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Pd-based Sol–Gel Catalysts for the Enantioselective Hydrogenation of (*E*)-2-Methyl-2-Butenoic Acid

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Abstract The enantioselective hydrogenation of the C=C double bond in (*E*)-2-methyl-2-butenoic acid was studied using Pd-based (5 wt.% on Al_2O_3, SiO_2 or TiO_2) catalysts, prepared by sol–gel methods and modified with cinchonidine (CD). The catalysts were characterized by XRD, NH_3–TPD, H_2-chemisorption analyses and N_2-physisorption for BET surface area measurements. In the absence of CD, some catalysts showed a satisfactory hydrogenation capacity, with best values for those supported on silica. However, when CD was added, the enantiomeric excess values obtained were lower than those previously observed using analogous commercial catalysts. The influence of preparation conditions on support texture and metal dispersion was evidenced and tentatively correlated with activity and enantioselectivity.

Keywords Enantioselective hydrogenation · (*E*)-2-methyl-2-butenoic acid · Cinchonidine · Pd/Al_2O_3 · Pd/SiO_2 · Pd/TiO_2 · Sol–gel preparation

1 Introduction

The enantioselective hydrogenation of α,β-unsaturated acids is a subject of high industrial significance in the pharmaceutical and agrochemical sectors, thanks to the different biological activity shown by pure enantiomers versus the corresponding racemic compounds [1, 2]. Numerous sophisticated homogeneous catalysts have been discovered that offer useful routes for the synthesis of chiral compounds [3, 4]. Enantioselective heterogeneous catalysts, which usually display a lower enantioselectivity than homogeneous catalysts, would be industrially preferable thanks to their technical advantages, such as separation properties, ease of handling, and possibility of reuse. More details on the general features of enantioselective heterogeneous catalysis can be found in some recent reviews [1–9].

The best solid catalysts for the enantioselective hydrogenation of olefins having an electron-withdrawing group in the α-position, such as α,β unsaturated carboxyl acids [10], contain Pd as the active phase, doped with different chiral auxiliaries. Values of enatiomeric excess (e.e.) varying between 20% and 92% have been achieved, depending on the structure of the unsaturated substrate [11–13]; the highest values are found when 1 or 2 aromatic rings are adjacent to the C=C double bond, while minor enantioselectivity is obtained with simple unsaturated aliphatic acids. The more selective modifiers appear to be cinchonine (CN), cinchonidine (CD) and their derivatives such as 10,11-dihydrocinchonidine and 10,11-dihydro-*O*-methylcinchonidine [14–16]. The main problems of the doped heterogeneous catalysts are: (i) the lower hydrogenation activity in comparison to unmodified catalysts; (ii) the loss of enantioselectivity due to leaching of chiral modifier from the metal surface; and (iii) the changes in the structure of the chiral dopant during the reaction due to its possible hydrogenation. In fact, it has been reported that CD may be transformed into several by-products under reaction conditions; in particular, the partial or total

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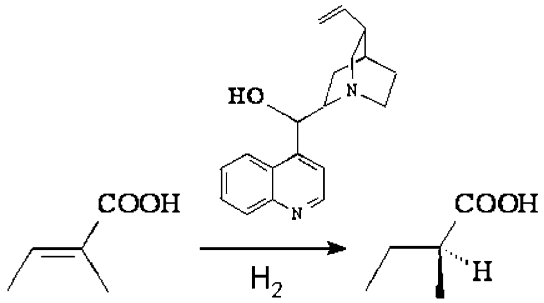

Fig. 1 Enantioselective hydrogenation of tiglic acid on CD-doped catalysts

hydrogenation of the quinoline ring causes a drop in enantioselectivity due to a lesser adsorption strength of the modifier on the metal surface [17].

In previous papers [18–21], some of us highlighted the specific activity of different noble metals as a function of the organic substrate fed, as well as the role of the reaction parameters and solvent polarity. In particular, with regard to catalysts, it was shown that metal dispersion, support acidity, surface area, metal crystallite size and preparation method play important roles. Sol–gel preparation methods are actually very versatile [22, 23] and make it possible to tune structure, surface properties, and activity of obtained catalysts, changing some factors, the most important being the ratio between precursors and water, temperature of gelification, nature of the gelification promoter, and calcination temperature. The aim of the present work was to develop a sol–gel preparation method capable of improving the catalytic activity and, by doping with CD, enantioselectivity in the hydrogenation of an aliphatic unsaturated model substrate, (*E*)-2-methyl-2-butenoic acid (also called tiglic acid) (Fig. 1).

