = 15, denoted as Z15c) were used as starting materials upon calcination at 550 °C for 5 h in air (rate of 100 °C h⁻¹). Post-synthetic desilication treatment was conducted following the methodology reported by Groen et al.,^[7] in which zeolites were treated with different concentrations of 100 mL NaOH solution (0.4 м for Z40c and 0.8 м for Z15c) for 30 min at 65 $^\circ C$ and 600 rpm. The solution was then filtered off and thoroughly washed with distilled water. Desilicated zeolites were subsequently treated in 100 mL of 0.1 M aqueous HCl under identical conditions during 6 h to remove alumina debris and obtain the ZSM-5 porous zeolites, as recently reported elsewhere.^[33] These NaOH concentrations were selected because they imparted good textural and acid properties onto the final materials.^[33] Hierarchical ZSM-5 materials after acid washing are denoted as Z40c H and Z15c-H.

Mechanochemical preparation of iron-containing materials: Hierarchical ZSM-5 materials with iron oxide nanoparticles were prepared using a mechanochemical protocol recently developed in our group.^[33,35] In a typical preparation, 2 g of the hierarchical ZSM-5 zeolites (Z40c-H and Z15c-H samples) were ground with the target quantity of metal precursor (FeCl₂.6H₂O, Sigma–Aldrich) in the solid phase to achieve the required iron loading in the final material. The mechanochemical protocol was performed using a planetary ball mill (Retsch PM 100) under previously optimized conditions (10 min milling at 350 rpm). The obtained materials were finally calcined in air at 400 °C for 2 h. The iron-containing materials are denoted as Fe1/Z40c-H (BM) and Fe0.5/Z15c-H (BM), where a theoretical iron incorporation of 1 or 0.5 wt % in the final material, respectively, was targeted and BM stands for (mechanochemical) ball-milling incorporation of the metal.^[13,44]

Materials characterization: The porosity of the materials was measured by $N_{\rm 2}$ adsorption at 77 K using an AUTOSORB-6 apparatus. Samples were previously degassed for 5 h at 373 K at 5.10 5 bar.



BET surface areas were estimated by using the multipoint BET method and adsorption data in the relative pressure (P/P_0) range of 0.05-0.30. The pore size distribution was calculated from the adsorption branch of the N_{2} isotherms using the DFT method. The mesoporous volume was calculated from the cumulative pore volume distribution curve. The micropore volume was calculated by using the *t*-plot method. Pyridine (PY) and 2,6-dimethylpyridine (DMPY) titration experiments were conducted at 200°C via gasphase adsorption of the basic probe molecules utilizing a pulse chromatographic titration methodology. Briefly, probe molecules (typically 1 to 2 µL) were injected in very small amounts (to approach conditions of gas chromatography linearity) into a gas chromatograph through a microreactor in which the solid acid catalyst was previously placed. Basic compounds were adsorbed until complete saturation, that is, until peaks of the probe molecules in the gas phase were detected by GC. The quantity of probe molecules adsorbed by the solid acid catalyst could then easily be quantified. To distinguish between Lewis and Brønsted acidity, we assumed that DMPY selectively titrates Brønsted sites (methyl groups hinder coordination of nitrogen atoms with Lewis acid sites) and that PY titrates both Brønsted and Lewis acidity. Thus, the difference between the amounts of PY (total acidity) and DMPY (Brønsted acidity) adsorbed should correspond to Lewis acidity in the materials. DRIFT spectra of adsorbed pyridine (PY) were carried out in an ABB IR-ATR instrument equipped with an environmental chamber. PY was adsorbed at room temperature for a certain period of time (typically 1 h) to ensure a complete saturation of the acid sites in the catalyst and then spectra were recorded at different temperatures ranging from 100 to 300°C in a similar way to previous reports.^[35] With this purpose, the different types of acid sites in the materials (Brønsted and Lewis) could be measured and quantified.

