Effect of impregnation sequence on oxidation activity and desorption properties of Ag-Pd/Ce0.8Zr0.2O2 catalyst

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Ce0.8Zr0.2O2 supported Ag-Pd catalysts have been prepared by the impregnation method and characterized by ethanol-TPD, CO-TPD and XRD. The effect of different impregnation sequences on catalytic activity for ethanol and CO oxidation has been investigated. The experimental results show that impregnation sequence has definite effect on the activity for ethanol and CO oxidation. Catalytic activity for ethanol and CO oxidation follows the order: Ag-Pd/Ce0.8Zr0.2O2 > Ag-Pd(Ce0.8Zr0.2O2) > Ag-Pd(F)/Ce0.8Zr0.2O2, and it corresponds with the temperature and intensity of the CO2 desorption peak in the CO-TPD process. Ethanol oxidation activity of the catalysts with different impregnation sequences correspond with the temperature and intensity of the desorption peak in ethanol-TPD process. XRD measurements show that there are two Ag2O phases, cubic and hexagonal, observed for all catalysts. Only hexagonal Ag2O may favor the oxidation of ethanol or CO. Hexagonal Ag2O formed in the catalyst prepared by co-impregnation is the most active to react with ethanol or CO adsorbed on the surface of the catalyst.

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Ce-Zr-O mixed oxides have been widely studied in recent years1-3 because Zr can enhance the capabilities of the redox, thermal stability and catalytic properties of CeO2. In catalysis, Ce-Zr-O mixed oxides have been widely used in the automotive three-way catalytic converter as oxygen storage media and thermal stabilizes. Ma et al.4 had reported that PdO/Ce0.8Zr0.2O2 catalyst exhibited high catalytic activity for CO oxidation. However, Ag as an industrial catalyst is often used for selective oxidation (such as epoxidation of ethylene5 and propylene5), and oxidation of volatile organic compounds (VOCs). Recently special attention has been focused on the cooperation catalytic activity of Ag and other metals. For examples, In Ag-Co/γ-Al2O3 and Ag-Mn/γ-Al2O3 catalysts, silver can promote the reduction of cobalt and manganese oxides and improve the VOCs oxidation activity of the catalyst5. The present work is concerned with the effect of impregnation sequence on ethanol and CO oxidation and with ethanol-TPD and CO-TPD of the catalysts.

Experimental

Preparation of catalysts

Ce0.8Zr0.2O2 mixed oxide was prepared by the citrate sol-gel method2. Ag-Pd(C)/Ce0.8Zr0.2O2 catalyst was prepared by co-impregnation method with the mixed aqueous solution containing Ag and Pd. This mixed solution was obtained with H3PdCl4 and AgNO3 mixed sample, which was liquefied by adding ammonia. The other two catalysts Ag-Pd(C)/Ce0.8Zr0.2O2 were prepared by step-by-step impregnation method. Pd/Co0.8Zr0.2O2 catalyst was prepared by conventional impregnation method2, and then impregnated Ag component using AgNO3 solution to give the first while Ag/Co0.8Zr0.2O2 catalyst was prepared first, then impregnated Ag-Pd(C)/Co0.8Zr0.2O2 with Pd component using H3PdCl4 solution to give the second. The catalyst prepared by the co-impregnation method was denoted as Ag-Pd(F)/Ce0.8Zr0.2O2, the catalyst impregnated first with Pd and then with Ag was denoted as Ag-Pd(F)/Co0.8Zr0.2O2, while the other was denoted as Ag(F)/Pd/Co0.8Zr0.2O2.

All catalysts were dried overnight in an oven at 120°C, then calcinated in air at 500°C for 4 h. The loading of Ag and Pd is 5% and 1.5%, respectively.

