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Article

Catalytic activity of Ag/SBA-15 for low-temperature gas-phase selective oxidation of benzyl alcohol to benzaldehyde

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ABSTRACT

Ag/SBA-15 catalysts with different Ag contents were prepared by an impregnation method and were used for the gas-phase selective oxidation of benzyl alcohol to benzaldehyde with O₂ as the oxidant. These catalysts were characterized using N₂ adsorption-desorption, X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, inductively coupled plasma mass spectrometry, and X-ray photoelectron spectroscopy. The effects of Ag loading, reaction temperature, and weight hourly space velocity of benzyl alcohol on the catalytic performance were investigated. The results showed that Ag was successfully incorporated into the mesoporous channels of SBA-15 and well dispersed on the surface as a result of the nano-confinement effect of SBA-15, which increased the specific surface area of the active components. Moreover, Ag/SBA-15 had a uniform pore size, a wall of thickness of 3–5 nm, and a high specific surface area of 411–541 m²/g. The catalytic activity of Ag/SBA-15 for the gas-phase selective oxidation of benzyl alcohol to benzaldehyde was enhanced by oxygen spillover of nucleophilic oxygen species from the Ag nanoparticles to the SBA-15 surface. The 5.3%Ag/SBA-15 exhibited excellent low-temperature catalytic properties; when the reaction temperature was 220 °C, the conversion of benzyl alcohol and the selectivity for benzaldehyde reached 87% and 95%, respectively. At 240 °C, the catalyst displayed the best catalytic properties, achieving a benzyl alcohol conversion of 94% and benzaldehyde selectivity of 97%, which remained almost constant at 240–300 °C. This showed that Ag/SBA-15 had excellent thermal gradient stability. The catalyst could be used for 40 h and retained high catalytic activity for oxidation after treatment at 500 °C.

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1. Introduction

Benzaldehyde is an important intermediate in organic synthesis [1] and is widely used in cosmetics, perfumery, food, and pharmaceutical industries [2]. At present, benzaldehyde is mainly produced by the gas-phase oxidation of toluene [3] or

liquid-phase oxidation of benzyl alcohol [4–6] on industrial and laboratory scales. However, these processes lead to generation of large amounts of by-products, which are difficult to separate, and the selectivity is poor; this limits benzaldehyde applications. Recently, gas/solid-phase selective oxidation of benzyl alcohol to benzaldehyde using O₂ as the oxidant in the presence

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of a heterogeneous catalyst in a packed bed reactor has attracted much attention because the process is solvent free and generates a small amount of by-products, and the products are easily separated. Supported metal catalysts such as Au-Cu/SiO₂ [7], Au/Ni fibers [8], Ag/SiO₂ [9], microfibrillar Ag [10,11], thin-sheet Ag/Ni fibers [12], and Ag-HMS [13] have been widely used in gas-phase selective oxidation of benzyl alcohol to benzaldehyde. Many of these catalysts showed good activities and selectivities, but the reaction temperature in most cases was above 300 °C. Galvanic deposition of Au onto sinter-locked Ni fibers delivered an excellent Au/Ni fiber catalyst [14] for low-temperature gas-phase benzyl alcohol oxidation. An Au catalyst loading of 4% and a reaction temperature of 240 °C were used, and a benzyl alcohol conversion of 99% and selectivity for benzaldehyde of 98% were achieved. Recently, a K-Cu-TiO₂ catalyst [15] was used in gas-phase benzyl alcohol oxidation to benzaldehyde at low temperature, i.e., 203–223 °C, giving a benzyl alcohol conversion of 72% and selectivity for benzaldehyde of 98%. However, the catalyst was temperature sensitive; a slightly higher reaction temperature (above 250 °C) led to total oxidation of benzyl alcohol to undesired benzyl acid. Low-temperature gas-phase selective oxidation of benzyl alcohol to benzaldehyde not only gives improved selectivity for benzaldehyde but also conforms to the guiding principles of green chemistry, so it has been attracting increasing attention [16].

SBA-15 mesoporous materials have highly ordered hexagonally arranged cylindrical pore structures, and the pore diameters can be systematically changed from 4.6 to 30 nm; they have thick walls, high specific surface areas, and good hydrothermal stabilities. Moreover, they have an abundance of surface Si-OH groups, and this is favorable for modification of SBA-15. The nano-confining effect of SBA-15 can be used to construct nanometer-scale active species; this is an effective method for producing functional nanomaterials [17–22], so it is widely used industrially for catalysts and adsorbents [23–31]. Ag-modified SBA-15 [32–37] has attracted the interest of many researchers for formaldehyde oxidation [38], selective oxidation of cycloalkanes [39], and CO oxidation [40–42] because of its remarkable catalytic performance. However, the application of Ag/SBA-15 in gas-phase selective oxidation of benzyl alcohol to benzaldehyde has rarely been reported.

In this study, a series of Ag/SBA-15 catalysts with different Ag loadings were synthesized using an impregnation method. The structure and active component of Ag/SBA-15 were characterized using N₂ adsorption-desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectrometry (ICP-MS). The catalysts were used in the gas-phase selective oxidation of benzyl alcohol to benzaldehyde with molecular oxygen as the oxidant, without any additives. The effect of Ag loading on the catalyst structure and the relationship between the structure and activity of the catalyst were investigated. The influence of reaction temperature on the conversion of benzyl alcohol and benzaldehyde selectivity was probed. The catalyst reusability was also investigated.

2. Experimental

2.1. Catalyst preparation

SBA-15 was synthesized according to the procedure reported in the literature [43,44]. A typical synthetic procedure was as follows. The triblock copolymer pluronic (P123, EO₂₀PO₇₀EO₂₀, *M_w* = 5800, Sigma-Aldrich, 4.2 g) was dissolved in 150 mL solution containing 60 g of HCl (4.0 mol/L) and 90 g of deionized water, and the solution was stirred for 2 h at 40 °C. Tetraethyl orthosilicate (8.5 g, AR, 98%) was then dropped into the solution and hydrolyzed at 40 °C for 24 h under vigorous stirring. The mixture was transferred to a Teflon vessel, and the vessel was sealed and heated at 100 °C for 24 h without stirring. The white solid formed was separated by filtration, washed three times with deionized water, dried at 60 °C overnight and calcined at 550 °C for 6 h, giving SBA-15 as a white powder.

A simple impregnation method was used to prepare Ag/SBA-15 catalysts based on previous reports [39,45]. Samples of SBA-15 support (1.0 g) were immersed in 50 mL of aqueous solutions containing different amounts of AgNO₃ under stirring. The slurry was stirred for 10 h at 50 °C. The wet samples obtained were dried at 80 °C for 12 h and calcined at 550 °C in air for 6 h. The samples were denoted by xAg/SBA-15, where x represents the Ag loading (mass fraction) determined using ICP-MS. In addition, after use for 40 h, 5.3%Ag/SBA-15 was washed with ethanol, filtered, dried at 80 °C for 12 h, and calcined at 500 °C for 2 h to giving regeneration catalyst and the sample was denoted by 5.3%Ag/SBA-15-A.

