



UNIVERSIDADE ESTADUAL DE CAMPINAS SISTEMA DE BIBLIOTECAS DA UNICAMP REPOSITÓRIO DA PRODUÇÃO CIENTIFICA E INTELECTUAL DA UNICAMP

Versão do arquivo anexado / Version of attached file:

Versão do Editor / Published Version

Mais informações no site da editora / Further information on publisher's website: https://www.sciencedirect.com/science/article/pii/S1387181120300202

DOI: 10.1016/j.micromeso.2020.110017

Direitos autorais / Publisher's copyright statement:

©2020 by Elsevier. All rights reserved.

DIRETORIA DE TRATAMENTO DA INFORMAÇÃO

Cidade Universitária Zeferino Vaz Barão Geraldo CEP 13083-970 – Campinas SP Fone: (19) 3521-6493 http://www.repositorio.unicamp.br



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: http://www.elsevier.com/locate/micromeso



Preparation of novel mesoporous Ca/P MCM-41-based materials for mechanochemical diphenyl sulfide oxidation

Henrique Brasil^{a,**}, Ana Letícia Gondim de Carvalho^a, Fabíola Fernandes Costa^b, Luís Adriano Santos do Nascimento^c, Sareena Mhadmhan^d, Antonio Pineda^d, Rafael Luque^{d,e,*}, Gustavo Paim Valença^a

^a School of Chemical Engineering, University of Campinas – UNICAMP, 13083-970, Campinas, SP, Brazil

^b Campus of Salinópolis, Federal University of Pará, CEP 68721-000, Salinópolis, Pará, Brazil

^c Laboratory of Oils of the Amazon, Federal University of Pará - UFPA, 66075-110, Belém, PA, Brazil

^d Departamento de Quimica Organica, Universidad de Cordoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km 396, E14014, Cordoba, Spain

^e Peoples Friendship University of Russia (RUDN University), 6 Miklukho Maklaya str., 117198, Moscow, Russia

ARTICLE INFO

Keywords: MCM-41 Mesoporous materials Mechanochemistry Oxidation

ABSTRACT

MCM-41 molecular sieve was synthesized by liquid crystal templating and modified by incipient wetness impregnation with different Ca/P ratios. The solids were characterized by XRD, XRF, N₂ physisorption and NH₃/CO₂-TPD. The impregnation of Ca/P considerably increased the acid and basic character of MCM-41 materials, which were subsequently tested as catalysts in the mechanochemical oxidation of diphenyl sulfide, showing good selectivity (ca. 62 and 76%) for the selective production of diphenyl sulfoxide.

1. Introduction

MCM-41 is a mesoporous material from the M41S family with a structured narrow pore size distribution, featuring hexagonal arrangement of one-dimensional pores with a diameter between 1.5 and 10 nm, a large specific surface area (700–1100 m² g⁻¹), high pore volume and good thermal stability [1]. MCM-41 is often used in the catalytic cracking of large molecules due to the rapid diffusion of the molecules in the mesopores [2].

When synthesized as purely siliceous, MCM-41 is only very weakly acidic. Possible ways of increasing the surface reactivity of these solids include isomorphic substitutions with the incorporation of other cations [3] or by supporting inorganic compounds/complexes such as metal oxides. The incorporation of metal oxides and/or complexes is highly relevant since solid acids are important catalysts currently in use in many different reactions [4].

The selective oxidation of sulfides to sulfoxides is a significant and challenging organic reaction [5]. The growth in the chemistry of organic sulfoxides during last decade was due to their importance as synthetic intermediates for the production of a wide range of chemically and biologically active molecules [6], being extensively employed in medicine, pesticide, heavy metal extraction, oil desulphurization, organic synthesis and also activation of enzymes [7].

