Complete oxidation of formaldehyde on Ag/CeO_2 nanosphere catalysts

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Introduction

Formaldehyde (HCHO) is one of the major pollutants for indoor air pollution, which becomes an incentive of a variety of diseases. It is recognized that catalytic oxidation technology is an effective way to eliminate the formaldehyde pollutants [1]. On the basis of present research, some of the catalysts based on precious metals could achieve complete catalytic oxidation of HCHO. However, with the price of precious metals continuing to increase, it is still a challenge for developing low cost catalysts. It was reported that Ag nanoparticles or supported Ag catalysts exhibited some remarkable ability in the catalytic oxidation reaction including HCHO oxidation [2-5]. Therefore, Ag should be a good choice for catalytic oxidation of HCHO.

In this work, we developed serial CeO_2 and Ag/CeO_2 nanosphere catalysts. The results showed that the HCHO oxidation ability was significantly improved on Ag/CeO_2 nanosphere catalysts compared to normal Ag/CeO_2 particle catalysts. The serial CeO_2 and Ag/CeO_2 catalysts were also characterized in detail, and the possible reaction mechanism for HCHO oxidation on Ag/CeO_2 nanosphere catalysts were proposed based on In-situ DRIFTS experiments.

Materials and Methods

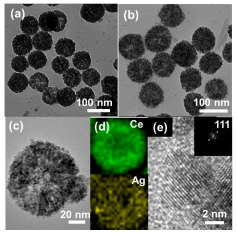
The CeO_2 nanospheres were synthesized by hydrothermal methods. Ag/CeO_2 nanospheres were prepared that a certain amount of $AgNO_3$ (AR) was added and dispersed in the mixed solution in the process of CeO_2 nanosphere preparation. The obtained catalysts are denoted as Ag/CeO_2-N and CeO_2-N, respectively. Meanwhile, the CeO_2 and Ag/CeO_2 bulk particles were prepared for comparison, and denoted as CeO_2-P and Ag/CeO_2-P, respectively.

The serial CeO_2 and Ag/CeO_2 catalysts were also characterized by BET, XRD, HRTEM, XPS, H_2-TPR, O_2-TPD, and Raman spectra. The possible reaction mechanism for HCHO oxidation on Ag/CeO_2 nanosphere catalysts were proposed based on In-situ DRIFTS experiments.

Results and Discussion

Figure 1 shows that both of CeO_2-N and Ag/CeO_2-N products are the nanosphere shapes with average sizes around 80-100 nm (Figure 2a and 2b). Ag/CeO_2-N crystallite size is estimated by the HRTEM results (Figure 2c), in which the Ag/CeO_2-N nanospheres are comprised of many small particles with a crystallite size of 2-5 nm, and there are clear voids among the small particles. The corresponding elemental maps of Ag/CeO_2-N nanospheres show that both Ce and Ag are well distributed throughout the individual Ag/CeO_2 nanosphere crystal (Figure 2d). The d lattice spacing is 0.312 nm, while FFT results indicate that the Ag/CeO_2 nanosphere crystals mainly exposure (111) planes of fluorite structure of CeO_2 (Figure 2e).

Figure 2 shows the catalytic activity of HCHO oxidation on different CeO_2 and Ag/CeO_2 catalysts. It can be seen that maximum HCHO conversion of the serial catalysts ranks in the sequence of Ag/CeO_2-N > Ag/CeO_2-P > CeO_2-N > CeO_2-P in the whole temperature range. The CeO_2-N catalysts show relatively higher catalytic activity than CeO_2-P. When the Ag nano particles are doped onto CeO_2-N support, surprisingly high HCHO conversions are gotten and reach approximately 100% conversion at 110 °C. Ag/CeO_2 nanospheres have relatively higher specific reaction rate and TOF implying that they should be potential catalysts for HCHO oxidation.



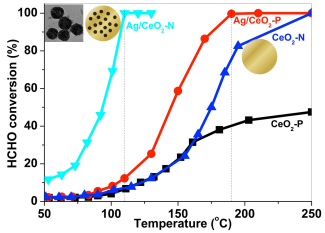


Figure 1 (left). (a) TEM image of the CeO_2-N nanosphere, (b) TEM image of Ag/CeO_2-N nanosphere, (c) HRTEM images of Ag/CeO_2-N nanosphere, (d) The distribution of element maps of Ce (green) and Ag (yellow) on Ag/CeO_2-N nanosphere, and (e) HRTEM image of the Ag/CeO_2-N nanosphere (Top-right inset show the corresponding FFT pattern).

Figure 2 (right). The performance of catalytic oxidation of HCHO on different CeO_2 and Ag/CeO_2 catalysts.

According to the results in XPS, H_2-TPR, O_2-TPD, and Raman spectra, surface chemisorbed oxygen easily formed on the Ag/CeO_2 nanosphere catalysts. The synergetic interaction might exist between Ag and CeO_2 nanosphere, and the presence of silver could facilitate surface chemisorbed oxygen activation, which mainly contributed to the HCHO oxidation. Based on In-situ DRIFTS results, formate species (HCOO-) were found to be the key intermediates and be activated on the surface active oxygen of Ag/CeO_2 nanosphere catalysts in the catalytic oxidation process of HCHO, which would be further oxidized into the final product water and carbon dioxides.

Significance

Ag/CeO_2 nanosphere catalysts exhibited much higher catalytic activity than normal Ag/CeO_2 particles prepared by conventional impregnation method. The synergetic interaction might exist between Ag and CeO_2 nanosphere, and the presence of silver could facilitate surface chemisorbed oxygen activation, which mainly contributed to the HCHO oxidation

References

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