CHEMISTRY LETTERS, pp. 1301-1304, 1988.

Preparation of Titania-Supported V-Mo-O Oxide as Highly Active Catalysts for the Simultaneous Removal of SO_2 and NO from Exhausts

Yasutake TERAOKA,† Akihiro YAMASHITA, and Noboru YAMAZOE*
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816
† Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852

The titania supported V-Mo-O prepared from $VOCl_3$ and $Mo(CO)_6$ was found to be very active for the simultaneous removal of SO_2 and NO. It was shown that the V-Mo-O oxide was supported as an amorphous phase and formed a surface compound similar to vanadium oxysulfate at a steady working state.

For removing sulfur oxides (SOx) and nitrogen oxides (NOx) from the flue gases emitted from stationary sources, the conventional systems adopt two consecutive processes; a dry process in which NO is reduced with NH_3 to N_2 and a wet process in which SO_2 is fixed as sulfates. For the exhaust produced from sulfur rich fuels, however, development of new removal processes to treat SOx and NOx simultaneously is awaited. One of such processes appears to be catalytic removal of SO_2 and NO in one reactor. For example, CuO-TiO_2 based oxides[1,2] and V_2O_5-loaded activated carbon[3] were reported to show catalytic activity for simultaneous removal of SO_2 and NO, in which SO_2 was fixed as $CuSO_4$ and H_2SO_4 adsorbed on activated carbon, respectively, and the regeneration process of catalysts was required. We have been investigating new solid catalysts on which NO is reduced with NH_3 to N_2 and SO_2 is oxidized to SO_3 to be removed as ammonium sulfates simultaneously and stationarily.[4] It has turned out that, of the two catalytic reactions, the oxidation of SO_2 is more difficult and need development of new active catalysts and that the V-Mo-O mixed oxide catalysts supported on TiO_2 prepared from aqueous solutions are most active for SO_2 oxidation among the oxide catalysts tested.[4] Subsequent study has revealed that preparation from $VOCl_3$ and $Mo(CO)_6$ dissolved in CCl_4 gives more active supported V-Mo-O catalysts with excellent reproducibility as reported in this letter.

The support TiO_2 (anatase type) was prepared from $TiCl_4$ as described before.[4] Resulting oxide calcined at 450 °C for 6 h had a specific surface area of ca. 100 m^2/g. V-Mo-O oxide was supported on TiO_2 by the following two methods. Type A catalysts were prepared by the conventional impregnation method. The support was impregnated with an aqueous solution containing $(NH_4)_6Mo_7O_{24}$, NH_4VO_3 and oxalic acid, and after evaporation it was dried at 150 °C for 24 h. Calcination in air was carried out either in two consecutive steps at 300 °C for 2 h and at 450 °C for 5 h (catalyst A-I), or in one step at 450 °C for 5 h (catalyst A-II).

The atomic ratio of V/Mo was set at 83/17 and the loaded amount of V-Mo-O oxide was fixed at 20 wt% (V/Mo/Ti=14/3/83 in atomic ratio). BET surface area of supported catalysts thus prepared was ca. 60 m^2/g. Type B catalysts were prepared by a sort of surface fixation method. The support was immersed in a CCl_4 solution of $Mo(CO)_6$ for 0.5 h at room temperature and, after evaporating CCl_4, it was subjected to the same two step calcination as done for catalyst A-I. The calcined sample was again immersed in a CCl_4 solution containing $VOCl_3$ for 0.5 h at room temperature. After decantation, remaining CCl_4 was evaporated from the solid phase. The obtained sample was then hydrolyzed in a moist air stream for 1 h at 120 °C, followed by the same two-step calcination as above. Although the concentration of the solutions was regulated to obtain a catalyst with a composition V/Mo/Ti=14/3/87, chemical analysis showed that the catalysts prepared in this way contained about 0.5 mmol of vanadium ions per gram catalysts, giving rise to the V/Mo atomic ratio of 59/41 and the loaded V-Mo-O amount of 9.4 wt% (V/Mo/Ti=4/3/93). BET surface area was ca. 70 m^2/g. Catalytic activity was tested in a conventional fixed bed reactor. A gaseous mixture of SO_2 (500 ppm), NH_3 (1000 or 1250 ppm), O_2 (5%), H_2O (10%), and N_2 (balance) was fed with or without NO (250 ppm) at a space velocity 12000 h^{-1}. The amount of NH_3 supplied was set at the same and twice amount of NO and SO_2, respectively, on the basis of the following equations; $NO + NH_3 + 1/4\ O_2 \rightarrow N_2 + 3/2\ H_2O$ and $SO_2 + 2\ NH_3 + 1/2\ O_2 + H_2O \rightarrow (NH_4)_2SO_4$. NO and SO_2 were analyzed by a chemiluminescence NO/NOx meter (Yanagimoto, ECL-77A) and iodometry, respectively.