The oxidation of sulfides to sulfoxides is the most straightforward synthetic route to the latter, and numerous reagents and oxidative procedures are available for this transformation [6]. However, a large number of such oxidation reactions often require the use of toxic metal reagents and/or large quantities of catalysts [8,9]. Among various oxidants employed in this transformation, hydrogen peroxide is an attractive and environmentally friendly oxidant due to its low cost, high availability and cleanliness [10]. However, hydrogen peroxide alone is a relatively weak electrophile and a catalytic activation is additionally required [11].

Moreover, many catalysts cause over oxidation to the corresponding sulfones, therefore, control of the reaction conditions plays an important role in avoiding the formation of oxidation side products [6]. Another fact to be considered is that some of these methods require a transition/noble metal catalyst for the selective oxidation of sulfides, which have a number of disadvantages such as complex preparation routes and the use of toxic transition metal compounds, among others [12].

https://doi.org/10.1016/j.micromeso.2020.110017 Received 16 October 2019; Accepted 9 January 2020 Available online 10 January 2020 1387-1811/© 2020 Elsevier Inc. All rights reserved.

^{*} Corresponding author. Departamento de Quimica Organica, Universidad de Cordoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km 396, E14014, Cordoba, Spain.

^{**} Corresponding author. School of Chemical Engineering, University of Campinas – UNICAMP, 13083-970, Campinas, SP, Brazil. *E-mail addresses:* hbrasil@feq.unicamp.br (H. Brasil), q62alsor@uco.es (R. Luque).

Considering this, in recent years, one of the main objectives of modernizations in catalytic processes have been the development of new and efficient technologies to improve environmental conditions and industries related to fine chemicals [12]. In order to switch the reaction to greener conditions, several alternatives have been proposed, with mechanochemistry being one of the most promising alternative methodologies to conduct selective catalytic processes under solvent-free or highly solvent-limited reactions at room temperature [13].

Based on these premises, the aim of this work was to study the influence of impregnation of aqueous solutions with different Ca/P ratios on the surface acidity and basicity of MCM-41, combining the large surface area of MCM-41 with the acid and basic properties of Ca/P impregnation. Synthesized transition-metal-free catalysts were subsequently tested in the mechanochemical selective oxidation of diphenyl sulfide to its respective sulfoxide.

2. Materials and methods

2.1. Synthesis of MCM-41

The MCM-41 (MCM-P) was prepared according to a procedure described elsewhere [14]. Briefly, 630 mL of NH₄OH (Merck, 25%) and 810 mL of deionized water were mixed (solution pH 11). Then 6 g of CTAB (Sigma Aldrich, 99%) were dissolved under magnetic stirring in the alkaline solution; subsequently, 30 mL of TEOS (Sigma Aldrich, 98%) was added to the mixture. The solution was kept under constant stirring for 2 h at room temperature. The precipitate was then vacuum filtered and the solids were dried at 400 K for 24 h and calcined in a U-shaped quartz reactor at 813 K for 11 h in synthetic air (100 mL min⁻¹).

2.2. Impregnations with Ca/P

Calcium and phosphorous were added to the MCM-P by incipient wetness impregnation (total of 5 wt%) in 3 different Ca/P ratios: 1.64, 1.67 and 1.70 (atom basis). The samples were denoted as 64-MCM, 67-MCM and 70-MCM. The precursors employed for such purpose were Ca $(NO_3)_2.4H_2O$ (Merck, 99%) and $(NH_4)_2HPO_4$ (Merck, 99%). For each Ca/P ratio, four impregnation steps were carried out. First, calcium was added and then phosphorous, followed by calcium and finally phosphorous. After each impregnation, the samples were dried at 393 K. Then, they were heated to 873 K to cause thermal decomposition of the precursors of Ca and P and formation of the respective oxides in the surface of MCM-41. The solids were heated with a ramp of 1 Kmin⁻¹ and remained at 873 K for 6 h.

