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REGENERATION OF V_2O_5-TiO_2 CATALYSTS FOR NITROGEN MONOXIDE REDUCTION POISONED BY POTASSIUM SALTS

Kaoru FUJIMOTO* and Tsutomu SHIKADA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The activities of V_2O_5-TiO_2 catalysts poisoned by potassium salts were recovered from 70 to 90% compared to that of the virgin catalyst by calcining in air to oxidized all vanadium species to fifth-valence, followed by treating with a solution of sodium sulfate or ammonium sulfate to remove the potassium salts of 97-98%.

The treatment with water or a acid solution has been reported as the regeneration methods of supported vanadium oxide catalysts for nitrogen monoxide reduction with ammonia poisoned by dust components.[1,2) However, the recovery of the catalytic activity is insufficient and in the case of acid treatment both the corrosive attack to reactors and the destruction of catalysts are unavoidable. On the other hand, the authors have shown in the preceding paper that the activities of supported vanadium oxide catalysts for nitrogen monoxide reduction are promoted by the addition of sodium or lithium salts while they are suppressed by added potassium salts.[3) Thus, only potassium ion shows a poisoning effect among alkali, suggesting that the recovery of the catalytic activity is attained by the removal of potassium component from the catalyst. In the present work, the regeneration methods of V_2O_5-TiO_2 catalysts poisoned by potassium ion were investigated. It was found that the treatment of the catalyst with a solution of $(NH_4)_2SO_4$ or Na_2SO_4 was more effective than that with hot water.

Catalyst was prepared by impregnating TiO_2 with an aqueous solution of vanadyl oxalate, followed by drying at 120°C for 24 h and then calcining in air at 450°C for 3 h. The addition of K_2SO_4 to the virgin catalyst was carried out by the impregnation from its aqueous solution. Reaction conditions and analytical methods were similar to those described in the preceeding paper.[3)

Removal of potassium component from the poisoned catalyst was performed by treating it with water. Five grams of the catalyst (No.2) which was used for the nitrogen monoxide reduction with ammonia at 250°C for 2 h was soaked in 300 ml of deionized water, treated at 80°C for 2 h with stirring and then filtreted. The filtrate shows a yellow color suggesting that a fairly large part of vanadium component was eluted. The recovery of the catalytic activity was quite insufficient (about 15%). Thus, the treatment of the spent catalyst with hot water as it was after the reaction was proven to be unfavorable for recovering activity because of the elution of vanadium component.

The vanadium component eluted was assumed to be fourth-valent vanadium compound. Therefore, it was thought that the vanadium component in the catalyst was necessary to be oxydized to fifth-valence by the calcination in air before treating with hot water. The catalyst (No.2) which was calcined in air at 450°C for 3 h after the reaction was treated with deionized water at 80°C for 2 h in a similar method as above. The catalyst was filtreted, dried and then calcined in air at 450°C for 3 h. In this case, the filtrate was colorless showing that little vanadium compound came out of the catalyst during the treatment. It was also supported by the data of elemental analysis shown in Table 2. The activity of the regenerated catalyst (No.2-a) are shown in Table 1. The activity of the catalyst increased in comparison with that of the poisoned catalyst (No.2). The extent of the activity recovery against the virgin catalyst (No.1) was about 50%.

Regeneration of the poisoned catalyst by treating with sulfate solutions such as $(NH_4)_2SO_4$ or Na_2SO_4 was investigated. The insufficient removal of potassium component and recovery of activity by treating with hot water were thought to be attributed to the formation of some chemical bond between potassium and vanadium oxide on the catalyst. Ion exchange of K^+ to NH_4^+ or Na^+ on the catalyst was expected by using a solution of $(NH_4)_2SO_4$ or Na_2SO_4.

$$K^+(c) + Na^+(s) \rightleftharpoons K^+(s) + Na^+(c) \tag{1}$$

$$K^+(c) + NH_4^+(s) \rightleftharpoons K^+(s) + NH_4(c), \tag{2}$$

where (c) and (s) denote to exist on the catalyst surface and in the solution, respectively. The catalyst (No.2) which was calcined at 450°C for 3 h after the reaction, was treated with 2 M $(NH_4)_2SO_4$ or Na_2SO_4 at 80°C for 2 h, followed by drying and calcination at 450°C for 3 h. As shown in Table 1, the activities of the regenerated catalysts (No.2-b and No.2-c) were recovered from 70 to 90% compared with that of the virgin catalyst.