2.2. Catalyst characterization

Powder XRD patterns were recorded with a Bruker D8 Advance (Germany) diffractometer using Cu K_α radiation (λ = 1.5418 Å); the scanning speed was 3°/min and the scanned area was 2θ = 0.5°–80°. N₂ adsorption isotherms were measured at –196 °C using a Quantachrome NOVA2000e instrument. The samples were degassed at 300 °C for 3 h under vacuum (1×10^{-3} Torr) before the measurements. The specific surface area, pore size, and pore volume were determined using the BET and BJH methods. The sample morphologies were observed by SEM using a Rigaku S-4300 spectrometer (Japan); the voltage was 20 kV, and the vacuum degree of the sample room was better than 1×10^{-4} . HRTEM images were obtained using a Tecnai G2 transmission electron microscope (USA) operated at an accelerating voltage of 200 kV. The surface chemical compositions of the samples were determined by XPS with an ESCALAB 250Xi spectrometer (Thermo Electron, UK) using a non-monochromatized Al K_α X-ray source (1486 eV). The actual Ag loadings of all the catalysts were determined by ICP-MS using an Agilent 7500ce spectrometer. Before the tests, the catalysts were dissolved in 3 mL of HCl, 1 mL of HF, and 1 mL of HNO₃, and then the solution volume was increased to 100 mL using 3% HNO₃.

2.3. Evaluation of catalytic performance

The gas-phase oxidation of benzyl alcohol over Ag/SBA-15 was carried out in a conventional continuous-flow fixed-bed reactor (stainless-steel tube, inner diameter 6 mm, length 450 mm) at atmospheric pressure. First, the catalyst (0.8 g) was sieved to 40–60 mesh powders and pretreated in a flow of N₂ and O₂ (O₂:N₂ volume ratio of 3:7 and flow rate 50 mL/min) at 550 °C for 2 h before testing. Second, the reactants, consisting of purified N₂ (35 mL/min), purified O₂, and benzyl alcohol at a weight hourly space velocity (WHSV) = 4.7–12.5 h⁻¹ vaporized at 220 °C, were fed into the reactor bed using a precious liquid pump; the molar ratio of O₂ to benzyl alcohol was 0.6. Vaporization of benzyl alcohol was performed in a preheating zone, placed before the catalyst bed, and the reaction was carried out at 220–380 °C. The products were collected using an ice-salt bath (–5 to –10 °C), and the products were periodically sampled and analyzed using a gas chromatograph (Cotrun GC9800(N)) fitted with an OV-17 capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. The column temperature was 140 °C, and the detector and injector temperatures were 200 °C. The yield of benzaldehyde was calculated by multiplying the benzyl alcohol conversion by the selectivity for benzaldehyde.

3. Results and discussion

3.1. Catalytic properties of Ag/SBA-15

3.1.1. Effect of Ag loading

The catalytic performance of Ag/SBA-15 in the gas-phase selective oxidation of benzyl alcohol to benzaldehyde is shown in Table 1. SBA-15 had hardly any catalytic activity in the gas-phase selective oxidation of benzyl alcohol at 240 °C. However, after Ag loading, the conversion of benzyl alcohol increased significantly. It was confirmed that Ag was the active species. With increasing Ag loading from 4.1% to 16.5%, the conversion of benzyl alcohol increased from 74.8% to 96.6%, but the selectivity for benzaldehyde first increased from 85.2% to 96.9%, and then decreased to 91.5%. Ag over-loading led to further oxidation of benzaldehyde to benzoic acid, thus the selectivity was reduced. A catalyst with 5.3% Ag gave the best results: a benzyl alcohol conversion of 93.9%, selectivity for benzaldehyde of 96.9%, and a TOF of 128.6 h⁻¹.

Table 1

Effect of Ag loading on catalytic performance of Ag/SBA-15 in selective oxidation of benzyl alcohol to benzaldehyde.

Catalyst	Conversion of benzyl alcohol (%)	Selectivity for benzaldehyde (%)	Yield of benzaldehyde (%)	TOF ^a (h ⁻¹)
SBA-15	2.0	60.5	1.24	—
4.1%Ag/SBA-15	74.8	85.2	63.7	116.5
5.3%Ag/SBA-15	93.9	96.9	90.9	128.6
8.1%Ag/SBA-15	94.2	96.0	90.4	83.7
16.5%Ag/SBA-15	96.6	91.5	88.4	40.2

Reaction conditions: catalyst 0.8 g, 240 °C, $n(\text{O}_2)/n(\text{benzyl alcohol}) = 0.6$, WHSV = 7.8 h⁻¹.

^a TOF = $m(\text{benzaldehyde})/[m(\text{catalyst}) \times x \times t]$, where $m(\text{benzaldehyde})$ (g) was calculated from the conversion at 1 h reaction and by assuming that the Ag are active sites, $m(\text{catalyst})$ is equal to 0.8 g, x is the content of Ag determined by ICP-MS, and t (h) is the reaction time.

3.1.2. Effect of reaction temperature

Temperature is an important factor in the conversion and selectivity of the gas-phase selective oxidation of benzyl alcohol [12–16]. The effect of reaction temperature on the gas-phase selective oxidation of benzyl alcohol was investigated using 5.3%Ag/SBA-15 as the catalyst (Fig. 1). It shows that the benzyl alcohol conversion and selectivity for benzaldehyde were 86% and 95%, respectively, at 220 °C. This indicates that low-temperature gas-phase selective oxidation of benzyl alcohol to benzaldehyde can be achieved using Ag/SBA-15 as a catalyst. When the temperature increased to 240 °C, a benzyl alcohol conversion of 94% and a selectivity for benzaldehyde of 97% were obtained. The results remained almost unchanged with increasing temperature from 240 to 300 °C. However, as the temperature continued to rise to 340 °C, the selectivity dropped to 90%, and the conversion increased slightly. A selectivity of 85% and conversion of 100% were achieved until the temperature reached 380 °C. Liquid chromatography-MS analysis showed that the benzaldehyde was partially oxidized to benzoic acid at high temperature, leading to decreased selectivity. These results show that Ag/SBA-15 can be used as the catalyst in the production of benzaldehyde from benzyl alcohol by gas-phase selective oxidation at low temperatures; a high selectivity can be achieved across a wide temperature range, and the catalyst displays excellent thermal gradient stability for the reaction. The reactivity and the selectivity for benzaldehyde can be controlled by regulating the reaction temperature and using an appropriate catalyst.

