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High surface area zincosilicates as efficient catalysts for the synthesis of ethyl lactate: an in-depth structural investigation⁺

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Novel Zn-MCM-41 mesoporous materials with a particle diameter ranging from 20 to 120 nm were successfully prepared following a straightforward synthesis route. The structural and textural properties of the solids were characterized by N₂physisorption, X-ray diffraction, ²⁹Si MAS-NMR, TEM and EDX. The results allow evidencing the presence of an ordered mesoporous structure with a very high specific surface area. The insertion of zinc as single site within the silica framework was investigated using XPS via Auger parameter in a Wagner plot representation. This is the first time that an in depth investigations of this type of solids using XPS techniques was performed. The presence of Brønsted and Lewis acidity was elucidated by following in the IR the interaction with ammonia and carbon monoxide. The materials were tested in the conversion of dihydroxyacetone into ethyl lactate with good results both in terms of yield and selectivity and the catalytic resulted excellent activity in agreement with IR and XPS analysis.

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1. Introduction

Mesoporous silica materials and, in particular, MCM-41 based solids have attracted considerable attention in the last two decades for their possible application in a broad range of research fields due to their textural properties as well as to the reduced diffusion barriers compared to typical microporous materials.¹⁻⁶ However, standard pure-silica MCM-41 solids have poor acidity which limits their use as heterogeneous catalysts.⁷⁻⁸ To overcome this problem, various metal elements have been incorporated within the silica framework via isomorphic substitution of silicon atoms. The introduction of elements such as Ti, Sn or Ga as single site in the silica architecture results in a combination of Brønsted and/or Lewis acid sites with relevant implications from a catalytic viewpoint.⁹⁻¹¹ A certain control of the type and strength of the acid sites may be also achieved by tuning the nature and the amount of hetero elements (with hetero different from silicon) within the silica framework. In this context it is evident that the choice of the heteroelement is a key parameter to attain both a high activity and selectivity for a given reaction even if the role of the textural properties as well as the hydrophilic/hydrophobic balance of the catalyst surface should not be underestimated.

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established concept in heterogeneous catalysis and it was recently extended to mesoporous solids.¹²⁻¹⁴ It was proved that the diffusion of reactants in a Ti-MCM-41 matrix can be improved by decreasing the particles dimension if the average pore size of the material remains unaltered.¹⁵⁻¹⁷ Recently, additional studies were carried out to prepare MCM-41 like solids with reduced (extra small) dimension and bearing both Sn and Ga inserted as single site in the silica framework.^{18,19} These materials were applied in different catalytic reactions with improved performance compared to analogous Sn- or Ga-MCM-41 solids with standard dimensions. The enhanced catalytic activity was attributed to a combination of factors including the small particle size warranting a good accessibility of the catalytic sites and the high specific surface area.^{18,19}

Moreover, the importance of the catalyst particle size is an

Zinc-based catalysts generate a great deal of attention in the scientific community mainly in the form of ZnO for their application in photocatalysis. A less explored field concerns the insertion of Zn as single site in the silica framework in order to investigate its capability to confer Lewis/Brønsted acidity to the solid. The isomorphic substitution of silicon by zinc within the mesoporous silica architecture of MCM-41 like materials can be still considered a challenging topic.

Only few examples can be found in literature and the characterization of the intra-framework insertion of Zn is still matter of debate due to the difficulties to analyse the local chemical environment of zinc.²⁰⁻²³ Concerning the possible catalytic applications, nowadays the development of sustainable processes plays a central role. In the context of green chemistry, a great attention has been devoted to the conversion of glycerol and one of its derivatives (dihydroxyacetone, DHA) into ethyl lactate (EL). EL is a valuable

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product which can find many uses as green solvent, in cosmetic or in pharmaceutical applications.²⁴⁻²⁶ In order to have an efficient conversion of DHA to EL, a combination of Lewis and Brønsted acid sites is needed.²⁷⁻³¹ The first step of the reaction mechanism is the dehydration and rearrangement of dihydroxyacetone to pyruvic aldehyde by Brønsted acid sites, although the contribution of Lewis acid sites cannot be excluded. The second step, catalysed by Lewis acid sites, converts pyruvic aldehyde into the desired alkyl lactates while strong Brønsted acid sites are detrimental because they favour (hemi)acetal products (Fig. 1).³²⁻³³

Herein, we describe a novel synthesis approach to embed Zn as single site in the MCM-41 network and obtain mesoporous solids with controlled extra-small particle dimensions and high specific surface area. The main objective of the work was the insertion and extensive characterization of Zn atoms within the silica architecture. Moreover a rapid and effective synthesis approach was envisaged in order to avoid time and energy consuming procedures. The materials were prepared via a straightforward procedure requiring a very short reaction time (2 h) and no additional thermal treatment under static conditions. The degree of metal insertion into the matrix was determined by XPS, using for the first time the Auger parameter in a Wagner plot representation. These materials resulted to be efficient catalyst in the conversion of dihydroxyacetone into ethyl lactate.

