Catal Lett (2007) 119:120–125
DOI 10.1007/s10562-007-9208-4

Well-dispersed Ceria-promoted Sulfated Zirconia Supported on Mesoporous Silica

Yingkui Guo · Zuowei Dong

Received: 21 May 2007 / Accepted: 9 July 2007 / Published online: 25 July 2007

Abstract Ceria-promoted sulfated zirconia (CeSZ) was supported on mesoporous molecular sieve of pure-silica MCM-41 (abbreviated as CeSZ/MCM-41). It was prepared by direct impregnation of metal sulfate onto the as-synthesized MCM-41, followed by solid state dispersion and thermal decomposition. The resultant catalysts were characterized by TG, XRD, nitrogen physisorption and TEM. It was showed that the hollow tubular structure of MCM-41 was retained, even with ZrO_2 loading as high as 60 wt.%. Most of CeSZ was well dispersed on the interior surface of the ordered mesopores, following a slight twist of the channels. The catalytic activity of CeSZ/MCM-41 was studied in the octadecanol oxidation. The improved performance of CeO_2-promoted catalysts was attributed to the high dispersion of sulfated zirconia (SZ) and the introduction of CeO_2 enhancing the oxidation ability of catalysts by retarding the transformation of zirconia from highly catalytic active metastable tetragonal phase to monoclinic phase.

Keywords Sulfated zirconia · Mesoporous silica · Ceria-promoted · Octadecanol oxidation

1 Introduction

Sulfated metal oxides, especially sulfated zirconia (SZ) first reported in 1979 by Hino et al. [1], have attracted great attention as superacid due to their highly catalytic activities in the isomerization of alkanes at relatively low temperature. However, the relatively small surface area (100–120 m^2/g) and short life of these catalysts may heavily limit their commercial application [2, 3]. Therefore, some researchers studied transition metals supported on porous materials, for instance, SiO_2 [4–6] and Al_2O_3 [7]. Although the catalytic activities of them can be improved properly, the pore distribution of these supports is not uniform and the surface area is <200–300 m^2/g.

Recently, well-ordered mesoporous materials with highly thermal stability (up to 800 °C), large surface area (around 1000 m^2/g), uniform-sized pores (20–100Å) and small diffusion hindrance, named as MCM-41 and MCM-48, were first reported by scientists at Mobil [8, 9]. The silica walls of mesoporous materials, however, usually lack of catalytic acidic sites and have little application without modifying them.

More recently, a new composite material of SZ supported on mesoporous silica such as MCM-41, has been reported by several research groups. For example, Xia et al. [10] have used $Zr(OPr^n)_4$ as the starting zirconium precursor to prepare SZ/MCM-41 by chemical liquid deposition and hydrolysis of zirconium salt in the organic solvent of n-hexane. Chen et al. [11] have prepared SZ supported on siliceous hollow tubular MCM-41 mesoporous molecular sieves by using a one-step incipient wetness impregnation method with zirconium sulfate as the precursor. Sun et al. [12] have successfully synthesized SZ supported on ordered mesoporous hexagonal materials by dispersion of $ZrOCl_2 \cdot 8H_2O$ into the mesopores, followed by the hydrolysis and sulfation. Wang et al. [13, 14] have found that Al- and Ga-promoted SZ/MCM-41 has higher catalytic activity in comparison with SZ/MCM-41, and the addition of promoters helps to retard the phase transformation of ZrO_2 from tetragonal phase to monoclinic phase.

Y. Guo (✉)
School of Materials Science and Engineering, Harbin University of Science and Technology, Harbin 150040, China
e-mail: gyk100@hrbust.edu.cn

Z. Dong
School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

In this work, the research focuses on the effect of ceria promotion in the SZ/MCM-41. Ceria is a good stabilizing agent [15–17] which can remarkably stabilize metastable tetragonal zirconia, known to be an ideal crystalline phase for catalytic activity [18–21]. We use direct impregnation method to prepare ceria-promoted sulfated zirconia (CeSZ) supported on as-synthesized MCM-41 whose retaining surfactants serve as a scaffold in stabilizing the mesostructure of CeSZ/MCM-41 during direct impregnation.

