Oxidation of Cyclopentene by H_2O_2 to Glutaraldehyde over the WO_3/SiO_2 Catalyst

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A novel WO_3/SiO_2 was designed for the catalytic oxidation of cyclopentene by H_2O_2 to glutaraldehyde. In comparison with those homogeneous catalysts, it seems more suitable for the industrial process owing to the high yield of glutaraldehyde and easy separation of the present catalyst from reaction products.

Glutaraldehyde(GA) has been used extensively for disinfection and sterilization in many areas.[1] Usually, it is produced through the ozonization of olefins. In recent years, many useful reactions using H_2O_2 as oxidant have been developed owing to their simple procedure, such as epoxidation of olefins and allylic cleavage of 1,2-diols and olefins to carboxylic acids.[2,3] However, very little attention has been paid to use of hydrogen peroxide for the oxidative cleavage of carbon-carbon double bonds to produce aldehydes. Recently, Furukawa et al.[4] reported that GA was obtained by oxidation of cyclopentene with H_2O_2 catalyzed by heterpoly in a non-aqueous medium. In our previous paper, we also reported the oxidation of cyclopentene by H_2O_2 catalyzed by tungstic acid dissolved in an aqueous solution as a homogeneous catalyst.[5] Although a high GA yield could be obtained, its application in industrial process seems impractical since the tungstic acid is not easily separated and recovered. One of the most promising way to overcome the above disadvantages is to design the heterogeneous catalysts. However, no such a work has been reported so far. In the present paper, we report the catalytic oxidation of cyclopentene by H_2O_2 over WO_3/SiO_2 with almost the same GA yield as that obtained in homogeneous catalytic oxidation.

The support SiO_2 was prepared by the sol-gel method.[6] Certain amount of ethanol was added to 150 ml tetraethylsilicate (TEOS) solution. After being stirred for 30 min, water and HCl solution were added to the above solution, in which the molar ratio between H_2O:TEOS:HCl was adjusted to be 4:1:0.09. The gel was heated up to 353 K for 24 h and turned to be a dried gel after being kept isothermally at 373 K for another 24 h. The powder of dried support was then ground with mortar and pestle, sieved to 80-100 mesh. The xerogel samples were heated programmed at 5 K/min in a nitrogen flow of 500 ml/min and kept for 1 h at 473 K to remove most of the organic residues. After cooling to 353 K, it was calcined at 5 K/min in an air flow of 500 ml/min and kept for 4 h at 823 K. The WO_3/SiO_2 was obtained by an incipient wetness impregnation with ammonium tungstate solution,[7] which was then dried at 393 K for 16 h following by a calcination at 823 K for another 16 h.

The activity test was performed at 308 K for 24 h with vigorous stirring in a regular glass reactor in which 340 mmol of cyclopentene, 680 mmol of 50% aqueous H_2O_2 solution, 50 ml of t-BuOH, and 2.0 g of each of the WO_3/SiO_2 catalysts were mixed. The reaction products were analyzed by a online gas chromatograph. According to the activity measurement, the following results were obtained: (1) As shown in Table 1, the GA yield is strongly dependent on the WO_3 loading and the calcination temperature, which revealed that the optimum catalyst in the present reaction is the WO_3/SiO_2 with 15 wt% WO_3 loading calcined at 823 K; (2) Over the optimum WO_3/SiO_2 catalyst, the GA yield was 59.9%, which is almost the same as that of the tungstic acid homogeneous catalyst containing the same W content(61.0%). After the reaction, only 2.3 ppm W was determined in the solution. By using the tungstic acid with 5.0 ppm W as the homogeneous catalyst, no significant activity was observed, indicating that the active sites in the present reaction are not the dissolved W species, but the WO_3 species deposited on SiO_2, and the loss of WO_3 due to dissolving in solution can be neglected. The main by-products in the present reaction are trans-1,2-cyclopentandiol and its mono-ether besides trace of the cyclopentanone and the cyclopentene oxide; (3) The initial molar ratio between cyclopentene and H_2O_2 was 1:2, which seems to be the optimum ratio since the less H_2O_2 will decrease the GA yield while the more H_2O_2 will result in more by-products. No significant H_2O_2 was determined after reaction. The extra H_2O_2 consumption of is possibly owing to its decomposition and to the formation of the by-products; (4) Superior over the corresponding homogeneous catalyst, the WO_3/SiO_2 catalyst can be used repetitively during the reaction. After reaction for 72 h, significant decrease in the GA yield was observed, indicating the deactivation of the WO_3/SiO_2 catalyst. However, it can be recovered easily by calcination at 823 K, as shown in Table 1. Although slightly decrease in the activity was observed after the first regeneration, no change in the activity occurred when the second or furthermore regeneration of the catalyst was performed; (5) Comparing to other solvents, such as methanol, ethanol, and acetonitrile etc., t-BuOH is the best reaction medium because it is a good solvent for both the reactants and the reaction products and can not be oxidized during the reaction.

Table 1. Effects on the surface area(S_{BET}) of the WO_3/SiO_2 catalysts and the glutaraldehyde(GA) yield

Catalyst	T/K	$S_{BET}/m^2 \cdot g^{-1}$	GA Yield/%
5 wt% WO_3/SiO_2	823	569	46.3
10 wt% WO_3/SiO_2	823	539	54.9
15 wt% WO_3/SiO_2	673	610	41.4
15 wt% WO_3/SiO_2	823	522	59.9
15 wt% WO_3/SiO_2	973	368	19.7
20 wt% WO_3/SiO_2	823	475	60.0
15 wt% WO_3/SiO_2[a]	823	502	57.5

[a]The catalyst after regeneration.

