Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.7 No.9, 2015
www.iiste.org

Synthesis of TS-1 from TiO_2 and Ludox Silica and Use as Catalyst for Cyclooctene Epoxidation

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Abstract

The aim of this work was the synthesis of a TS-1 zeolite starting from Si and Ti precursors more adapted to scale-up than TEOS and tetra-alkyl orthotitanates. Silica and titania were used here. The resulting TS-1 material was characterized and its catalytic performance evaluated in the oxidation of cyclooctene in liquid-phase (acetonitrile) using anhydrous H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as oxidants. The TS-1 with Ti/Si = 0.0046 (XRF) was prepared via a hydrothermal treatment and characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR), UV-Vis. spectroscopy. A MFI structure with high crystallinity was obtained in which the titanium atoms are tetrahedrally coordinated to four oxygen atoms. Using titanosilicalite TS-1 with MFI structure in heterogeneous catalytic oxydations of cyclooctene with aqueous H_2O_2 and Tert-butyl hydroperoxide the epoxide of cyclooctene is detected to be highest among the obtained variety of compounds. The reaction progress is monitored by GC-MS.

Keywords: Zeolite, XRF, TS-1, XRD, IR, UV-Vis., catalyst, cyclooctene, epoxidation

1. Introduction

Catalysts derived from solid acids and bases play an important role with respect to economic and ecological aspects [1]. Both are extensively applied in various chemical reactions [2,3] but, up to now, the number of processes using solid acid catalysts is overwhelmingly larger than those considering solid bases[4]. Among the solid acids, natural and synthetic zeolites have attracted a great interest due to their catalytic and exchange properties. Such microporous materials-based catalysts have also shown great potential for the epoxidation of various olefins[5]. The most successful systems for heterogeneous liquid phase epoxidation are obtained with the Shell catalyst[6] or titanium silicalite (TS-1) [7]. Titanium silicalite (TS-1) which belongs to the class of manufactured zeolites was first patented by Enichem in 1983[7]. For a titanium content below 1-2wt%, TS-1 presents an ordered crystalline microporous structure where titanium ions are incorporated as isolated sites within the MFI lattice.

In this work, we report on the synthesis of TS-1 using silica and titania as Si and titanium sources instead of TEOS and a tetra-alkyl orthotitanate. Crystallization was carried out at 175°C but for a shorter time than usual when using silica and titania (24 h). The resulting solid was characterized by XRD, FT-IR and UV-Vis. and its catalytic performances evaluated through an epoxidation test.

2. Experimental

2.1. TS-1 synthesis procedure

Titanium silicalite was synthesized from Ludox silica and titanium dioxide used as silicon and titanium sources, respectively, in the presence of a template, tetrapropylammonium hydroxide (TPAOH), under hydrothermal conditions.

Hence, 7.5 g of Ludox (40 wt.% in H_2O) in 6.08 g of H_2O, 1.686 g of TPAOH (40 wt.% in H_2O) and 0.114 g of TiO_2 mixed in a flask were stirred for 2 h at room temperature. At this step, the reaction mixture had the following molar composition: $1SiO_{2,}$ $0.01TiO_{2,}$ 0.13TPAOH, $13H_2O$. The xerogel obtained was transferred into a stainless steel autoclave which was heated for 24 h in an oven at 175°C. To stop the crystallization process, the autoclave was removed from oven and cooled at room temperature. The autoclave mixture was filtered and washed several times with distilled water. The resulting powder was dried overnight at 90°C and calcined in air at 550°C for 6 h.

2.2. Instruments

The silicon and titanium compositions of TS-1 were determined by X-Ray Fluorescence spectroscopy using an energy dispersive XEPOS spectrometer (Spectro Ametek). The sample was analyzed in its powder form. Quantitative data were determined using the MicroPowder method. X-ray diffraction patterns of the same material were recorded between 10 and 50° on a Bruker AXS D8 Advance diffractometer with a graphite monochromator using the Cu K radiation (λ = 1.5418 Å). The IR spectrum of TS-1 (KBr pellet) was recorded with a Bruker Vector 22 spectrophotometer. The Diffuse Reflectance UV-Vis. spectrum was recorded at room temperature between 200 and 800 nm on a Varian Cary 5E spectrophotometer equipped with a double monochromator and an integrating sphere coated with polytetrafluoroethylene (PTFE) as reference.