2 Experimental

2.1 Chemicals

(*E*)-2-methyl-2-butenoic acid, cinchonidine (CD), undecane, n-hexane, tetraethylorthosilicate (TEOS), methytrimethoxylsilane (MTMS), aluminum *i*-propoxide, titanium *i*-propoxide, zirconium *i*-propoxide, $PdCl_2$, palladium acetylacetonate [Pd(AcAc)], trioctylamine (TOA), and NaF were purchased from Aldrich Chemicals (purity $\geq$ 98%) and used without further purification.

2.2 Catalyst Preparation

Pd-based (5 wt.%) catalysts were prepared on various supports using the sol–gel technique and recipes found in literature [22–26]. As a general procedure, a support precursor solution and a solution of the metal precursor and the gelification promoter were mixed together, before starting the gelification process, by adding the required amount of water. The mixtures were mixed for 1 h at room temperature (r.t.) to achieve a good homogeneity. A minimum amount of water was used for the complete hydrolysis of the support precursors; in fact, the molar ratio between H_2O- and Si-containing reagents (TEOS and MTMS) and titanium *i*-propoxide or zirconium *i*-propoxide was 1:4, or 1:3 in the case of Al *i*-propoxide. The role of the different parameters in the catalyst preparation (solvent, temperature, gelification time, and promoter, calcination temperature, and time) has been investigated as a function of the support nature (Table 1).

After gelification, CAT 1 (Pd/SiO_2) [23] and CAT 2 ($Pd/\gamma\text{-}Al_2O_3$) [25] were dried at 298 K for 24 h. In CAT 3 (Pd/TiO_2) [25] and CAT 4 (Pd/ZrO_2) [25] the solvent was removed under vacuum in a rotavapor for 1 h at 298 K, with CAT 4 being further dried at atmospheric pressure at 373 K for 12 h. Since the catalyst supported on SiO_2 showed notable activity and selectivity (see below), the conditions of catalyst preparation have been modified in an attempt to improve the catalytic performances (some details are shown in Table 1). According to literature [24, 27], in CAT 5 (Pd/SiO_2) and CAT 6 (Pd/SiO_2), $PdCl_2$ or Pd(AcAc) was pre-reduced to metal Pd in a solution of THF, in the presence of TOA as the stabilizer (molar ratio TOA/Pd precursor = 1:1), under $P_{H2} =$ 0.5 MPa at 298 K for 6 h; this colloidal suspension was then mixed with Si-containing reagents and NaF. The resulting gel was maintained at r.t. for 48 h and dried at 323 K for 96 h. CAT 7 (Pd/SiO_2) [20, 23] was prepared by incipient wetness impregnation on SiO_2 obtained by the sol–gel method using the conditions of CAT 1, without Pd species, to compare the two preparation methods. CAT 8 (Pd/SiO_2) [25] was obtained by changing the gelification promoter and using aqueous ammonia at pH = 9; after gelification, the solvent was removed in a rotavapor for 1 h at 298 K and the resulting gel was dried at 373 K for 1 h. Lastly, CAT 9 (Pd/SiO_2) [22, 26] and CAT 10 (Pd/SiO_2) [22, 26] were prepared using a molar ratio between TEOS and H_2O of about 1:10, thus increasing the amount of water as compared to CAT 1; after gelification the solvent was removed in a rotavapor for 1 h at 298 K and the gel was dried at 323 K for 24 h to remove the residual water.

Before the catalytic tests, CAT 1–4 and CAT 7–10 were activated in a flow of H_2 (10 mL/min) and N_2 (20 mL/min) at 623 K in order to reduce Pd(II) completely to Pd(0). CAT 5 and CAT 6 were used without this activation.