3.1.3. Effect of WHSV

The influence of WHSVs of benzyl alcohol on the conversion, selectivity, and TOF over 5.3%Ag/SBA-15 is shown in Fig. 2. As the WHSV increased from 4.7 to 12.5 h⁻¹, the selectivity for benzaldehyde increased to above 95%, and the TOF increased from 77.1 h⁻¹ to a maximum of 134.9 h⁻¹ and then decreased to 127.6 h⁻¹; when the WHSV was 7.8 h⁻¹, the conversion of benzyl alcohol and the selectivity for benzaldehyde achieved maximum values of 94% and 97%, respectively, and the TOF was 128.6 h⁻¹. The maximum TOF value, 134.9 h⁻¹, was found when

Fig. 1. Conversion of benzyl alcohol (1) and selectivity for benzaldehyde (2) versus reaction temperature over 5.3%Ag/SBA-15 for selective oxidation of benzyl alcohol. Reaction conditions: catalyst 0.8 g, $n(\text{O}_2)/n(\text{benzyl alcohol}) = 0.6$, WHSV = 7.8 h⁻¹.

Fig. 2. Influence of different WHSVs (h^{-1}) of benzyl alcohol on conversion (1), selectivity (2), and TOF (3) over 5.3%Ag/SBA-15. Reaction conditions: catalyst 0.8 g, 240 °C, $n(\text{O}_2)/n(\text{benzyl alcohol}) = 0.6$.

the WHSV was 9.4 h^{-1} , but the benzyl alcohol conversion was only 82.8%. It was concluded that the optimum conditions were reaction temperature 240 °C, amount of catalyst 0.8 g, WHSV 7.8 h^{-1} , and $n(\text{O}_2):n(\text{benzyl alcohol}) = 0.6$, giving a benzyl alcohol conversion of 94% and selectivity for benzaldehyde of more than 97%.

3.2. Relationship between structure and catalytic activity of Ag/SBA-15

To investigate the relationship between the structure of Ag/SBA-15 and the catalytic performance, the structure and active ingredients of the catalyst in the gas-phase selective oxidation of benzyl alcohol were determined using N_2 adsorption-desorption, XRD, SEM, HRTEM, XPS, and ICP-MS.

The morphology of Ag and its content on the Ag/SBA-15 surface were analyzed using the XPS surface probe technique. The Ag 3d XPS spectra of 5.3%Ag/SBA-15 are shown in Fig. 3. The Ag 3d binding energy region consisted of asymmetric peaks that could be fitted to two doublets; the energy difference, $\Delta E = 6.1 \text{ eV}$, was ascribed to the Ag $3d_{3/2}$ (374.4 eV) and Ag $3d_{5/2}$ (368.3 eV) core levels of two different species [46,47]: metallic Ag (atomic ratio 90% of the total Ag $3d_{5/2}$ XPS signal,

Fig. 3. XPS spectra of 5.3%Ag/SBA-15.

368.4 eV) and Ag_2O (10%, 367.8 eV) [48]. These results show that the Ag particles on the Ag/SBA-15 surface consist of metallic Ag and oxidized Ag species [13] at 0.33% of the mass fraction of Ag. In addition, ICP-MS analysis showed that the percentage content of Ag was 5.3% for the 5.3%Ag/SBA-15 sample, so it can be estimated that the mass fraction of Ag in the SBA-15 mesopores was about 4.93%, i.e., more than 93% of the Ag was in the channels of mesoporous SBA-15. Combining the catalytic performance tests, it was concluded that Ag is the active species for gas-phase selective oxidation of benzyl alcohol to benzaldehyde.

The N_2 adsorption-desorption isotherms of the catalyst and the BJH pore size distribution curves are shown in Fig. 4. The N_2 adsorption-desorption isotherms of all the samples are type IV at high relative pressures ($0.6 < p/p_0 < 0.8$) because capillary condensation under N_2 presents an H1 hysteresis loop, Fig. 4(a). The adsorption and desorption branches across a narrow range of pressures displayed clear parallel trends. This is consistent with the SBA-15 molecular sieves having uniform open cylindrical pores ($d > 6 \text{ nm}$) [43–45,49]; however, with increasing Ag loading, the Ag/SBA-15 samples showed a wide range of relatively flat pressure hysteresis loops, and the adsorption and desorption branches closed at slightly lower pressures. According to Kelvin's law, the low pressure of capillary condensation when the aperture size decreased indicated

Fig. 4. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of Ag/SBA-15. (1) SBA-15; (2) 4.2%Ag/SBA-15; (3) 5.3%Ag/SBA-15; (4) 8.1%Ag/SBA-15; (5) 16.5%Ag/SBA-15; (6) 5.3%Ag/SBA-15-A.

Table 2
Physicochemical properties of Ag/SBA-15.

Catalyst	A_{BET}^a (m^2/g)	D^b (nm)	V^c (cm^3/g)	D_{Ag}^d (nm)
SBA-15	676	6.57	0.87	—
4.2%Ag/SBA-15	541	6.28	0.73	5.5
5.3%Ag/SBA-15	546	6.19	0.67	6.4
8.1%Ag/SBA-15	476	6.20	0.66	10.2
16.5%Ag/SBA-15	411	6.18	0.60	17.4
5.3%Ag/SBA-15-A	452	5.57	0.55	15.5

^a Surface area derived from BET equation.

^b Pore diameter derived by BJH method using desorption branch.

^c Pore volume obtained from the volume of N_2 adsorbed at a relative pressure of 0.99.

^d Ag particle size calculated using HRTEM images.

that the sample has ink-bottle-type channels [13,50]. Channel formation may be caused by Ag entering the pores. It can be seen from Fig. 4(b) that the average pore size became smaller and the pore size distribution broadened. The pore size distributions of 4.2%Ag/SBA-15 and 5.3%Ag/SBA-15 appeared at $d = 3.7$ nm. This is an illusion that originates from the narrow orifice of the ink-bottle-shaped channel, and further demonstrates the presence of Ag in the SBA-15 channels. The structural parameters of Ag/SBA-15 are shown in Table 2. As the Ag loading increased from 0 to 16.5%, the specific surface area, pore volume, and pore size of the catalyst decreased from 676 m^2/g , 0.886 cm^3/g , and 6.57 nm, respectively, to 411 m^2/g , 0.607 cm^3/g , and 6.19 nm, respectively. This may be caused by the Ag particles in the channels occupying part of the pore space in the channels, so the specific surface area, pore volume, and pore size decrease. A pore size of $d = 6\text{--}7$ nm was calculated from the desorption branch, which indicated that channels with $d = 3.7$ nm were not present in the samples. The N_2 adsorption-desorption isotherms and BJH pore size distribution curves further proved that the Ag loading did not affect the ordered porous structure of SBA-15, and the active Ag species entered the SBA-15 channels.

