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EFFECT OF ADDED ALKALI SALTS ON THE ACTIVITIES OF SUPPORTED VANADIUM OXIDE CATALYSTS FOR NITRIC OXIDE REDUCTION

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It was found that the activities of supported vanadium oxide catalysts for nitric oxide reduction with ammonia were promoted by the addition of sodium or lithium salts while they were suppressed by added potassium salts.

Supported vanadium oxide catalysts have been known to show high activities for reduction of nitric oxide in flue gas with ammonia.[1-3] Especially, V_2O_5-TiO_2 and V_2O_5-TiO_2-SiO_2 catalysts are highly active at temperatures as low as 200°C or lower and resistant to sulfate or hydrogen sulfate which is formed on the catalyst surface during the reaction of flue gas containing sulfur oxides.[4-7] It has been reported that potassium compounds contained in the dust in flue gas show a marked poisoning effect.[8-10] A counterplan for the dust is required accompaning an increase of the relative frequency of the treatment of flue gas from coal-fired boiler. In the present work, the effects of various added alkali salts on the activities of supported vanadium oxide catalysts have been investigated. It has been found that both sodium and lithium compounds act as an accelerator rather than a catalyst poison. The details are described here.

Catalysts were prepared by impregnating TiO_2 and TiO_2-SiO_2 supports with an aqueous solution of vanadyl oxalate, followed by drying at 120°C for 24 h and calcining in air at 350°C for 3 h. The content of V_2O_5 in all catalysts tested was 5 wt%. The preparative method of TiO_2-SiO_2 support has been described in the previous paper.[5] The addition of alkali salt to parent catalysts was carried out by the physical mixing or the impregnation from aqueous solution. The catalysts were calcined in air at 250°C for 1 h after the addition of alkali salt. The amount of added alkali salt was 10 wt% based on the parent catalyst. A conventional tubular flow reactor was used for the reaction. Inlet gas composition was NO 300 ppm, NH_3 450 ppm, SO_2 100 ppm, O_2 5 %, H_2O 10 %, balanced N_2. Space velocity was 20000 cm^3/g-cat·h and the catalyst weight was calculated on the basis of alkali free state. Analysis of NO was made with a chemiluminescence NO/NO_x meter.

Experimental results are summerized in Table 1. Catalyst 3 and Catalyst 4 which were prepared by adding potassium sulfate to V_2O_5-TiO_2-SiO_2 and V_2O_5-TiO_2 by physical mixing method showed nearly the same activities as those of alkali free catalysts (No 1 and 2), respectively. When K_2SO_4 was added by the impregnation method, on the other hand, the activity of TiO_2-SiO_2-supported catalyst (No 5) decreased to from one-fourth to one-fifth compared with that of alkali free catalyst while the activity of TiO_2-supported catalyst (No 6) decreased slightly. Catalyst 7 which was calcined in air at 450°C for 24 h after impregnating V_2O_5-TiO_2 with K_2SO_4 solution showed very low activity. Thus, the activities of supported vanadium oxide catalysts decreased with the addition of potassium salt by impregnation but the features of activity decrease differed between the supports. With V_2O_5-TiO_2 series catalysts, heat treatment at higher temperature after the impregnation of K_2SO_4 may result in the formation of a certain bond between potassium and catalyst, leading to a poisoning effect.

It is interesting that the activities of both V_2O_5-TiO_2-SiO_2 and V_2O_5-TiO_2 catalysts which contain Na_2SO_4 (Catalyst 8 and Catalyst 9) are higher than those of original ones. With Catalyst 10 which was calcined in air at 450°C for 24 h after impregnating V_2O_5-TiO_2 with Na_2SO_4 solution, only slight decrease in activity was observed compared with Catalyst 9. The addition of other sodium salts such as $NaHSO_4$ NaCl and Na_2HPO_3 resulted in an increase of the activity as well. Especially, the activity of the Catalyst 12 containing NaCl is by more than two times higher than that of alkali free catalyst. Similar accelerating effects were observed in the case of lithium salt addition (Catalyst 14 and Catalyst 15).

Kasaoka et al. have been reported that the activities of V_2O_5-TiO_2 catalysts are suppressed by the addition of sodium salts.[11)] They are markedly different from the results in this study. Although the difference in the results is considered to be due to that in the method of catalyst preparation or alkali addition, the details are not clear.

Table 1 Effect of addition of alkali salts to V_2O_5-TiO_2-SiO_2 and V_2O_5-TiO_2 catalysts on NO conversion

No	Catalyst[a]	Addition of alkali		Conversion of NO (%)[c]			
		Alkali salt[b]	Method	150°C	180°C	200°C	250°C
1	V_2O_5-TiO_2-SiO_2	-	-	-	-	32.9	72.5
2	V_2O_5-TiO_2	-	-	17.3	53.3	80.6	100
3	V_2O_5-TiO_2-SiO_2	K_2SO_4	Physical mixing	-	-	30.0	70.3
4	V_2O_5-TiO_2	K_2SO_4	Physical mixing	20.0	56.7	79.2	98.5
5	V_2O_5-TiO_2-SiO_2	K_2SO_4	Impregnation	-	-	7.9	14.5
6	V_2O_5-TiO_2	K_2SO_4	Impregnation	16.7	53.3	64.2	93.5
7	V_2O_5-TiO_2	K_2SO_4	Impregnation[d]	-	18.7	35.7	85.0
8	V_2O_5-TiO_2-SiO_2	Na_2SO_4	Impregnation	22.3	57.3	71.7	97.7
9	V_2O_5-TiO_2	Na_2SO_4	Impregnation	40.8	84.7	99.6	100
10	V_2O_5-TiO_2	Na_2SO_4	Impregnation[d]	28.6	76.4	96.4	100
11	V_2O_5-TiO_2	$NaHSO_4$	Impregnation	18.2	65.2	92.6	100
12	V_2O_5-TiO_2	NaCl	Impregnation	47.3	90.7	99.1	100
13	V_2O_5-TiO_2	Na_2HPO_3	Impregnation	34.2	84.1	98.6	100
14	V_2O_5-TiO_2-SiO_2	Li_2SO_4	Impregnation	16.7	55.0	72.3	98.5
15	V_2O_5-TiO_2	Li_2SO_4	Impregnation	40.6	81.0	95.7	100

a. 5wt%V_2O_5-3wt%TiO_2-SiO_2, 5wt%V_2O_5-TiO_2; Calcination temp. 350°C.

b. Alkali salt/Catalyst = 1/10 (weight ratio). c. Reaction conditions: NO 300ppm, NH_3 450ppm, SO_2 100ppm, O_2 5%, H_2O 10%, N_2 balance; SV 20000 cm^3/g-cat h (STP). d. Calcined at 450°C for 24 h after impregnation.

It was found that the addition of sodium or lithium salts to supported vanadium oxide catalysts led to an marked increase of the catalytic activity, whereas the addition of potassium salt led to the activity decay. The reason why the activity changes with the addition of alkali salt is not clear. However, these facts may have a significant meaning in the stand point of catalyst protection against potassium or the development of regeneration method of poisoned catalyst.

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