Catalysis Letters 4 (1990) 157–162

ALKALI NITRATE PROMOTED RANEY Ru CATALYST AS A SUPERIOR CATALYST FOR AMMONIA SYNTHESIS

Tokihisa HIKITA, Ken-ichi AIKA * and Takaharu ONISHI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received 16 August 1989; accepted 1 December 1989

Alkali nitrates, Raney Ru catalyst, hydrogenolysis of alkali nitrates, ammonia synthesis

Alkali nitrate promoted Raney Ru catalysts were prepared by hydrogenolysis of alkali nitrates ($CsNO_3$, $RbNO_3$, KNO_3, and $NaNO_3$) over Raney Ru. These catalysts were even more active in ammonia synthesis than Raney Ru promoted with metallic potassium. The promotion behaviour was different from that for the supported Ru catalysts, where metallic potassium was more effective than $CsNO_3$. Per-weight activity of $CsNO_3$ promoted Raney Ru was higher than that for any catalysts so far reported in ammonia synthesis under 80 kPa and at 573 K.

1. Introduction

Ruthenium has been known to become quite active for ammonia synthesis when promoted with electron donors [1]. Two series of ruthenium catalysts, supported Ru [2,3] and Raney Ru [4] have been studied. For supported catalysts metallic potassium gives higher activity than the alkali nitrate promoter such as $CsNO_3$ [2,5,6]. However, the metallic potassium is difficult to handle, while the alkali nitrate is easy to handle for preparing the catalysts. Alkali nitrate is decomposed in hydrogen over the ruthenium surface to give an active form. The promoter action of alkali nitrates has previously been studied on supported Ru catalysts [5,6]. It is believed that the alkali interacts not only with the Ru surface directly, but with the support as well. Thus, the direct interaction should be studied in detail without the support. The Raney Ru-alkali nitrate system was thus chosen as a model system, although the surface was covered partly by residual Al [7]. Meanwhile, however, the alkali nitrates were found to be even better promoters than metallic potassium for Raney Ru, which had not been expected before. We will report the preliminary results here.

---

* To whom correspondence should be addressed.

2. Experimental

Raney Ru catalyst was prepared from Ru-Al alloy (Ru/Al = 1/1 wt/wt) by leaching with 5N KOH aqueous solution at 373 K for 3 h [4,7]. Alkali nitrates (M/Ru = 6 to 10 mol%, M: alkali) were added as solutions on Raney Ru in water (impregnation). After evacuation of water, Raney Ru with alkali nitrate catalysts were treated with 80 kPa of H_2 at 573 K for 2 h. Ammonia synthesis rate was measured at 573 K or lower temperatures by the volume decrease of $N_2 + 3H_2$ under constant pressure (80 kPa) in a closed circulation system (flow rate = 80 mL min^{-1}) with a liquid nitrogen trap. The trapped product was examined to be ammonia by mass spectroscopy. Usually 1 g of Ru-Al alloy was used, which turned out to be about 0.5 g of Raney Ru after leaching. Shimadzu ESCA 750 was used for the XPS measurements. The binding energy was determined by comparing the peak of Au $4f_{7/2}$ to be 83.8 ± 0.1 eV.

3. Results and discussion

Ammonia synthesis rates at 573 K on various alkali nitrate promoted Raney Ru are shown in table 1. Activity is expressed as mmol NH_3 per hour per weight of catalyst which is not added with a promoter. Turn over frequency (TOF) at the footnote is represented as ammonia synthesis rate per sec per surface Ru atom. The number of surface Ru atoms was estimated from hydrogen or CO adsorp-

Table 1
Ammonia synthesis activity of various catalysts

Catalyst	Activity [a] (mmol h^{-1} g^{-1})	Apparent activation energy (kcal mol^{-1})	Binding energy of Ru $3d_{5/2}$ (eV)	Ref.
$CsNO_3$-Raney Ru	2.73 [b]	19	278.9	This work
$RbNO_3$-Raney Ru	2.12		278.6	This work
KNO_3-Raney Ru	1.54		279.6	This work
$NaNO_3$-Raney Ru	0.62		279.9	This work
Raney Ru	0.081	22	280.8	This work, [4]
Raney Ru-K	1.12	22		[4]
4.7% Ru-K/AC [c]	2.0 [d]	22		[2]
Ru powder	0.0013	23	280.0	[1,2,3]
$Fe-Al_2O_3-K_2O$	0.21		–	[1,2]
$Fe-Al_2O_3-K_2O-CaO$	1.03		–	[8]
Fe powder	0.0018		–	[1,2]

[a] Reaction under 80 kPa of N_2+3H_2 at 573 K.