3. Results and discussion

The following theoretical molar composition: $1SiO_2$, $0.01TiO_2$, 0.13TPAOH, $13H_2O$ was used (see experimental part) allowing the formation of TS-1. XRF showed that the synthesized sample contains 47.0 wt.% of Si and 0.22 wt.% of Ti, *i.e.* a Ti/Si atomic ratio of 0.0046 instead of 0.01. Half of the titanium species was incorporated. Such loading of titanium is compatible with its location inside tetrahedral sites in the structure lattice of TS-1. Physicochemical properties of the sample are detailed below.

3.1. Characterization of TS-1

3.2.1. X-Ray Diffraction (XRD)

XRD patterns of the silicalite-1 ($10 < 2\theta < 50°$) synthesized in this paper are shown in Figure 1. Diffraction peaks centered at $2\theta = 21$, 23.04, 23.22, 23.71, 23.93, 24.37 and 29.18° indicate the presence of a MFI-type phase in accordance with the data published by the International Zeolite Association[6,8] for the diffraction patterns of ZSM-5 (orthorhombic symmetry)[9,10]. Peaks in Figure 1 are related to the incorporation of titanium in the framework of TS-1[11]. No characteristic peaks of anatase were observed at 25.4, 37.8 and 48°.

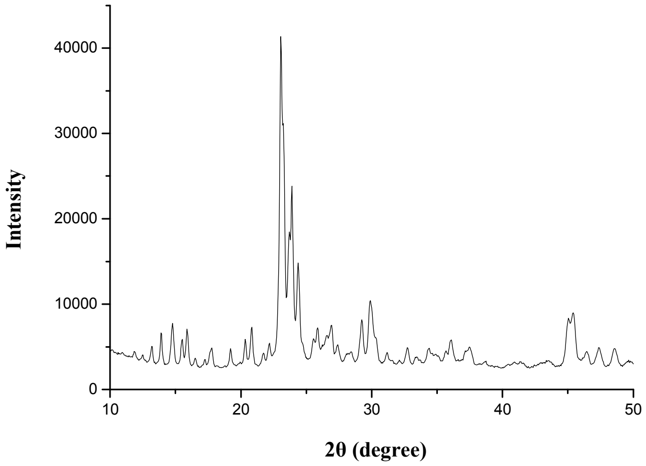


Fig 1: XRD patterns of TS-1.

3.2.3. IR spectroscopy

It is worth noting that wavenumbers around 450-1230 cm^{-1} are of strong interest to differentiate zeolite types. Absorption bands of tetrahedral structure typical of MFI zeolite at 1228, 1103, 798, 551 and 451 cm^{-1} are observed here[9]. The absorption band at 1103 cm^{-1} with a shoulder around 1228 cm^{-1} can be assigned to the asymmetric stretching vibration of Si-O-Si, while that at 798 cm^{-1} is for the stretching/bending symmetry vibration of the Si-O-Si bridge. Absorption bands at 551 and 451 cm^{-1} can be attributed to the rocking vibration of Si-O-Si[12]. The insertion of titanium in the TS-1 framework[8,13] is usually demonstrated by the existence of the stretching vibration mode of the Si-O-group of $[SiO_4]$ units bound to Ti(IV) atoms at 960-970 cm^{-1}. This band has been assigned to the asymmetric stretching vibration mode of the bridge Si-O-Ti by Boccuti and Thangaraj et al.[14,15]In the present case, only a shoulder could be observed due to the low loading of Ti in our sample[6].

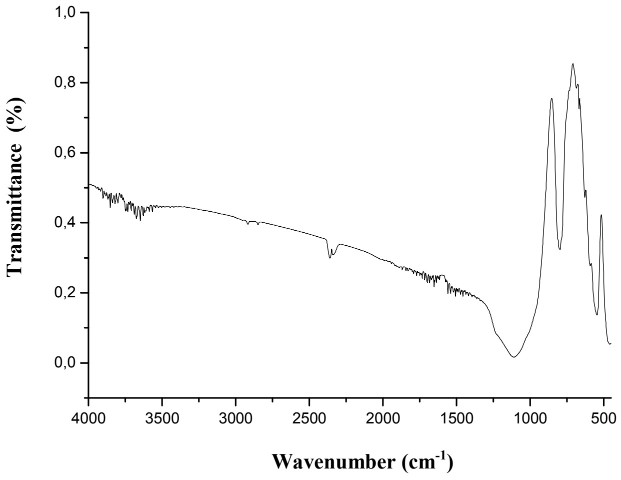


Fig 2: IR spectrum (transmission) of TS-1.