Figure 1 shows the time course of the conversion of SO_2 at 350 °C over types A and B catalysts in the absence of NO. The initial conversions were all apparently high, because the adsorption of SO_2 was counted. After this adsorption, type A catalysts either went down to a modest steady conversion level below 60% (A-I), or fell down rapidly to a very low activity level (A-II). It was found that, even when the same preparation method was applied, the activities of A-I catalysts were dispersed rather widely. On the other hand, type B catalyst tended to increase activities for an initial short period (induction period) and reached a steady conversion level as high as 83%. Moreover, reproducibility of the catalyst preparation was satisfactory for type B catalysts.

Type B catalysts were further tested for the SO_2 conversion in the presence and absence of NO (Fig. 2). Catalysts from B-1 to B-5 in Fig. 2 were prepared in the same way but in separate batches. In the NO free system the conversion was high from the initial stage as shown by curves B-1 and B-2. In the presence of NO, however, the induction period where the conversion remained lower was more con-

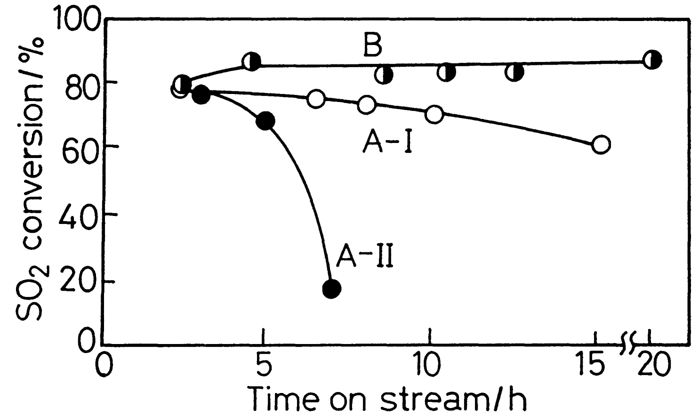

Fig. 1. Time course of SO_2 removal over V-Mo-O/TiO_2 catalysts at 350 °C. Feed: SO_2(500 ppm)+NH_3(1000 ppm)+O_2(5%)+H_2O(11%)+N_2(balance).

spicuous than in NO free system, and then went up to a steady level of ca. 80% which was only a few percents less than the level attained in the absence of NO, as shown by curves B-3, 4,and 5. It follows that the catalytic activity of type B catalysts are not affected seriously by the presence of NO in the steady state.

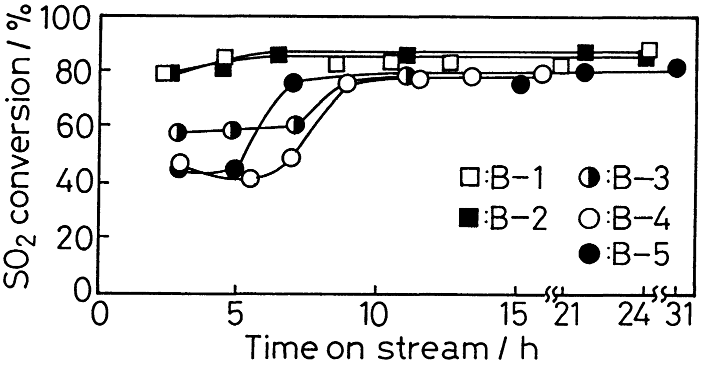

Fig. 2. Time course of SO_2 removal over type B catalysts at 350 °C in the absence (B-1, 2) and presense (B-3,4,5) of NO. Feed: **[B-1,2]** SO_2(500 ppm)+NH_3(1000 ppm)+O_2(5%)+H_2O(11%)+N_2 (balance), **[B-3,4,5]** SO_2(500 ppm)+NO(250 ppm) +NH_3(1250 ppm)+O_2(5%)+H_2O(11%)+N_2(balance).

Figure 3 shows the steady state activity of a type B catalyst for the simultaneous removal of SO_2 and NO as a function of temperature. The conversion of NO was 75% at 200 °C and reached 100% at 250-350 °C, whereas the conversion of SO_2 was 40% at 200 °C and increased gradually with increasing temperature to reach 80% at 350 °C. The high SO_2 conversion level (80%) attained at 350 °C would assure that type B catalysts are promising for the simultaneous removal of NO and SO_2.

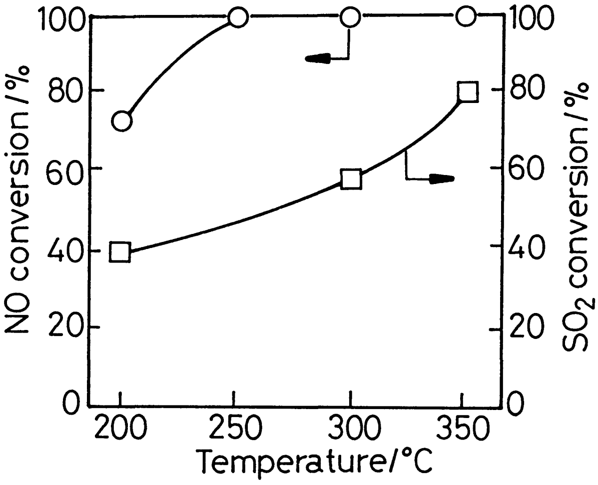

Fig. 3. Temperature dependence of steady state activity of a type B catalyst for the simultaneous removal of SO_2 and NO. Feed: SO_2(500 ppm)+NO(250 ppm)+NH_3(1250 ppm)+O_2(5%)+H_2O(11%)+N_2(balance).

