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PREPARATION OF RHODIUM NIOBATE COMPOUND BY CHEMICAL MIXING METHODS: EFFECT OF PREPARATION METHOD ON SMSI BEHAVIOR OF $RhNbO_4/SiO_2$ CATALYSTS

Y.G. YIN [1], T. WAKASUGI, H. SHINDO, S. ITO, K. KUNIMORI [2]
and T. UCHIJIMA
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

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Rhodium niobate was prepared as a complex oxide supported on silica via tetra-alkyl ammonium and citrate complexation. After calcination at 750 °C, the complex oxide was formed essentially in the monophasic columbite structure as determined by means of XRD. The two silica-supported $RhNbO_4$ catalysts were tested for their activity toward ethane hydrogenolysis, and a large difference in SMSI behavior was observed for the two preparations.

Keywords: Rhodium niobate, chemical mixing methods, ethane hydrogenolysis, SMSI, metal-oxide interaction

Recently, Hu et al. [1,2] studied in detail the mutual interaction between Rh and niobia, both supported on silica, during air calcination at high temperature (700 °C–900 °C). They demonstrated that $RhNbO_4$ complex oxide forms via a solid phase reaction between a Rh salt and niobia on silica, and showed that typical SMSI phenomena appear when the rhodium niobate was reduced by hydrogen [1,2]. However, a higher calcination temperature (e.g., 900 °C) was usually needed to attain a complete reaction to rhodium niobate [2]. Chemical mixing techniques, such as the sol-gel method, seem to have the potential for giving mixed/complex oxide catalysts with intimately mixed components [3,4]. In this paper, new chemical mixing methods using tetra-alkyl ammonium and citrate complexes [5] have been applied to prepare the $RhNbO_4/SiO_2$ catalysts and to compare the catalytic properties for ethane hydrogenolysis reaction.

Spinners et al. [6] have studied a new family of Nb(V) isopolyanions, prepared by reacting niobia with tetra-alkyl ammonium hydroxide. The Rh niobate can be prepared via the tetra-alkyl ammonium hydroxide complex of niobate [5]. On the other hand, the citrate complexation method, originally proposed by Marcilly et

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[1] Visiting professor from Beijing Institute of Chemical Fiber Technology, Beijing, China.
[2] To whom correspondence should be addressed.

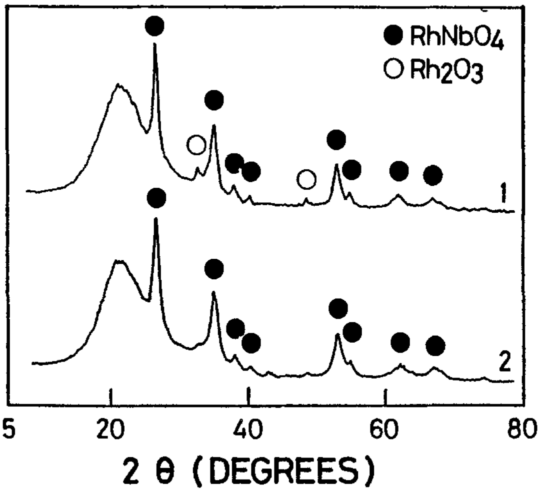

Fig. 1. X-ray diffraction pattern of the silica-supported complex oxide catalysts prepared by the chemical mixing methods: 1. RNSA, 2. RNSC.

al. [7], has been widely used recently for the preparation of complex oxides used as catalysts [8,9]. However, the application to the preparation of complex oxides containing noble metal (Rh) has not been reported as yet.

A silica-supported Rh-Nb oxide catalysts was prepared by double decomposition of aqueous solutions of $Rh(NO_3)_3$ and tetra-propyl ammonium niobate in the presence of SiO_2 (JRC-SIO-7) [10]). The precipitate was filtered and washed, and then dried at 120 °C overnight (designated as RNSA). Another Rh-Nb oxide catalyst (designated as RNSC) was prepared from citrate complexes of Rh and Nb, followed by vacuum-drying [5]. The Rh content of both catalysts was 5.0 wt%, with an atomic niobium-to-rhodium ratio of unity. The RNSA and RNSC catalysts were calcined in air at 750 °C. Prior to each activity test, the sample in the reactor was heated in O_2 at 500 °C for 1 h, followed by the H_2 reduction at different temperatures. The ethane hydrogenolysis reaction was carried out as a probe reaction for SMSI behavior of the complex oxides. Detailed procedures for the activity test were described previously [1]. X-ray diffraction (XRD) patterns of the abovementioned complex oxides were obtained by means of an X-ray diffractometer (Rigaku Co. Ltd.) equipped with a graphite monochromator for CuK_α (40 kV, 30 mA) radiation.

