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Superior performance of nano-Au supported over Co_3O_4 catalyst in direct N_2O decomposition

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Au nanoparticles supported over Co_3O_4 lead to a highly active and stable catalyst for N_2O decomposition even in the presence of excess oxygen and steam.

Nitrous oxide (N_2O) has been identified as a strong greenhouse effect gas with a global warming potential per molecule *ca.* 300 times that of carbon dioxide and as a contributor to the destruction of ozone in the stratosphere.[1,2] The emission of N_2O comes from both natural sources and human contributions, such as the production of adipic acid and nitric acid. The direct catalytic decomposition of N_2O into N_2 and O_2 is an attractive end-of-pipe solution to reduce N_2O emission, but few of the catalysts proposed in the literature show a good activity and stability for N_2O decomposition in the presence of excess oxygen and steam.[2,3] Gold was recognized as a poor catalyst,[4] however, when Au nanoparticles are highly dispersed on some metal oxides and hydroxides such as TiO_2, α-Fe_2O_3, Co_3O_4, NiO and $Mg(OH)_2$, they exhibited activity for CO oxidation even at a temperature as low as −70 °C.[5,6] Such unusually high activity of gold strongly interacting with the support has later been confirmed by many research groups.[7–10] Kalback and Sliepcevich studied N_2O decomposition over an Au catalyst above 720 K in the absence of oxygen and steam.[11] In this study, nanoparticles of Au supported on Co_3O_4 catalysts were shown to be very active and stable in direct N_2O decomposition even in the presence of excess oxygen and steam.

The catalysts were prepared by a co-precipitation method. Adding dropwise an aqueous solution of Na_2CO_3 (10 wt%) to an mixed aqueous solution containing desired amounts of cobalt nitrate and $HAuCl_4{\cdot}4H_2O$ at 60 °C until the pH of the solution reached 8, and stirring for 3 h, led to the resultant precipitate which was washed until there were no chloride ions in the filtrate. The catalyst was then dried at 80 °C overnight followed by calcination at 550 °C in air for 5 h. The samples were characterized by XPS, XRD, TEM, AAS and N_2 adsorption/desorption. The catalytic reaction was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of N_2O (1200 ppm), O_2 (10 v/v%) and H_2O (5 v/v%) in a He flow at a total flow rate 100 ml min^{-1} over 300 mg catalyst (total pressure: 1 atm; space velocity: 20 000 h^{-1}). The products were monitored by two on-line gas chromatographs (PE autosystem XL) equipped with Molecular sieve 5A and Porapak Q columns, respectively.

The characterization results of the different catalysts and the conversion of N_2O to N_2 over different Au loading catalysts at 250 °C are shown in Table 1. These showed that the Au particle size increased with an increase of Au loading and the BET surface area was slightly decreased. The catalytic activity of N_2O decomposition reaches the highest level at a loading of 1.1 wt% Au, then decreases to constant level with increasing of Au loading. The reason for the decrease of the activity with increasing of the Au loading was that the gold nanoparticles were sintered to larger particles at higher loadings, as verified by the characterization results of TEM. The differences in activity of the different Au loading samples can be related to the Au particle size. A comparison of the Au particle size and TOF suggested a correlation (Table 1): the TOF increases with decreasing average Au particle size, 1–5 nm Au particles show much higher activity than larger particles. Compared to the results of Fe-ZSM-5 catalyst at similar reaction conditions,[9] the TOF of Au/Co_3O_4 at low Au loading is higher, which indicates that such catalysts were more active than Fe-ZSM-5 for the direct N_2O decomposition reaction.[12] Fig. 1 shows N_2O conversions in different reaction systems (over Co_3O_4 and 1.1 wt% Au/Co_3O_4 catalysts), respectively. Pure Co_3O_4 was active for the N_2O decomposition at 250–400 °C, which is consistent with results of the literature,[13] however, the presence of excess O_2 and steam severely inhibited the reaction, and the N_2O conversion curve shifted to higher temperature. The presence of Au nanoparticles significantly promoted the catalytic activity and stability, causing the N_2O conversion curve to shift 100 °C to lower temperature, which indicated that gold strongly interacted with the Co_3O_4 support to form active gold species. The active gold species are highly dispersed on cobalt oxide to lead to the enhanced activity. Addition of O_2 to the feed gases scarcely affected the activity of 1.1 wt% Au/Co_3O_4. Apparently, molecular oxygen does not dissociate over 1.1 wt% Au/Co_3O_4 and does not compete with N_2O for active sites. Water inhibited the reaction mainly at low temperatures. An H_2O-TPD study

Table 1 Data of the used catalysts

Catalyst	Au (wt%)	BET area/ $m^2\ g^{-1}$	d^a/nm	$10^{-4}TOF^b$/ s^{-1}	Conv. of N_2O (%)
Co_3O_4	0	24.0	—	—	6.2
Au/Co_3O_4	0.53	23.5	1–4	75.6	67.8
Au/Co_3O_4	1.10	23.6	3–6	50.7	84.3
Au/Co_3O_4	2.02	21.4	5–15	22.6	74.6
Au/Co_3O_4	3.18	21.1	9–20	14.3	75.1
Au/Co_3O_4	3.69	20.2	13–35	12.5	75.8
FeZSM-5[c]	0.64	—	1–2	48.6	—

[a] Au particle size distribution determined by TEM. [b] Mol of N_2O converted (mol Au)$^{-1}$ s^{-1}, determined at 250 °C; feed composition: 1200 ppm N_2O in He, 1 atm, GHSV = 20 000 h^{-1} [c] Cited from reference 12.

