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Spontaneous Nitridation of Ultrafine Particles of Ni during NO/CO Reaction

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Ultrafine particles of Ni (UFP Ni) are highly active in the catalytic reduction of NO by CO, showing a complete conversion of NO to N_2 at 573 K even for a large space velocity of 1.2×10^8 h^{-1}, but is subject to severe deactivation. Nitridation of UFP Ni, which occurred spontaneously during the cyclic operation of the reaction with deactivation followed by reactivation with CO reduction, remarkably suppresses the tendency toward deactivation.

While some combinations of precious metals are effectively used in catalytic de-NO_x systems for automobiles,1-5) their replacement by base metals is quite desirable from the viewpoint of resources conservation and economics.6-8) In an attempt to study the catalysis of UFP Ni, we observed novel phenomena which will hopefully lead to the development of an excellent catalytic system.

UFP Ni, prepared by the gas evaporation method9) and supplied by ULVAC Co., was used. The reactor was a U-tube made of glass (I.D. 8 mm), equipped with a temperature-control system working between room temperature and 773 K, and with a liquid nitrogen bath used for *in situ* BET surface area measurement. A stream of He containing 1000 ppm of NO and 5000 ppm of CO was supplied to the reactor tube. The effluent gas stream from the reactor flowed through a gas sampler attached to a gas chromatograph which could analyze NO, CO, N_2O, N_2, CO_2, and O_2. A temperature-programed reduction (TPR) analysis was carried out by using this flow type-reactor system with the gas chromatograph. The gas stream was exchanged to a line connected directly to a thermal conductivity detector when surface area analysis by nitrogen adsorption at its boiling temperature was performed.

In advance of a catalytic reaction run, a measured quantity of UFP Ni was reduced in the reactor tube by a stream of H_2 at 473 K. During the reduction process, the surface area decreased from the original value of 40 m^2/g due to thermal sintering, but became constant at 20 m^2/g. It should be noted that no distinguishable changes of surface area took place except for this initial decrease.

Figure 1 typifies the catalysis of UFP Ni in terms of fraction of NO converted against time elapsed. Curve (a) clearly shows the initial high activity and the rapid deactivation of UFP Ni. Even for a space velocity as large as 1.2×10^8 h^{-1}, the initial conversion of NO at 573 K amounts to 100%. In Fig. 1, the remarkable effects of the reducing species, H_2 or CO, on the catalysis of UFP

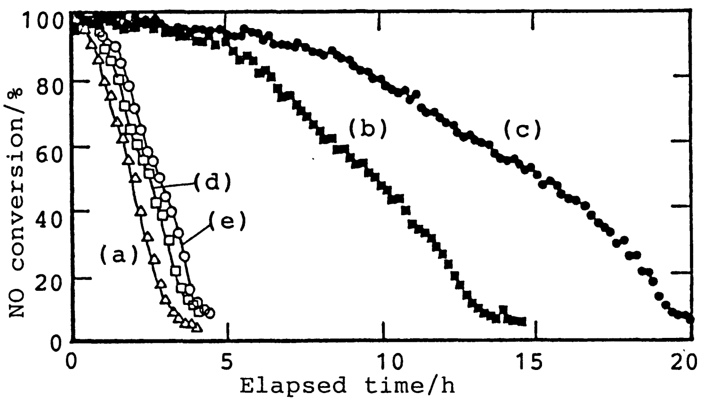

Fig. 1.
Time dependence of catalytic activities of UFP Ni.

T=423 K; [NO]=1000 ppm; [CO]=5000 ppm; SV=5×10^5 h^{-1}.

Pretreatment for respective runs was:
a) H_2 reduction only
b) reduction by CO at 473 K after run (a)
c) reduction by CO at 473 K after run (b)
d) reduction by H_2 at 423 K after run (a)
e) reduction by H_2 at 423 K after run (d)

Ni after reduction are noticed. When the deactivated catalyst is reduced by H_2 at 423 K it recovers the original performance, characterized by high activity and a strong tendency toward deactivation. On the other hand, reduction by CO at 473 K, as demonstrated by curves (b) and (c), results in considerable improvement in catalytic life in addition to recovery of the initial activity.