3.2.4. UV-Vis. spectroscopy

The shape of the DRUV spectrum is similar to those already published in the literature for this type of zeolite[16,17]. The Ti/Si atomic ratio of the synthesized TS-1 sample is 0.0046 which should not favor the formation of octa-coordinated titanium species at the expense of the expected tetra-coordinated ones. UV-Visible spectroscopy was used to confirm the absence of these extra framework titanium ions which are not active for oxidation reactions and participate to the degradation of H_2O_2[18]. Hence, the UV-Vis. spectrum of TS-1 shows an intense band at 212 nm corresponding to a charge transfer transition involving isolated tetra-coordinated framework titanium and oxide ions[14,18,21]. The absence of peaks at 260-270 nm indicates a large ordered arrangement of Ti-O-Si bond[22].

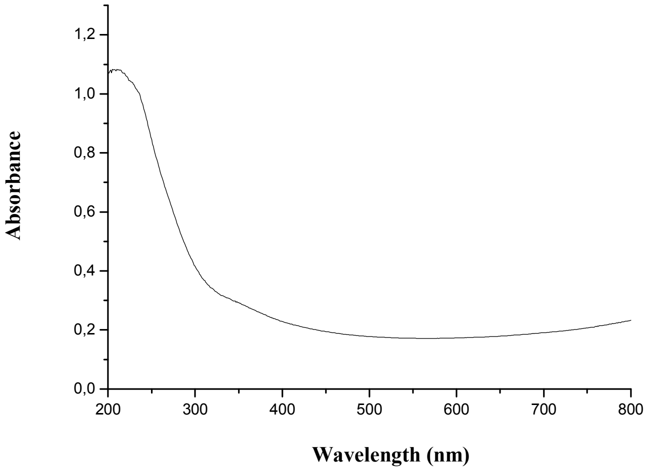


Fig 3: Diffuse reflectance UV-Vis. spectrum of TS-1.

3.3. Oxidation tests

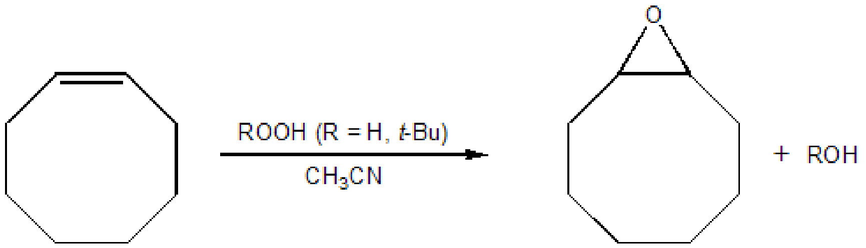
Cyclooctene, urea-hydrogen peroxide, *tert*-butyl hydroperoxide (5.5 M in decane) were purchased from Sigma-Aldrich and used as received. Oxidation reactions were carried out in a two-neck round-bottom flask equipped with a reflux condenser. The reaction system was magnetically stirred. The reaction progress was monitored by GC-MS (Trace GC equipped with a Optima 5 MS column (30 m length, 0.25 m film thickness, 0.025mm internal diameter) coupled to a MS spectrometer). To identify the epoxidation products, 1 L was taken from the crude reaction mixture after cooling and was injected into the GC/MS.

Case of hydrogen peroxide: 0.5 M anhydrous hydrogen peroxide (CH_3CN / H_2O_2) was prepared by extracting H_2O_2 from its urea adduct using acetonitrile. The oxidation reaction was carried out at 50°C. First, the flask was charged with 100 mg of TS-1, then 30 mL (15 mmol) of CH_3CN / H_2O_2, 0.50 mL (4 mmol) of cyclooctene and 0.77 mL (4 mmol) of decane, used as an internal standard, were introduced.

Case of *tert*-butylhydroperoxide (TBHP): First, the flask was charged with 100 mg of TS-1, then 10 mL of CH_3CN, 0.91 mL (7 mmol) of cyclooctene, 2.2 mL (11 mmol) of *tert*-butyl hydroperoxide (5.5 M in decane) were introduced. The mixture was heated at 70°C.

3.3.1 Catalytic reactions:

The existence of tetrahedral type coordinated titanium in the framework structure of TS-1 is important for the catalyst activity[8,21]. The TS-1 sample was tested in the catalytic epoxidation of cyclooctene in acetonitrile using either anhydrous H_2O_2 (0.5 M) or *tert*-butyl hydroperoxide in decane (TBHP) at 50 or 70°C, respectively (scheme 1).