2. Experimental section

2.1. Catalyts preparation

The reagents employed in this study are cetyltrimethylammonium bromide (CTAB purity \geq 99%), ammonium hydroxide solution (NH₄OH 28.0%), sodium hydroxide (NaOH purity \geq 97%), absolute ethanol (EtOH purity \geq 99.5%), tetraethylorthosilicate (TEOS purity \geq 99,999%) and zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O purity \geq 99,9%. All of them purchased from Sigma-Aldrich.

Extra-small Zn-MCM-41 nanoparticles (XS-Zn-MCM-41) were prepared according to two methods: a concentrated route and a dilute route. In the both methods, a basic solution (NaOH 2.0 M or NH_4OH 28%) was added slowly to a mixture of milli-Q

water and CTAB. The resulting solution was stirred during 30 minutes. Then the $Zn(NO_3)_2.6H_2O$ (dissolved previously in 1.0 mL of ethanol) and TEOS were added separately to the homogeneous solution under stirring at 800 rpm. The composition of the reaction mixture for the concentrated route was 1 TEOS : 0.0135 Zn(NO₃)₂.6H₂O : 4.25 NH₄OH : 0.125 CTAB : 1.43 EtOH : 135 H_2O and for the dilute route 1 TEOS : 0.0135 Zn(NO₃)₂.6H₂O : 0.33 NaOH : 0.125 CTAB : 0.90 EtOH : 1212 H₂O (Table 1). A second batch of materials was prepared by varying the quantity of zinc precursor while keeping constant the concentration of all other reactants. After being stirred for 2 hours at room temperature (RT), the resulting solid was filtered, washed three times with milli-Q water and ethanol alternatively. Finally the catalysts were dried at 60 °C for 16 h and the resulting powder was calcined in air at 550 °C for 6 h (at a heating rate of 3 °C/min).

2.2 Catalysts Characterization

Nitrogen adsorption-desorption isotherms were measured at -196 °C on a volumetric adsorption analyser (Micromeritics Tristar 3000). Prior to the measurements, the samples were degassed at 150 °C for 24 h under 10⁻⁴ bar. The specific surface areas were calculated using BET method³⁴ and the pore size distribution were estimated by the BJH method³⁵ using the Powder X-ray diffraction (XRD) desorption branch. measurements were carried out on a PANalytical X'pert diffractometer with Cu K α radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) images were obtained on a Philips Tecnai with an accelerating voltage of 80 kV. The samples were prepared by dispersing the catalyst powder in absolute ethanol. After 15 minutes in an ultrasound bath, 2 droplets of the solution were deposited on holey carbon coated Cu grids. The chemical composition was determined by an energy-dispersion X-ray analysis (EDX) system using an acceleration potential of 7.5 kV and a working distance of 8 mm. An average of 40 measurements per samples was used to calculate the final ratio of the catalyst. The environment of the silicon atoms were studied via ²⁹Si Magic-Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra measured on a VARIAN 400 spectrometer. Diffuse reflectance UV-Vis spectra were recorded with a Varian Cary 5000 UV-Vis-NIR Spectrophotometer with a Harrick single-beam Praying Mantis Diffuse Reflectance cell. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a ThermoFisher ESCALAB 250Xi instrument. This spectrometer uses a monochromatic Al Ka X-ray source (1486.6 eV) and a hemispherical deflector analyser (SDA) working at constant pass energy (CAE). This mode allows a constant energy resolution on the whole spectrum. The intrinsic resolution of the spectrometer is 0.47 eV, measured on the Ag $3d_{5/2}$ line. The experiments were performed using a 300 µm diameter Xray spot. The charge neutralization of the sample was achieved with a flood gun using low energy electrons and Ar^{+} ions. The base pressure in the analyser chamber was 2.10⁻⁸ Pascal, and during experiments an argon partial pressure of 3.10⁻⁵ Pascal was maintained for the flood gun operation. Survey spectra

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Entry	Sample	Si/Zn	Si/Zn ratio		
		In the reaction mixture	In the final material ^a	synthesis	
1	XS-Zn-MCM-41-A	74	77	Concentrated 2h RT	
2	XS-Zn-MCM-41-B	74	76	Dilute 2h RT	
3	XS-Zn-MCM-41-C	41	47	Concentrated 2h RT	
4	XS-7n-MCM-41-D	41	45	Dilute 2h BT	