2.3. Materials characterization

The crystalline structure of MCM-P was determined by powder X-ray diffraction (XRD) in a Philips PW 1710 diffractometer, $0.01^{\circ} \text{ s}^{-1}$, 40 kV and 30 mA. The hexagonal unit cell parameter (a_0) was calculated from the interplanar distance d_{100} , according to the expression $a_0 = 2d_{100}/\sqrt{3}$. The Ca and P contents were determined by X-ray fluorescence (XRF) in a Panalytical Axios 1 KW equipment. The textural properties were measured by N₂ physisorption at 77 K on a Micromeritics ASAP 2020 equipment. Prior to analysis, samples (ca. 200 mg) were pretreated for 24 h at 673 K. The density of acid and base sites was determined by NH₃ and CO₂ temperature-programmed desorption (TPD) in a Micromeritics AUtoChem II 2920 equipment. Prior to TPD analysis, the samples were pretreated at 673 K, saturated with the probe molecule at 308 K (CO₂) or 323 K (NH₃) and heated up to 873 K.

2.4. Oxidation of diphenyl sulfide to diphenyl sulfoxide

The oxidation reaction of diphenyl sulfide under ball milling was



Fig. 1. X-ray diffraction pattern of (a) pure and (b) Ca/P doped MCM-41.

used to evaluate the influence of Ca/P impregnation on the acid and base properties of MCM-41. In a typical procedure diphenyl sulfide (0.5 mmol), 30% H_2O_2 (8 equiv.) and catalyst (0.042%mol) were added in 25 mL jar with eight stainless steel balls (Ø10 nm). Then the planetary ball milling was performed at 350 rpm for 25 min. The crude reaction was recover from the jar by using 0.5 mL of toluene. Then the liquid phase was analyzed by GC-FID equipped with a Supelco 2-8047-U capillary column. All results were finally confirmed by GC-MS.

3. Results and discussion

MCM-41 material exhibited the main characteristic reflections of MCM-41, i.e., 3 peaks at $2\theta = 2.86^{\circ}$, 4.72° and 5.40° , typical of the hexagonal cell of its mesoporous structure (Fig. 1a). Broad peaks suggest the formation of small MCM-41 crystals. The hexagonal unit cell parameter (a_0) was 3.6 nm, which is the sum of the pore diameter (D_P) plus the silica wall thickness. The thickness of the wall and the average pore diameter are equal to 1.1 nm and 2.5 nm (Table 1).

The characteristic peaks of MCM-41 were no longer detected at low angles after Ca/P impregnation on MCM-41 (Fig. 1b). The absence of these MCM-41 characteristic peaks in the impregnated samples may be related to the mesoporous collapse or to a disorganization of the mesoporous structure which turned into an amorphous silica phase [15–17]. The impregnated samples showed low resolution peaks associated with a carbonated calcium hydroxyphosphate phase, as well as a clear amorphous silica phase as evidenced by the broad band at ca. 22-23° (Fig. 1b).

The results from XRF (chemical composition) indicated a higher value of the Ca/P ratio as compared to the nominal values in the three impregnated samples. The experimental Ca/P ratios were 1.86, 1.90 and

Table 1

Morphology, acid and basic sites distribution (%) and results of the mechanochemical oxidation of diphenyl sulfide using synthesized Ca/P-MCM-41 mesoporous materials.

Sample	$S_{BET}\!/m^2~g^{-1}$	Acid sites ^a				Basic sites ^a				Conversion/%	Selectivity/%	
		l.t.p.	m.t.p.	h.t.p.	Total/µmol $NH_3 m^{-2}$	l.t.p.	m.t.p.	h.t.p.	Total/µmol $CO_2 m^{-2}$		Sulfoxide	Sulfone
Blank										<15	29	71
MCM-P	705	47.3	44.7	8.0	0.57	14.3	1.4	84.3	0.59	<15	40	60
64-MCM	141	46.4	41.2	12.4	4.10	31.3	32.8	35.9	1.52	29	64	36
67-MCM	104	31.1	22.7	46.2	2.18	22.2	34.0	43.8	1.56	32	62	38
70-MCM	159	50.8	21.0	28.2	3.09	25.4	24.2	50.4	1.46	28	76	24

