CHEMISTRY LETTERS, pp. 1069-1070, 1990.

Silver-promoted Cobalt Oxide Catalysts for Direct Decomposition of Nitrogen Monoxide

Hideaki HAMADA,* Yoshiaki KINTAICHI, Motoi SASAKI, and Takehiko ITO
National Chemical Laboratory for Industry, Higashi, Tsukuba, Ibaraki 305

Silver as a catalyst additive showed an excellent effect to improve the catalytic activity of cobalt oxide for the decomposition of nitrogen monoxide below 773 K. Reaction inhibition by oxygen was very much relieved by using Ag-Co oxide catalysts.

Direct decomposition of nitrogen monoxide is the most desirable method for the removal of NOx from exhaust streams. A lot of catalysts have been reported such as supported metals,1) metal oxides,1) Cu ion-exchanged zeolites,2) and perovskite oxides.3) In this paper, we report an excellent additive effect of silver on the catalytic activity of cobalt oxide, which has the highest activity among simple metal oxide catalysts.4)

The catalysts were prepared with precipitation method from metal nitrate and Na_2CO_3 solutions. The precipitate was washed, dried at 373 K and calcined in air at 673 K for 4 h. The deposition of Ag by precipitation on cobalt oxide prepared in advance was also attempted. The reactions were carried out with a fixed-bed flow reactor by feeding 2% NO (and 5% O_2) in He at a rate of 30 cm^3 min^{-1} over 1 g catalyst. The effluent gas was analyzed by gas chromatography using a Molecular Sieve 5A column. The catalytic activity was evaluated by NO conversion to N_2. For catalyst characterization, NO chemisorption measurements (at room temp , NO pressure : 6.7 kPa) using a constant volume adsorption system were made on catalysts pre-evacuated at 673 K. X-Ray diffraction analysis was also performed.

Table 1 shows that the activity of cobalt oxide is clearly enhanced below 773 K by adding Ag. It is interesting that the promoting effect was also recognized for Ag deposited on cobalt oxide. Surface area is not responsible for the activity increase because there is no change in the amount of NO chemisorbed (NO/Co = 0.64 for Co, 0.67 for Ag-Co). We think that the combination of Ag and Co is essential since the activity of Ag alone has not yet been confirmed. At higher temperatures catalyst deactivation occured.

Table 1. Results of NO decomposition

Catalyst Co-M oxide	Prepn. method	O_2 concn. /%	NO conv. to N_2/% at			
			673 K	773 K	873 K	973 K
Co	a)	0	4.7	9.3	17	36
		5		0.7	2.6	12
Ag-Co	a)	0	19	45	38	47
(1/20)		5		18	25	20
Ag/Co	b)	0	17	42	30	24
(1/20)		5	0.55	18	17	

a) Precipitation or co-precipitation.

b) Deposition of Ag by precipitation.

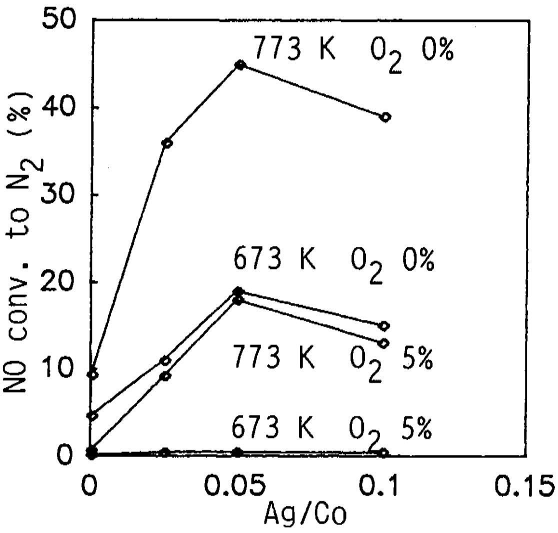

Fig. 1. Effect of Ag amount.

The most prominent feature of the Ag-promoted cobalt oxide catalyst is that the reaction inhibition by oxygen is very much relieved. This can be seen by comparing the extent of the decrease in conversion for Co oxide with that for Ag-Co oxide in the presence of oxygen. Oxygen usually inhibits NO decomposition especially at lower temperatures. The effect of the amount of Ag on the activity of Ag-Co oxide catalyst is shown in Fig. 1. A small amount of Ag was sufficiently effective. Maximum activity was obtained at around Ag/Co = 1/20 (mole ratio).

X-Ray diffraction analysis of Ag-Co oxide (Ag/Co = 1/20) shows no diffraction peaks other than those of Co_3O_4, suggesting that Ag is highly dispersed. Therefore, the active species in this catalyst may be a complex oxide of Co and Ag. For deactivated Ag-Co oxide catalyst used at above 873 K, distinct diffraction peaks of Ag metal were detected. This agrees well with the fact that no more Ag effect was observed for the deactivated catalyst. At present we think that the favorable effect of silver is closely related to its weak affinity for oxygen.

References

1) J. W. Hightower and D. A. Leirsburg, "Catalytic Chemistry of Nitrogen Oxides," ed by R. L. Klimsch and J. G. Larson, Plenum Press, London (1975), p.63.
2) M. Iwamoto, H. Yahiro, Y. Mine, and S. Kagawa, Chem. Lett., 1989, 213.
3) Y. Teraoka, H. Fukuda, and S. Kagawa, Chem. Lett., 1990, 1.
4) G. K. Boreskov, Discuss. Faraday Soc., 41, 263 (1966).

(Received March 17, 1990)