Microwave-assisted oxidation of benzyl alcohol: In a typical reaction, 0.2 mL benzyl alcohol, 0.3 mL H_2O_2 50% (*v*/*v*), 2 mL acetonitrile, and 0.05 g catalyst were added to a Pyrex vial and microwaved in a pressure-controlled CEM Discover microwave reactor for 5 min at 300 W (maximum temperature reached was 120–125 °C, maximum pressure 240 PSI) under continuous stirring. Samples were then withdrawn from the reaction mixture and analyzed by GC using an Agilent 6890N fitted with an HP-5 capillary column (30 m×0.32 mm×0.25 m) and a flame ionization detector (FID). The identity of the products was confirmed by GC–MS. The microwave method was generally temperature-controlled (by an infrared probe) where the samples were irradiated with the required power output (settings at maximum power, 300 W) to achieve the desired temperature.

Microwave-assisted epoxidation of cyclohexene: In a typical reaction, 10.3 mmol cyclohexene (1 mL), 0.4 mL H_2O_2 50% (v/v), 2 mL acetonitrile, and 0.05 g catalyst were added to a Pyrex vial and microwaved for 15 min in a pressure-controlled CEM Discover microwave reactor at 300 W (120–130 °C maximum temperature reached, maximum pressure 240 PSI) under continuous stirring. Samples were then withdrawn from the reaction mixture and analyzed as similarly described for the other microwave-assisted reactions. Response factors of the reaction products were determined with respect to the corresponding starting material from GC analysis, using known compounds in calibration mixtures of specified compositions.

Microwave-assisted conversion of DMF: In a typical reaction, 2 mL DMF, 0.3 mL H_2O_2 50% (*v*/*v*), and 0.05 g catalyst were added to a Pyrex vial and microwaved in a pressure-controlled CEM Discover microwave reactor at 300 W (120–130 °C maximum temperature reached, maximum pressure 240 PSI) under continuous stirring. Samples were then withdrawn from the reaction mixture and

These are not the final page numbers! 77

analyzed as similarly described for the other microwave-assisted reactions.

Acknowledgements

R.L. gratefully acknowledge support from the Spanish MICINN via the concession of a RyC contract (RYC 2009-04199) and funding under projects P10-FQM-6711 (Consejeria de Ciencia e Innovacion, Junta de Andalucia) and CTQ2011 28954-C02-02 (MICINN). J.G.M. gratefully aknowledges funding under project PCIN-2013-164 (MINECO and UE). Both R.L. and J.G.M. acknowledge support from MICINN under cooperation project CTQ2011-28954.

