Applied Catalysis A: General 345 (2008) 195–200

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Titanium and cerium-containing mesoporous silicate materials as catalysts for oxidative cleavage of cyclohexene with H_2O_2: A comparative study of catalytic activity and stability

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ARTICLE INFO

Article history:
Received 12 February 2008
Received in revised form 6 April 2008
Accepted 29 April 2008
Available online 3 May 2008

Keywords:
Cyclohexene
Oxidation
Hydrogen peroxide
Adipic acid
Titanium
Cerium
Mesoporous silicate materials

ABSTRACT

Catalytic properties of transition-metal-containing silicate materials with hexagonally packed mesopore-channels, Ti-MMM-2 and Ce-SBA-15, have been studied in oxidative cleavage of cyclohexene (CyH) to adipic acid using aqueous H_2O_2 as oxidant. In a solvent-free system, the yield of adipic acid reached 10–15% at H_2O_2/CyH 3.6 mol mol^{-1} and 80 °C after 72 h. The stepwise addition of the oxidant to the reaction mixture allowed increasing the yield of the target product up to 33 and 18% for Ti-MMM-2 and Ce-SBA-15, respectively. For both catalysts, the yield of adipic acid decreased significantly in the second run despite CyH conversion attained 100%. The catalyst stability and the reasons of the deactivation have been explored. For both catalytic materials, partial decrease of the mesopore surface area and mesopore volume was observed after the CyH oxidation run. DRS–UV–vis study revealed irreversible formation of oligomerized TiO_2-like species on the Ti-MMM-2 surface due to interaction of Ti centres with the oxidant and the reaction products. The elemental analysis data showed that adipic acid causes leaching of titanium from Ti-MMM-2 into solution. Ce-SBA-15 was found to be more stable with respect to the active metal leaching but prone to deactivation due to agglomeration of cerium ions to form cerium oxide nanocrystallites; partial reduction of Ce(IV) to Ce(III) also occurred.

1. Introduction

Adipic acid is a key intermediate in the manufacture of Nylon-66 polymer. Traditionally, adipic acid is produced via a two-step process that involves cyclohexane oxidation with dioxygen to -ol/-one mixture and further catalytic oxidation of this mixture with HNO_3 [1–3]. The development of a one-step synthesis of adipic acid is a challenging goal. The oxidative cleavage of cycloalkenes to yield carboxylic acids is widely used in organic synthesis [4]. Specifically, the selective oxidation of cyclohexene (CyH) is viewed as a possible alternative route for the production of adipic acid. Various oxometal reagents, including permanganate [1] and ruthenium tetroxide [5], were tried to achieve this goal. The activity of these reagents can be increased by addition of oxygen donors, such as NaOCl [6], $NaIO_4$ [7] and peracetic acid [8]. A combination of peroxotungstates and lipophilic quaternary ammonium salts was found to catalyze effectively the selective oxidative cleavage of CyH under phase-transfer conditions [9,10].

Although many types of catalytic systems have been tried in the title reaction, most of them were homogeneous. Since heterogeneous catalysis may offer advantages of an easier catalyst separation and recycling, a few research groups were focused on the development of a heterogeneous catalyst for CyH oxidation with environmentally friendly oxidants. Recently, mesostructured titano-aluminosilicate Ti-AlSBA-15 prepared using a grafting methodology was found to be highly active in the “one-pot” synthesis of adipic acid under mild conditions using *tert*-butyl hydroperoxide as oxidant [11]. The yield of adipic acid was as high as 70–80% after 24–48 h of CyH oxidation in CH_3CN at 80 °C. Fairly good catalyst recyclability was demonstrated.

Aqueous hydrogen peroxide is the most attractive oxidant (after dioxygen) because it is green, quite cheap and easy to handle [1,3,4,12]. Cyclohexene epoxidation with H_2O_2 over various micro- and mesoporous catalysts has been reported in many papers [13–18]. The catalytic activity of microporous titanium-substituted aluminophosphates was found to reduce in the order TAPO-5 > TAPO-11 > TAPO-36, with TAPO-5 being just slightly less active

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doi:10.1016/j.apcata.2008.04.039

than titanium silicalite TS-1 [14]. Afterward, TAPO-5 was successfully employed as catalyst for H_2O_2-based CyH oxidation to adipic acid in a solvent-free system [19]. CyH conversion reached 100%, while the yield of adipic acid was ~30% after 72 h at 80 °C. However, the question on the Ti-catalyst stability and the possibility of recycling has not been addressed in [19] and in other related papers.

In our previous work, we demonstrated that Ti-containing mesoporous mesophase materials Ti-MMM and Ti-MMM-2 prepared by hydrothermal synthesis at pH 9 and 3, respectively, using cetyltrimethyl ammonium bromide as surfactant are effective catalysts for selective oxidation of a few bulky organic substrates [20–25]. Specifically, Ti-MMM with Si/Ti atomic ratio 49–129 and mesopore diameter 3.4–3.8 nm showed fairly good activity in CyH oxidation with H_2O_2 in CH_3CN [20,21]. Cyclohexene oxide and *trans*-cyclohexane-1,2-diol prevailed among the oxidation products. No titanium leaching occurred during the oxidation process, and the catalysis nature was proved to be true heterogeneous. Meanwhile, Ti-MMM, like most of known mesoporous Ti,Si-catalysts (Ti-MCM-41, Ti-MCM-48, TiO_2–SiO_2 mixed oxides, etc.) suffered from hydrolytic instability, which led to catalyst deactivation and made problematic its recycling in H_2O_2-based processes [21,24–26].