 Table 1 Physicochemical parameters for the synthesis of XS-Zn-MCM-41 materials

were recorded with a 150 eV pass energy, and this energy was decreased to 25 eV for high-resolution spectra. Auger spectra were fitted (least square method) with symmetric Gaussian-Larentzian lineshapes, using the Thermo Avantage software (Thermo Fisher Scientific). Four parameters were adjusted during this procedure: Gaussian-Larentzian (L/G) ratio, Full Width at Half Maximum (FWHM), kinetic energy and intensity (peak area). The only constraints were that L/G and FWHM must be the same for all the components of one spectrum. The analysis of Brønsted and Lewis acidity of the catalysts was performed by adsorption/desorption of ammonia and carbon monoxide monitored by Fourier transform infrared spectroscopy (FT-IR). The measurements were performed on a Bruker Tensor 27 spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector, operating at 2 cm⁻¹ resolution. Pre-treatments were carried out using a standard vacuum frame, in an IR cell equipped with KBr windows. Wafers were outgassed 1 hour at 673 K before adsorption of carbon monoxide at nominal 77 K and ammonia at room temperature. Adsorption of ammonia and carbon monoxide were studied in the pressure range 0.01-20.0 mbar: the reversible fraction of the adsorbates was then removed by prolonged outgassing at room temperature.

2.3. Catalytic experiments

The catalytic reactions for the conversion of dihydroxyacetone (DHA) to ethyl lactate in the presence of ethanol were carried out following a procedure already reported in the literature.^{18,19}

Typically, 0.180 g of DHA (2 mmol, in the form of 1,3dihydroxyacetone dimer) and 0.0215 g of nonane (as GC internal standard) were dissolved in 3.92 g ethanol (as solvent and reactant) at 45 °C for 30 min. Then 50 mg of the catalyst were added to the solution and the mixture was heated at 90 °C under vigorous stirring (1200 rpm) for 6 h. At the end of the test, the mixture was cooled down and the catalyst was separated by centrifugation (10 min at 4500 rpm). The products were analysed by gas chromatography (GC) on a Trace GC Ultra from Interscience (RTX-1 column, 5 m, 0.1 mm). The assignment of the products was confirmed by gas chromatography-coupled mass spectroscopy analysis (GC-MS) on a Thermo-Finnigan Trace GC 1300 gas chromatograph (Supelco SPB-5 column, 30 m, 0.32 mm) coupled to TraceMS single-quadrupole mass spectrometer working in electronic ionization mode. Recyclability tests were carried out by

washing the catalyst with absolute ethanol (5 times) after separation from the mixture. Finally the samples were dried overnight at 100 °C and calcined at 500 °C for 2 h (heating rate of 2° C min⁻¹).

Leaching tests were performed under the same conditions used for the catalytic tests with the double amount of catalyst (100 mg). After 3 h of reaction, the catalyst was removed from the mixture *via* hot filtration procedure and the filtrate was allowed to react for additional 3 h. The reaction mixture was analysed by GC after 3h and 6 h.

3. Results and discussion

Porous solids with extra-small (XS) dimensions and bearing the Zn embedded as single site in the silica architecture (XS-Zn-MCM-41) were prepared following two different synthesis protocols. The experimental procedures were inspired to the ones already reported for the preparation of XS-Sn- and XS-Ga-MCM-41 solids.^{18,19} The first method (concentrated route, Table 1) was a modification of the synthesis approach followed for the preparation of MCM-41 solids with standard dimensions while the second (dilute route, Table 1) was characterized by the use of a larger amount of water in the reaction mixture (see experimental). In both cases, the formation of porous particles with reduced dimensions was expected to be favoured by the mild reaction conditions (room temperature and absence of further hydrothermal treatment under static conditions) as well as by the short reaction time. In order to study the influence of the zinc content on the textural properties of the final materials, two different Si to Zn weight ratio were used. Table 1 shows a summary of the reaction parameters used for the preparation of the XS-Zn-MCM-41 particles.

All the solids were characterized by a combination of various physicochemical techniques. Due to the similarities between the materials, only the complete characterization of the samples XS-Zn-MCM-41-A and B (Table 1, entries 1 and 2) is presented and discussed in details in the text while the analogous data for the samples C and D (Table 1, entries 3 and 4) can be found in the supplementary information material (SI).