Keywords: dehydrations • mesoporous materials microwaves • oxidations • zeolites

- [1] J. Weitkamp, Solid State Ionics 2000, 131, 175–188.
- [2] J. Kärger, R. Valiullin, Chem. Soc. Rev. 2013, 42, 4172-4197.
- [3] J. Pérez-Ramírez, C. H. Christensen, K. Egebla, C. H. Christensen, J. C. Groen, *Chem. Soc. Rev.* **2008**, *37*, 2530–2542.
- [4] C. H. Christensen, K. Johannsen, E. Törnqvist, I. Schmidt, H. Topsøe, C. H. Christensen, *Catal. Today* 2007, *128*, 117–122.
- [5] E. Li, J. Garcia-Martinez, in Mesoporous Zeolites, Wiley VCH, 2014.
- [6] M. Ogura, S. Y. Shinomiya, J. Tateno, Y. Nara, E. Kikuchi, M. Matsukata, Chem. Lett. 2000, 882–883.
- [7] D. Verboekend, S. Mitchell, M. Milina, J. C. Groen, J. Pérez-Ramírez, J. Phys. Chem. C 2011, 115, 14193–14203.
- [8] L. Zhao, J. Gao, C. Xu, B. Shen, Fuel Process. Technol. 2011, 92, 414-420.
- [9] J. C. Groen, J. A. Moulijn, J. Perez-Ramirez, J. Mater. Chem. 2006, 16, 2121-2131.
- [10] a) K. Sadowska, A. Wach, Z. Olejniczak, P. Kustrowski, J. Datka, *Microporous Mesoporous Mater.* 2013, *167*, 82–88; b) G. Bellussi, A. Carati, C. Rizzo, R. Millini, *Catal. Sci. Technol.* 2013, *3*, 833–857.
- [11] I. I. Ivanova, E. E. Knyazeva, Chem. Soc. Rev. 2013, 42, 3671-3688.
- [12] C. Perego, R. Millini, Chem. Soc. Rev. 2013, 42, 3956-3976.
- [13] Mesoporous Zeolites: Preparation, Characterization and Applications (Eds.: J. Garcia-Martinez, K. Li), Wiley-VCH, 2015, p. 616.
- [14] D. P. Serrano, J. M. Escola, P. Pizarro, Chem. Soc. Rev. 2013, 42, 4004– 4035.
- [15] K. Na, M. Choi, R. Ryoo, Microporous Mesoporous Mater. 2013, 166, 3– 19.
- [16] Y. Tao, H. Kanoh, L. Abrams, K. Kaneko, Chem. Rev. 2006, 106, 896-910.
- [17] J. García-Martínez, M. Johnson, J. Valla, K. Li, J. Y. Ying, *Catal. Sci. Technol.* 2012, 2, 987–994.
- [18] J. García-Martínez, K. Li, G. Krishnaiah, Chem. Commun. 2012, 48, 11841–11843.
- [19] K. Li, J. Valla, J. Garcia-Martinez, *ChemCatChem* **2014**, *6*, 46–66.
- [20] K. Möller, T. Bein, Chem. Soc. Rev. 2013, 42, 3689-3707.
- [21] A. Silvestre-Albero, A. Grau-Atienza, E. Serrano, J. Silvestre-Albero, J. Garcia-Martinez, Catal. Commun. 2014, 44, 35–39.
- [22] L. Su, L. Liu, J. Zhuang, H. Wang, Y. Li, W. Shen, Y. Xu, X. Bao, Catal. Lett. 2003, 91, 155–167.
- [23] M. Spangsberg Holm, E. Taarning, K. Egeblad, C. H. Christensen, Catal. Today 2011, 168, 3–16.
- [24] F. Thibault-Starzyk, I. Stan, S. Abello, A. Bonilla, K. Thomas, C. Fernandez, J. P. Gilson, J. Perez-Ramirez, J. Catal. 2009, 264, 11–14.
- [25] M. Milina, S. Mitchell, Z. D. Trinidad, D. Verboekend, J. Perez-Ramirez, Catal. Sci. Technol. 2012, 2, 759–766.
- [26] L. Zhou, M. Shi, Q. Cai, L. Wu, X. Hu, X. Yang, C. Chen, J. Xu, *Microporous Mesoporous Mater.* 2013, 169, 54–59.
- [27] P. Pescarmona, K. Janssen, C. Delaet, C. Stroobants, K. Houthoofd, A. Philippaerts, C. De Jonghe, J. Paul, P. Jacobs, B. Sels, *Green Chem.* 2010, 12, 1083–1089.
- [28] M-L. Tsai, R. G. Hadt, P. Vanelderen, B. F. Sels, R. A. Schoonheydt, E. I. Solomon, J. Am. Chem. Soc. 2014, 136, 3522 – 3529.
- [29] A. A. Fokin, P. R. Schreiner, Adv. Synth. Catal. 2003, 345, 1035-1052.