Since the first syntheses of mesoporous titanium silicates in 1992, a considerable progress seems to be achieved in solving the problem of the hydrothermal instability of mesoporous titanium-silicates [22,23,27,28]. In particular, Ti-MMM-2 showed quite good stability and recyclability in H_2O_2-based oxidation of thioethers, alkenes and alkylphenols under rather mild reaction conditions [22,23]. In contrast to Ti-MMM prepared under weak alkaline conditions, both structural and textural properties of Ti-MMM-2, which is prepared under weak acidic conditions, remained unchanged after treatment with boiled water [22]. Note that the structure of Ti-MMM-2 is less ordered compared to Ti-MMM and Ti-SBA-15. The silicate wall thickness of Ti-MMM-2 (1.0 nm) is comparable with that of Ti-MMM (0.8–1.0 nm) but less than that of Ti-SBA-15 (1.6–2.0 nm) [22,25]. At the same time, mesopore diameter of Ti-MMM-2 (3.2 nm) is comparable to that of Ti-MMM (3.5 nm) and significantly smaller compared to Ti-SBA-15 (10.6 nm) [22,25].

Recently, some of us reported that cerium-containing mesoporous materials Ce-SBA-15 (Si/Ce = 15–60) synthesized by hydrothermal method using a triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$) are able to catalyze cyclohexene oxidation with H_2O_2 [29]. Catalytic activity of these materials strongly depended on the amount and agglomeration of cerium atoms as well as the concentration of OH-groups on the surface.

In the present work, we explore the possibility of using Ti-MMM-2 and Ce-SBA-15 catalysts for CyH oxidation to adipic acid using clean and cheap oxidant—aqueous H_2O_2. Special attention is drawn to the questions of the catalysts stability under the reaction conditions and their recyclability, both crucial for heterogeneous liquid-phase oxidations.

2. Experimental

2.1. Materials and catalysts

H_2O_2 was used as 28 wt% solution in water and was determined iodometrically. Cyclohexene (99%, Aldrich) was purified by distillation prior to use. Cyclohexene oxide, *trans*-cyclohexane-1,2-diol, 2-cyclohexene-1-ol and 2-cycloxehene-1-one were purchased from Aldrich and used without further purification. Ce-SBA-15 was synthesized according to [29]. Ti-MMM-2 was prepared following a procedure described in [22]. The transition metal content along with the main textural characteristics of both Ce-SBA-15 and Ti-MMM-2 are given in Table 1.

2.2. Instrumental measurements

DR–UV–vis spectra were recorded on a UV-2501 PC Shimadzu spectrometer with a IRS-250A diffusion reflection attachment in the 190–900 nm range with a resolution of 2 nm. $BaSO_4$ was used as standard for measurements. Textural characteristics of catalyst samples were determined from nitrogen adsorption isotherms (77 K, ASAP-2400 Micromeritics) as described in [30]. The products were identified by GC–MS using a Saturn 2000 gas chromatograph equipped with a CP-3800 mass spectrometer employing a 40-m capillary column (Carbowax 20M/Lukopren G 1000 = 1/3). A gas chromatograph Tsvet-500 equipped with a flame ionization detector and a 3 m × 3 mm column filled with 5% SE-30 on Chromosorb W was used for quantitative GC analysis.

2.3. Catalytic tests

CyH oxidation runs were carried out in a temperature-controlled autoclave under vigorous stirring. Typically, 4.9 mmol of CyH, 5.9–20.6 mmol of H_2O_2 and 50 mg of catalyst were charged into the reactor and heated at 80 °C for 24–72 h. *o*-Dichlorobenzene was used as an internal standard for GC. Aliquots were taken during the reaction course and analyzed by GC. Adipic acid was determined as its methyl ether after addition of α-methyl-α-nitrosourea into the aliquots [31].

The study on H_2O_2 degradation was carried out in a temperature-controlled magnetically stirred reactor. Typically, 17.6 mmol of H_2O_2 and 50 mg of the catalyst (fresh or recycled) were charged into the reactor and heated at 80 °C for 3–4 h under vigorous stirring. Aliquots of the solution (25 μL) were taken during the reaction course by a syringe, and the concentration of H_2O_2 was determined by iodometric titration.

2.4. Catalyst stability tests

The catalysts were examined in two consecutive runs. After the first cycle of CyH oxidation, the catalyst was washed with 50 mL of

Table 1
Physicochemical characteristics of Ti-MMM-2 and Ce-SBA-15

Catalyst	Metal[a] (wt.%)	D[b] (nm)	A_{BET}[c] ($m^2\ g^{-1}$)	A_{meso}[d] ($m^2\ g^{-1}$)	V_{meso}[e] ($cm^3\ g^{-1}$)	V_{micro}[f] ($cm^3\ g^{-1}$)
Ti-MMM-2	1.5 (1.3,[g] 0.9[h])	3.2 (3.0)[g]	1147 (788)[g]	1096 (73)[g]	0.58 (0.27)[g]	0 (0.32)[g]
Ce-SBA-15	2.0 (2.0,[g] 1.9[h])	7.7 (6.9)[g]	1093 (585)[g]	928 (621)[g]	1.38 (1.01)[g]	0 (0)[g]

[a] Weight percent of metal in the sample.
[b] Average pore diameter ($4V/A_{BET}$).
[c] BET surface area.
[d] Mesopore surface area (BJH).
[e] Mesopore volume (BJH).
[f] Micropore volume.
[g] After 72 h of the reaction of CyH oxidation.
[h] After treatment with adipic acid (for the reaction and treatment conditions see Section 2).