Nitrogen physisorption measurements revealed a very high specific surface area for all samples and a narrow pore size distribution (PSD) centred at 2.6 and 2.2 nm for the solids obtained *via* the concentrated and dilute method respectively

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Table 2 Textural properties of XS-Zn-MCM-41 series

Entry	Sample	a₀ (nm)	d ₁₀₀ (nm)	Average pore size [nm]	Wall thickness (nm) ^a	BET surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]	Internal pore volume [cm ³ g ⁻¹] ^b
1	XS-Zn-MCM-41-A	4.3	3.7	2.6	1.7	1188	0.77	0.73
2	XS-Zn-MCM-41-B	4.7	4.0	2.2	2.5	953	1.22	0.48
3	XS-Zn-MCM-41-C	4.3	3.7	2.6	1.7	1130	0.85	0.79
4	XS-Zn-MCM-41-D	4.7	4.0	2.2	2.5	927	1.24	0.43
$^{\circ}$ calculated as a ₀ - pore size ^b data calculated for p/p ₀ from 0.0 to 0.8								

(Table 2, Fig. 2 and Fig. S1, SI). This difference may be tentatively ascribed to the different reaction conditions or to a different incorporation of Zn within the silica architecture. It was previously observed that the amount of isomorphically substituted Si does not depend linearly on the relative concentration of inorganic precursors in the synthesis gel and is influenced by a combination of parameters including pH and amount of solvent.³⁶ The different insertion of heteroelement could also cause a different organization of the silica architecture with a more important distortion of the silica framework expected for materials with higher percentage of Zn as single site specie. The specific surface areas of the materials obtained via the concentrated route are particularly elevated, with XS-Zn-MCM-41-A reaching the remarkable values of 1188 m² g⁻¹and sample C of 1130 m² g⁻¹ despite its higher Zn loading. The comparison between the XS-Zn-MCM-41-B and D revealed a similar trend evidencing that the specific surface area is not strongly affected by the increasing concentration of zinc in synthesis gel.

Nitrogen adsorption/desorption profiles evidence a type IV isotherm typical of the MCM-41-like materials. Sample A displays a linear increase of adsorbed volume at low pressure, followed by a sharp inflection due to capillary condensation inside the mesopores.



Fig. 2 Nitrogen adsorption desorption isotherms (top) and pore size distribution (bottom) of XS-Zn-MCM-41-A (a) and XS-Zn-MCM-B (b).

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The solid B, obtained through the dilute route, presents a smaller inflection peak at lower pressure and an evident hysteresis loop at higher pressure indicating the existence of a second mesoporosity. The pore size distribution of XS-Zn-MCM-41-B (Fig. 2b) further evidences the presence of this second porosity with a broad band between 15 to 45 nm probably due to inter-particular cavities. In order to neglect the contribution due to the inter-particles aggregation, the pore volume of the samples was also calculated by excluding the contribution of the larger pores, corresponding to adsorption/desorption branch at the highest relative pressures $(p/p_0 = 0.8-1.0)$. These values give a better estimation of the internal mesopore volume which is nearly identical to the total pore volume for sample A (compare last two columns in Table 2) and present an evident drop for the solid B confirming the great contribution of the larger mesopores to the total pore volume (samples C and D show the same trend). Small angle powder XRD analysis of sample A exhibits a typical pattern of an MCM-41 mesoporous structure with a sharp peak which can be indexed as d₁₀₀ and two smaller signals attributed to d_{110} and d_{200} (Fig. 3 and Fig. S2, SI). These reflections correspond to a hexagonal array of channels with cylindrical pores. Interestingly, in the materials prepared by the dilute route only a main broad d_{100} reflection is visible suggesting a decrease in the long range order. The analysis of the diffraction patterns reveals other minor differences between the two solids. The inter-reticular distance, calculated from a₀ = $(2/3^{1/2}).d_{100}$ (Table 2), is slightly higher for the samples obtained via the dilute route. Combing the information obtained via XRD (a_0) with the pore diameter



Fig. 3 X-ray diffraction pattern of XS-Zn-MCM-41-A (a) and B (b) in the small angle range ($2\theta = 1-10^{\circ}$).

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Fig. 4 TEM pictures of XS-MCM-41-A (a,b) and XS-MCM-41-B (c,d).

coming from N₂ physisorption measurements, the wall thickness was calculated as well (Table 2). From the analysis of these data emerged that the solids formed through the dilute approach present thicker pore walls and smaller average pore size compared to the concentrated route.

Based on these preliminary investigations, it is evident that the major difference between the solids can be ascribed to the synthesis protocol rather than to Si/Zn weight ratio. In order to have a deeper understanding of the differences observed in the two series of materials, electron microscopy analysis of the samples was performed as well. TEM investigation revealed a homogeneous particle size distribution centred at 100 nm for XS-Zn-MCM-41-A (Fig. 4a). The majority of the particles display a spherical shape while a smaller percentage of elongated spheres can also be observed. High magnification (Fig. 4b) images allow confirming the presence of a highly ordered hexagonal organization. Sample XS-Zn-MCM-41-B displayed smaller particles with a particle size distribution ranging (Fig. 4c) from 20 to 50 nm and internal mesoporosity (Fig. 4d).