2 Experimental

2.1 Preparation of Catalysts

The MCM-41 sample was synthesized under hydrothermal condition with the molar composition of $0.15C_{16}TABr:1.0 TEOS:1.64NH_3 \cdot H_2O:130 H_2O$. The gel was crystallized in static condition at 100 °C for 72 h. Then the solid product was filtered, washed with deionized water and finally dried in air at room temperarure. The as-synthesized mesoporous material in powder form was suspended in an ethanol solution of the desired amount of zirconium sulfate and cerium sulfate mixture and stirred at 50 °C for 60 min, then dried to remove the solvent. The solid sample was heated at 450 °C for 5 h to decompose the remaining surfactants and the solid-state dispersion of sulfates. Finally, the solid was calcined at a desired temperature for 3 h in static air. In order to investigate the effect of ceria, ZrO_2 content was kept at 60 wt.% on every support.

2.2 Characterization

XRD patterns of the samples were obtained on an X′ Pert Philips instrument with Cu K_α radiation at 50 kV and 35 mA. The TGA data was collected with a TGA/SDTA 851 analyzer. The surface area and pore size distribution measurements were carried out on a Quantachrome automated adsorption instrument using nitrogen as analytic gas. TEM observation was performed on a Philips CM20 microscope operating at 200 kV. Sulfur content in the catalysts was measured by a chemical method. The sulfated was turned into BaSO4 and determined by a gravimetric method.

2.3 Catalytic Experiments

For the oxidation of the octadecanol, which is a model reaction for characterizing the catalytic activity of these superacid catalysts, approximately 0.3 g of power catalyst was placed in a glass flask with four necks for a stirring rod, a thermometer, a feed funnel and a reflux condenser, respectively, before 20 g of pure octadecanol was introduced into the flask using an oil bath as the heater. The reaction was carried out in the range of 130–140 °C for 5 h under vigorous stirring. The alcohol conversion and corresponding carboxylic acid yield were detected by a hydroxyl-value quantitative analysis method and a standard titration procedure, respectively.

3 Results and Discussion

3.1 Thermal Decomposition Analysis

Figure 1 shows the TG profile taken in air of the precursor of CeSZ/MCM-41, in comparison with those of as-synthesized MCM-41 and $Ce(SO_4)_2 \cdot 4H_2O$. Curve (a) shows that most of the surfactant decomposed at around 200–400 °C. Curve (b) shows that the crystal water and the structure water of $Ce(SO_4)_2 \cdot 4H_2O$ were removed at the temperature range of 100–450 °C and 450–750 °C, respectively, and after 750 °C $Ce(SO_4)_2$ began to decompose. According to the curve (c), there were several weight loss steps. In comparison with the other two profiles, the weight loss at temperature lower than 400 °C is mainly due to the decomposition of surfactant in light of minute quantity of $Ce(SO_4)_2 \cdot 4H_2O$. The weight loss occurred at temperature higher than 600 °C is primarily due to the decomposition of $Zr(SO_4)_2$ which decomposes at around 650–700 °C [22]. TG analysis shows that the complete decomposition of cerium sulfate occurs at relatively higher temperature, ca. 900 °C. Therefore, CeO_2 may play an important role in preserving sulfate on the catalyst surface.

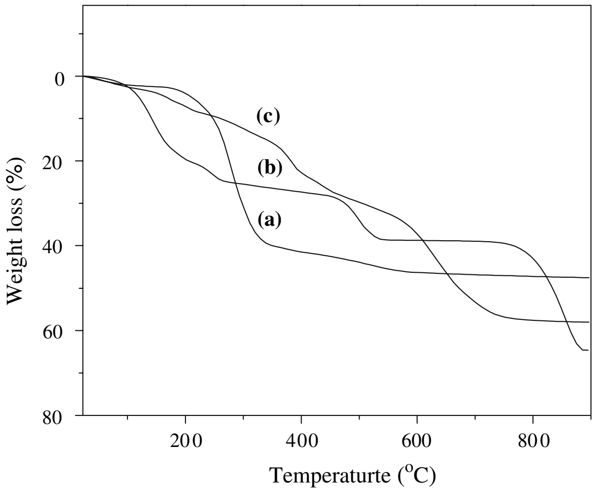

Fig. 1 TG analysis of (**a**) as-synthesized MCM-41, (**b**) $Ce(SO_4)_2 \cdot 4$ H2O and (**c**) the precursor of CeSZ/MCM-41 with 60 wt.% ZrO_2 and 3.4 wt.% CeO_2