^a l.t.p. = low-temperature peak (<433 K), m.t.p. = middle-temperature peak (433–723 K), h.t.p. = high-temperature peak (723 K). Reaction conditions: diphenyl sulfide (0.5 mmol), 30% H₂O₂ (8 equiv.), catalyst (0.042%mol), eight stainless steel balls (Ø10 nm), 350 rpm, 25 min.



Fig. 2. N₂ adsorption-desorption isotherms obtained at 77 K.

1.93 for the 64-MCM, 67-MCM and 70-MCM samples. Previous work has shown only 66% impregnation of the P atoms on silica [18]. Here, the number of sites initially available for impregnation in pure MCM-41 could be estimated from the density of acid and basic sites (Table 1). For a 5 wt% impregnation, the number of available sites in MCM-41 is ca. 4.5×10^{20} . Thus, the sites available for impregnation were occupied after two impregnations of Ca and one impregnation of P. Therefore, some of the P used in the fourth impregnation could be lost, thus resulting in higher similar Ca/P ratios (deviations less than 1.5%). In addition, the mean value of P loss in all samples is 12.0%, indicating a good reproducibility of results and preparation.

The nitrogen adsorption-desorption isotherms of all solids are type IV isotherms that changed their shape with Ca/P impregnation. All the impregnated solids had an H3-type hysteresis loop, typically interpreted as slit-like pores, low degree of pore curvature and the non-rigidity of the adsorbent structure [19,20]. The considerable decrease in the surface area after Ca/P impregnation indicates a partial pore blocking due to the collapsing of the MCM-41 structure upon impregnation and pore opening (crystal sintering) upon generation of Ca and P oxide particles (Fig. 2).

The impregnation with Ca and P increased the density of acid and basic sites on the MCM-41 surface (Fig. 3). The effect of the Ca/P ratio on the distribution of surface solids sites is more pronounced for acid sites than for basic sites. A small variation in the Ca/P ratio results in a large change in acidity of the solids (Table 1). As the Ca/P ratio increases, the amount of strong acid sites also increases. Impregnation causes an increase of more than 600% in the surface acidity of MCM-41 suggesting that Ca²⁺ adsorbed on the surface of MCM-41 creates Lewis-type acid sites [21]. The sample 64-MCM had the highest density of acid sites while 67-MCM had the lowest. The density of strong acid sites (mmol g⁻¹) was the only parameter that had a linear relationship with the increase of Ca/P ratio.

Oxidation of diphenyl sulfide to the corresponding sulfoxide under



Fig. 3. Desorption profiles of CO₂ and NH₃.

mechanochemical conditions was selected as a model reaction to investigate the selectivity and affectivity of the prepared materials in the presence of H₂O₂ (Table 1). The catalytic tests were performed at room temperature under solventless conditions by using hydrogen peroxide as oxidant [22]. Low conversion was observed in the absence of catalyst (blank run) as well as in the presence of MCM-P. The three synthesized catalysts exhibited a moderate conversion (ca. 30%) even at very low catalyst loadings, with a generally good selectivity for diphenyl sulfoxide production (62-76%). The ratio of strong acid sites to strong base sites follows the same trend as the conversion values, with a maximum value for the 67-MCM catalyst. In addition, the conversion follows an inverse trend towards the number of basic sites. Regarding selectivity, no direct correlation was observed. However, we speculate that the ratio of weak acid sites to weak basic sites may be an influential parameter for sulfoxide selectivity. As previously stated, the Lewis acid sites and the interaction of metal and support are important features for the catalytic activity of oxides in oxidation reactions [23].