Table 1 Experimental conditions for the preparation of Pd catalysts on different supports

CAT [ref]	Precursors	Solvent	Gelification temperature (K)	Time[a] (h)	Temperature and calcination time	Gelification promoter
CAT 1 (Pd/SiO_2) [23]	Pd(AcAc), TEOS	i-Propanol	298	5	773 K for 7 h	NaF, water
CAT 2 ($Pd/\gamma\text{-}Al_2O_3$) [25]	Pd(AcAc), aluminium i-propoxide	Hexileneglycol, acetone	373	7	973 K for 1 h	Water
CAT 3 (Pd/TiO_2) [25]	Pd(AcAc) titanium i-propoxide	i-Propanol, acetone	323 → 343	29	973 K for 4 h	NH_3, water
CAT 4 (Pd/ZrO_2) [25]	Pd(AcAc) zirconium i-propoxide	i-Propanol, acetone	298	2	973 K for 4 h	Nitric acid, i-propanol, water
CAT 5 (Pd/SiO_2) [24, 27]	$PdCl_2$, MTMS, TEOS	THF, TOA	298	4	773 K for 17 h	NaF, water
CAT 6 (Pd/SiO_2) [24, 27]	Pd(AcAc), MTMS, TEOS	THF, TOA	298	4	773 K for 17 h	NaF, water
CAT 7 (Pd/SiO_2) [20, 23]	Pd(AcAc)/sol–gel silica	Acetic acid	373	2	673 K for 5 h	–
CAT 8 (Pd/SiO_2) [25]	Pd(AcAc), TEOS	EtOH, acetone	323 → 373	25	773 K for 4 h	NH_3,water
CAT 9 (Pd/SiO_2) [22, 26]	$PdCl_2$, TEOS	Ethanol	351	6	773 K for 2 h	NaF, water
CAT 10 (Pd/SiO_2) [22, 26]	$PdCl_2$, TEOS	Ethanol	351	6	1173 K for 2 h	NaF, water

[a] Referred only to gelification time

2.3 Characterization Methods

The catalysts were characterized by X-ray diffraction (XRD), H_2 chemisorption, BET N_2 physisorption, and NH_3-temperature programmed desorption (NH_3–TPD) analyses. XRD powder patterns were obtained using a Philips PW 1050/81 diffractometer (40 kV, 25 mA) equipped with a PW 1710 unit and a Cu Kα radiation ($\lambda = 0.154118$ nm); a 2θ range from 10° to 80° was studied at a scanning rate of 0.10°/s. The H_2 chemisorption and BET N_2 physisorption analyses were carried out using an AUTOCHEM 2910 (Micromeritrics). Before H_2 chemisorption, the catalyst were pre-treated under H_2 (5% with Ar) at 673 K for 25 min. The samples were then treated at 333 K with Argon for 20 min, and subsequently treated with H_2 (5% with Ar). Before BET N_2 physisorption, the samples were pre-treated for 1 h at 373 K and 10^{-4} Pa. The catalyst surface acidity was determined by using a Thermo Quest TPD/R/O 1100, equipped with TCD. Samples were pre-treated under a 100 mL/min He flow at 673 K for 60 min, then adding 10 pulses of NH_3 (every 5 min) at 433 K, and maintained at this temperature for 60 min. Lastly, under the same He flow, samples were heated up to 823 K (heating rate 10 K/min) and maintained at this temperature for 60 min.

2.4 Catalytic Tests

Unless stated otherwise, the following experimental conditions were applied using a 300 mL stainless steel Parr autoclave with mechanical stirring: 54 µmol of Pd, 25 mmol of tiglic acid, 170 µmol of CD, 75 mL of solvent (*n*-hexane), 4.0 MPa of H_2 and 298 K. The reaction time was 2 h. The metal surface was doped with CD during a preliminary 1 h step in air under stirring [28], then the autoclave was purged three times with He at 0.3 MPa before H_2 and tiglic acid were introduced at the set pressure. 2 mL of the reaction mixture were periodically sampled, 100 µL of undecane added as an internal standard, and the sample diluted to 10 mL with the solvent. The products were analyzed using a Perkin Elmer Autosystem XL gas chromatograph, equipped with FID and a wide bore PS086 chiral column (DEtTbuSililBETACDX 25 m × 0.25 mm, film width 0.25 µm). The e.e. was expressed as:

$$\text{e.e.}\ \% = [(S - R)/(S + R)] \times 100).$$

3 Results and Discussion

3.1 Catalyst Characterization

Table 2 shows the values of surface area, metal dispersion, average Pd particle size and total surface acidity for unit