3.2 X-ray Diffraction

Figure 2 shows the XRD patterns of the CeSZ/MCM-41 composites with 60 wt.% ZrO_2 and different CeO_2 contents calcined at 700 °C for 3 h. All the samples show a diffraction peak assigned to (100) reflection in the low 2θ region, which indicates that the ordered mesoporous structure is preserved on CeSZ/MCM-41. At high 2θ ranges, all the patterns show the peaks at 30°, 50° and 60°, indicating the presence of tetragonal zirconia nanocrystalline phase. The peaks at 28° can be indexed as monoclinic zirconia. It has been reported by many researchers that sulfated ZrO_2 of metastable tetragonal phase has higher catalytic activity than the monoclinic phase [18–21]. Huang et al. [23] have found that both tetragonal and monoclinic zirconia phases can be observed for the samples of high ZrO_2 contents (above 50 wt.%). However, the CeSZ/MCM-41 sample with 3.4 wt.% CeO_2 only shows the peaks of tetragonal zirconia. It is known that CeO_2 is an excellent stabilizer which can retard the transformation of ZrO_2 from tetragonal phase to monoclinic phase. Since the small peaks of ZrO_2 are observed in the region of 20–70°, most of the CeSZ was highly dispersed on the interior surface of MCM-41 at a high loading of 60 wt.% ZrO_2. Figure 3 shows the XRD patterns of CeSZ/MCM-41 with 3.4 wt.%CeO_2 after different heating treatment. The pure tetragonal zirconia phase was obtained only when the calcination temperature was at 700 °C.

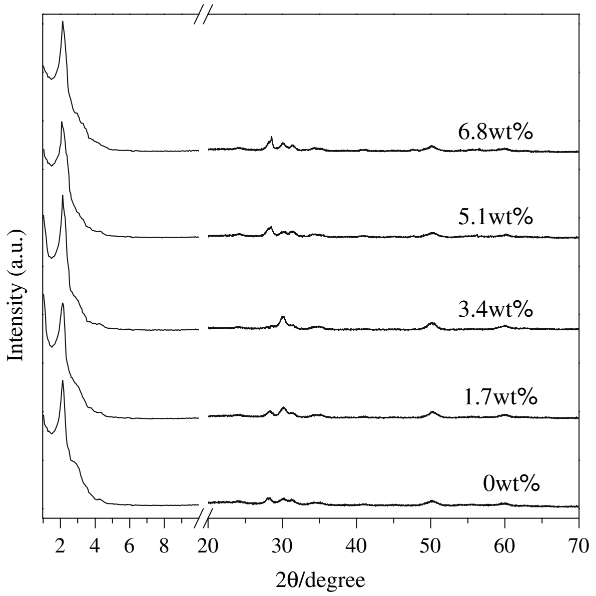

Fig. 2 XRD patterns of the composites of CeSZ/MCM-41 with 60 wt.% ZrO_2 and different CeO_2 contents calcined at 700 °C for 3 h in air

3.3 Physico-Chemical Properties of the Samples

Figure 4 shows the N_2 adsorption–desorption isotherms and pore size distribution of CeSZ/MCM-41 in comparison with those of pristine MCM-41. The isotherm for MCM-41 has a type IV shape. Upon supporting CeSZ on MCM-41 to form CeSZ/MCM-41, the N_2 adsorption amount decreased and the respective steps shift to lower values of P/P_0. The average pore diameter of MCM-41 decreased from 3.6 nm to 2.8 nm when the CeSZ was introduced. It is also noticeable that the pore size distribution still remains narrow for CeSZ/MCM-41. These results imply that the CeSZ was dispersed on the inner surface of MCM-41. Table 1 shows the surface areas, total pore volumes and sulfur contents of series CeSZ/MCM-41 samples. It is noticed that the surface area and pore volume decrease with the deposition of SZ-modified samples in comparison with that of pure silica-based MCM-41. However, the surface areas of various CeSZ/MCM-41 samples are still larger than those of the traditional SZ (around 100–120 m^2/g). Both CeO_2 contents and calcination temperatures affect the surface area. For CeSZ/MCM-41 with 3.4 wt.% CeO_2, the surface areas increase from 364 m^2/g upon 660 °C calcination to 480 m^2/g at 720 °C. The increase in the surface area is due to the decomposition of sulfate in the internal mesopores to form SZ. These results can be explained in connection with the change in XRD patterns of CeSZ/MCM-41 calcined at different temperatures. It can also be seen that the sulfur content decreases with the calcination temperature because more SO_3 should be released when the sample is calcined at higher temperature. On the other hand, it is found that the sulfur content increases with the