In contrast to sample A, the material B shows particles of irregular shape and some zones of condensation in agreement with the nitrogen physisorption analysis (vide infra). The samples prepared with higher zinc loading displayed the same characteristics (Fig. S3, SI). The smaller particle size distribution of the solids obtained via the diluted route could be attributed to the preference of nucleation compared to growth as consequence of the reduced concentration of inorganic precursors and allow explaining the lower degree of long range ordering observed in the XRD pattern. It is known that high water/inorganic precursor ratios induce the formation of silica networks with high porosity and smaller particles size distribution.³⁷ The good degree of condensation, was confirmed by solid state ²⁹Si MAS-NMR (Fig. 5).^{18,19} The broad band centred at -107 ppm can be deconvoluted into two different contributions corresponding to a Q³ [(SiO)₃SiOH] and Q^4 species [(SiO)₄Si]. In both cases, a lower Q^4 to Q^3 ratio



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 $(Q^4/Q^3 = 1.30 \text{ and } 1.15 \text{ for XS-Zn-MCM-41-A and } -B \text{ respectively})$ compared to conventional MCM-41 is observed (Fig. 5).³⁸ The elevate amount of Q³ species is related to the high concentration of surface silanol groups, as consequence of extra-small nanoparticles dimensions.

The XS-Zn-MCM-41 solids display a series of promising characteristics for catalytic application such as the good condensation degree of the silica framework, the excellent specific surface area, narrow pore size distribution and the extra-small particles dimensions. However, the complete characterization of the materials should involve a correct interpretation of the coordination of zinc embedded in the MCM-41 like matrix or present as extra-framework species. The characterization of the chemical environment of Zn via solid state nuclear magnetic resonance (SSNMR) represents a challenging aspect. The acquisition of high-quality SSNMR spectra was hindered by the low wt % of zinc in the mesoporous solids combined with the intrinsic drawbacks of ⁶⁷Zn (the sole NMR-active isotope of Zn) such as the quadrupole moment, the low γ and the poor natural abundance. Diffuse reflectance UV-Vis spectroscopy is a largely used technique to highlight the coordination of different elements inserted as single sites in silica architecture. 39,40

The UV-Vis spectra of XS-Zn-MCM-41 solids were recorded (Fig. 6 and Fig. S4, SI). Both materials displayed a broad band in which an evident maximum of adsorption at 238 nm can be distinguished for the sample A, while Zn-MCM-41-B show two maxima (at 239 and 262 nm). Although a difference between the two samples can be clearly claimed, the lack of literature references on zincosilicates with a rigorous assignment of these two bands to a specific chemical environment of Zn made difficult the analysis of the samples via UV-Vis spectroscopy.^{22,23} By analogy with Ti- or Sn-MCM-41 solids, the two maxima were tentatively attributed to Zn species inserted as single site in the silica framework (238 nm) and to Zn-O-Zn





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extra-framework species (262 nm) present as polymeric chains or small ZnO aggregates. To confirm the absence of large separate domain of zinc oxide, EDX elemental mapping using SEM was performed. This analysis confirmed the homogeneous distribution of zinc and silica and allow excluding the presence of large separate aggregates of ZnO and/or SiO₂ (Fig. S5, SI).

Aiming to a deeper understanding of the coordination of Zn in the samples and due to the aforementioned difficulties, the investigation of the solids thought X-ray photoelectron spectroscopy was performed as well. The analysis of the standard Zn 2p_{3/2} level is not useful due to the close proximity of the transitions corresponding to Zn(II) and metallic Zn selected as reference (less than 0.4 eV). On the other hand, zinc has some interesting Auger features in the kinetic energy range which can be advantageously exploited.⁴¹ The shape of the Zn $L_3M_{45}M_{45}$ (Zn LMM) Auger region has been studied more than 30 years ago for ZnO based solids and shows significant differences between metallic zinc and zinc oxide.^{41,42} The analysis of the Zn LMM Auger transition displays a broad band that can be considered as an overlapping of two different contributions (in green and blue in Fig. 7 and Fig. S6, SI). Both the green band centred at a kinetic energy of 984.5 eV and the blue one at 987 eV are in the region usually assigned to Zn(II).^{21,43} The deconvolution of this band into the two different contributions is rarely observed in the literature. The entire signal is generally attributed to Zn(II) species and used as proof of the insertion of Zn within the silica framework.