Figure 5(a) shows the small-angle XRD patterns of the Ag/SBA-15 catalysts. All the samples showed two diffraction peaks in the range $2\theta = 1.4^\circ\text{--}2^\circ$. This shows that Ag/SBA-15 retains the typical hexagonal mesoporous structure [43]. When

the Ag loading was 16.5%, the intensities of the diffraction peaks declined significantly. An Ag loading that is too high results in aggregation of Ag in the SBA-15 channels, so the channel structure changes. Figure 5(b) shows the wide-angle XRD patterns of the samples. When the Ag loadings were 4.2% and 5.3%, the Ag diffraction peaks were not obvious. This shows that Ag nanoparticles were highly dispersed on the carrier surface. When the Ag loading was increased to 16.5%, the intensities of four diffraction peaks at $2\theta = 38.4^\circ$, 44.0° , 64.3° , and 77.5° , corresponding to the four crystal planes, i.e., (111), (200), (220), and (311), of cubic Ag (JCPDS No. 4-07830) [13,34,48] increased and narrowed. This illustrated that the form of Ag changed from a highly dispersed state to an aggregated state. These results are consistent with the XPS and N_2 adsorption-desorption results.

Figure 6 shows SEM and HRTEM images of the SBA-15 and Ag/SBA-15 catalysts. It shows that the SBA-15 support (Fig. 6(a)) was a long rope connected with short rods, with clear corrugations and minor grooves on the surface. There are no significant differences among the appearances of 5.3%Ag/SBA-15 (Fig. 6(b)) and pure SBA-15, and they are identical to those reported in the literature [43,44]. This shows that the Ag loading using the impregnation method did not affect the appearance of SBA-15. Figure 6(d) shows that the SBA-15 channels were ordered and the cross-section was hexagonal (the figure shows a TEM image of SBA-15 perpendicular to the C6 axis). This is a typical two-dimensional hexagonal mesoporous structure [51]. The aperture is about 6–8 nm, and the wall thickness is about 3–5 nm. Figure 6(e–h) show that the Ag/SBA-15 still has a long-range ordered and uniform pore structure after Ag loading. This is in agreement with the reported results [49,50]. When the Ag loadings were 4.2% and 5.3%, the Ag (~6 nm) was highly dispersed on the SBA-15 carrier. As the Ag loading increased to 16.5%, some of the Ag particles gathered in the SBA-15 channels and formed nanorods of length 10–30 nm, and occupied part of the channels. This is in agreement with the XPS, N_2 adsorption-desorption, and XRD results.

Structural analysis of the catalysts and catalytic performance experiments showed that Ag is the active species in Ag/SBA-15, and the Ag loading, particle size, and dispersion

Fig. 5. XRD patterns of Ag/SBA-15 in small-angle range (a) and wide-angle range (b). (1) SBA-15; (2) 4.2%Ag/SBA-15; (3) 5.3%Ag/SBA-15; (4) 8.1%Ag/SBA-15; (5) 16.5%Ag/SBA-15; (6) 5.3%Ag/SBA-15-A.

Fig. 6. SEM (a–c) and HRTEM (d–i) images of SBA-15 and Ag/SBA-15. (a, d) SBA-15; (e) 4.2%Ag/SBA-15; (b, f) 5.3%Ag/SBA-15; (g) 8.1%Ag/SBA-15; (h) 16.5%Ag/SBA-15; (c, i) 5.3%Ag/SBA-15-A.

degree directly affect the catalytic activity and reaction conditions. In 5.3%Ag/SBA-15, the active Ag species size is about 6 nm and uniformly dispersed on the carrier surface. This increases the specific surface area of the active components, which enables low-temperature selective catalytic oxidation of benzyl alcohol; a conversion of 95% and selectivity of 86% were obtained at 220 °C. The catalytic activity of 5.3%Ag/SBA-15 is significantly higher than those of the other catalysts; the ordered channel structure and appropriate pore size of SBA-15 promote uniform dispersion of Ag on the support surface, resulting in a nano-confinement effect. Even when the reaction temperature reached 340 °C, the active component remained highly dispersed and active, and the conversion of benzyl alcohol and selectivity for benzaldehyde were more than 97% and 90%, respectively. If the Ag content is not less than 16.5%, Ag aggregation in the SBA-15 channels results in formation of Ag nanorods and partial occupation of the channels. This hinders mass transfer of the reactants and products, and they remain in the channels for a long time. Thus, some of the generated benzaldehyde continues to be oxidized, so the selectivity is lower than 92%. For 4.2%Ag/SBA-15, although the Ag particle size is smaller its loading is lower, so there are fewer active sites; a proportion of the reactants passing through the fixed bed does not react, leading to lower catalytic activity.

In catalytic reactions, O_2 is present as O^{2-} , O^- , and O_2^- . Nucleophilic oxygen (O^{2-}) is mainly responsible for the partial oxidation of organic compounds (hydrocarbons), and electrophilic oxygen (O^- and O_2^-) participates in the peroxidation reaction, leading to the formation of CO_x [52]. Benzaldehyde production depends on nucleophilic oxygen (O^{2-}) [53]. The characterization of Ag/SBA-15 shows that the active species were mainly Ag and a small amount of Ag_2O . Moreover, the active Ag species were almost uniformly dispersed on the support surface as a result of the nano-confinement effect of the porous SBA-15. The highly dispersed Ag nanoparticles helped to increase the specific surface area of the active components and therefore accelerated the formation of active oxygen species and promoted the migration of oxygen species to the sup-

port surface, i.e., oxygen spillover [54]; the combination rate of reactive oxygen species with benzyl alcohol was increased as a result of the larger specific surface area, ordered channel structure, and appropriate pore size of the SBA-15. These factors improved the catalytic activity of Ag/SBA-15. Literature reports [9,10,13] suggest that in the gas-phase selective oxidation of benzyl alcohol to benzaldehyde with gas-phase oxygen (O_2) as the oxidant and Ag/SBA-15 as the catalyst, gaseous O_2 is first adsorbed on the surface of the Ag particles and receives electrons, and is then dissociated to form nucleophilic oxygen species. These species migrate to the SBA-15 surface by oxygen spillover, and benzyl alcohol molecules adsorbed on the support surface are oxidized by the nucleophilic oxygen species. Active nucleophilic oxygen species can activate the C–H and O–H bonds in benzyl alcohol, and the subsequent reactions produce benzaldehyde.

