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Valence State Transformation of Rh on CeO_2NR/γ-Al_2O_3 Composite Support

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Oxide supported catalysts are widely used in the heterogeneous catalysis industry nowadays. One of the most common industrial applications for oxide supported catalysts is in the automotive three-way catalytic converter (TWC). The reactions in TWC consist of CO oxidation, unburnt hydrocarbon oxidation and nitrogen oxides reduction. In the TWC application, CeO_2 is used as a support or promoter material to simultaneously promote two oxidation and one reduction reactions mentioned above, owing to the easy reversible valence state change between Ce^{3+} and Ce^{4+}. γ-Al_2O_3 possesses high surface area with porous structure which promotes the dispersion of metal catalysts and reactant gas adsorption. In this study, ceria nanorods (CeO_2 NR), gamma alumina (γ-Al_2O_3) and their composites are chosen as the support materials for rhodium (Rh) catalyst to explore the origin of support prompting effect for low temperature CO oxidation.

CeO_2 NR were synthesized by a hydrothermal method. Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 0.1 M) and sodium hydroxide (NaOH, 6M) were mixed in a 200 mL Teflon-lined autoclave and kept in a box furnace at 90 ℃ for 48 h. After the hydrothermal reaction, the sample was filtered and washed with 500 mL DI water and 50 mL ethanol. CeO_2 NR were obtained by drying the sample at 60 ºC for 12 h. γ-Al_2O_3 was synthesized by sol-gel method. Aluminum nitrate nonahydrate ($Al(NO_3)_3$) was first dissolved in DI water with urea and then the suspension was stirred for 1 h on a magnetic stirrer, filtered and dried. The dry powder was treated at 250 ℃ for 3 h and then heated at 500 ℃ for 3 h to obtain γ-Al_2O_3 powder. The composites were obtained by mixing two supports (CeO_2 NR and γ-Al_2O_3) powders in solution with magnetic stirring. The catalysts with 0.5 wt.% Rh loading were prepared by direct wet-chemical deposition. An appropriate amount of rhodium chloride was dropwise added into the suspension solution of support powders and stirred for 24 h. Then sodium borohydride was added into the solution and stirred for 1 h. After filtering and drying, the catalyst powders were oxidized at 300 ℃ for 5 h in air and then reduced at 300 ℃ for 5 h under 5% H_2/Ar flow. Finally, the catalysts were labelled as Rh-CeO_2NR-r, Rh-γ-Al_2O_3-r and Rh-50%CeO_2NR/50%γ-Al_2O_3-r (r refers to reduction treatment). The samples were characterized by XRD, BET surface area, Raman spectroscopy, XPS, and TEM. H_2 temperature programmed reduction (H_2-TPR)/O_2 temperature programmed desorption (O_2-TPD) were studied using a Micrometric AutoChem II 2920 chemisorption analyzer. The catalytic oxidation of CO was conducted using a fixed bed plug flow reactor system. The presence of CO and CO_2 were analyzed using an online gas chromatograph (SRI multiple gas analyzer GC, 8610C chassis).

Figure 1(a) shows the XPS spectra of Rh 3d for all three catalysts. A significant difference was observed in regard to the valence states of Rh among three catalysts: 0.5Rh-γ-Al_2O_3-r only contains Rh^{3+} species whereas 0.5Rh-CeO_2NR-r contains Rh^0, and no Rh was detected on the surface of 0.5Rh-50%CeO_2NR/50%γ-Al_2O_3-r. The different valence states were due to the respective support effect of CeO_2 NR and γ-Al_2O_3 or Rh-support interaction. On γ-Al_2O_3 support, it was reported that the existence of Rh^{3+} is because Rh reacts with alumina irreversibly and forms an irreducible oxide phase [1]. On CeO_2 NR support, a strong interaction called oxygen ions back-spillover occurs between CeO_2 NR and RhO_x at the interface [2]. It is not clear why there was little signal of Rh species for 0.5Rh-50%CeO_2NR/50%γ-

