



Kinetic analysis of reduction process of supported Rh/Al₂O₃ catalysts by time resolved in-situ UV–vis spectroscopy

Qiang Lin^a, Ken-ichi Shimizu^b, Atsushi Satsuma^{a,*}

^a Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

^b Catalysis Research Center, Hokkaido University, Kita21, Nishi10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

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ABSTRACT

Kinetic analysis of reduction of Rh/Al₂O₃ with low Rh-loadings (0.01–0.1 wt%) has been carried out by time resolved in-situ UV–vis spectroscopy. Based on XAFS and UV–vis spectra, it was indicated that Rh was present as surface isolated Rh³⁺ on catalyst calcined at 773 K in air. The rate of reduction of Rh³⁺ to metallic Rh⁰ was determined by in-situ UV–vis measurements under a flow of 1% H₂/He at 523–823 K. The reduction rate increased with Rh-loading but decreased as the calcination temperature elevated. The decrease of metallic Rh⁰ formation with the calcination temperature was in harmony with the reaction rate of CO oxidation. The apparent activation energy (*E*_a) for the reduction of Rh³⁺ to Rh⁰ was found to be constant around 60–62 kJ mol^{−1} and independent of the calcination temperature and the Rh-loading, indicating the equivalent intrinsic activity of supported Rh species on Rh/Al₂O₃ with the low Rh-loadings.

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1. Introduction

Three-way catalysts (TWC) have been widely used for controlling automobile emissions [1–4]. As an essential constituent of TWC, rhodium (Rh) is widely recognized as the most efficient noble metal to promote the reduction of NO_x [1,2]. Due to the merits of both relatively high surface area and thermal stability, alumina is a common support for TWC [2,5]. It has been well known that supported Rh/Al₂O₃ catalyst lose its activity at high temperatures (≥873 K) in an oxidizing atmosphere [5,6]. This deactivation of Rh/Al₂O₃ is caused by the formation of hardly reducible Rh species on alumina support [5–7], and has been investigated by use of various techniques [5–18], mainly TPR [5,7,11,13,16], XPS [12,14,15], and chemisorption [5,6,8]. It is well accepted that the deactivation of Rh/Al₂O₃ is due to the diffusion of Rh ions from surface into alumina bulk under oxidizing conditions, especially at the temperatures above 1073 K. The most of these studies have been carried out based on comparison of the state of Rh/Al₂O₃ before and after aging at a high temperature. For the better understanding of the deactivation, in-situ characterization of Rh/Al₂O₃ under working states would give us more fruitful information.

So far, in-situ Raman and in-situ XAFS spectroscopy have been applied to monitor the redox behaviors of Rh species under

reaction conditions [16,17]. Weng et al. studied the effects of calcination temperature on the catalytic performance of Rh/Al₂O₃ using in-situ Raman spectroscopy to monitor the bands of RhOx species under CH₄/O₂ atmosphere [16]. They found that calcination of catalyst at a higher temperature led to the lower reduction property of surface RhOx species due to substitution of Rh into Al site of Al₂O₃. Using in-situ XAFS, Dohmae et al. successfully traced the formation of metal Rh⁰ during reduction of Rh/Al₂O₃ [17]. The reduction rates of Rh were estimated at different temperatures (373–523 K) with the time interval of 0.2 s, and the obtained rates were on a line in an Arrhenius plot. Furthermore, in-situ XAFS measurements of reduction at 1173 K were performed using catalysts after oxidation at high temperatures. Although a portion of Rh was reduced in a few minutes, the residual Rh was hardly reduced, which was considered to be caused by a reaction with Al₂O₃ support. Although above two in-situ spectroscopic techniques successfully analyzed the dynamics of Rh species on alumina, both of them are not sensitive enough for Rh/Al₂O₃ with Rh-loadings as low as TWC. The most of the studies about the deactivation of Rh/Al₂O₃ were devoted to the catalysts containing sufficiently high Rh concentrations (≥0.5 wt%). However, the Rh concentrations of practical TWC are very small, for instance, 0.2 g/L [3] or 0.03 wt% [4]. Consequently, it is meaningful to investigate the deactivation of Rh/Al₂O₃ catalysts with low Rh-loadings close to a practical TWC.

Generally, quantitative measurements of transition metals are possible by in-situ UV–vis spectroscopy especially at low metal loadings [32,33]. Furthermore, UV–vis spectroscopy is known to

* Corresponding author. Tel.: +81 52 789 4608; fax: +81 52 789 3193.

E-mail address: satsuma@apchem.nagoya-u.ac.jp (A. Satsuma).