3.3. Deactivation and regeneration of 5.3%Ag/SBA-15 catalyst

Figure 7 shows the deactivation and regeneration of 5.3%Ag/SBA-15 in the gas-phase selective oxidation of benzyl alcohol. It can be seen that the conversion of benzyl alcohol and the selectivity for benzaldehyde initially reached 97% and 80%, respectively. After reaction for 5 h, the conversion dropped to 94%, the selectivity rose to 97%, and then stabilized. After 11 h, the catalytic activity declined sharply to 60%; there were no obvious changes in the selectivity. At this time, the raw material feed was stopped, and the temperature of the catalyst bed was increased to 500 °C and maintained for 2 h to activate the catalyst. Benzyl alcohol was then fed into the reactor, and the conversion of benzyl alcohol and the selectivity for benzaldehyde increased to 92% and 95%, respectively. Catalyst deactivation may result from carbon deposition on the catalyst surface during the reaction [11]. The activity of the spent catalyst could therefore be recovered by simple oxidation. After two reaction-regeneration cycles, the catalytic activity and selectivity were both above 90%, and the changes were slight. However, after three activation cycles, the catalytic activity and selectivity of the regenerated catalyst were significantly lower

Fig. 7. Reaction/regeneration cycle tests of 5.3%Ag/SBA-15 catalyst in gas-phase selective oxidation of benzyl alcohol to benzaldehyde. Reaction conditions: catalyst 0.8 g, 240 °C, WHSV = 7.8 h⁻¹, $n(\text{O}_2)/n(\text{benzyl alcohol}) = 0.6$. Regeneration in N₂ + O₂ (O₂:N₂ volume ratio of 3:7 and flow rate 50 mL/min) at 500 °C for 2 h.

than those of fresh one. The conversion was less than 90% and began to decline after only 4 h; after 6 h the conversion was lower than 80%. Deactivation of the catalyst may be caused by the reduction of the active components or irreversible inactivation during long-term use and repeated treatment at high temperature. After three activation cycles, the catalyst 5.3%Ag/SBA-15-A, which had been used in the reaction for 40 h, was washed, calcined, and then characterized using N₂ adsorption-desorption, XRD, SEM, and TEM. The results showed that 5.3%Ag/SBA-15-A still showed typical type IV isotherms (Fig. 4(a)) with H1-type hysteresis; the pore size distribution was broader (Fig. 4(b)), and the specific surface area and pore volume were smaller (Table 2) than the fresh one. The XRD pattern (Fig. 5(b)) of 5.3%Ag/SBA-15-A shows that the intensity of the Ag diffraction peak increased, showing aggregation of some of the Ag after reaction for 40 h (Fig. 5(b)). There were clear stripes on the surface of 5.3%Ag/SBA-15-A, and the SEM image showed no obvious changes in the surface morphology (Fig. 6(c)), indicating that the catalyst had good mechanical stability. The appearance of the catalyst samples after reaction was not as neat as that of fresh one, and some fragmentation was observed; this may be the result of damage during tableting, crushing, and other operations in the catalyst-molding process. The 5.3%Ag/SBA-15-A catalyst had an ordered hexagonal mesoporous structure (Fig. 6(i)), its Ag content was significantly reduced, and Ag aggregation clearly occurred in the channels, so the channels were clogged. These results are in agreement with the N₂ adsorption-desorption and XRD results. Based on these results, it can be concluded that Ag/SBA-15 had a neat and ordered pore structure and thick pore walls, which significantly improved the activity and selectivity for benzaldehyde.

4. Conclusions

SBA-15 mesoporous materials have highly ordered hexagonally arranged cylindrical pore structure, thick pore walls, and high specific surface area. As a result of the nano-confinement

effect of the SBA-15 ordered channels, Ag was successfully incorporated into the mesoporous channels and dispersed uniformly on the SBA-15 surface. This is beneficial for generation of nucleophilic oxygen species via oxygen spillover from Ag to the SBA-15 surface and improves the catalytic activity in the low-temperature selective gas-phase oxidation of benzyl alcohol to benzaldehyde. When the reaction temperature was 220 °C, the conversion of benzyl alcohol and the selectivity for benzaldehyde reached 87% and 95%, respectively. The best catalytic properties were obtained at 240 °C, with benzyl alcohol conversion of 94% and benzaldehyde selectivity of 97%. The benzyl alcohol conversion and benzaldehyde selectivity were almost unchanged with increasing temperature from 240 to 300 °C, showing that the catalyst had excellent thermal gradient stability.

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Graphical Abstract

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Catalytic activity of Ag/SBA-15 for low-temperature gas-phase selective oxidation of benzyl alcohol to benzaldehyde

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Ag/SBA-15 catalyst for the gas-phase selective oxidation of benzyl alcohol to benzaldehyde with O₂ was prepared using an impregnation method. Ag/SBA-15 displayed good catalytic activity at low temperature and excellent thermal gradient stability.

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Ag/SBA-15低温气相选择性催化氧化苯甲醇合成苯甲醛

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摘要: 以SBA-15为载体, 采用浸渍法制备了不同Ag含量的Ag/SBA-15, 通过N₂吸附-脱附、X射线衍射、扫描电子显微镜、高分辨透射电子显微镜、X射线光电子能谱和电感耦合等离子体质谱对催化剂进行了表征。将Ag/SBA-15用于苯甲醇气相选择性催化氧

合成苯甲醛,研究了反应条件对转化率和选择性的影响。结果表明,Ag/SBA-15具有均一的一维孔道结构、较厚的孔壁(3–5 nm)及较大的比表面积(411–541 m²/g),其规整纳米空间的限域作用使一定负载量的Ag以纳米尺寸均匀分散于介孔SBA-15孔道内,增加了活性组分的比表面积。亲核性氧物种从Ag到SBA-15表面的氧溢流,提高了低温下Ag/SBA-15对苯甲醇气相选择性氧化合成苯甲醛的催化性能。5.3%Ag/SBA-15中的Ag粒径为5–6 nm,且均匀分散于载体孔道中,反应温度为220 °C时,苯甲醇转化率为87%,苯甲醛选择性为95%;240 °C时,苯甲醇转化率和苯甲醛选择性分别高达94%和97%;并在240–300 °C范围内,其催化活性和选择性保持不变,表现出了良好的温度耐受能力。催化剂经活化再生可以连续使用40 h,选择性基本保持不变。

关键词: 银; SBA-15; 低温气相氧化; 苯甲醇; 苯甲醛

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1. 前言

苯甲醛是一种重要的有机合成中间体^[1],广泛应用于化妆品、香料、食品和医药工业^[2]。目前工业和实验室中多采用甲苯气相氧化^[3]或苯甲醇液相氧化^[4–6]制备苯甲醛,但往往副产物多,选择性低,产物难分离,因而限制了苯甲醛的应用。近年来,以分子氧为氧化剂,利用固定床反应器,气固相选择性催化氧化苯甲醇制备苯甲醛,由于无溶剂,副产物少,产物易分离及反应工艺绿色环保而备受人们的关注。反应多采用负载型金属催化剂,如Au-Cu/SiO₂^[7], Au/Ni-纤维^[8], Ag/SiO₂^[9], Ag-纤维^[10,11], Ag/Ni-纤维^[12]和Ag-HMS^[13]等,反应温度均在300 °C以上。Zhao等^[14]采用电沉积法将Au颗粒负载在Ni-纤维载体上,制得了Au/Ni-纤维型催化剂,Au负载量为4%,280 °C反应时,苯甲醇的转化率达到99%,苯甲醛选择性高达98%。Fan等^[15]使用K-Cu-TiO₂催化剂,在接近苯甲醇沸点203–223 °C条件下,获得苯甲醇转化率72%,苯甲醛选择性大于98%;该催化剂对反应温度的控制要求比较严格,温度高于250 °C时,目的产物苯甲醛过氧化几乎完全生成苯甲酸。低温气相选择性催化氧化苯甲醇生成苯甲醛,反应温度低,不仅有利于提高目的产物选择性,提高活性位的寿命,而且节能环保,引起人们越来越多的重视^[16]。