Table 2 Chemical-physical properties of the investigated catalysts

Catalyst	Surface area (m^2/g)	Pd(0) particle size (nm)	Pd(0) dispersion (%)	Surface acidity (μmol NH_3/g_{cat})	Specific surface acidity (μmol NH_3/m^2)
CAT 1 (Pd/SiO_2)	123	8.6	13.0	211	1.7
CAT 2 ($Pd/\gamma\text{-}Al_2O_3$)	353	29.2	3.8	294	0.8
CAT 3 (Pd/TiO_2)	35	26.2	4.3	488	13,9
CAT 4 (Pd/ZrO_2)	45	24.6	4.5	n.d.	n.d.
CAT 5 (Pd/SiO_2)	64	n.d.	n.d.	≈0	≈0
CAT 6 (Pd/SiO_2)	60	106.1	1.1	≈0	≈0
CAT 7 (Pd/SiO_2)	110	10.5	10.7	150	1.4
CAT 8 (Pd/SiO_2)	74	6.8	16.4	456	6.2
CAT 9 (Pd/SiO_2)	50	194.8	0.6	≈0	≈0
CAT 10 (Pd/SiO_2)	15	383.0	0.3	49	3.3
Eng-1 ($Pd/\gamma\text{-}Al_2O_3$)[a]	185	5.8	19.3	1329	7.2
Eng-2 ($Pd/\gamma\text{-}Al_2O_3$)[a]	101	7.1	15.8	580	5.7
JM ($Pd/\gamma\text{-}Al_2O_3$)[a]	148	8.0	14.0	670	4.5
Eng-3 (Pd/TiO_2)[a]	200	2.6	43.5	150	0.8

n.d. = not determined

[a] Ref. [19]

either of weight or surface area. All these properties depended largely on the preparation conditions: in particular, the characteristics of Pd/SiO_2 catalysts were strongly affected by the gelification rate which, in turn, depended on the gelification conditions (temperature, solvent and inducer). Usually it was faster with NaF than with aqueous ammonia at pH = 9; in the former case a silicon oxide network was primarily characterized by linear or randomly branched polymers [20], while in the latter case the structure was more branched and packed. It is noteworthy that the pre-reduction of Pd(II) to Pd(0) (CAT 5 and CAT 6) or a high gelification rate (CAT 9 and CAT 10) gave rise to low surface area and metallic dispersion, with a further decrease associated with the increase in calcination temperature (CAT 10 vs. CAT 9) [21].

Some catalysts did not show significant peaks of ammonia desorption, suggesting a very low surface acidity. CAT 2 ($Pd/\gamma\text{-}Al_2O_3$) showed an acidity and metallic dispersion lower than analogous commercial catalysts, having the same support but higher surface area values. CAT 3 (Pd/TiO_2) exhibited low surface area and metallic dispersion values. In general, the catalysts supported on SiO_2 had acidity values lower than those supported on TiO_2 or $\gamma\text{-}Al_2O_3$, which ranged between 456 (CAT 8) and 0 μmol NH_3/g_{cat} (Table 2), highlighting the role of the preparation method on this property. Analyzing the characteristics of these new catalysts with those of previously investigated commercial catalysts (Table 2) [19], it may be noted that CAT 1 and CAT 7 exhibit particle size, surface area, and metal dispersion values in line with those of commercial $Pd/\gamma\text{-}Al_2O_3$ catalysts, but with lower surface acidity values. Conversely, CAT 8 had similar particle size, metal dispersion and surface acidity (in particular, the value of the specific surface acidity), but showed a lower surface area. The other catalysts showed very different properties, thus making it possible to correlate a wide range of features to the activity and/or enantioselectivity.

The XRD patterns of some Pd/SiO_2 catalysts (CAT 7–10) are reported in Fig. 2, where the typical reflections of metal Pd (reference code 01-1310 JCPDS) ($2\theta = 39$–$40°$, 46–47°, 67–68°) and a large band, due to amorphous silica, are evident [29]. On the contrary, CAT 5 and CAT 6, not reported here, did not show the reflection of metal Pd, but only the large band of the amorphous silica, suggesting a high metal dispersion, probably associated with a partial

