

Selective reduction of NO on Pd/NiO added Y(Ba) 203 catalyst with C₃H₆

柳, 琳

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氏 名 : 柳 琳

論 文 名 : Selective reduction of NO on Pd/NiO added Y(Ba)₂O₃ catalyst with C₃H₆ (プロペンを用いて Pd と Ni を添加した Y(Ba)₂O₃ 触媒による NO の選択還元反応)

区 分 : 甲

論 文 内 容 の 要 旨

NO_x are not only be harmful to human body but also be responsible to photochemical smog and acid rain. NO_x are mainly formed from powder station, industrial boiler and exhaust gas from diesel and gasoline engines. It is reported that more than half of NO_x are formed by vehicles. Therefore, removing NO_x from the automobiles are still remaining an important issue to be resolved. It was found Y(Ba)₂O₃ catalyst could show high activity to NO direct decomposition reaction, however, the reaction temperature is too high to practical use. Selective reduction of NO usually occurred at lower temperature, as it could take advantage of hydrocarbons which are already existed in the exhausted gas. The objective of this study is to develop a new catalyst for NO_x removal under co-existence of oxygen. This thesis consists of 5 chapters. In Chapter 1, the current state of NO_x removal system from vehicles are reviewed. NO direct decomposition catalysts are also introduced from reaction mechanism.

In Chapter 2, modification of Y(Ba)₂O₃ catalysts were studied for selective reduction of NO with C₃H₆. Among noble metal (Rh, Pt, Pd) loaded MO_x (M=Ni, Co, Fe)/ (Y_{0.99}Ba_{0.01})₂O₃, it is found that 1 wt% Pd–3.2 wt% NiO/ (Y_{0.99}Ba_{0.01})₂O₃ catalyst shows a relatively high activity in the selective NO reduction below 300 °C with C₃H₆ in excess of O₂. NO_x conversion was achieved to about 70% at 260 °C on this catalyst. NO conversion was hardly affected by 3wt% water addition and high activity was sustained under 15000 h⁻¹. In addition, the catalytic activity is well maintained under lean burn conditions, which is advantageous comparing with the current TWCs. The effect of CeO₂ addition was also studied. On 1wt%Pd–3.2wt%NiO/(Y_{0.99}Ba_{0.01})₂O₃ catalyst for selective reduction of NO under oxygen excess (O₂:2.5%) condition, increased selective reduction activity of NO as well as lower reaction temperature was achieved by CeO₂ added to 1wt%Pd–3.2wt%NiO/(Y_{0.99}Ba_{0.01})₂O₃ catalyst. CeO₂ was considered to have positive effect on the oxidation of C₃H₆.

In Chapter 3, the author described the reaction mechanism of Pd–NiO/(Y_{0.99}Ba_{0.01})₂O₃ on selective reduction of NO reaction. TPD, pulsed reaction analyses and *insitu*-FTIR were applied to investigate the adsorption of NO, C₃H₆ and O₂, as well as the possible reaction mechanism. The results suggest that three main nitrate species are adsorbed on the catalyst, which formed by the disproportionation of NO on Pd and NiO. Pd and NiO also assist in activation of NO decomposition at lower temperatures as well as increasing the extent of NO adsorption. These surface active species including nitrate and -C₂H_x or -CH₃ react to form intermediate C₂H_xNO_y (x, y=2, 3) and CNO species. These intermediates readily react with NO to form the products N₂ and part of CO₂ as by-products. Oxygen play a role of react with hydrocarbons and acetate existed

on the surface of catalyst to recover of active sites.

In Chapter 4, based on the reaction mechanism shown in chapter 3, strain effect on the Y_2O_3 based catalyst through High Pressure Torsion (HPT) or Au dispersion for increasing the oxygen vacancy amount and oxygen diffusivity to achieve NO direct decomposition at lower temperature. From XRD, TEM and XPS measurement, it is confirmed HPT increased formation of oxygen vacancies and the decrease in particle size. Therefore, based on these changes, during the NO pulsed reaction, a higher NO conversion as well as N_2 yield was observed, however, no oxygen desorption was observed. In contrast, for gold dispersed sample, tensile strain was introduced into $Y(Ba)_2O_3$ sample which is confirmed by the XRD pattern. This tensile strain could increase the oxygen diffusivity resulting in the increased NO decomposition activity at low temperature and oxygen formation at around 600 °C was confirmed. This suggest that increase in diffusivity of oxygen is effective for increasing NO decomposition activity.

In Chapter 5, major studies discussed on Chapters 1-4 and perspective of this study were summarized.