5



- [30] a) P. Pescarmona, J. Van Noyen, P. Jacobs, J. Catal. 2007, 251, 307-314;
 b) P. Pescarmona, P. Jacobs, Catal. Today 2008, 137, 52-60.
- [31] R. Rinaldi, F. Y. Fujiwara, W. Hölderich, U. Schuchardt, J. Catal. 2006, 244, 92-101.
- [32] A. Jia, L.-L. Lou, C. Zhang, Y. Zhang, S. Liu, J. Mol. Catal. A 2009, 306, 123-129.
- [33] A. Grau-Atienza, R. Campos, E. Serrano, M.Ojeda, A. A. Romero, J. Garcia-Martinez, R. Luque, *ChemCatChem* **2014**, DOI: 10.1002/ cctc.201402555.
- [34] a) J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero, J. J. Calvino, M. P. Rodriguez-Luque, J. Catal. 2005, 230, 327–338; b) B. Gil, L. Mokrzycki, B. Sulikowski, Z. Olejniczak, S. Walas, Catal. Today 2010, 152, 24–32; c) D. Tzoulaki, A. Jentys, J. Perez-Ramirez, K. Egeblad, J. A. Lercher, Catal. Today 2012, 198, 3–11.
- [35] a) A. Pineda, A. M. Balu, J. M. Campelo, A. A. Romero, D. Carmona, F. Balas, J. Santamaria, R. Luque, *ChemSusChem* 2011, 4, 1561–1565; b) A. M. Balu, A. Pineda, K. Yoshida, J. M. Campelo, P. L. Gai, R. Luque, A. A. Romero, *Chem. Commun.* 2010, 46, 7825–7827.
- [36] a) M. L. Kuznetsov, Y. N. Kozlov, D. Mandelli, A. J. L. Pombeiro, G. B. Shulpin, *Inorg. Chem.* 2011, *50*, 3996–4005; b) W. Wang, Y. Jiang, M. Hunger, *Catal. Today* 2006, *113*, 102–114; c) D. Mandelli, M. C. A. van Vliet, R. A. Sheldon, U. Schuchardt, *Appl. Catal. A* 2001, *219*, 209–213; d) H. L. Xie, Y. X. Fan, C. H. Zhou, Z. X. Du, E. Z. Min, Z. H. Ge, X. N. Li, *Chem. Biochem. Eng. Q.* 2008, *22*, 25–39.

- [37] a) A. Cihanoğlu, G. Gündüz, M. Dükkancı, *Appl. Catal. B* 2015, *165*, 687–699; b) Y. Hu, Y. Zhang, Y. Tang, *RSC Adv.* 2012, *2*, 6036–6041; c) K. A. Sashkina, E. V. Parkhomchuk, N. A. Rudina, V. N. Parmon, *Microporous Mesoporous Mater.* 2014, *189*, 181–188.
- [38] a) L. M. D. R. S. Martins, A. Martins, E. C. B. A. Alegria, A. P. Carvalho, A. J. L. Pombeiro, *Appl. Catal. A* **2013**, *464–465*, 43–50; b) R. Ohno, K. Taniya, S. Tsuruya, Y. Ichihashi, S. Nishiyama, *Catal. Today* **2013**, *203*, 60– 65.
- [39] A. Fusi, R. Ugo, G. M. Zanderighi, J. Catal. 1974, 34, 175-190.
- [40] X. Zhu, R. G. Mallinson, D. E. Resasco, Appl. Catal. A 2010, 379, 172-181.
- [41] M. J. Beier, W. Kleist, M. T. Wharmby, R. Kissner, B. Kimmerle, P. A. Wright, J.-D. Grunwaldt, A. Baiker, Chem. Eur. J. 2012, 18, 887–898.
- [42] M. H. Baghal-Vayjooee, J. L. Collister, H. O. Pritchard, Can. J. Chem. 1977, 55, 2634–2636.
- [43] A. C. Filippou, W. Grünleitner, C. Völkl, J. Organomet. Chem. 1991, 413, 181–203.
- [44] K. Yoshida, C. Gonzalez-Arellano, R. Luque, P. L. Gai, Appl. Catal. A 2010, 379, 38–44.

Received: January 23, 2015 Published online on

COMMUNICATIONS

Ambitious not siliceous: Desilicated hierarchical zeolites hold promise as catalytic systems. The feasibility of using these hierarchical zeolites, with and without iron oxide nanoparticles, in selective oxidation processes is investigated, taking advantage of terminal Al–OH groups to generate redox sites in zeolites. The test reactions, under microwave irradiation, are the oxidation of benzyl alcohol to benzaldehyde, the epoxidation of cyclohexene, and the multistep conversion of *N*,*N*-dimethyl formamide (DMF).



M. Ojeda, A. Grau-Atienza, R. Campos, A. A. Romero, E. Serrano, J. Maria Marinas, J. García Martínez,* R. Luque*



Hierarchical Zeolites and their Catalytic Performance in Selective Oxidative Processes