In addition to the study of the Auger signal, the Auger parameter and the representation in a Wagner plot gives the most relevant information on the chemical environment of the zinc.^{44,45} In order to have a deeper understanding of the two observed contributions, the modified Auger parameter α' (1) and the Wagner parameter A (2) were considered as well^{44,45}:

$$E_{k}^{F}(c_{1}c_{2}c_{3}) = \alpha' - E_{B}^{F}(c_{1})$$
(1)

where $E_k^F(c_1c_2c_3)$ is the kinetic energy of $c_1c_2c_3$ Auger level and $E_B^F(c_1)$ is the binding energy of the c_1 level. The F "superscript" indicates that both these energies are measured compared to the Fermi level.

$$E_{k}^{F}(c_{1}c_{2}c_{3}) = -3 E_{B}^{F}(c_{1}) + A$$
(2)



Fig. 8 Wagner plot (Zn L3M45M45 Auger vs. XPS Zn2p3/2) of XS-Zn-MCM-41-A (points 1 and 2) and –B (points 3 and 4). Filled circle/square represents the most intense contributions and empty circle/square the less important.

where $A=K^0-2(\Phi+qE_M)-2kQ$; K^0 is a constant depending on the atom, Φ is the work function of the solid, qE_M is the local Madelung energy and kQ is the local valence charge.

The linear plot of the two equations performed for XS-Zn-MCM-41-A and B as well as for metallic Zn and commercial ZnO as references are displayed in Fig. 8. This analysis allows highlighting that two different Zn(II) species are present in both MCM-41 like solids. The points defined as "ref" in Fig. 8 represent metallic Zn and ZnO respectively. As expected no metallic Zn is present in the extra-small silica particles. On the other hand evidences of ZnO can be clearly observed (Fig. 8, points 1 and 3). The points 1 and 3 are close enough to be considered as the same ZnO species (similar kinetic and binding energy); however both contributions are slightly different from pure ZnO nanoparticles. These contributions can be assigned to the presence of extra-framework ZnO present as extremely small nanoparticles (not visible in the EDX analysis) adsorbed on the silica surface hence of the same nature but with a different local environment compared to the commercial ZnO nanoparticles used as reference. As previously announced a second contribution clearly different from pure ZnO is also present (point 2 and 4). This second low energy component was attributed to the Zn (II) atoms inserted as single site in the silica framework. It is worth to mention that the relative percentage of the two contributions due to extra (points 1 and 3) and intra-framework (points 2 and 4) zinc is different for the two samples XS-Zn-MCM-41-A and B. The Zn silicate B displays the higher percentage of extra-framework ZnO. A similar behaviour was observed for the sample XS-Zn-MCM-41-C and -D (see Fig. S7, SI). From this analysis we can conclude that the dilute route led to a larger formation of extra-framework ZnO nanoparticles while the concentrated

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Table 3. Catalytic conversion to ethyl lactate over XS-Zn-MCM-41 catalysts

Entry	Catalyst	Conv. [%]ª	Y _{ethyl lactate} [%]	Y _{hemiacetal} [%]	Y _{acetal} [%]	S _{ethyl lactate} [%]	TON ^b
1	XS-Zn-MCM-41-A	26	24	2	0	92	63
2	XS-Zn-MCM-41-B	14	13	1	0	93	35
3	XS-Zn-MCM-41-C	37	36	1	0	97	46
4	XS-Zn-MCM-41-D	20	18	2	0	90	27
5	XS-Zn-MCM-41-A ^c	92	89	3	0	96	57
Conditions: 50 mg of catalyst, 2.00 x 10 ⁻³ mol of DHA in ethanol and 1.68 x 10 ⁻⁴ mol of nonane used as internal standard for GC analysis.							

Reaction time: 6h. ^asum of the yields of the reactants products; ^bTON = mol of DHA converted/mol of Zn atoms; ^ctest realized with 200 mg of catalyst.



Fig.9 IR difference spectra concerning NH₃ adsorption at r.t. on XS-Zn-MCM-41-A (a) and on XS-Zn-MCM-41-B (b) outgassed 673 K. Curve 1-2 are related to spectra obtained, respectively, under ca. 20 mbar ca. 5 mbar NH₃ equilibrium pressures. Curve 3: prolonged outgassing at RT after ammonia dosages. Spectra show breaks in the 2600-2200 cm-1 range.

approach allow a higher incorporation of Zn as single site in the silica matrix.

The elevated concentration of intra-framework Zn atoms can induce some distortions in silica architecture as evidenced after N_2 physisorption analysis of the samples (Table 2). These results are in agreement with the UV-Vis diffuse reflectance curves and allow confirming the correct attribution of the band around 240 nm to single site Zn species. It is worth to mention that this is the first time that a deep analysis of the Auger electrons and its correlation with UV-Vis spectroscopy investigation is reported for zincosilicate materials bearing the Zn inserted as single site in the silica architecture.