Attempts were made to elucidate the mechanism underlying these kinetic results, by means of TPR and X-ray diffraction (XRD). The results are summarized in Table 1. The TPR analysis was started by cooling the catalysts in the reactor to room temperature, flowing a stream of He containing a reducing gas (5000 ppm CO or 10 000 ppm H_2), and raising the temperature. The composition of the effluent gas was determined gas-chromatographically. Since the analysis of a sampled gas took 12 min, the heating rate in TPR was kept a low value of 0.33 K/min. A good resolution of the TPR spectrum achieved by this slow heating rate allowed the quantitative analysis of the composition of the deactivated catalysts. Figure 2 shows the results.

When CO was used as a reducing gas, CO_2 and N_2 were evolved from the deactivated catalysts. CO_2 evolution occurred at around 473 K and became more extensive at temperatures higher than 530 K. The molar ratios of consumption of CO to evolution of CO_2 at the lower and the higher temperatures were 1 and 2, respectively. Hence the CO_2 evolution at around 473 K is attributed to the reduction of the oxide ($CO+O=CO_2$), and that at higher temperatures to the Boudart reaction ($2CO=CO_2+C$). Formation of nickel nitride is evidenced by evolution of N_2 at around 593 K. N content of the UFP Ni increased remarkably during the repetition of deactivation and activation cycles, from 8.5% (b, cycle 1) to 16.2% (d, cycle 3). An XRD analysis showed that the nitride formed after the first deactivation is Ni_4N and that formed after the third deactivation is Ni_3N. The fraction of Ni_4N and Ni_3N to total Ni of each catalyst amounts to 42.0% and 68.5%, respectively. These results demonstrate that both Ni oxide and Ni nitride are formed during the CO/NO reaction, and that the reaction with CO at 473 K reduces the oxide without decomposing the nitride.

When H_2 was used in the TPR study, it was consumed at around 403 K but N_2 was not evolved in the same temperature range as in the TPR by CO. While no direct determination of the products corresponding to consumption of H_2 was attempted, it is estimated that the oxide and nitride in the deactivated catalysts were reduced by H_2 at 403 K to yield H_2O and NH_3 which could not be determined by the present gas chromatography. This estimation is confirmed by the fact that their catalysis is essentially identical with that of the original UFP Ni, as shown in Fig. 1 (d) and (e).

It is concluded that the cause of deactivation is formation of the Ni oxide during the reaction, and that the growth of nitrides is responsible for the improved durability in the case of CO reduction.

Another feature characteristic of the TPR spectrum by CO reduction is that the evolution of CO_2 begins at a lower temperature for the deactivated catalyst containing Ni_3N than for the catalyst containing Ni_4N, as shown by a comparison of curves (a) and (b) in Fig. 2. This may suggest an important role of the nitridation of Ni in lowering the binding force of oxygen to the surface. The weakened affinity of oxygen for the surface may be responsible for the improved durability of catalyst containing Ni_3N because surface reduction with CO in the catalytic redox cycle is facilitated.