纯硅SBA-15介孔分子筛具有长程有序的一维孔道结构,介孔尺寸可在4.6–30 nm范围内调控,孔壁较厚,比表面积高,水热稳定性好,且表面存在大量的硅羟基,易于改性。同时,利用其规整纳米空间的限域作用制备纳米活性相是制备功能性纳米材料的有效方法之一^[17–22],因此被广泛应用于催化和吸附工业^[23–31]。其中Ag改性的SBA-15^[32–37]由于在甲醛氧化^[38]、环烷烃的选择性氧化^[39]和CO氧化^[40–42]等反应中表现出较好的催化性能,

引起了研究者的广泛兴趣。然而,将Ag/SBA-15用于苯甲醇气相选择性催化氧化制备苯甲醛鲜有报道。

本文以介孔SBA-15为载体,采用浸渍法合成了一系列不同Ag负载量的Ag/SBA-15,利用N₂吸附-脱附、X射线衍射(XRD)、扫描电镜(SEM)、高分辨透射电镜(HR-TEM)、X射线光电子能谱(XPS)和电感耦合等离子体质谱(ICP-MS)等手段对催化剂结构及活性组分进行了表征。并以分子氧为氧源,在不添加任何助剂的情况下,将其用于苯甲醇气相选择性催化氧化反应,考察了Ag的负载量对催化剂结构的影响,以及催化剂结构与性能之间的关系,研究了反应温度对苯甲醇转化率和苯甲醛选择性的影响,在此基础上考察了催化剂的使用寿命。

2. 实验部分

2.1. Ag/SBA-15催化剂制备

载体SBA-15参考文献[43,44]方法制备。40 °C下,将4.2 g P123 (EO₂₀PO₇₀EO₂₀, *M_w* = 5800, 美国Sigma-Aldrich公司)加入到60 g HCl (4.0 mol/L)与90 g去离子水混合溶液中,磁力搅拌2 h得溶液A。将8.5 g正硅酸乙酯(TEOS, AR, 98%)缓慢滴加到溶液A中。40 °C下搅拌24 h后,将所得混合液转移到带有聚四氟乙烯内衬的不锈钢水热反应釜中,100 °C恒温晶化24 h。经过滤得到白色固体,用去离子水洗涤三次,60 °C干燥过夜。研磨后于550 °C焙烧6 h,即得到白色粉末状固体SBA-15。

取1.0 g新制SBA-15载体浸渍在50 mL不同浓度的AgNO₃溶液中,50 °C下磁力搅拌10 h,然后于100 °C干燥过夜,500 °C焙烧6 h,即得不同Ag含量的Ag/SBA-15催化剂^[39,45],记为xAg/SBA-15,其中x代表利用ICP-MS测定的Ag的质量分数)。将反应40 h后的5.3%Ag/SBA-15用乙醇洗涤,过滤,于80 °C干燥过夜,500 °C焙烧2 h,所得再生催化剂记为5.3%Ag/SBA-15-A。

2.2. 催化剂表征

XRD在德国Bruker D8 Advance型粉末衍射仪上测定, Cu靶 K_{α} 射线, Ni滤波器, 管电压60 kV, 管电流300 mA, 功率18 kW, 扫描速度 $3^{\circ}/\text{min}$, 扫描范围 $2\theta = 0.5^{\circ}$ – 80° . N_2 吸附-脱附等温线在Quantachrome NOVA 2000e型物理吸附仪上测量, 吸附质为 N_2 , 吸附温度为 -196°C , 测试前样品在 300°C 真空条件下预处理3 h, 样品的比表面积、孔径和孔体积分别用BET和BJH法计算得到. SEM在日本日立公司S-4300型场发射扫描电子显微镜上拍摄, 电压20 kV, 样品室真空度优于 1×10^{-4} . HR-TEM在美国FEI公司Tecnai G2型透射电子显微镜上拍摄, 电压200 kV. 采用英国Thermo Electron公司ESCALAB 250Xi型X射线光电子能谱(XPS)仪分析样品中Ag的结合态, 激发源为Al K_{α} 射线(1486 eV). 利用Agilent 7500ce型电感耦合等离子体质谱仪测定催化剂中Ag的含量, 测试前将催化剂用HCl (3 mL), HF (1 mL)和 HNO_3 (1 mL)溶解, 使用3% HNO_3 溶液定容到100 mL.

2.3. 催化剂评价

采用常压连续固定床反应器(内径6 mm, 长450 mm)进行苯甲醇气相选择性催化氧化反应. 将0.8 g催化剂(40–60目)装入反应器中, 两端用石英砂和石英棉封堵. 在 N_2 和 O_2 体积比为3:7, 总流速为50 mL/min的条件下于 500°C 活化2 h. 随后通入载气 N_2 (35 mL/min)、反应物 O_2 和苯甲醇, 重时空速(WHSV)为 4.7 – 12.5 h^{-1} , O_2 /苯甲醇摩尔比为0.6. 使用微量进样控制器调节苯甲醇进料速率, 在 220°C , 气化后通入反应器. 反应温度 220 – 380°C , 反应产物经冰盐浴(-5 到 -10°C)冷却后收集. 用GC-9800型气相色谱仪对产物进行定量分析. 使用OV-17毛细管柱($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$), FID检测器, 柱温 140°C , 检测器温度 200°C , 进样器温度 200°C , 载气(N_2)流速180 mL/min, 空气0.3 MPa, 氢气0.35 MPa, 柱前压0.07 MPa, 进样量 $0.04 \mu\text{L}$. 根据反应产物中各物质的含量、总投料量及产物质量计算苯甲醇转化率、苯甲醛选择性、苯甲醛收率及TOF.