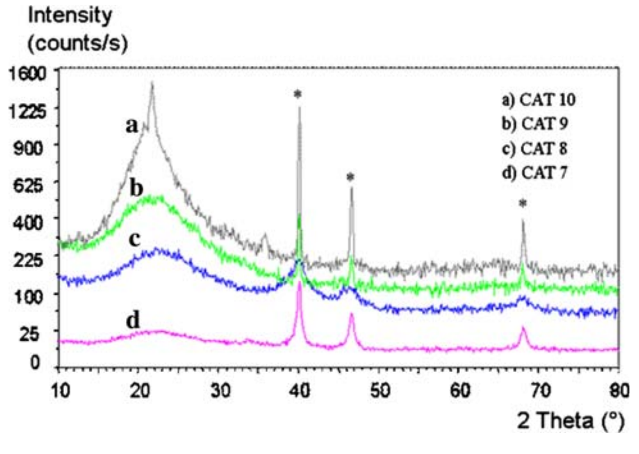

Fig. 2 XRD powder patterns for Pd/SiO_2 catalysts Cat 7–10 [Pd(0) (*)]

re-oxidation of metal Pd and stabilization during calcination, unlike that suggested by H_2-chemisorpition results.

The reflections of metal Pd were also evident (reference code 01-1310 JCPDS) in the XRD patterns of CAT1 (Pd/SiO_2) and CAT 2 (Pd/Al_2O_3), while in CAT 3 (Pd/TiO_2) they were not detectable because of high-intensity reflections of the support which, because of the calcination temperature, was present as anatase (reference code 04-0477 JCPDS) [29]. Lastly, the reflections of both metal Pd (reference code 01-1310 JCPDS) and zirconium oxide (reference code 80-2155 JCPDS) were evident in the XRD pattern of CAT 4 (Pd/ZrO_2) [29].

CAT 1–4 were preliminarily tested without CD to assess their hydrogenation activity (Table 3a): CAT 1 gave rise to a total substrate conversion already after 45 min; CAT 2 and CAT 3 showed a high hydrogenating activity only after 120 min, while CAT 4 showed a very low conversion. However, the CAT 3 (Pd/TiO_2) activity was lower than that obtained with an analogous commercial catalyst [19] probably on account of its low surface area (Table 2): in fact, CAT 2 with similar metal properties but a higher surface area showed a improved conversion value.

The adsorption of CD on the catalyst surface significantly reduced the activity (Table 3b), according to the proposed reaction mechanism [27], although the reduction was higher than that previously observed with commercial catalysts [18, 19] (Table 4). In particular, the rather unsatisfactory results obtained with CAT 2–4 in the presence of CD may be attributed to the low metal dispersion and the subsequent presence of large Pd particles, which may be covered by CD, considerably reducing the number of active sites.

Since CAT 1 (Pd/SiO_2) presented the highest conversion value combined with a fine enantioselectivity, further Pd/SiO_2 catalysts (CAT 5–10) were studied to highlight the role of the preparation variables. Unfortunately, only CAT 7 gave rise to a total conversion after a 120-min reaction (Table 5); this generally low activity may be attributed to various factors: in CAT 5 and CAT 6, the metal surface seems to have been covered by amorphous SiO_2 during the gelification step. CAT 9 and CAT 10 exhibited very large metal particles, with subsequent very low active surfaces, which worsened later on by increasing the calcination temperature. Surprisingly, CAT 8, which exhibited excellent chemical-physical properties (Table 2), showed a very low hydrogenation activity. This may be attributed to the gelification conditions: as previously reported, the silicon oxide network formed in NH_3-catalyzed conditions had a highly branched and packed structure, thus making the metal phase poorly accessible to the substrate.

In consideration of these unsatisfactory hydrogenation activities, only CAT 7 was doped with CD and tested, obtaining conversion and e.e. values similar to those observed for CAT 1 (Table 4). CAT 7 was prepared by incipient wetness impregnation of a silica obtained by the sol–gel method (operating under the same conditions as for CAT 1), while in CAT 1 the metal precursor (Pd-acetylacetonate) was introduced at the beginning of the preparation method. The comparable results between CAT 1 and CAT 7 show that the two preparation methods are equivalent. Lastly, we attempted to improve the yield and e.e. by varying the reaction conditions such as the molar ratio between Pd and CD and the reaction temperature, using CAT 1. However, a higher conversion was observed with both a decrease in the amount of the chiral modifier and an increase in temperature, although in both cases a decrease in e.e. was observed.