To know why the catalytic activity depended fairly on the preparation methods, types A-I, A-II,and B catalysts were subjected to XRD and IR measurements. From X-ray diffraction analyses, crystalline V_2O_5 phase was always detected in type A-II catalysts prepared separately, infrequently detected in type A-I, and never detected in type B. Comparison of this tendency with the catalytic performances just mentioned indicates that the supported V-Mo-O oxide should be amorphous to be an active and stable catalyst. In addition, marked difference between types A and B catalysts was observed in IR measurements, as stated below.

The infrared spectra of fresh and used catalysts are shown in Fig. 4. Type A catalyst (both A-I and A-II) showed a band near 1013 cm^{-1}, which was ascribable to V=O stretching vibration, and no significant changes were observed between the fresh and used catalysts. In type B catalyst, the V=O band was not visible as a peak, probably because it shifted to lower wave number to become a shoulder overlapping with the strong absorption of TiO_2. In the used catalyst, new bands appeared at 1046, 1136,and 1400 cm^{-1}. The last band disappeared after evacuation at 300 °C for 1 h, and was assigned to adsorbed NH_4^+ ion. The other two bands are in the wave number regions corresponding to the stretching vibration modes of S=O and S-O, and in fact they coincided fairly well with the spectrum of $VOSO_4$ as shown in the same figure. We consider therefore that SO_2 molecules are adsorbed oxidatively to form a surface compound very similar to vanadium oxysulfate which may be responsible for the steady-state activity of a type B catalyst. As stated above, the induction periods were observed only for type B catalysts irrespective to the presence and absence of NO, though it was more conspicuous in the presence of NO. Taking IR results into account, the induction period observed over type B catalysts seem to be a time necessary to activate the catalyst surface to the oxysulfate, and the coexistance of NO impedes the formation of oxysulfate. Anyway, type B catalysts have a steady surface state quite different from that of type A catalysts, and this difference in surface state may explain the high and stable catalytic activity of type B catalysts, although the roles of the oxysulfate in the catalysis are not clear at present.

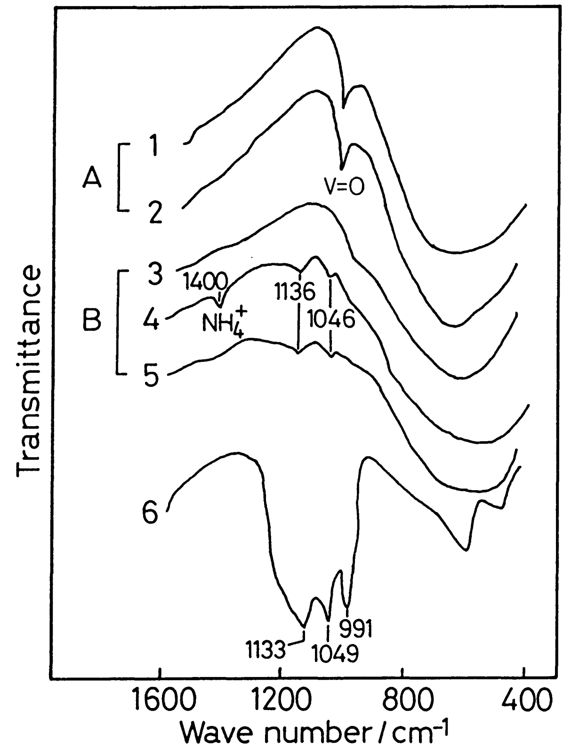

Fig. 4. Infrared spectra of V-Mo-O/TiO_2 catalysts. **1.** Fresh type A (I and II) catalyst, **2.** Used type A (I and II) catalyst, **3.** Fresh type B catalyst, **4.** Used type B catalyst, **5.** Used type B catalyst after evacuation at 300 °C for 1 h, **6.** $VOSO_4$ (reference).

In summary, V-Mo-O/TiO_2 catalysts prepared from $VOCl_3$ and $Mo(CO)_6$ dissolved in CCl_4 were found to show high activity for both the reactions of NO and SO_2 removal. Although the problems such as the removal of ammonium sulfate and the prevention of ammonia leakage from the system remain unresolved, the present results show the possibility of removing SO_2 and NO simultaniously in one reactor using a solid catalyst.

References

1) S. Kasaoka, E. Sasaoka, M. Funahara, and S. Nakashima, J. Fuel Soc. Jpn., 61, 126(1982).

2) S. Kasaoka, E. Sasaoka, and S. Nakashima, J. Fuel Soc. Jpn., 63, 54(1984).

3) K. Gomi, T. Komura, N. Arashi, Y. Hishimura, O. Kanda, and H. Kuroda, Nippon Kagaku Kaishi, 1986, 527.

4) Y. Teraoka, K. Shimanoe, and N. Yamazoe, Chem. Lett., 1987, 2047.

(Received May 9, 1988)