Catalysis Letters 1 (1988) 155–158

EFFECT OF HIGH-TEMPERATURE REDUCTION ON AMMONIA DECOMPOSITION OVER NIOBIA-SUPPORTED AND NIOBIA-PROMOTED RHODIUM CATALYSTS

A. MAEDA, Z. HU, K. KUNIMORI * and T. UCHIJIMA *

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Received 5 April 1988

The high-temperature reduction at 773 K (HTR) of both Rh/Nb_2O_5 and $Nb_2O_5//Rh/SiO_2$ catalysts caused severe suppression in the capacity of H_2 chemisorption (SMSI behavior). However, in contrast to the case of hydrogenolysis reactions, the HTR caused only a small change in the activity of NH_3 decomposition, which is, like hydrogenolysis, a structure sensitive reaction. SMSI was not reversed during the reaction, as revealed by in situ H_2 chemisorption study.

In the studies of the effects of reduction temperature on the catalytic activities (e.g., Rh/TiO_2 [1], Rh/Nb_2O_5 [2]), it has been shown that the high-temperature reduction at 773 K (HTR) caused a strong activity suppression, i.e., several orders of magnitude, for ethane hydrogenolysis reaction but only a modest suppression for cyclohexane dehydrogenation reaction. It is thus recognized that SMSI (defined as a reversible effect on chemisorption capacity or catalytic activity induced by HTR) has a great influence on structure sensitive reactions but only a minor effect on structure insensitive reactions. The decomposition of NH_3 is generally considered to be a structure sensitive reaction [3]. This paper first reports the effect of SMSI on the activity of NH_3 decomposition over both Nb_2O_5-supported and Nb_2O_5-promoted Rh catalysts (Rh/Nb_2O_5 and $Nb_2O_5//Rh/SiO_2$) [2,4].

The 5.0 wt% Rh/Nb_2O_5 catalyst was prepared by the incipient wetness technique followed by reduction in H_2 at 773 K [2]. The Nb_2O_5-promoted 0.5 wt% Rh/SiO_2 catalyst (atomic ratio of $Nb/Rh = 11.4$) was prepared by the same method as in ref. [4]. The NH_3 decomposition reaction was carried out in a closed circulating system (2.5% NH_3/He, 760 Torr). The chemisorption value (H/Rh) was measured in situ at room temperature before and after the reaction. Analysis was performed by an on-line gas chromatograph. The catalysts were treated in O_2 at 673 K for 1 h followed by H_2 reduction for 1 h at 373 K (LTR) or 773 K (HTR) before each activity measurement.

---

* To whom correspondence should be sent.

Table 1
The NH_3 decomposition on Rh catalysts

Catalyst	Treatment	H/Rh [a] before	H/Rh [a] after	Rate [b] at 602 K
Rh/Nb_2O_5	LTR	0.15	–	0.31
	HTR	0.00	0.01	0.08
$Nb_2O_5//Rh/SiO_2$	LTR	0.16	0.12	0.66
	HTR	0.03	0.03	0.64

[a] The H_2 chemisorption was measured before and after the reaction (for 1 h) followed by the evacuation in vacuo at 723 K.

[b] Molecules converted per total Rh atoms per h.

Table 1 shows the in situ H_2 chemisorption data and the catalytic activities of the Rh/Nb_2O_5 and $Nb_2O_5//Rh/SiO_2$ catalysts. The suppression of the H_2 chemisorption capacity after HTR was observed for both catalysts. It should be noted that the H/Rh values were reversed if the catalysts were treated in O_2 at 673 K followed by the low-temperature reduction at 373 K (LTR). As shown in table 1, the activity of NH_3 decomposition on the $Nb_2O_5//Rh/SiO_2$ catalyst did not change between LTR and HTR. For the Rh/Nb_2O_5 catalyst, the HTR caused only a modest suppression (a factor of 4) in the activity. These results are in contrast with those from the ethane hydrogenolysis studies: the catalytic activity after HTR decreased by about 6 or 7 orders of magnitude, compared with LTR for both catalyst system [2,4].

Another independent study by a pulsed reaction system also showed that the HTR caused only a minor change in the activity of NH_3 decomposition [5]. The activation energy appeared to be almost constant (ca. 20 kcal/mol) between LTR and HTR. These results are in good agreement with those on a Rh/TiO_2 catalyst [6]. Haller et al. [6] also reported that this reaction on Rh/TiO_2 was not affected by HTR, and discussed a possibility that SMSI was reversed by the reactant NH_3 during the reaction. However, the H/Rh values after the reaction (see table 1) did not change significantly, which indicates that SMSI was not broken during the reaction on the Nb_2O_5-supported and Nb_2O_5-promoted Rh catalysts. Therefore, it became evident that the T.O.F. values, based on the H/Rh values after HTR, were much higher than those after LTR. In a current model of SMSI, the presence of an oxide species (TiO_x, NbO_x etc.) on the metal surface is responsible for the suppression of the H_2 chemisorption capacity after HTR (the decoration model) [1,2]. The relevance of the metal surface structure to the enhanced activity should be further investigated in both Rh/Nb_2O_5 and $Nb_2O_5//Rh/SiO_2$ catalyst systems.

In summary, although the NH_3 decomposition is one of "demanding" reactions [3], the observed SMSI behavior in the activity was quite different from those of the hydrocarbon hydrogenolysis reactions [1,2].

Acknowledgement

One of the authors (Z. Hu) gives his thanks to Tianjin University, China. This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 62540316, No. 62550575).

References

[1] D.E. Resasco and G.L. Haller, J. Catal. 82 (1983) 279.
[2] K. Kunimori, K. Ito, K. Iwai and T. Uchijima, Chem. Lett. (1986) 573.
[3] R.P.H. Gasser, *An Introduction to Chemisorption and Catalysis by Metals* (Clarendon Press, Oxford, 1986) p. 185.
[4] K. Kunimori, Y. Doi, K. Ito and T. Uchijima, J. Chem. Soc., Chem. Commun. (1986) 965.
[5] A. Maeda, K. Kunimori and T. Uchijima, to be published.
[6] G.L. Haller, V.E. Henrich, M. McMillan, D.E. Resasco, H.R. Sadeghi and S. Sakellson, Proc. of the 8th Int. Congr. Catal., Vol. V (1984) p. 135.