The BET surface areas(S_{BET}) of the WO_3/SiO_2 samples were determined by N_2 adsorption at 77 K using ASAP 2010 Micromeriticsm, as shown in Table 1. One can see that the S_{BET} decreased gradually with the increase in WO_3 loading, possibly due to the gathering or overlap of the catalyst particles since no significant structural conversion was observed on the XRD patterns. The XRD analysis indicate the all those samples are present in amorphous state when they were calcined at the temperature below 823 K. However, crystalline WO_3 was

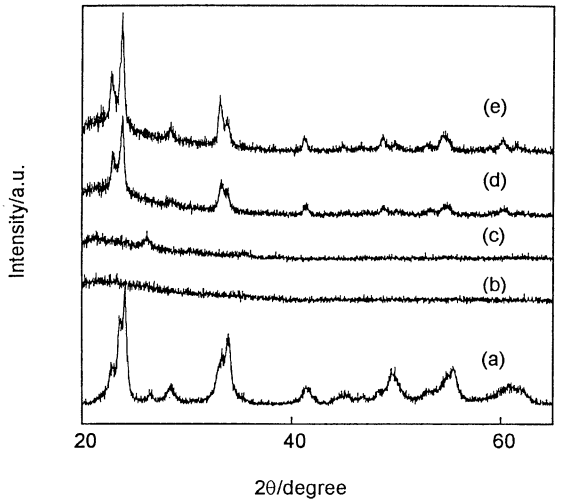

Figure 1. XRD spectra of WO_3/SiO_2 catalysts. (a) WO_3 bulk. (b) 15% before the reaction. (c) 15% after the regeneration. (d) 15% after the reaction. (e) 15% calcination at 973 K.

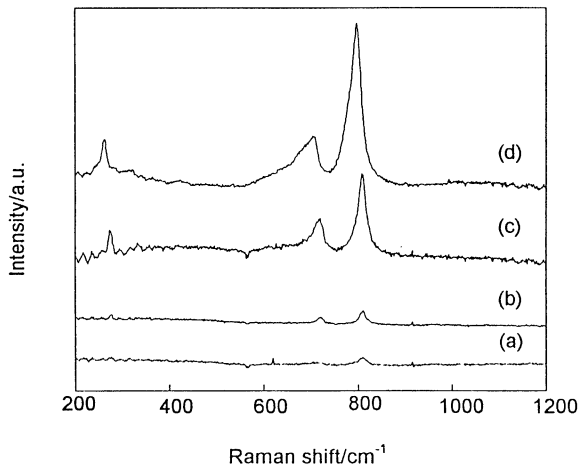

Figure 2. Raman spectra of the 15% WO_3/SiO_2 catalysts. (a) before the reaction. (b) after the regeneration. (c) after the reaction. (d) calcination at 973 K.

observed when the catalyst was obtained by calcination at 973 K or the optimum catalyst was employed in the catalysis for more than 72 h, as shown in Figure 1. This was further confirmed by the Raman spectra, as shown in Figure 2, the Raman spectra of the WO_3/SiO_2 catalyst also exhibit very strong Raman bands due to crystalline at 800, 709, 270 cm^{-1} which have been assigned to the symmetric stretching mode of the W-O, bending mode of the W-O, and deformation mode of the W-O-W bonds, respectively,[8,9] when the catalyst was obtained by calcination at 973 K or the optimum catalyst was employed in the catalysis for more than 72 h. However, only the weak peaks at those bands appeared in the other samples when they were calcined at the temperature below 823 K.

According to the above characterizations, we concluded that the active site of WO_3/SiO_2 catalyst was amorphous WO_3 and the change of its activity could be explained as follows: (1) The increase in the WO_3 loading has both the positive and negative effect on the activity of the WO_3/SiO_2. On one hand, as the amorphous WO_3 is the active site for the present oxidation, the increase in the WO_3 loading will increase the active sites, while, on the other hand, will decrease the S_{BET} as discussed above. Those two effects reach a balance at about 15 wt% WO_3 loading since no significant increase in the GA yield was observed when the WO_3 loading increased from 15 wt% to 20 wt%, showing that the 15 wt% is the optimum WO_3 loading. (2) The increase in the calcination temperature from 673 K to 823 K resulted in a slightly decrease in the S_{BET}. However, the increase in the interaction between WO_3 and SiO_2 can effectively prevent the WO_3 from dissolving in the solution, resulting in the higher GA yield. The extremely high calcination temperature(973 K), however, caused a greatly decrease in the S_{BET} owing to the structural conversion, which resulted in an abrupt decrease in the number of active sites(amorphous WO_3), responsibly for the rapid decrease in the GA yield, as shown in Table 1. Therefore, 823 K is the optimum calcination temperature. (3) After reaction for 72 h, significant decrease in the activity of WO_3/SiO_2 catalyst was observed, possibly due to the structural conversion from the amorphous state to the crystalline WO_3, resulting in the decrease in active sites. After being calcined at 823 K for 6 h, the catalyst turned to be amorphous state again, as shown in Figure 1,2, which resulted in almost the completely recovery of the activity of the WO_3/SiO_2 catalyst.

Thus, the WO_3/SiO_2 catalyst with 15 wt% calcined at 823 K exhibited almost the same oxidation activity as that of the corresponding homogeneous catalyst. The convenient separation of the WO_3/SiO_2 from the reaction products and the simple procedure for the catalyst regeneration make it more powerful than the corresponding homogeneous catalyst during the industrial catalysis for the oxidation of cyclopentene by H_2O_2 to produce glutaraldehyde. Detailed research works are being underway.

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