3. 结果与讨论

3.1. Ag/SBA-15的催化性能

3.1.1. Ag负载量的影响

表1为不同Ag负载量的Ag/SBA-15催化剂上苯甲醇气相选择性催化氧化制苯甲醛反应性能. 反应温度为 240°C 时, SBA-15无催化活性, 负载Ag后催化活性显著增加, 随着Ag负载量由4.1%逐渐增至16.5%, 苯甲醇转

化率由74.8%逐步升到96.6%, 而苯甲醛选择性由85.2%先增加到96.9%, 之后下降到91.5%. 可能是由于Ag负载量过多时, 苯甲醛过氧化生成苯甲酸, 导致其选择性降低. 可见, 当Ag负载量为5.3%时催化剂性能较佳: 苯甲醇转化率94%, 苯甲醛选择性97%, TOF值 128.6 h^{-1} .

3.1.2. 反应温度的影响

温度是影响苯甲醇气相选择性催化氧化反应转化率和选择性的重要因素^[12–16]. 图1为5.3%Ag/SBA-15催化剂上反应温度对苯甲醇气相选择性催化氧化反应的影响. 由图可知, 反应温度 220°C 时, 苯甲醇转化率和苯甲醛选择性分别为86%和95%. 可见, 在较低温度下, Ag/SBA-15可有效实现选择性催化氧化苯甲醇生成苯甲醛. 升温至 240°C , 苯甲醇转化率上升到94%, 苯甲醛选择性为97%, 并在 240 – 300°C 范围内保持不变; 继续升至 340°C , 选择性降至90%, 转化率略有上升; 至 380°C 时, 苯甲醛选择性为85%, 苯甲醇转化率接近100%, 液质联用分析表明, 高温下部分苯甲醛氧化生成了苯甲酸, 从而使其选择性下降. 上述实验表明, Ag/SBA-15在较低的温度下可选择性催化氧化苯甲醇生成苯甲醛, 并在较宽的宽度内保持高选择性, 具有很好的温度耐受性; 而且通过选择合适的催化剂和反应温度可调控反应活性及苯甲醛选择性.

3.1.3. 重时空速的影响

图2为反应重时空速与催化性能的关系. 由图可知, 当 $\text{WHSV} = 4.7$ – 12.5 h^{-1} , 5.3%Ag/SBA-15上苯甲醛选择性均在95%以上, 同时TOF由 77.1 h^{-1} 上升到最大值 134.9 h^{-1} 后下降至 127.6 h^{-1} . $\text{WHSV} = 7.8 \text{ h}^{-1}$ 时, 苯甲醇转化率和苯甲醛的选择性达到最大值, 分别为94%和97%, TOF值为 128.6 h^{-1} ; $\text{WHSV} = 9.4 \text{ h}^{-1}$, TOF值达最大, 为 134.9 h^{-1} , 然而此时苯甲醇转化率仅为82.8%. 综上所述, 最优反应条件为: 反应温度 240°C , WHSV 为 7.8 h^{-1} . 此时, 苯甲醇转化率为94%, 苯甲醛选择性大于97%.

3.2. Ag/SBA-15催化活性与其结构的关系

利用XPS表面探针技术研究了Ag/SBA-15表面Ag的形态及其含量. 图3是5.3%Ag/SBA-15中Ag 3d的XPS谱. 电子结合能为374.4和368.3 eV的谱峰分别对应Ag $3d_{3/2}$ 和Ag $3d_{5/2}$ 能带^[46,47], 差值 $\Delta E = 6.1 \text{ eV}$; 同时Ag $3d_{5/2}$ 的特征峰略有不对称, 分峰后得到368.4和367.8 eV处的两个特征谱峰, 分别对应于单质Ag (90%)和 Ag_2O (10%)^[48]. 这说明在5.3%Ag/SBA-15表面中Ag物种主要以单质Ag和少量 Ag_2O 形式存在^[13], Ag质量分数为0.33%. 另外ICP-MS分析表明, 5.3%Ag/SBA-15样品中

Ag含量为5.3%, 可以估算出进入介孔孔道内的Ag含量约为4.93%, 也就是说93%以上的Ag进入到SBA-15的介孔孔道。结合评价结果表明, 单质Ag为苯甲醇气相选择性催化氧化制苯甲醛反应的活性物种。

图4为各Ag/SBA-15催化剂的 N_2 吸附-脱附等温线和BJH孔径分布曲线。由图可见, 所有样品等温线均为IV型, 并在较高的相对压力($0.6 < p/p_0 < 0.8$)下出现因 N_2 的毛细凝聚而产生的H1型滞后环。其中吸附支与脱附支在窄的相对压力范围内显示平行显著变化的趋势, 与SBA-15分子筛具有规则、均一的开口圆筒形孔道($d > 6$ nm)特征相一致^[43–45,49]。同时, 随着Ag负载量增加, Ag/SBA-15样品显示有较宽相对压力范围的扁平滞后环, 并且吸附与脱附分支闭合于略低的相对压力。根据开尔文定律, 孔径小时发生毛细凝聚的相对压力低, 表明样品中出现墨水瓶形孔道^[13,50]。该孔道的形成, 可能是Ag进入孔道造成的; 由图4(b)可知, 最可几孔径变小且孔径分布宽化, 其中4.2%Ag/SBA-15和5.3%Ag/SBA-15样品还出现了孔径为3.7 nm的小孔径, 它源于墨水瓶形孔道的孔口过窄带来的假象, 进一步说明Ag进入到SBA-15的孔道。

表2为Ag/SBA-15催化剂的结构参数。可以看出, 随Ag负载量从0增至16.5%, 催化剂的比表面积、孔体积和孔径分别从676 m²/g、0.886 cm³/g和6.57 nm降低至411 m²/g、0.607 cm³/g和6.19 nm。这可能是由于Ag粒子占据了部分孔道空间, 使比表面积、孔体积和孔径减小。同时由脱附分支计算出孔径为6–7 nm, 说明样品中并不存在3.7 nm孔道。由图4还可以看出, Ag的负载对载体SBA-15的规则孔道结构基本无影响, 且活性物种Ag进入了SBA-15孔道。

图5(a)为Ag/SBA-15的小角度XRD谱。由图可知, 在 $2\theta = 1.4^\circ$ – 2° 范围内, 所有样品均出现两个衍射峰, 说明样品仍保持了分子筛的典型六方介孔结构^[43]。当Ag负载量达到16.5%时, 衍射峰强度明显减弱, 可能是由于Ag含量过高而使Ag在SBA-15孔道内聚集, 导致SBA-15结构发生变化。图5(b)为各样品的广角XRD谱。可以看出, 当Ag负载量为4.2%和5.3%时, Ag的衍射峰不明显, 说明Ag高分散于载体表面。 $2\theta = 38.4^\circ$, 44.0° , 64.3° 和 77.5° 处出现的特征衍射峰分别归属于Ag的(111), (200), (220)和(311)晶面(JCPDS No. 4-07830)^[13,34,48]; 随着Ag负载量的增加, Ag特征衍射峰强度变大, 峰形更加尖锐, 说明Ag在SBA-15载体表面由高度分散状态转变为聚集状态, 与XPS和 N_2 吸附-脱附结果相一致。