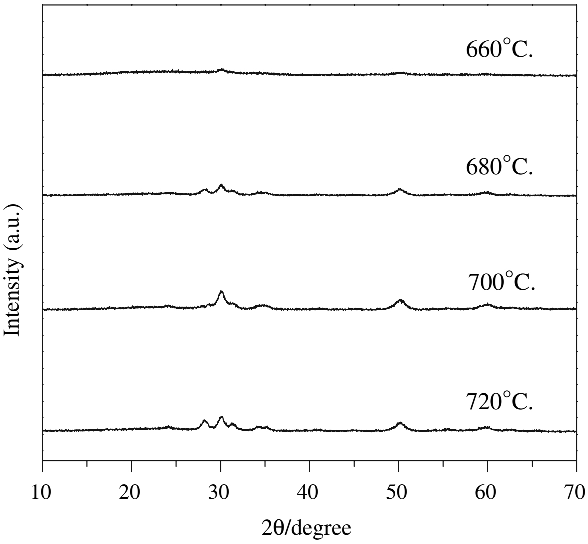

Fig. 3 XRD patterns of the composites of CesSZ/MCM-41 with 3.4 wt% CeO_2 content calcined at different temperatures for 3 h in air

Fig. 4 Nitrogen adsorption-desorption isotherms and pore size distribution curves of (**a**) MCM-41 and (**b**) CeSZ/MCM-41 with 3.4 wt.% CeO_2 content

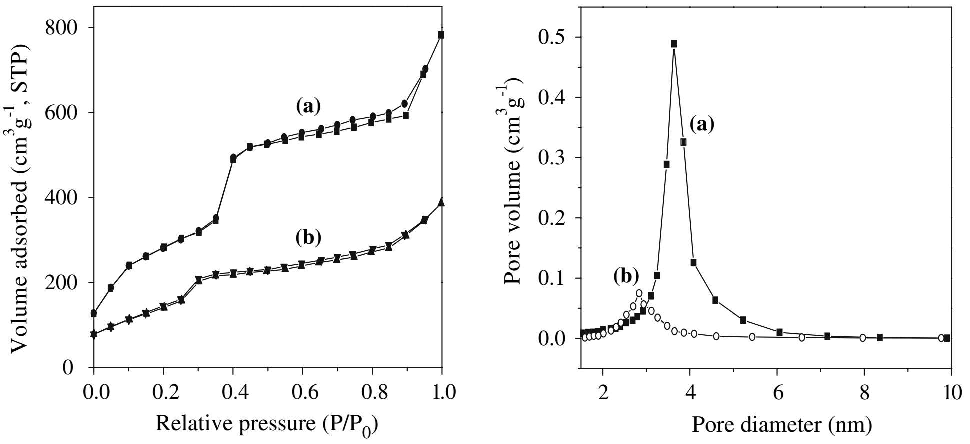

Table 1 Physico-chemical properties of the catalysts and support

Catalysts	Calc. temperature (°C)	CeO2 content (wt.%)	Sulfur content (wt.%)	BET S. A. (m^2/g)	Pore volume (mL/g)
SZ/MCM-41	700	0.0	0.76	425	0.41
CeSZ/MCM-41	700	1.7	1.03	438	0.42
CeSZ/MCM-41	700	3.4	1.53	447	0.46
CeSZ/MCM-41	700	5.1	2.01	441	0.44
CeSZ/MCM-41	700	6.8	2.62	435	0.42
CeSZ/MCM-41	660	3.4	1.97	364	0.35
CeSZ/MCM-41	680	3.4	1.73	402	0.40
CeSZ/MCM-41	720	3.4	1.39	480	0.49
MCM-41	700	–	–	1054	1.13

addition of CeO_2. Therefore, CeO_2 probably plays an important role in preserving sulfate on the catalyst surface.