The proved isomorphic substitution of Si with Zn together with the aforementioned textural and morphological features made of the extra-small mesoporous zincosilicate promising candidates for the selected catalytic application. The four materials were, hence, tested as catalysts for the conversion of dihydroxyacetone (DHA) to ethyl lactate (EL). The results of the catalytic tests are summarized in Table 3. Due to the different wt% of Zn present in the various solids and in order to allow a meaningful comparison the turnover number (TON) defined as moles of DHA converted/moles of Zn was calculated as well. All solids displayed good catalytic performances with an excellent selectivity and a high TON. The apparent low conversion displayed in table 3 (entries 1 to 4) does not represent a serious drawback since an almost total conversion with only a slight decrease in the TON value can be achieved just increasing the amount of catalyst (entry 5). The best catalysts (XS-Zn-MCM-41-A and C) exhibited good catalytic performances as compared with literature data and selectivity higher than most of reference solids for this type of the reaction.^{19,46,47}

In order to correlate the good catalytic performances with the acidity of the samples, Brønsted and Lewis acidity of XS-Zn-MCM-41-A and XS-Zn-MCM-41-B were investigated by following in the IR the interaction with ammonia and carbon monoxide, a strong and weak base respectively, able to interact with both acidic hydroxyl groups (Brønsted sites) and coordinatively unsaturated cations (Lewis sites). Fig. 9 reports the IR difference spectra (spectrum of naked sample outgassed at 673 K has been subtracted) related to the adsorption of NH₃ on XS-Zn-MCM-41-A (Fig. 9a) and on XS-Zn-MCM-41-B (Fig. 9b) where the negative bands indicate the species consumed during the experiment.

Adsorption of ammonia on XS-Zn-MCM-41-A evidences the formation of three negative bands in the -OH region (ca. 3740, 3710, and 3550 cm⁻¹) due to different kinds of hydroxyls interacting with NH₃. With reference to the literature, the first band (3740 cm⁻¹) was assigned due to free silanols, the signal at 3710 cm⁻¹ may corresponds to terminal silanols in hydroxyls chains while the last contribution (3550 cm-1) was ascribed to H-bonded silanols.⁴⁸⁻⁵⁰

The other important region in IR spectrum is the one lying between 1700 and 1400 cm⁻¹ whose signals can be directly correlated with the Lewis/Brønsted acidity. At lower

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correlated with the Lewis/Brønsted acidity. At lower wavenumbers (1635 cm⁻¹) a signal due to the bending mode of ammonia molecules H-bonded to silanols can be observed.^{48,49} The broad band at about 1465 cm⁻¹ is related to the bending vibration of NH4⁺ species formed by proton-transfer reaction with Brønsted hydroxyls. The formation of the ammonium ion definitely evidences the presence of acid hydroxyl species strong enough to protonate ammonia, at variance with -OH groups of un-doped amorphous silica. This suggest that when Zn(II) atoms are introduced into the silica framework more acidic hydroxyl species are probed, whose nature most likely coincides with Si-OH groups interacting through the oxygen site with neighbour Zn(II) framework species. The exact infrared frequency of these species is not directly visible as negative band in the difference spectrum, probably as consequence of the great amount of surface -OH groups. Prolonged outgassing at room temperature does not allow the complete removal of adsorbed ammonia: weak signals due to ammonia molecules still interacting with the surface are observed in the corresponding spectrum (curve 3). The band due to ammonium ion almost disappears upon evacuation, indicating a reversible proton-transfer reaction to ammonia, typical of weak Brønsted acidic sites and in fair agreement with the expected acidity strength. On the other hand, upon outgassing the band ascribed to ammonia physisorbed on silanols massively decreases in intensity and a red-shift up to ca. 1620 cm⁻¹ is observed. This behaviour was attributed to the presence of ammonia adducts with uncoordinated Zn(II) ions (Lewis acidic centres), exposed at the surface.

Ammonia adsorption on XS-Zn-MCM-41-B sample evidenced a different behaviour in terms of Brønsted acidity: no signal due ammonium ion is disclosed in the difference spectra (Fig. 9b), even at higher ammonia equilibrium pressure (curve 1), suggesting that -OH species proposed as the source of Brønsted acidity in XS-Zn-MCM-41-A are no longer present or not detectable due to very low concentration. It is worth to note that the negative band at around 3710 cm⁻¹ results more intense and well-defined compared to that observed for XS-Zn-MCM-41-A, suggesting slightly higher abundance of terminal H-bonded silanol groups for sample XS-Zn-MCM-41-B. The other spectroscopic features result very similar to those displayed in Fig. 9a, except for the intensity of residual band upon outgassing at around 1620 cm⁻¹, which appears more intense compared with the corresponding signal observed for XS-Zn-MCM-41-A. This suggests that, on equal outgassing conditions (curves 3), the concentration of uncoordinated Zn(II) centres appears higher in sample B.