图6为SBA-15和Ag/SBA-15的SEM和HR-TEM照片。可以看出, SBA-15载体外观形貌呈短棒相接的长绳状, 表面呈现清晰波纹, 且带有细微的凹槽; Ag/SBA-15外观形貌与纯SBA-15没有明显区别, 与文献[43,44]结果一致, 说明采用浸渍法负载Ag不影响SBA-15的形貌。由图6(d)可知, SBA-15孔道排列规则, 横截面呈有序六边形排列(插图为SBA-15垂直于C6轴方向的TEM图), 为典型的二维 $p6mm$ 六方相结构^[51], 孔径约为6–8 nm, 孔壁厚度大约在3–5 nm。由图6(e–h)可知, 负载Ag后各样品仍具有长程有序、孔径均一的孔道结构, 与文献一致^[49,50]。当Ag含量为4.2%和5.3%时, Ag (≈ 6 nm)在SBA-15载体表面均匀分散; 至16.5%时, 部分Ag在SBA-15孔道中发生聚集形成长度为10–30 nm的纳米棒, 占据部分孔道, 与前文结果一致。

综上所述, Ag/SBA-15中Ag是活性相, 且Ag的负载量、颗粒大小与分散程度直接影响其催化性能。5.3%Ag/SBA-15中的活性物种Ag以 ~ 6 nm颗粒均匀分散在载体表面中, 增加了活性组分的比表面积, 显著提高了5.3%Ag/SBA-15的催化活性, 有利于实现低温选择性催化氧化, 220 °C时, 苯甲醇转化率和苯甲醛选择性分别达86%和95%; SBA-15规则的孔道结构和适宜的孔径对Ag的分散起到了很好的限域作用, 即使反应温度达到340 °C, Ag仍保持较好的高分散状态, 因而其催化活性较高, 苯甲醇转化率大于97%, 苯甲醛选择性达到90%以上。对于Ag含量较高的16.5%Ag/SBA-15, 由于Ag在SBA-15孔道中部分发生聚集形成Ag纳米棒, 占据了部分SBA-15孔道, 不利于传质, 反应物在孔道中停留时间过长, 从而使部分生成的苯甲醛继续被氧化, 其选择性低于92%; 而对于4.2%Ag/SBA-15, Ag虽然粒径较小, 但是负载量少, 以致活性位较少, 因而其催化活性仍不高, 苯甲醇转化率低于75%。

O_2 在催化反应中的化学态有 O^{2-} , O^- 和 O_2^- , 亲核氧(O^{2-})主要参与有机化合物(碳氢化合物)的部分氧化反应, 亲电氧(O^- 和 O_2^-)参与深度氧化反应, 导致 CO_x 的形成^[52]。苯甲醛的生成取决于亲核氧(O^{2-})^[53]。由Ag/SBA-15的表征结果可知, 活性物种Ag以单质Ag和少量 Ag_2O 存在。由于载体SBA-15规则孔道结构对活性物种Ag的限域作用, Ag在载体表面均匀分散。一方面, 高度分散的纳米Ag使活性组分比表面积增大, 有益于活性氧物种的生成, 也促进了活性氧物种迁移到载体表面, 形成氧溢流现象^[54]; 另一方面, 载体较大的比表面积、规则的孔道结构和适宜的孔径大小加速了活性氧物种

与反应物苯甲醇的结合速率,使Ag/SBA-15具有较好的催化活性.结合文献报道^[9,10,13],以气相氧(O₂)为氧化剂,Ag/SBA-15气相选择性催化氧化苯甲醇制备苯甲醛反应中,气相O₂首先吸附于富集电子的Ag颗粒表面并不断得到电子,发生解离形成亲核性氧物种,后者溢流到SBA-15载体表面,与吸附于载体表面的苯甲醇分子发生氧化反应.活化的亲核性氧物种可以激活苯甲醇中的C-H键和O-H键,进而发生反应生成苯甲醛.

3.3. 5.3%Ag/SBA-15催化剂的失活与再生

图7为5.3%Ag/SBA-15在苯甲醇气相氧化反应中的失活与再生情况.由图可知,在初始阶段,苯甲醇的转化率达到97%,产物选择性为80%;反应至第5 h,苯甲醇转化率降至94%,而苯甲醛选择性上升至97%,之后趋于平稳;至11 h,苯甲醇转化率急剧降至60%,而选择性无明显变化.此时停止通入原料,床层温度升至500 °C对催化剂进行活化处理2 h,之后继续通入苯甲醇,可以看到,苯甲醇的转化率和苯甲醛的选择性分别恢复至92%和95%.这可能是由于催化剂在反应过程中发生积炭失活^[11],因此简单的高温处理便可使催化剂再生.同时可以看到,催化剂经过两个使用周期和两次活化后,催化活性和选择性变化不大,均在90%以上.当进行三次活化后,再生催化剂活性和选择性明显低于新鲜催化剂,且使用4 h后,催化剂活性便开始下降;第6 h时,苯甲醇转化率低于80%,可能是由于催化剂经长时间使用和多次高温处理后,活性组分减少或发生不可逆失活.取出

经过三次活化且反应40 h后的催化剂,洗涤,过滤,焙烧后(5.3%Ag/SBA-15-A)对其表征发现该催化剂仍呈IV型吸附-脱附等温线(图4(a)),H1型滞后环,孔径分布变宽(图4(b)),比表面积与孔体积(表2)较反应前有所下降.另外,反应后催化剂的XRD谱(图5(b))中Ag衍射峰较反应前的增强,表明部分Ag发生了聚集.从SEM结果(图6(c))可以看出,反应后的催化剂单节表面均呈清晰的条纹状且主体形貌没有发生明显变化,说明催化剂具有很好的机械稳定性;外部存在少量碎片,外观形貌不如反应前的规整,这可能是催化剂成型过程中压片和粉碎等操作造成的.反应后的催化剂仍保持SBA-15的规则孔道结构(图6(i)),Ag明显减少并在孔道中发生聚集,出现堵塞孔道现象.综上可以推断,Ag/SBA-15规整的形貌、排列有序的孔道结构和较厚的孔壁显著提高了催化剂活性和苯甲醛选择性.

4. 结论

Ag/SBA-15具有均一的一维孔道结构、较厚的孔壁和较大的比表面积,其规整纳米空间的限域作用使Ag以纳米尺度高度分散在介孔SBA-15孔道内,促进了亲核性氧物种从Ag到SBA-15的氧溢流,有利于提高低温下苯甲醇气相选择性氧化合成苯甲醛的选择性.反应温度为220 °C时,苯甲醇转化率和苯甲醛选择性分别为87%和95%,240 °C时,分别为94%和97%,并在240–300 °C范围内保持不变,催化剂表现出了良好的温度耐受能力.