4 Conclusions

The gelification conditions played a fundamental role on the final properties of the catalysts obtained by sol–gel method, such as, for example, size and accessibility of metal particles or surface acidity. Although the conditions for obtaining a highly active and dispersed metal phase

Table 3 Activity and selectivity or enantioselectivity in the hydrogenation of tiglic acid using undoped and CD-doped CAT 1–4 catalysts

Catalyst	Conversion (%)	TON[a]	Yield (%)	Selectivity (%)	e.e. (%)
Undoped					
CAT 1 (Pd/SiO_2)	99	48.0	32	96	–
CAT 2 ($Pd/\gamma\text{-}Al_2O_3$)	89	24.2	20	95	–
CAT 3 (Pd/TiO_2)	83	107.9	26	92	–
CAT 4 (Pd/ZrO_2)	26	26.0	23	89	–
CD-doped					
CAT 1 (Pd/SiO_2)	33	15.4	32	97	30
CAT 2 ($Pd/\gamma\text{-}Al_2O_3$)	22	5.4	20	91	33
CAT 3 (Pd/TiO_2)	12	9.1	7	59	14
CAT 4 (Pd/ZrO_2)	6	5.0	5	83	10

$T = 298$ K, $P_{H2} = 4$ MPa; solvent (*n*-hexane) = 75 mL; tiglic acid/solvent = 1:30 v/v, reaction time = 120 min (45 min for undoped CAT 1). For the doped catalysts: tiglic acid/CD = 50:1 mol/mol; Pd/CD = 1:3 mol/mol, reaction time = 120 min

Table 4 Activity in the enantioselective hydrogenation of tiglic acid using some homemade and commercial catalysts doped with CD

Catalyst	Conversion (%)	TON[a]	Yield (%)	Selectivity (%)	e.e. (%)
CAT 1 (Pd/SiO_2)	33	15.4	32	97	30
CAT 2 (Pd/γ-Al_2O_3)	22	5.4	20	91	33
CAT 7 (Pd/SiO_2)	27	7.8	26	96	30
Eng-1 (Pd/γ-Al_2O_3)[b]	>99	96.0	95	96	48
Eng-2 (Pd/γ-Al_2O_3)[b]	>99	117.2	95	96	45
JM (Pd/γ-Al_2O_3)[b]	94	128.5	92	98	38
Eng-3 (Pd/TiO_2)[b]	77	31.4	70	91	36

$T = 298$ K, $P_{H2} = 4$ MPa; solvent (*n*-hexane) = 75 mL; tiglic acid/solvent = 1:30 v/v, tiglic acid/CD = 50:1 mol/mol; Pd/CD = 1:3 mol/mol, reaction time = 120 min

[a] mmol of saturated acid obtained/[Pd-metal surface area (m^2) × h]

[b] Ref. [19]

Table 5 Activity in the hydrogenation of tiglic acid using undoped Pd/SiO_2 CAT 5–10 catalysts

Undoped Pd/SiO_2 catalysts	Yield (%)	Selectivity (%)
CAT 5 (Pd/SiO_2)	5	83
CAT 6 (Pd/SiO_2)	7	44
CAT 7 (Pd/SiO_2)	75	76
CAT 8 (Pd/SiO_2)	13	72
CAT 9 (Pd/SiO_2)	3	23
CAT 10 (Pd/SiO_2)	4	67

$T = 298$ K, $P_{H2} = 4$ MPa; solvent (*n*-hexane) = 75 mL; tiglic acid/solvent = 1:30 v/v, reaction time = 120 min

have been optimized, with optimum metal particle size (6–10 nm), it was not possible to combine these properties with a high surface acidity, something that has been proved to be fundamental to stabilize the interaction between substrate, CD, and catalytic surface. This may justify enantiomeric excess values lower than those previously reported for commercial catalysts. According to the remark of one of the Peer, this is not surprising considering that industrial catalysts have been optimised to have very small particle size of supported Pd nanocrystals and well tuned acidity. However, it is noteworthy that the sol–gel methods offer significant potential advantages (for example, absence of any contamination, high homogeneity, controlled surface area and porosity, tuning properties, etc.) due to the high number of parameters that may be varied [22, 23, 31]. Thus, further work will be performed to tune the surface acidity and, in consequence, optimize the catalytic properties, by introducing heteroatoms (such as Al, Ti or Zr) into the siliceous framework during the sol–gel preparation, that, according to that reported in literature [32–34] can increase the acidity. It is noteworthy that Zr-containing mesoporous silica have already shown excellent behaviour as an acid catalyst [32, 33].