3.4 TEM Analysis

Figure 5a shows the TEM image of the sample MCM-41. From the TEM micrograph of MCM-41, well-ordered channels with one-dimensional parallel arrangement and continuous walls are clearly observed. However, some sulfate particles with around 10 nm did not decompose and located outside the mesopores when they were supported on MCM-41, as shown in Figure 5b. It is clear that the sizes of those particles on the external surface exceeded the sum of the mesopore diameter and the wall thickness. Notably, the mesoporous silica framework was slightly disordered with the introduction of foreign particles and some mesopores were even blocked. Figure 5c is a TEM image of the sample CeSZ/MCM-41 with 3.4 wt.% CeO_2 calcined at 720 °C for 3 h. The TEM photograph shows that sulfate particles in the internal mesopores decomposed completely, forming CeSZ components and attaching to the internal surface of channels. Due to the introduction of foreign particles, the average pore size of MCM-41 decreases from 3.6 nm to 2.8 nm, following an increase in the wall thickness. On the other hand, there is a slight decline in the parallelism of channels and some mesopores are partially blocked, indicating that 60 wt.% ZrO_2 should be very close to the dispersion threshold of zirconia sulfate on MCM-41. Although the use of elevated temperature can result in the formation of large CeSZ particles outside the mesopores, the dispersed particles inside the channels of MCM-41 are still very small. In other words, mesoporous structure of MCM-41 plays a very important role in preventing the formation of large CeSZ agglomerates, avoiding the choke of mesopores.

3.5 Catalytic Activity in Octadecanol Oxidation

Figure 6 shows the effect of the CeO_2 content on the catalytic activity of CeSZ/MCM-41 catalysts calcined at 700 °C. Both the octadecanol conversion and corresponding carboxylic acid yield increased with the CeO_2 content up to 3.4 wt.%, and then decrease as the CeO_2 content was further increased. The optimal activity, a 99% of selectivity to octadecanoic acid, was observed when the CeO_2 content reached about 3.4 wt.% in the CeSZ/MCM-41 sample. Further increasing the CeO_2 content decreased the catalytic activity, although CeO_2 is usually used as a promoter

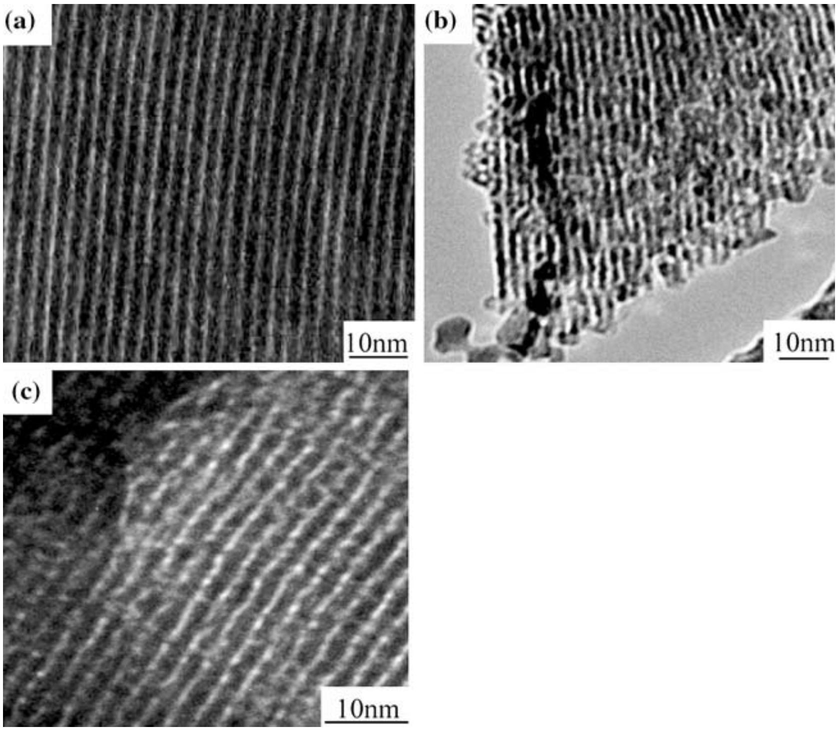

Fig. 5 High-resolution transmission electron micrographs of (**a**) MCM-41; CeSZ/MCM-41 with 3.4 wt.% CeO_2 calcined at (**b**) 660 °C and (**c**) 720 °C for 3 h