Fig. 1 shows the XRD patterns of the RNSA and RNSC catalysts after calcined at 750 °C. Both patterns indicate essentially a monophasic $RhNbO_4$ [2], although small peaks of rhodium oxide were observed. It should be noted that the intensities of the Rh_2O_3 peaks were somewhat larger in the RNSA catalyst than in the RNSC catalyst. The average crystallite size of the $RhNbO_4$ particles was almost the same (8 nm) for both catalysts. In the case of the conventional impregnation/calcination procedure [2], the calcination treatment at 700 °C

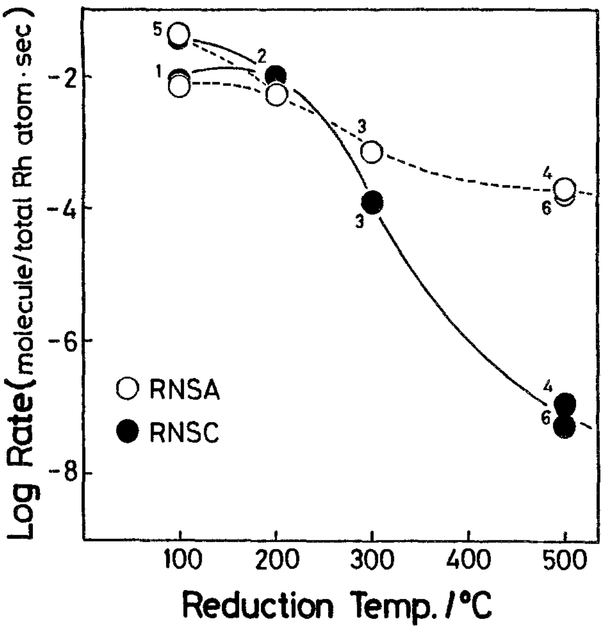

Fig. 2. Effect of the catalyst reduction temperature on the ethane hydrogenolysis activity (at 162 °C). The numbers in the figure mean the order of the H_2 treatment preceded by the O_2 treatment at 500 °C.

resulted in a formation of three phases (Nb_2O_5, Rh_2O_3, and $RhNbO_4$) on the silica surface, and the $RhNbO_4$ phase was formed almost completely only at 900 °C, but a small contribution of Rh_2O_3 was still observed in the XRD pattern [2,11]. Therefore, the Rh double oxide can be formed at a much lower temperature by these chemical mixing methods.

The ethane hydrogenolysis activities of the two catalysts are shown in fig. 2. The activity pattern of the RNSC catalyst shows a span of 5 orders of magnitude between the low-temperature reduction (LTR) and high-temperature reduction (HTR) treatments (No. 1 to No. 4). The activity change was reversible; i.e., the catalytic activity was increased by the O_2 treatment at 500 °C followed by LTR at 100 °C (No. 5), and decreased again by HTR at 500 °C (No. 6). Thus, the rhodium niobate in the RNSC catalyst exhibits typical SMSI behavior. The extent of the activity suppression was larger than the $RhNbO_4$ catalyst prepared by the conventional solid phase reaction (i.e., suppression by ca. 3.5 orders of magnitude) [2,11]. However, the activity pattern of the RNSA catalyst shows a span of only about one order of magnitude between the LTR and HTR treatments. The curve obviously indicates that the RNSA catalyst exhibits only slight SMSI behavior.

On the basis of a decoration model, generally accepted for the model of SMSI [12], the niobium oxide, probably NbO_2 [2], is formed after the decomposition of the rhodium niobate by HTR, migrates onto the Rh metal particles on the silica support, and, thus, blocks the latter. However, the extent of the Rh-niobia interaction depends strongly on the preparation method. At the present stage, it seems to be difficult to rationalize the difference in the SMSI behavior for catalysts with morphological characteristics that are almost the same. One possible explanation might be that a larger amount of Rh_2O_3 (including amorphous phase) which did not interact with niobia was present in the RNSA catalyst (fig. 1). This case is even more intriguing than the case reported by Asakura et al. [13]. They reported a different behavior of Rh-TiO_2 toward SMSI when Rh allyl complex was used as the precursor for Rh metal, as compared with those prepared from $RhCl_3$ [13]. The study of the mechanism of the preparation reactions and the characterization by several techniques is now in progress, and may provide information to give more insight into the SMSI phenomena.

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