In summary, in the catalytic reduction of NO with CO over UFP Ni it was found that 1) UFP Ni shows quite a high initial activity; 2) rapid deactivation takes place, associated with formation of oxide and nitride in the Ni; 3) the deactivation is caused by the oxidation of Ni; 4) the nitridation proceeds to

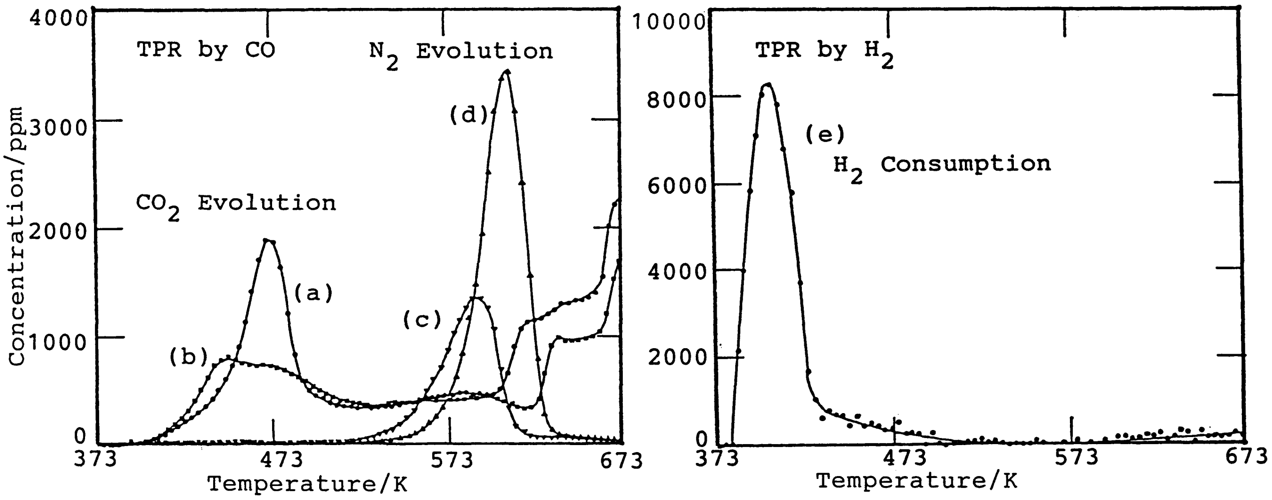

Fig. 2.

Temperature-programed reduction of deactivated catalysts. Desorption/consumption rate of each species is expressed as its concentration of effluent gas. UFP Ni 0.1 g; Flow rate=10 ml/min; heating rate=0.33 K/min.

TPR by CO as reducing gas:

a) CO_2 evolution from the catalyst after one deactivation

b) CO_2 evolution from the catalyst after three deactivation/CO reduction cycles

c) N_2 desorption from the catalyst after one deactivation

d) N_2 desorption from the catalyst after three deactivation/CO reduction cycles

TPR by H_2 as reducing gas:

e) H_2 consumption by the catalyst after one deactivation

Table 1. Characterization of deactivated UFP Ni catalyst

	Catalyst after one deactivation	Catalyst after three deactivation/CO reduction cycles
Temperature corresponding to peak maximum of TPR profiles (CO as reducing gas)	593 K (N_2)$^{a)}$	608 K (N_2)$^{a)}$
	473 K (CO_2)$^{b)}$	443 K (CO_2)$^{b)}$ (473 K: satellite)
	>623 K (CO_2)$^{c)}$	>623 K (CO_2)$^{c)}$
Phases determined by XRD	Ni, Ni_4N	Ni, Ni_3N
Compositions calculated from TPR evolution amounts	Ni 45.1% Ni_4N 42.0% NiO 12.9%	Ni 13.5% Ni_3N 68.5% NiO 18.0%

a) Assigned to Ni nitride decomposition.
b) Assigned to Ni oxide reduction.
c) Assigned to Boudart reaction ($2CO=CO_2+C$).

yield bulk Ni_3N by the repetitive operations of reaction with deactivation and reactivation with CO reduction; and 5) the catalyst containing Ni_3N is also deactivated, but much more slowly than the virgin UFP Ni. The improved durability of catalyst containing Ni_3N is tentatively understood in terms of the weakened affinity of oxygen for the surface, as indicated by a TPR analysis. Whether or not the present results observed for ultrafine particles represent characteristics common to all forms of Ni catalysts should be studied.

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