Chemistry

NW10A/2009G574

Local structure analysis of thermostable Rh/$AlPO_4$ catalyst

Keita IKEUE,[1]* Satoshi HINOKUMA,[1] Kyosuke MURAKAMI,[1] Madoka OKAMOTO,[1] Mitsuhiro MATSUDA,[1] Yunosuke NAKAHARA,[2] Takahiro SATO[2] and Masato MACHIDA[1]
[1]Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan.
[2]Catalyst Division, Engineered Marerials Sector, Mitsui Mining & Smelting Co., Ltd., 1013-1, Ageoshimo, Ageo, Saitama 362-0025

Introduction

Although precious metals including Rh are highly dispersed in a fresh automotive catalyst, they are gradually agglomerated into large grains with a low surface area and hence a low catalytic activity in a long period of operation at high temperatures. The strategy to develop more stable catalysts requiring less precious metal loadings, especially for the very expensive Rh, is therefore of paramount importance. Recently, we have reported that $AlPO_4$ becomes an efficient and robust support material to produce optimum metal-support interactions that can reduce significantly Rh loading, owing to thermally-stable and highly-dispersed Rh nano-particles anchored strongly onto the phosphate surface [1]. In the present work, the metal-support interaction of the Rh/$AlPO_4$ catalyst has been studied.

Experimental

The Rh/$AlPO_4$ catalyst (50 mg) was heated from room temperature to 600 °C at constant rate of 10 °C•min^{-1} with supplying a simulated exhaust gas mixture containing NO (0.050%), CO (0.510%) C_3H_6 (0.039%), O_2 (0.400%) and He (balance) supplied at 100 cm^3•min^{-1}.

EXAFS of Rh K-edge was recorded at room temperature in a transmission mode on NW10A station at PF-AR. The XAFS data were processed by a REX 2000 program (Rigaku). The EXAFS oscilation was extracted by fitting a cubic spline function through the post-edge region. The k^3-weighted EXAFS oscillation in the 3.0-14 $Å^{-1}$ regions was Fourirer–tansformed.

Results and Discussion

As prepared Rh/$AlPO_4$ initiated the reaction at the lowest temperature of ≤ 200 °C and reached complete conversion at around 300 °C. The thermal ageing caused the light-off shifting about 100 °C toward higher temperatures, but the steep rise of conversion efficiencies within a narrow temperature range remained unchanged. This is in complete contrast to more than 500 °C required for 0.4 wt% Rh/La-γ-Al_2O_3. More drastic difference was observed after ageing at 900 °C for 500 h; the activity of the Rh/La-γ-Al_2O_3 was totally lost, whereas Rh/$AlPO_4$ preserved the light-off characteristic, which evidences a high thermal stability under oxidizing atmosphere.

To elucidate factors enabling marked difference in thermal stability and catalytic light-off characteristics, the local structure of Rh species was investigated by XAFS.

Fig. 1 shows the Fourier transforms of Rh K-edge EXAFS for as-prepared Rh/$AlPO_4$ and Rh/La-Al_2O_3 without corrections for phase shifts. The both EXAFS indicate the same peak due to Rh-O shell, but the shape and position of their second peaks are quite different. Our curve fitting analysis gave the best fit when they are assigned to Rh-O-P and Rh-O-Al shells. Although such interactions at the interface would be effective for stabilizing RhO_x nano-particles against sintering, the bonding of Rh-O-Al would finally cause the deactivation as a result of bulk-type reactions to form a solid solutions or compounds between RhO_x and Al_2O_3. By contrast, RhO_x did not cause such solid-state reactions with $AlPO_4$. Thus, non-reactive anchoring effect can be considered to be a reason for the thermal stability against sintering even during high-temperature ageing.

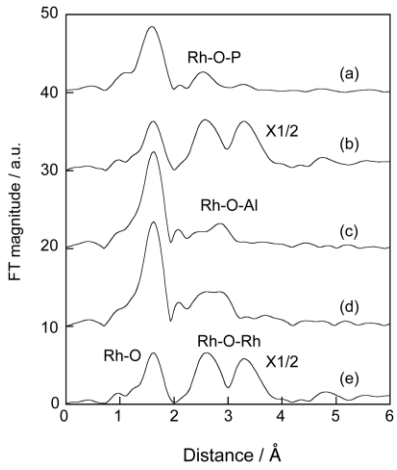

Fig. 1 Fourier transformed Rh K-edge EXAFS for (a) as-prepared 0.4wt% Rh/$AlPO_4$, (b) 0.4wt% Rh/$AlPO_4$(500h), (c) as-prepared 0.4wt% Rh/La-Al_2O_3, (d) 0.4 wt% Rh/La-Al_2O_3(500h) and (e) Rh_2O_3 as a reference. The times in parentheses are for ageing in a stream of 10% H_2O/air at 900 °C.

References

[1] M. Machida et al., Chem. Mater. 21, 1976 (2009).

*ikeue@kumamoto-u.ac.jp