Al_2O_3-r. Two possible hypotheses are that, (a) due to the significant amount of surface defects on CeO_2 NR and strong CeO_2-γ-Al_2O_3 interaction, Rh species diffuses in the lattice of the composite support; (b) Rh was encapsulated by porous layer of γ-Al_2O_3 or reacted with γ-Al_2O_3 to form rhodium aluminate ($Rh(AlO_x)_y$). The existence of Rh in all three samples was confirmed by the EDX analysis shown in Figure 1(b). The distribution of Rh species on these supports was characterized by TEM and STEM. Figure 1(d~g) show the TEM images of 0.5Rh-γ-Al_2O_3-r (d), 0.5Rh-CeO_2NR-r (e and g) and 0.5Rh-CeO_2NR/γ-Al_2O_3-r (f), respectively. The STEM-HAADF images were shown in Figure 1(h) and (i) corresponding to the 0.5Rh-γ-Al_2O_3-r and 0.5Rh-50%CeO_2NR/50%γ-Al_2O_3-r catalysts, respectively. Small RhO_x nanoclusters can be observed only in 0.5Rh-γ-Al_2O_3-r (h). No apparent RhO_x clusters are found in 0.5Rh-50%CeO_2NR/50%γ-Al_2O_3-r (i) which is consistent with the XPS results (Figure 1(a)). Figure 1(b) shows the CO conversion of three catalysts. The brighter contrast clusters in Figure 1(h) represent the RhO_x on γ-Al_2O_3 surface due to Z-contrast. For the CO oxidation performance, shown in Figure 1(c), it is clear that 0.5Rh-CeO_2NR-r shows the best low-temperature performance (below 120 ^oC) while 0.5Rh-50%CeO_2NR/50%γ-Al_2O_3-r has a similar catalytic activity as 0.5Rh-CeO_2NR-r at higher temperature range (above 120 ^oC). Metallic Rh has been considered as the active site for CO oxidation in comparison with RhO_x [3]. As a result of the strong CeO_2 NR- γ-Al_2O_3 interaction, the diffusion and/or transformation of RhO_x to other Rh species was promoted leading to the improved catalytic activity [4]. We will present more detailed interfacial structure and composition analysis.

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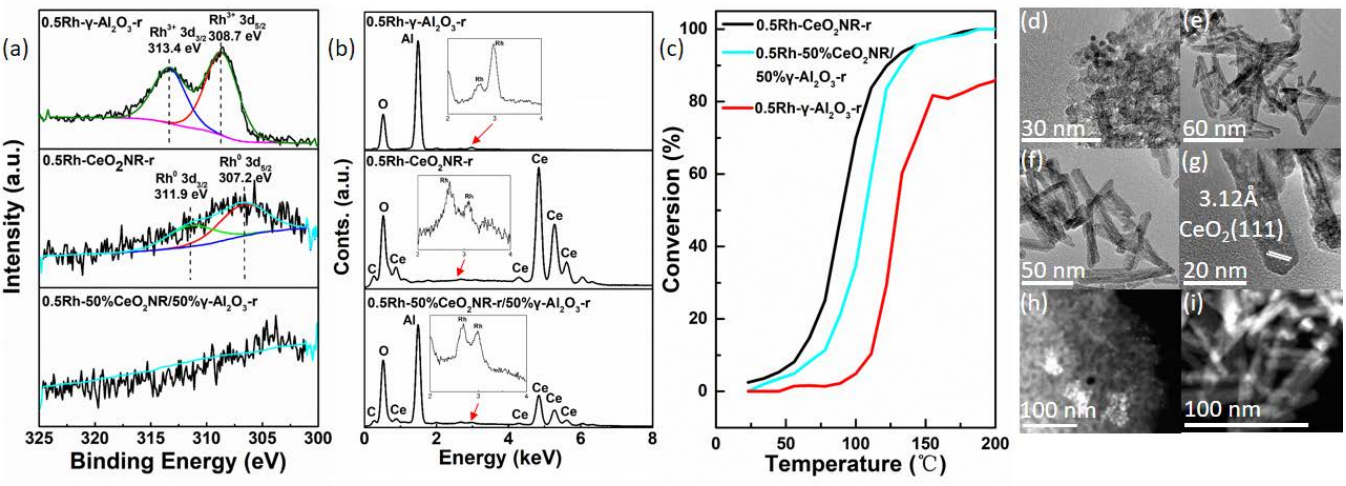

Figure 1. (a) XPS spectra, (b) EDX results, (c) CO conversion, TEM images of (d) 0.5Rh-γ-Al_2O_3-r, (e, g) 0.5Rh-CeO_2NR-r, (f) 0.5Rh-50%CeO_2NR/50%γ-Al_2O_3-r, and Z-contrast images of (h) 0.5Rh-γ-Al_2O_3-r and (i) 0.5Rh-50%CeO_2NR/50%γ-Al_2O_3-r.

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