Pronounced Catalytic Activity of Specially Prepared MoO_3–TiO_2 for Reduction of Nitrous Oxide with Hydrogen

By Susumu Okazaki, Naoki Ohsuka,
(*Department of Industrial Chemistry, Faculty of Technology, Ibaragi University, Hitachi-shi* 316, *Japan*)
and Tokio Iizuka and Kozo Tanabe*
(*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo* 060, *Japan*)

Summary Although an MoO_3–TiO_2 (α) catalyst prepared from orthotitanic acid showed only 2·5% conversion in the reduction of nitrous oxide with hydrogen at 250 °C, an MoO_3–TiO_2 (β) catalyst prepared from metatitanic acid showed 100% conversion, and its activity was markedly higher than that of MoO_3–SiO_2, MoO_3–Al_2O_3, MoO_3–MgO, or MoO_3–active carbon.

The catalyst carrier often plays an important role in catalytic activity. We now report a surprising effect of the method of preparation of TiO_2 on the activity of MoO_3–TiO_2 for the reduction of nitrous oxide with hydrogen.

MoO_3 was mounted on the carriers as follows. The carrier was immersed in an aqueous solution of a known amount of ammonium paramolybdate, which was then evaporated to dryness over a water bath, dried at 120 °C

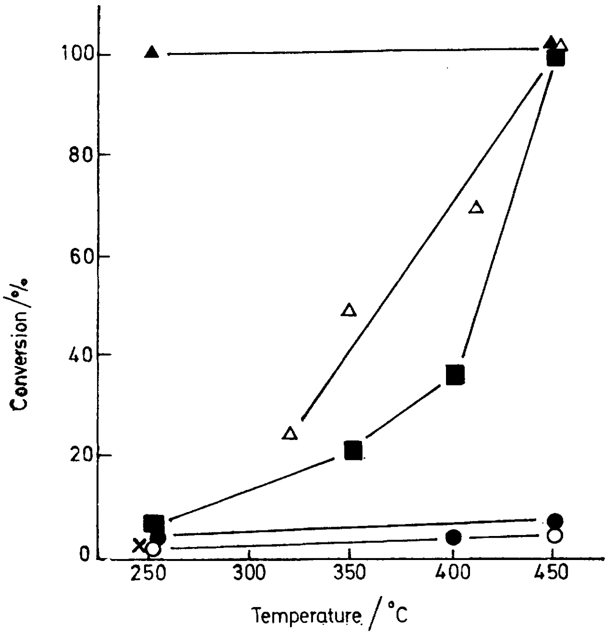

FIGURE. Effect of carriers of supported MoO_3 catalysts on % conversion in the reduction of N_2O. (Catalyst weight: 4·5 g; space velocity: 2020 h^{-1}.) ▲ MoO_3–TiO_2 (β), △ MoO_2–Al_2O_3, ■ MoO_3–active carbon, ● MoO_3–SiO_2, ○ MoO_3–MgO, × MoO_3–TiO_2 (α).

for 24 h, and calcined in air at 600 °C for 3 h. The content of MoO_3 was 7 wt. % in all cases. Orthotitanic acid (α-titanic acid)[1] was prepared by hydrolysis of an aqueous solution of $TiCl_4$ cooled in an ice bath with 28% aqueous ammonia until the pH became 7, washing with distilled water until no chloride ion was detected, and drying at 120 °C for 24 h. Metatitanic acid (β-titanic acid)[1] was prepared by hydrolysis of $TiOSO_4$ with boiling water, washing with boiling water until no sulphate ion was detected, and drying as above. $Mg(OH)_2$ was prepared by hydrolysis of an aqueous solution of $Mg(NO_3)_2$ with 28% aqueous ammonia, followed by washing with distilled water, and drying as above. Alumina (Mizusawa Chem. Co., spherical neobead C), SiO_2 (Nissan Chem. Co., Colloidal silica), and active carbon (Takeda Chemicals Inc., HGN933) were also used as catalyst carriers.

The surface areas of the MoO_3–active carbon, MoO–Al_2O_3, MoO_3–SiO_2, MoO_3–MgO, and MoO_3–TiO_2 systems calcined at 600 °C in air for 3 h and in a stream of hydrogen for 2 hr were determined by the B.E.T. method using N_2 gas as adsorbate to be 860, 266, 233, 78, and 68 m^2/g, respectively.

The reduction of nitrous oxide with hydrogen was carried out at 250—450 °C by using a conventional flow apparatus wrapped with a tape heater to prevent the condensation of the water vapour formed. The molar ratio of nitrous oxide to hydrogen was 1 : 9, the space velocity being 2020 h^{-1}. Prior to reaction, the catalysts were reduced with hydrogen at 600 °C for 2 h and cooled to the reaction temperature; the reaction was then started. Unchanged N_2O and the H_2O formed were analysed by gas chromatography with a 2 m column of Porapeak Q. The formation of ammonia was negligible, as shown by titration with 0·1 M H_2SO_4 using methyl red as an indicator.

The results are shown in the Figure. At 450 °C, MoO_3–TiO_2(β), MoO_3–Al_2O_3, and MoO–active carbon showed 100% conversion, while MoO_3–SiO_2 and MoO_3–MgO were almost completely inactive. Without a catalyst, the conversion was 2% at 450 °C. At 250 °C, only MoO_3–TiO_2(β) showed 100% conversion and the activities of the other catalysts including MoO_3–TiO_2(α) were <10%.

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[1] J. Barksdale, 'Titanium, its Occurrence, Chemistry and Technology,' 2nd edn., Ronald Press, New York, 1966, p. 78.