Notably, the results indicated that the over-oxidation to diphenyl sulfone could easily take place (see blank run and for MCM-41) but was minimized for the synthesized catalysts, particularly for 70-MCM (76% selectivity to the sulfoxide). These results clearly pointed out that selectivity in the systems could be maximized under mechanochemical conditions (reactions taking place on the external surface) rather than in the pores of the materials.

4. Conclusion

The impregnation of calcium and phosphorus in the MCM-41 rendered amorphous silica-based materials of high surface acidity and basicity. The impregnated Ca/P ratio was higher than the nominal values and the number of atoms corresponding to a 5 wt% impregnation was higher than the available sites in MCM-41. The density of acid sites, unlike the basic sites, is sensitive to variations in the Ca/P ratio. Prepared mesoporous Ca/P MCM-41-based materials can be used as transition-metal-free and efficient catalysts for the mechanochemical selective oxidation of diphenyl sulfide to sulfoxide using 30% H_2O_2 at room temperature, with conversions of ca. 30% and selectivities up to 76% to the corresponding sulfoxide.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank Dr. Lisandro Cardoso and Guilherme Calligaris from Laboratório de Preparação e Caracterização de Materiais (IFGW/UNICAMP) by low angle DRX analyses. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The researchers would also like to thank BASA (grant number 2018/212) and CNPq (Grant numbers 140940/2017-0 and 432221/2018-2) for financial support. The publication has been prepared with support from RUDN University, Program 5–100.

References

- [1] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. W.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, A new family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc. 114 (1992) 10834–10843, https://doi.org/10.1021/ja00053a020.
- [2] A. Corma, From microporous to mesoporous molecular sieve materials and their use in catalysis, Chem. Rev. 97 (1997) 2373–2420, https://doi.org/10.1021/ cr960406n.
- [3] N. La-Salvia, J.J. Lovón-Quintana, A.S.P. Lovón, G.P. Valença, Influence of aluminum addition in the framework of MCM-41 mesoporous molecular sieve synthesized by non-hydrothermal method in an alkali-free system, Mater. Res. (2017), https://doi.org/10.1590/1980-5373-mr-2016-1064.