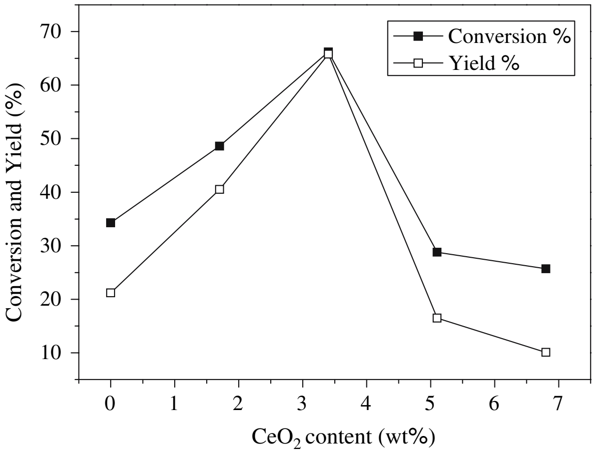

Fig. 6 Catalytic activity of catalysts calcined at 700 °C at constant ZrO_2 content 50 wt.% with various CeO_2 content

retarding the phase transformation of ZrO_2 from highly catalytic active metastable tetragonal phase to monoclinic phase. The appearance of an optimal CeO_2 loading on the catalytic activity implies that excess amount of CeO_2 can not means a more amount of tetragonal ZrO_2 with highly catalytic activity, and that it may cover the zirconia surface and reduce the catalytically active sites. These results indicate that the amount of tetragonal ZrO_2 in the CeSZ/MCM-41 catalysts plays a very important role in catalizing octadecanol to corresponding octadecanoic acid .On the other hand, the catalytic activity of CeSZ/MCM-41 after reaction can be restored by thermal treatment at 450 °C in air.

Figure 7 shows the effect of calcination temperature on the catalytic activity of CeSZ/MCM-41 with 3.4 wt.% CeO_2. The catalytic activity of the samples increased with the final calcination temperature up to 700 °C, and then decreased at higher temperature. The result is reasonable because more amount of sulfate zirconium decomposed at higher temperature according to the reaction $Zr(SO_4)_2 \rightarrow ZrO_2 + 2SO_3$, following an decrease in the sulfur content of the CeSZ/MCM-41 catalysts. The optimal activity was obtained when the CeSZ/MCM-41 sample was calcined at about 700 °C. Since the sulfur content decreases as the

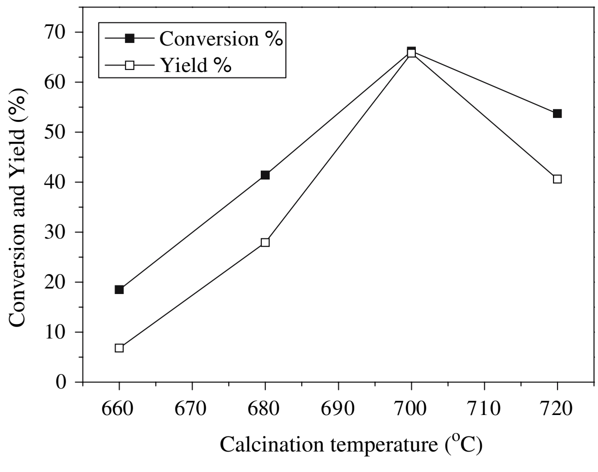

Fig. 7 Effect of calcination temperature on the catalytic activity of CeSZ/MCM-41 with 60 wt.% ZrO_2 and 3.4 wt.% CeO_2

calcination temperature increases, the 700 °C calcination temperature for optimal catalytic activity is probably a compromise between the sulfur content and the amount of tetragonal ZrO_2 phase.