The contribution due to uncoordinated Zn(II) centres can be attributed to ZnO species thus in fair agreement with XPS results, which evidenced for XS-Zn-MCM-41-B a larger formation of extra-framework ZnO nanoparticles with a consequent lower amount of intraframework Zn atoms. Surface properties of the solids XS-Zn-MCM-41-C and D, investigated through ammonia adsorption on the samples outgassed at 673 K (Fig. S8), displayed a similar trend, in



Fig. 10 FT-IR difference spectra concerning CO adsorption (CO stretch range) at nominal 77 K on XS-Zn-MCM-41-A (a) and on XS-Zn-MCM-41-B (b) outgassed 673 K (CO equilibrium pressures: 0.010–20.0 mbar).

terms of Brønsted and Lewis acidity, to those observed for samples A and B respectively. All the solids exhibited improved acid properties as compared with the standard MCM-41 material. $^{\rm 51}$

To assess more in detail the nature and the relative abundance of Lewis acid sites, dosage of carbon monoxide at nominal 77 K was carried out for the most promising catalyst XS-Zn-MCM-41-A and for the sake of comparison a similar investigation was conducted also for sample B. Fig. 10 shows the difference IR spectra related to carbon monoxide adsorption on XS-Zn-MCM-41-A (Fig. 10a) and on XS-Zn-MCM-41-B (Fig. 10b) outgassed 673 K in the CO stretching range. For XS-Zn-MCM-41-A three bands at 2138 cm^{-1} , 2157 cm^{-1} and ca. 2190 cm⁻¹ can be clearly distinguished. The first corresponds to the formation of a liquid-like phase,⁵² the second is attributed to CO molecules H-bonded to all types of hydroxyls, whose difference in acidity is not large enough to impart to the CO molecule different stretching frequencies, and the third, rather low in intensity, is related to CO molecules interacting with a limited number of exposed Zn(II) ions, acting as Lewis acidic centres. Adsorption of CO on XS-Zn-MCM-41-B (Fig. 10b) evidences the presence of the same the bands described for XS-Zn-MCM-41-A plus one additional signal at 2168 cm⁻¹. With reference to the literature, the latter band is assigned to CO adsorbed on weak Lewis sites,49 where cation is supposed partially shielded by neighbouring oxygen or hydroxyl groups and thus not fully accessible to the probe. This attribution is consistent with the formation of larger amount of extraframework ZnO nano-clusters for the sample prepared via the dilute route as evidenced by XPS data elaboration as well as by and FT-IR analysis of adsorbed ammonia.

From this analysis emerged a different acid nature of the two series of samples. In the analysis of the catalytic behaviour the textural parameters such as the higher surface area of XS-Zn-MCM-41-A and C and the absence of inter-particles condensation zones should be considered. However, the superior activity of the materials A and C compared to the analogous solids B and D can be mainly ascribed to the almost

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Fig. 12 Leaching tests of XS-Zn-MCM-41-A and -B catalysts (100 mg of catalyst).

complete incorporation of Zn as single site in the silica architecture with a consequent better combination of Lewis/Brønsted acidity in the samples prepared through the concentrated route. The presence of Zn as single site favoured the selective formation of alkyl lactate, in agreement with the general accepted reaction mechanism reported in Fig. 1.

The stability of the catalyst under the selected reaction conditions was considered as well. Recycle experiments performed on the most promising catalyst (XS-Zn-MCM-41-A, Fig. 11) proved that the catalytic activity is preserved in consecutive uses. Moreover hot filtration leaching tests were performed as well for both samples XS-Zn-MCM-41-A and B (see experimental for details) thus further confirming the heterogeneous nature of the catalysts (Fig. 12). The slight increase in the conversion after filtration of the materials can be attributed to presence of very small solid particles not trapped by the filter rather than to the leaching of active Zn based species.

4. Conclusions

In conclusion a novel class of Zn-MCM-41 heterogeneous catalysts with extra-small particles sizes were synthesized via two different routes. The characterization showed a high specific surface area and a homogeneous particle size distribution. The insertion of zinc inside the mesoporous matrix was confirmed for the first time by using the Auger parameter in a Wagner plot representation. The XS-Zn-MCM-41 materials were tests for the conversion of DHA into ethyl

lactate with good yield and excellent selectivity and the catalytic activity resulted in excellent agreement with IR and XPS analysis. Moreover the best catalyst was successfully used in multiple catalytic runs thus proving the stability of the solid under the selected reaction conditions.

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