Table 1 Activities of catalysts regenerated by treatment with water and aqueous solutions of ammonium sulfate and sodium sulfate

No.	Catalyst	Regeneration conditions	Conversion of NO (%)[a]			
			150°C	180°C	200°C	250°C
1	V_2O_5-TiO_2[b]	-	33.5	75.3	93.0	100
2	V_2O_5-TiO_2 + K_2SO_4[c]	-	-	18.7	35.7	85.0
2-a	V_2O_5-TiO_2 + K_2SO_4	H_2O, 80°C, 2 h	-	35.7	74.2	100
2-b	V_2O_5-TiO_2 + K_2SO_4	$(NH_4)_2SO_4$ soln 80°C, 2 h	14.5	55.0	80.6	100
2-c	V_2O_5-TiO_2 + K_2SO_4	Na_2SO_4 soln 80°C, 2 h	18.5	57.8	83.3	100

a. Reaction conditions : NO 300 ppm, NH_3 450 ppm, SO_2 100 ppm, O_2 5%, H_2O 10%, N_2 balance; SV 20000 cm^3/g-cat·h (STP).

b. Calcination temp. 450°C; $V_2O_5/TiO_2 = 1/19$ (weight ratio).

c. Calcined at 450°C for 24 h after addition of K_2SO_4; $V_2O_5/TiO_2/K_2SO_4 = 1/19/2$ (weight ratio).

The elemental analysis data of the catalysts, before and after the reaction, were given in Table 2. The amounts of vanadium in three catalysts regenerated were close to that in the catalyst unregenerated, indicating that little vanadium component was eluted. On the other hand, the amounts of potassium in the regenerated catalysts decreased markedly. Especially, the treatment with a solution of $(NH_4)_2SO_4$ or Na_2SO_4 increased the removal of potassium compared to that with hot water. The concentration of sodium component in the catalyst (No.2-c) which was treated with a solution of Na_2SO_4 was 0.15 wt% calculated as Na_2SO_4. The adsorbed amount of sodium on the catalyst was smaller than expected.

It was found that an effective removal of potassium and recovery of the activity of V_2O_5-TiO_2 catalyst poisoned by potassium salt was attained by calcining in air at about 450°C after the reaction, followed by treating with a solution of $(NH_4)_2SO_4$ or Na_2SO_4. A higher removal of potassium can be expected by repeated treatment because K^+ and NH_4^+ or Na^+ on the catalyst surface or in the solution are

Table 2 Elemental analysis of regenerated catalysts

Catalyst No.	Amount (mg/g of Ti)		
	V	K	Na
2	24.3	40.9	-
2-a	22.6	1.3	-
2-b	23.8	1.0	-
2-c	24.2	1.0	0.4

assumed to be at equilibrium. It is also noteworthy that the catalytic activity may be promoted by the adsorption of a small amount of sodium component on the catalyst during the treatment with a Na_2SO_4 solution.

The regeneration method by use of a solution of sodium or ammonium salt is more effective than that of hot water. In addition, both the corrosive attack to reactors and the destruction of catalysts by acid treatment can be avoided in the case of salt solution treatment. Therefore, the method which is developed in this study might be effective one for the practical *in-situ* regeneration.

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References

1) A. Nishijima, M. Kurita, T. Sato, Y. Kiyozumi, H. Hagiwara, A. Ueno, and N. Todo, Nippon Kagaku Kaishi, 1976, 276.

2) T. Hatanaka, T. Okouchi, H. Rikimaru, K. Abe, and T. Asafuji, Research Report from the Steel Industry Foundation for the Advancement of Environmental Protection Technology, No.2-20 (1980).

3) T. Shikada and K. Fujimoto, Chem. Lett., 1983, 77.

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