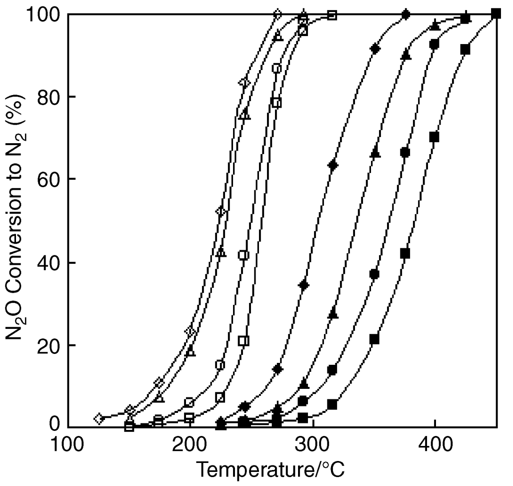

Fig. 1 N_2O conversion to N_2 in different feed compositions: (◇,◆) 1200 ppm N_2O, (△,▲) 1200 ppm N_2O + 10% O_2, (○, ●) 1200 ppm N_2O + 5% H_2O (□, ■) 1200 ppm N_2O + 10% O_2 + 5% H_2O over 1.1 wt% Au/Co_3O_4 and Co_3O_4 catalysts, respectively.

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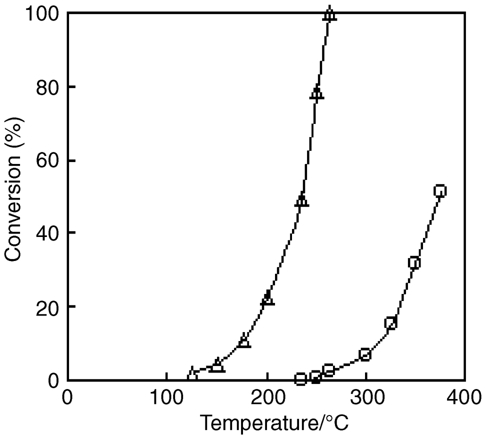

Fig. 2 Conversion of N_2O and CH_4 at different temperature over 1.1 wt% Au/Co_3O_4 catalyst: (△) N_2O, (○) CH_4. *Reaction conditions*: 1200 ppm N_2O, 300 ppm CH_4, He as balance gas.

Table 2 T_{50} and T_{90} of the N_2O decomposition and apparent activation energies for various reaction systems

Catalyst	Composition of feed gas	T_{50}/°C	T_{90}/°C	Apparent activation energy/ kJmol^{-1}
1.1 wt% Au/Co_3O_4	N_2O	223	265	48
	$N_2O + O_2$	229	270	51
	$N_2O + H_2O$	254	281	65
	$N_2O + O_2 + H_2O$	263	287	73
Co_3O_4	N_2O	307	348	69
	$N_2O + O_2$	341	373	82
	$N_2O + H_2O$	368	397	87
	$N_2O + O_2 + H_2O$	387	425	94
1.1 wt% Au/Co_3O_4	$N_2O + CH_4$	225	263	46
	$N_2O + CH_4$[a]	375	—	—

[a] CH_4 conversion to CO_2. Reaction conditions as described in Fig. 1 and Fig. 2.

revealed there are desorption peaks of H_2O at 210 and 430 °C. This suggested that the water was adsorbed on the active sites at low temperature so suppressing the decomposition of N_2O. As the temperature increased, water was desorbed from the surface, and the activity for the N_2O decomposition was recoved. Moreover, 1.1 wt% Au/Co_3O_4 catalyst was highly stable in the presence of excess oxygen and steam, which was confirmed by the fact that the catalytic activity of N_2O decomposition scarcely varied in the presence of excess O_2 and water vapor after reaction for 40 h.

The presence of reductant can significantly lower the conversion temperature of N_2O over many catalysts.[14–17] In this study, we also studied the selective catalytic reduction (SCR) of N_2O with CH_4 as reducant over 1.1 wt% Au/Co_3O_4 catalyst. Addition of 300 ppm CH_4 to the feed gases scarcely affected the conversion of N_2O as shown in Fig. 2, when N_2O has completely converted to N_2 and O_2, CH_4 was scarcely consumed and started to be converted to CO_2 and H_2O only above 300 °C. This showed that the N_2O decomposition mechanism over Au/Co_3O_4 catalyst might be different from that over Fe-ZSM-5 which can form a special oxygen species (α-O) intermediate by N_2O decomposition to oxidize methane at lower temperature.[18] Table 2 shows the temperture at 50 and 90% N_2O conversion and apparent activation energies of N_2O decomposition for various reaction systems over 1.1 wt% Au/Co_3O_4 and Co_3O_4 catalysts, respectively. The apparent activation energies of N_2O decomposition scarcely depended on the presence of O_2 and CH_4 for the 1.1 wt% Au/Co_3O_4 catalyst. Compared to the apparent activation energies for different reaction systems the 1.1 wt% Au/Co_3O_4 catalyst is more active and stable than Co_3O_4.

The present results have demonstrated that the catalytic decomposition of N_2O in the presence of excess O_2 and steam occurs effectively over the nano-Au/Co_3O_4 catalyst. We are currently undertaking further investigations in our laboratory with respect to the detailed mechanism, the effect of coexistent gases (SO_2, NO, *etc*) and the characterization of active sites.

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