- [4] A. Corma, Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions, Chem. Rev. 95 (1995) 559–614, https://doi.org/10.1021/cr00035a006.
- [5] W. Dai, S. Shang, Y. Lv, G. Li, C. Li, S. Gao, Highly chemoselective and enantioselective catalytic oxidation of heteroaromatic sulfides via high-valent manganese(IV)–Oxo cation radical oxidizing intermediates, ACS Catal. 7 (2017) 4890–4895, https://doi.org/10.1021/acscatal.7b00968.
- [6] H. Golchoubian, F. Hosseinpoor, Effective oxidation of sulfides to sulfoxides with hydrogen peroxide under transition-metal-free conditions, Molecules 12 (2007) 304–311, https://doi.org/10.3390/12030304.
- [7] X.-F. Wu, A general and selective zinc-catalyzed oxidation of sulfides to sulfoxides, Tetrahedron Lett. 53 (2012) 4328–4331, https://doi.org/10.1016/j. tetlet.2012.06.003.
- [8] M. Mba, L.J. Prins, G. Licini, C3-symmetric Ti(IV) triphenolate amino complexes as sulfoxidation catalysts with aqueous hydrogen peroxide, Org. Lett. (2007), https:// doi.org/10.1021/ol062395i.
- [9] G.C. Tsui, Q. Glenadel, C. Lau, M. Lautens, Rhodium(I)-Catalyzed addition of arylboronic acids to (Benzyl-/Arylsulfonyl)acetonitriles: efficient synthesis of (Z)-β-Sulfonylvinylamines and β-keto sulfones, Org. Lett. 13 (2011) 208–211, https://doi.org/10.1021/ol102598p.
- [10] G. Abdi, A. Alizadeh, M.M. Khodaei, Highly carboxyl-decorated graphene oxide sheets as metal-free catalytic system for chemoselective oxidation of sulfides to sulfones, Mater. Chem. Phys. 201 (2017) 323–330, https://doi.org/10.1016/j. matchemphys.2017.08.062.
- [11] J.-W. Chu, B.L. Trout, On the mechanisms of oxidation of organic sulfides by H 2 O 2 in aqueous solutions, J. Am. Chem. Soc. 126 (2004) 900–908, https://doi.org/ 10.1021/ja036762m.
- [12] A. Rostami, N. Saedmocheshi, Z. Shirvandi, Zeolite nanoparticles (H-ZSM5) as a highly efficient, green, and reusable heterogeneous catalyst for selective oxidation of sulfides to sulfoxides under mild conditions, Compt. Rendus Chem. 21 (2018) 835–839, https://doi.org/10.1016/j.crci.2018.05.004.
- [13] R. Luque, F. Leung-Yuk Lam, Sustainable Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2018, https://doi.org/10.1002/9783527693030.
- [14] E.L. Pires, E.A. Miranda, G.P. Valença, Gas-phase enzymatic esterification on immobilized lipases in MCM-41 molecular sieves, Appl. Biochem. Biotechnol. Part A Enzyme Eng. Biotechnol. (2002) 963–976, https://doi.org/10.1385/ABAB:98-100:1-9:963.
- [15] K.S.N. Kamarudin, N. Alias, Adsorption performance of MCM-41 impregnated with amine for CO2 removal, Fuel Process. Technol. 106 (2013) 332–337, https://doi. org/10.1016/j.fuproc.2012.08.017.
- [16] S.L. Suib (Ed.), New and Future Developments in Catalysis: Activation of Carbon Dioxide, 2013, https://doi.org/10.1016/B978-0-444-53882-6.00005-X.
- [17] B. Yilmaz, K.G. Shattuck, P.Q. Miraglia, J. Warzywoda, A. Sacco, Recent advances in the science and technology of zeolites and related materials, in: Proceedings of the 14th International Zeolite Conference, 2004, https://doi.org/10.1016/S0167-2991(04)80882-6.
- [18] M. Vallet-Regí, I. Izquierdo-Barba, A. Rámila, J. Pérez-Pariente, F. Babonneau, J. M. González-Calbet, Phosphorous-doped MCM-41 as bioactive material, Solid State Sci. 7 (2005) 233–237, https://doi.org/10.1016/j.solidstatesciences.2004.10.038.
- [19] M.J. Ramírez-Moreno, I.C. Romero-Ibarra, M. González-de Gortari, Á. Hernández-Pérez, H. Pfeiffer, CO2 adsorption at high pressures in MCM-41 and derived alkalicontaining samples: the role of the textural properties and chemical affinity, J. Porous Mater. 23 (2016) 1155–1162, https://doi.org/10.1007/s10934-016-0173-4
- [20] J.B. Condon, Surface Area and Porosity Determinations by Physisorption, Elsevier Science, Amsterdam, 2006.
- [21] T. Wang, G. Wu, N. Guan, L. Li, Nitridation of MgO-loaded MCM-41 and its beneficial applications in base-catalyzed reactions, Microporous Mesoporous Mater. 148 (2012) 184–190, https://doi.org/10.1016/j.micromeso.2011.07.024.
- [22] V. Trombettoni, A. Franco, A.G. Sathicq, C. Len, G.P. Romanelli, L. Vaccaro, R. Luque, Efficient liquid-assisted grinding selective aqueous oxidation of sulfides using supported heteropolyacid catalysts, ChemCatChem 11 (2019) 2537–2545, https://doi.org/10.1002/cctc.201900296.
- [23] A. Corma, H. García, Lewis acids as catalysts in oxidation reactions: from homogeneous to heterogeneous systems, Chem. Rev. (2002), https://doi.org/ 10.1021/cr010333u.