Activity measurement

Catalytic activity measurements were carried out in a fixed bed reactor (6 mm i.d.) using 150 mg catalyst. The total flow rate of the feed gas was 80 ml/min. The catalysts were directly exposed to reaction gas as the reactor temperature stabilized at the reaction temperature without any pretreatment. For ethanol oxidation, the concentration of ethanol was 4000mg/m3. The analysis of CO2 in the reactor effluent was performed on a gas chromatograph equipped with thermal conductivity detector (TCD). The analysis of the reactant and the organic compound in production were performed on a gas chromatograph with flame ionization detector (FID). For CO oxidation, the gas consisted of 2.4% CO and 1.2% O2 in N2. CO2 and CO were analysed with a TCD similar to the former.
Ethanol-TPD and CO-TPD

Ethanol-TPD and CO-TPD were carried out in TPD equipment homemade. The effluents from the reactor were analyzed on-line by a mass spectrometer (Balzers Omnistar MS200). A 100 mg sample was placed in the middle of a quartz tubular reactor, heated in O₂ (20 ml/min) at 500°C for 0.5 h and after cooling to the room temperature, the purging gas was switched to He (20 ml/min) for 0.5 h. Then ethanol or CO for ethanol-TPD or CO-TPD was injected until it was absorbed to saturation. Excess of adsorbate was removed by allowing the sample to remain in He flow until the baseline was balanceable approximately 1 h. The sample was then ramped to 900°C at a liner heating rate of 20°C/min. The mass spectrum monitored the changing signals of CH₄,CH₂OH (m/z=45), CH₃CHO (m/z=43), C₂H₅ (m/z=27), CH₂OH (m/z=31), O₂ (m/z=28), CO (m/z=28), CO₂ (m/z=44) and H₂(m/z=2) simultaneously for ethanol-TPD; CO (m/z=28) and CO₂ (m/z=44) for CO-TPD.

XRD Characterization

X-ray diffraction (XRD) patterns were collected on a PHILIPS PW3040/60 powder diffractometer, using Cu Kα radiation. The working voltage of the instrument was 40 kV and the current was 40 mA. The intensity data were collected at room temperature over a 20 range 25~75° with a scan rate of 0.1°/s.

Results and discussion

Effect of impregnation sequence on CO and ethanol oxidation

Figure 1 shows the activity of Ag-Pd/Ce₀.₅Zr₀.₂O₂ catalysts with different impregnation sequences for ethanol oxidation. It is found that impregnation sequence has great effect on the ethanol oxidation. The oxidation activity of the catalysts follows the order: Ag-Pd(C)/Ce₀.₅Zr₀.₂O₂ > Ag-Pd(F)/Ce₀.₅Zr₀.₂O₂ > Ag(F)/Pd/Ce₀.₅Zr₀.₂O₂. It is possible that on the surface of Ag-Pd(C)/Ce₀.₅Zr₀.₂O₂ catalyst active oxygen is easily formed which can favor the oxidation of ethanol. For the catalysts prepared by step-by-step impregnation methods, the substance impregnated later will cover the active site of the substance impregnated first, so active oxygen is difficult to form, which results in the decrease of activity. Figure 2 shows the activity of Ag-Pd/Ce₀.₅Zr₀.₂O₂ catalysts with different preparation methods for CO oxidation. The effect of impregnation sequence on CO oxidation activity is the same as ethanol oxidation.

Ethanol-TPD

Figure 3 shows the ethanol-TPD spectra of Ag-Pd/Ce₀.₅Zr₀.₂O₂ catalyst preparation by different impregnation sequences. For all catalysts, the desorption species are CO₂ and CO besides ethanol. No other desorption species are shown in Fig. 3 because their signals are very weak. From Fig. 3, it can be seen that there is only weak ethanol desorption peak in low temperature section (<100°C); in high temperature section (>200°C) there are obvious CO₂ and CO desorption peaks except ethanol desorption peak. This indicates that at high temperature ethanol absorbed can react with the oxygen absorbed on the surface of the catalyst to produce CO₂, and the oxidation reaction cannot take place until the temperature is higher than 200°C. There is a larger
CO₂ and CO desorption peak at about 350°C for all catalysts. For the area of CO desorption peak, Ag(F)-
Pd/Ce₀.₅Zr₀.₅O₂ catalyst is the largest, and Ag-
Pd(C)/Ce₀.₅Zr₀.₅O₂ catalyst is larger than Ag-
Pd(C)/Ce₀.₅Zr₀.₅O₂ catalyst, and reversible for the area of CO₂ desorption peak. This indicates that ethanol absorbed on the surface of the catalyst can be oxygenated to CO₂ easily on Ag-Pd(C)/Ce₀.₅Zr₀.₅O₂ catalyst. There are two CO₂ desorption peaks, at 180°C and at 250°C for Ag-Pd(C)/Ce₀.₅Zr₀.₅O₂ catalyst, and there is one CO desorption peak at about 250°C for Ag(F)-Pd/Ce₀.₅Zr₀.₅O₂ catalyst. During the reaction process, when there is sufficient oxygen existing in the gaseous phase, the ethanol absorbed on the surface of the catalysts can be oxygenated to CO₂, in spite of the desorption peak being comparatively weak. From the ethanol-TPD spectra, it is found that the desorption temperature of CO₂ is related to ethanol oxidation activity. Lower the temperature of CO₂ desorption, higher is the ethanol oxidation activity.