[b] TOF = 2.0×10^{-3} NH_3/H(a)/s

[c] AC: Active carbon.

[d] TOF = 13×10^{-3} NH_3/CO(a)/s (ref. [2]).

tion. The activity depends on the amount of alkali nitrates. 6 to 10 mol% of nitrate against Ru gave the maximum activity. All the activities cited in table 1 were measured on catalysts with 6–10 mol% nitrates. The activity of KNO_3 promoted Raney Ru (1.54 mmol h^{-1} g^{-1}) was found to be similar to that of Raney Ru-K (1.12) mmol h^{-1} g^{-1}) [4] or that of 4.7% Ru-K/A.C. (2.0 mmol h^{-1} g^{-1}) which were the most active ammonia catalysts below atmospheric pressure [2,3]. On $CsNO_3$ promoted Raney Ru, the ammonia synthesis rate was found to be highest (2.73 mmol h^{-1} g^{-1}) at 573 K, and it was measurable even at around 373 K. The activity of these catalysts was not changed for a week during the measurement of activation energy (443 to 573 K). The apparent activation energy for Raney Ru-$CsNO_3$ (19 kcal mol^{-1}) was lower than that on Raney Ru-K (22 kcal mol^{-1}), but the difference was not much. The activity of Raney Ru-$CsNO_3$ is also higher than that reported for commercial iron catalysts Fe-Al_2O_3-K_2O-CaO (1.03 mmol h^{-1} g^{-1}) [8] or Fe-Al_2O_3-K_2O (0.21 mmol h^{-1} g^{-1}) [3] under the same conditions. Among alkali nitrates, the heavier the alkali element, the more effective is promotion of the catalyst (Cs > Rb > K > Na). This tendency was consistent with the order of electron donating ability of alkali metals. These results suggest electron donation from a metallic alkali to the ruthenium metal surface, which might promote N_2 dissociation over the ruthenium surface. Although the per-weight activity is the highest, the turn over frequency (TOF) of Raney Ru-$CsNO_3$ (2.0×10^{-3}) is still lower than the 4.7% Ru-K/AC (active carbon) (13×10^{-3}) at 573 K as is shown in table 1.

The hydrogenolysis of alkali nitrate on Raney Ru was not studied in detail here; however, the temperature programmed reaction has been studied on Ru/Al_2O_3 [6], where $CsNO_3$ is thought to be converted to Cs_2O and/or CsOH on Ru/Al_2O_3 as is shown in eqs. (1) to (4) [5,9].

$$2CsNO_3 + 8H_2 \rightarrow Cs_2O + 2NH_3 + 5H_2O, \quad (1)$$

$$2Cs_2O \rightarrow Cs_2O_2 + 2Cs, \quad (2)$$

$$Cs_2O_2 + H_2 \rightarrow 2CsOH, \quad (3)$$

$$Cs + OH(a) \rightarrow CsOH. \quad (4)$$

Similar reactions are suggested for Raney Ru, although eq. (4) is inferred to proceed to less extent than for the supported catalyst system where more surface OH exists. A part of alkali element is inferred to exist in "metallic" by eq. (2). Indeed, the catalyst was irreversibly deactivated by addition of water. XPS spectra of these catalysts were measured after the reaction. The binding energy of Ru $3d_{3/2}$ is shown in table 1. The binding energy of Ru $3d_{5/2}$ was found to shift to lower energy by 0.1–1.3 eV from that of Ru metal powder or Raney Ru (280.0 eV). One of the cause of this shift is considered to be due to the electron transfer from "metallic" alkali element to Ru surface. The nitrates are hydrogenolized on Raney Ru through eqs. (1) to (3) and some to eq. (4). The binding energies of alkali elements of alkali nitrates before and after the hydrogenolysis were also

Table 2
XPS binding energy of alkali metal element of alkali nitrate and those of alkali element on the active Raney Ru-alkali nitrate catalyst

	B.E. of alkali element of alkali nitrate (eV)	B.E. of alkali element on the active catalyst (eV)
Na $1s_{1/2}$	1073.2	1073.2
K $2p_{3/2}$	293.4	293.1
Rb $3d_{5/2}$	110.7	108.7
Cs $3d_{5/2}$	726.0	725.2

measured and shown in table 2. It was found that the binding energy was decreased by the hydrogenolysis, although all the absolute values for alkali nitrates are somewhat higher than that in the literature [10]. The change of the binding energy might also be correlated with the presence of "metallic" alkali element on the active catalyst. Even KOH has been known to be reduced to K by carbon at 1073 K [11,12].