Scheme 1: Oxidation of cyclooctene.

Due to its stability to oxidation processes, acetonitrile was selected as solvent. Its rather high polarity allows the miscibility of the oxidizing agent in the reaction mixture and, therefore, favors the access of the oxidant and of cyclooctene to the active sites[22]. Hydrogen peroxide or *tert*-butyl hydroperoxide interacts with Ti-O-Si affording Si-O-Ti-OOR (R = H or t-Bu).

Using H_2O_2 as the oxidant, a low amount of cyclooctene oxide with traces of allylic products, 2-cyclooctene-1-ol and 2-cyclooctene-1-one, were formed after 24 h. With a longer time (48 h), the epoxide yield was very slowly increased (Table 1).

Table 1: Relative areas of compounds detected by GC-MS for H_2O_2 / TS-1 vs. time.

	RT (min)	A_i/A_{is}*	
		24 h	48 h
Cyclooctene	4.2	0.63	0.69
Cyclooctene oxide	10.2	0.0001	0.005

*A_i and A_{is} correspond to the areas of the studied compound and the internal standard, respectively.

Using TBHP as oxidant, the reaction had to be performed at 70°C and lead to a mixture of compounds. Among the various products, cyclooctene oxide was found to be formed with the highest selectivity (Table 2). TBHP is advantaged compared to hydrogen peroxide due to the absence of water formation resulting from the reduction of this oxidant. Water is indeed considered to be at the origin of the TS-1 catalyst deactivation.

Table 2: Relative areas of compounds detected by GC-MS for TBHP / TS-1 vs.time.

	RT (min)	A_i/A_{is}*	m/z
cis cyclooctene	4.5	5.1	110
cyclooctene oxide	10.3	1.5	126
2-cycloctene-1-ol	10.9	0.2	108 ; 111 ; 126
2-cyclooctene-1-one	11.4	0.24	125.3 ; 124 ; 110
2-OH-cyclooctanone	16.5	0.2	141,9 ; 137.9 ; 123.9 ;110.10 ; 108 ; 125,9 ;
trans 1,2-cycloctanediol	19.3	0.1	145.2; 143.9;142.7;126.1;124.9;108.4

*A_i and A_{is} correspond to the area of the studied compound and the internal standard, respectively.

Besides cyclooctene oxide, trans 1,2-cyclooctanediol, 2-cycloctene-1-ol, 2-hydroxy-cyclooctanone, 2-cyclooctene-1-one were also produced (Table 2). The diol is probably derived from the hydrolysis of cyclooctene oxide due to the presence of some water molecules coordinated to the TS-1 centers in an acidic environment. Other compounds mentioned before are resulting from dehydration of the diol and/or over-oxidation.

The weak catalytic performances of TS-1 synthesized in this work are related to the use of cyclooctene as a substrate. This molecule has a relatively high kinetic diameter (5.5Å)[23] and does not easily reach the titanium species included in the pores. Therefore, only those located on the external surface of the crystals are involved here.

The higher temperature of the test performed with TBHP leads to a higher yield of epoxide due to side reactions not involving titanium. In the latter case, tert-butoxyl (*t*-BuO$^{\cdot}$), hydroxyl (HO$^{\cdot}$) then *tert*-butylhydroperoxyl (*t*-BuOO$^{\cdot}$) radicals may be produced by thermal decomposition of TBHP[24]. The latter are able to produce cyclooctene oxide from cyclooctene.

4. Conclusion

TS-1 zeolite with Ti/Si = 0.0046 (XRF) was prepared from silicate and titanium dioxide under hydrothermal conditions and characterized as a orthorombic structure (XRD) with tetrahedrally coordinated titanium ions (cf. UV-Vis, FT-IR data). Possible uses as a catalyst were evidenced in the oxidation of a rather sterically hindered substrate, i.e. cyclooctene, in the presence of hydrogen peroxide and TBHP in acetonitrile. With TBHP, at 70°C, the oxidation reaction gave mixtures consisting in the epoxide, allylic compounds and products derived from the opening of the oxirane ring. TBHP led to a bigger amount of cyclooctene oxide than hydrogen peroxide. A non-metalled centered mechanism could explain the relatively good oxidation results with this oxidant. In the continuation of our work we focused on the synthesis of new microporous materials and the study on their properties in heterogeneous catalyst reactions.

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