CO-TPD

Figure 4 shows the CO-TPD spectra of Ag-
Pd/Ce₀.₅Zr₀.₅O₂ catalyst preparation by different impregnation sequences. Almost no CO (m/e=28) is observed during CO-TPD. So only CO₂ desorption peaks after CO absorption is shown in Fig. 4. The reason is that the absorbed CO can react with the oxygen species on the surface of the catalyst to produce CO₂. The temperature and intensity of the desorption peaks depend on impregnation sequences very much. There is a desorption peak at about 110°C on Ag-Pd(C)/Ce₀.₅Zr₀.₅O₂ and Ag-Pd(F)/Ce₀.₅Zr₀.₅O₂ catalysts while there is a desorption process on Ag(F)-
Pd/Ce₀.₅Zr₀.₅O₂ catalyst over 200°C. This indicates that the CO absorbed on Ag-Pd(C)/Ce₀.₅Zr₀.₅O₂ and Ag-Pd(F)/Ce₀.₅Zr₀.₅O₂ catalysts is easy to react with the oxygen species and produces CO₂ for desorption. Combined with the CO oxidation activity result, we believe that there have been corresponding relation between the CO oxidation activity and the peak temperature and intensity of CO₂ desorption. Lower the temperature and the more intensive is the CO₂ desorption peak and the higher it is for the oxidation activity of CO.

XRD characterization

Figure 5 shows the XRD patterns of Ag-
Pd/Ce₀.₅Zr₀.₅O₂ catalysts with different impregnation sequences. There are no visible peaks due to Pd or PdO crystal phase to be observed because the contents of Pd were comparative lower or Pd (PdO) is finely dispersed on Ce₀.₅Zr₀.₅O₂. From Fig. 5, only for Ag-
Pd(F)/Ce₀.₅Zr₀.₅O₂ catalyst diffraction peaks of Ag appear. However the Ag diffraction peaks for Ag-
Pd(C)/Ce₀.₅Zr₀.₅O₂ and Ag(F)-Pd/Ce₀.₅Zr₀.₅O₂ cannot be found. Two Ag₂O phases cubic and hexagonal are observed for all catalysts, is the intensity of hexagonal Ag₂O diffraction peaks at 46.3° and 59.4° follows the
Fig. 5—XRD patterns of Ag-Pd/Ce0.8Zr0.2O2 catalysts with different impregnation sequences. A, Ag(Pd(F)/Ce0.8Zr0.2O2; B, Ag-Pd(C)/Ce0.8Zr0.2O2; C, Ag-Pd(C)/Ce0.8Zr0.2O2.

order: Ag-Pd(C)/Ce0.8Zr0.2O2 > Ag-Pd(F)/Ce0.8Zr0.2O2 > Ag(Pd(F)/Ce0.8Zr0.2O2, it is corresponding with the oxidation activity of ethanol or CO. So we consider that the forming of hexagonal Ag2O may favor the oxidation of ethanol or CO.

Conclusions
Ag-Pd/Ce0.8Zr0.2O2 catalysts are prepared by different impregnation sequence. The impregnation sequence has great effects on the catalysts oxidation activity, ethanol-TPD and CO-TPD. The catalytic activity for both ethanol and CO oxidation follows the order: Ag-Pd(C)/Ce0.8Zr0.2O2 > Ag-Pd(F)/Ce0.8Zr0.2O2 > Ag(Pd(F)/Ce0.8Zr0.2O2. The oxidation activity of ethanol or CO is corresponding with ethanol-TPD or CO-TPD. The XRD patterns indicate that the forming of hexagonal Ag2O may favor the oxidation of ethanol or CO.

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References