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References

1. Blaser HU (1991) Tetrah Asymm 2:843
2. Mallat T, Baiker A (2001) In: Sheldon RA, van Bekkum H (eds) Fine Chemicals through Heterogeneous Catalysis. Wiley-VCH, Weinheim (D), p 449
3. Noiory R, Hashiguchi S (1996) In: Cornils B, Herreman WA (eds) Applied homogeneous catalysts with organometallic compounds, vol 1. VCH, Weinheim (D), p 552
4. van Koten G, van Leeuwen P (1999) In: van Santen RA, van Leeuwen PWNM, Moulijn JA, Averill BA (eds) Catalysis: an integrated approach, vol 123, 2nd edn. Studies in Surface Science and Catalysis, Elsevier, Amsterdam (NL), p 289
5. Mallat T, Baiker A (2004) Chim Ind (Milan) 86:110
6. Baiker A (1998) Curr Opin Solid State Mater Sci 3:86
7. Sípos É, Tungler A, Bitter I (2003) J Mol Catal A: Chemicals 198:167
8. Cserényi S, Felföldi K, Balázsik K, Szöllősi G, Bucsi I, Bartók M (2006) J Mol Catal A: Chemical 247:108
9. Masesane I (2006) Synthetic Page 239 (www.syntheticpages.org)
10. Borszeky K, Mallat T, Baiker A (1999) Catal Lett 59:95
11. Borszeky K, Mallat T, Baiker A (1996) Catal Lett 41:199
12. Sugimura T, Watanabe J, Uchida T, Nitta Y (2006) Catal Lett 112:27
13. Sugimura T, Watanabe J, Nitta Y, Okuyama T (2005) Tetrah Asymm 16:1573
14. Tungler A, Fogassy G (2001) J Mol Catal A: Chemical 173:231
15. Orglmeister E, Mallat T, Baiker A (2005) J Catal 233:333
16. Busygin I, Toukoniitty E, Leino R, Murzin D (2005) J Mol Catal A: Chemical 236:227
17. Morawsky V (2000) Catal Commun 1:15
18. Franceschini S, Vaccari A (2005) In: Sowa JR (ed) Catalysis of Organic Reactions. Taylor & Francis, Boca Raton (USA), p 547
19. Bisignani R, Franceschini S, Piccolo O, Vaccari A (2005) J Mol Catal A: Chemical 232:161
20. Casagrande M, Franceschini S, Lenarda M, Piccolo O, Vaccari A (2006) J Mol Catal A: Chemical 246:263

21. Toukoniitty E, Franceschini S, Vaccari A, Yu D (2006) Murzin, Appl Catal A300:174
22. Hench LL, West JK (1990) Chem Rev 9:33
23. Brinker CJ, Scherer GW (1990) Sol–gel Science. Academic Press, Boston (USA), p 98
24. Pagliaro M, Ciriminna R (2001) Tetrah Lett 42:4511
25. Aristizàbal B, González C, Barrio I, Montes M, Montes de Correa C (2004) J Mol Catal A: Chemical 222:189
26. Guimaraes AP, Viana P, Lago R (2002) J Non-Crystalline Solids 304:70
27. Troitski SYu, Serebriakova MA, Fedotov MA, Ignashin SV, Chuvilin AL, Moroz EM, Novgorodov BN, Kochubey DI, Likholobov VA, Blanc B, Gallezot P (2000) J Mol Catal A:Chemical 158:461
28. Griffiths SP, Johnston P, Wells PB (2000) Appl Catal A191:193
29. Podwer Diffraction Files (1991) Alphabetical Indexes Inorganic Phases. ICDD, Swarthmore (USA)
30. Nitta Y, Ueda Y, Imanaka T (1994) Chem Letters 23:1095
31. Campanati M, Fornasari G, Vaccari A (2003) Catal Today 77:299
32. Rodríguez-Castellón E, Mérida-Robles J, Díaz L, Maireles-Torres P, Jones DJ, Rozière J, Jiménez-López A (2004) Appl Catal A260:9
33. Jones DJ, Jiménez-Jiménez D, Jiménez- López A, Maireles-Torres P, Olivera-Pastor P, Rodríguez-Castellón E, Rozière J (1997) Chem- Commun 431
34. Rodríguez-Castellón E, Jiménez-López A, Maireles-Torres P, Jones DJ, Rozière J, Trombetta M, Busca G, Lenarda M, Storaro L (2003) J Solid State Chem 175:159