Previously, Tsukuma et al. had associated the increase in tetragonal ZrO_2 of ZrO_2-CeO_2 system with the increased amount of CeO_2 [15–17]. However, the amount of tetragonal ZrO_2 in the CeSZ/MCM-41 samples does not increase strictly with the CeO_2 content, as shown in Figure 2. Therefore, to some extent, the mesoporous structure of MCM-41 is responsible for the relative quantity of tetragonal and monoclinic ZrO_2 phases. Canton et al. had attributed the increased catalytic activity of Al_2O_3-promoted SZ to the reduction in particle size of ZrO_2 [24]. Here we also reach the high dispersion of ZrO_2 through using the mesopores of MCM-41 as confined space. Finally, we note that Wang et al. had related the increase in oxidation ability of Ga_2O_3-doped SZ/MCM-41 with the enhancement effect of Ga_2O_3 [13, 14]. In our case, this is expected since a proper amount of CeO_2 can retard the phase transformation of ZrO_2 from tetragonal phase to monoclinic phase.

4 Conclusion

In this work, CeSZ was successfully dispersed in the channels of silicon-based mesoporous MCM-41. The mesoporus framework was slightly disordered because of CeSZ particles supported on MCM-41. On the other hand, under high ZrO_2 loading, some CeSZ clusters were dispersed outside the channels of MCM-41. The proper addition of Ceria increased the amount of tetragonal zirconia with high catalytic behavior and product selectivity for octadecanoic acid. The optimal Ceria loading in these catalysts calcined at 700 °C is around 3.4 wt.% and only leads to the formation of tetragonal zirconia. The improved catalysis performance of CeO_2-promoted SZ/MCM-41 is attributed to the reasons that the mesopores of MCM-41 are conducive to a better dispersion of sulfated tetragonal ZrO_2, and that CeO_2 can prevent the transformation of tetragonal sulfated ZrO_2 into monoclinic ZrO_2.

References

1. Hino M, Kobayashi S, Arata K (1979) J Am Chem Soc 101:6439
2. Corma A, Fornes V, Navarro MT, Perez-Pariente J (1994) J Catal 148:569
3. Sayari A (1996) Chem Mater 8:1840
4. Yamaguchi T, Jin T, Ishida T, Tanabe K (1987) Mater Chem Phys 17:3
5. Huang YY, Zhao BY, Xie YC (1998) Appl Catal A General 171:65
6. Ishida T, Yamaguchi T, Tanabe K (1998) Chem Lett 1869
7. Lei T, Xu JS, Tang Y, Hua WM, Gao Z (2000) Appl Catal A General 192:181
8. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Nature 359:710
9. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, Mccullen SB, Higging JB, Schlenker JL (1992) J Am Chem Soc 114:10834
10. Xia QH, Hidajat K, Kawi S (2000) Chem Commun 2229
11. Chen C-L, Cheng S, Lin HP, Wong ST, Mou CY (2001) Appl Catal A General 215:21
12. Sun YY, Zhu L, Lu HJ, Wang RW, Lin S, Jiang DZ, Xiao F-S (2002) Appl Catal A Gen 237:21
13. Wang W, Chen C-L, Xu N-P, Han S, Li T, Cheng S, Mou C-Y (2002) Catal Lett 83:281
14. Wang W, Wang J-H, Chen C-L, Xu N-P, Mou C-Y (2004) Catal Today 97:307
15. Tsukuma K, Shimada M (1985) J Mater Sci 20:1178
16. Gogot GA, Zavada VP, Swain MV (1996) J Eu Ceram Soc 16:545
17. Tani E, Yoshimura M, Somiya S (1983) J Am Ceram Soc 66:506
18. Jin T, Yamaguchi T, Tanabe K (1986) J Phys Chem 90:4797
19. Yadav GD, Nair JJ (1999) Micropor Mesopor Mater 33:1
20. Morterra C, Cerrato G, Pinna F, Signotretto M (1995) J Catal 157:109
21. White RL, Sikabwe EC, Coelho MA, Resasco PE (1995) J Catal 157:755
22. Chen C-L, Li T, Cheng S, Xu NP, Mou C-Y (2002) Catal Lett 78:223
23. Huang Y-Y, Zhao B-Y, Xie Y-C (1998) Appl Catal A General 173:27
24. Canton P, Olindo R, Pinna F, Strukul G, Riello P, Meneghetti M, Cerrato G, Morterra C, Benedetti A (2001) Chem Mater 13:1634