Raney Ru surface is partly covered with Al^0 and Al^{3+} [7]. Quantitative analysis by XPS suggests that the intensity of Al is decreased by alkali addition. This suggests that the alkali compounds might localize more on aluminum than on Ru atoms on the Raney catalyst surface. Potassium has been reported to react with Al_xO_y on an iron single crystal [13]. However, direct interaction between Ru and the alkali metal is also suggested by the binding energy shift for Ru $3d_{5/2}$. Thus, the exact model might not be so simple and we may need further studies.

Fe-Al_2O_3-K_2O catalyst is composed of reduced iron mostly, about 3% of Al_2O_3, and about 1% of K_2O. Both Al_2O_3 and K_2O exist mainly on the catalyst surface. It has been understood that Al_2O_3 is a structural promoter, and K_2O is an electronic promoter [1]. For alkali nitrate promoted Raney Ru catalysts, it is suggested that the remaining aluminum acts as a structural promoter which stabilizes the ruthenium fine structure [7] and alkali compounds act as electronic promoters which donate electrons to the ruthenium surface. In this sense, alkali nitrate promoted Raney Ru catalysts resemble Fe-Al_2O_3-K_2O, and should be called "doubly promoted ruthenium catalysts", although the states of Al and the alkali might be more reduced in the case of the promoted Raney Ru catalyst.

Why does alkali nitrate work better on Raney Ru than on supported Ru? It is suggested that the alkali nitrate may give some alkali metal (eq. (2)), which could react with surface hydroxyl on the support (eq. (4)). Since Raney Ru has less hydroxyl, the alkali metal might survive and act as a strong promoter. Why does alkali nitrate work better than alkali metal (potassium vapor) on Raney Ru? Alkali metal nitrate may penetrate more effectively into the micro pore structure during impregnation of the Ru than potassium does during preparation of the catalyst by alkali metal vaporization. We need further studies.

References

[1] A. Ozaki and K. Aika, in: *Catalysis-Science and Technology*, eds. J.R. Anderson and M. Boudart, Vol. 1 (Springer-Verlag, Berlin/Heidelberg, 1981) ch. 3, pp. 87.
[2] K. Aika, H. Hori and A. Ozaki, J. Catal. 27 (1972) 424.
[3] A. Ozaki, K. Aika and Y. Morikawa, in: *Proc. 5th Int. Congr. Catal.*, 1972, Florida, ed. J.W. Hightower (North-Holland/American Elsevier, 1973) pp. 1251.
[4] K. Urabe, T. Yoshioka and A. Ozaki, J. Catal. 54 (1978) 52.
[5] K. Aika, K. Shimazaki, Y. Hattori, A. Ohya, S, Oshima, K. Shirota and A. Ozaki, J. Catal. 92 (1985) 296.
[6] K. Aika, A. Ohya, A. Ozaki, Y. Inoue and I. Yasumori, J. Catal. 92 (1985) 305.
[7] Y. Ogata, K. Aika and T. Onishi, J. Catal. 112 (1988) 496.
[8] H. Amariglio and G. Rambeau, in: *Proc. 6th Int. Congr. Catal.*, eds. G.C. Bond et al. (Chem. Soc., London, 1977) pp. 1113; The activity was recalculated by assuming the total pressure dependence of 1.5 order and the apparent activation energy of 17 kcal/mol.
[9] In: *Gmelins Handbuch der Anorganischen Chemie*, ed. E. Pietsch (Verlag Chemie, Weinheim, 1955) System-Number 25, pp. 107.
[10] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg, in: *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Co., Eden Prairie, 1978).
[11] A.N. Wennerberg and T.M. O'Grady, U.S. Pat. 4, 082, 694, 4 (April, 1978).
[12] T. Otowa, M. Yamada, R. Tanibata and G. Tanaka, 64th Cat. Soc. Jap. Meeting Abstracts: No. 2A11 (1989).
[13] S.R. Bare, D.R. Strongin and G.A. Somorjai, J. Phys. Chem. 90 (1986) 4726.