Catalytic Oxidation of CO on Ni–Y

Zeolite-Y ion-exchanged with transition metal ions has been extensively studied as oxidation catalysts (1–5). In general, the oxidation activity is enhanced by the presence of transition metal ions. The degree of enhancement depends on the nature of the metal ion, the nature of reaction, the oxidation state of the metal ion, and the method of preparation of the catalyst. The latter is true when the catalytic activity is believed to be due to clusters of metal ions instead of isolated ions (6–9). The distribution of metal ions in sites inside the hexagonal prism, the sodalite cage, and the supercage (10) is another interesting aspect. That some of the ions are located in sites inaccessible to the reactants can mask the true activity of the ions.

Among the first-row transition metal ions, Ni–Y is among the least active catalysts for oxidation reactions. However, NiO is rather active. This could be due to the fact that either most of the Ni ions in the zeolite are at the inaccessible sites, or isolated Ni ions are inactive. It has been suggested that CO chemisorption detects Ni ions in the supercage (11, 12). It should then be possible to determine the oxidation activity of isolated Ni ions by performing CO chemisorption and kinetic measurements on the same catalyst. We report here the results of such measurements for CO oxidation.

Ion exchange of Ni onto washed powder Na–Y (Linde) was accomplished by slow addition of dilute $Ni(NO_3)_3$ solution into an aqueous suspension of zeolite. After washing, the catalyst was dried at 70°C and stored. The degrees of exchange of the four batches of catalysts used were between 55 and 64%. Analysis of Ni and Na in the exchange solution indicated stoichiometric exchange to within 5%. Before use, the catalyst was activated by heating in vacuo (10^{-4} Pa) for at least 36 h at 370°C that was reached by slowly increasing the temperature.

CO oxidation was carried out at 200 or 225°C in a differential reactor using a feed with a O_2/CO ratio of 4. CO, supplied as 5% CO in He, was purified by first passing through a glass tubing at about 300°C and then a silica gel trap at -196°C. O_2 was purified by molecular sieve 13X at -78°C. When a freshly prepared Ni–Y was exposed to the reactants, the rate of production of CO_2 typically declined with time as shown in Fig. 1a. The decline was rapid initially and did not cease even after 3 h of reaction. If the deactivated catalyst was evacuated to 10^{-4} Pa at 370°C for over 10 h, about 75% of the initial activity of the fresh catalyst was restored. The activity of this regenerated catalyst also declined in a similar manner (Fig. 1b). Unlike that of a fresh catalyst, the lost activity of a regenerated catalyst was recovered to within a few percent by evacuation at 370°C.

When a fresh, a regenerated, or a deactivated catalyst was studied with CO chemisorption at 0°C after evacuating the reactor, it was found that within experimental error, the shape of the adsorption isotherm and the amount chemisorbed were the same independent of the state of the catalyst, the evacuation time, and the evacuation temperature (reaction temperature or 370°C). The isotherms were similar to those reported (12), and the chemisorption capacity of our Ni–Y was about 9×10^{-5} gmole CO/g zeolite. Zeolite-Y containing no Ni ion did not chemisorb CO.

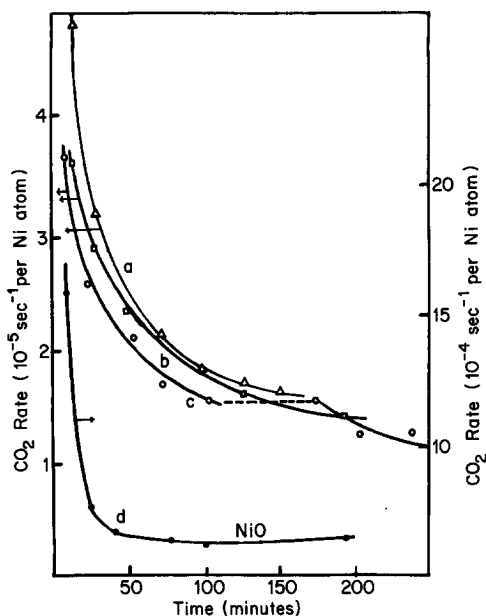For comparison, NiO powder was also found to deactivate in CO oxidation. A typ-

FIG. 1. Typical CO oxidation activity of Ni–Y and NiO. Reaction conditions: 200°C, flow rate about 70 ml m^{-1}, 0.79 g of Ni–Y, and 0.0042 g of NiO. Curves a and b are for a fresh and a regenerated Ni–Y catalyst, respectively. Curve c is for a regenerated Ni–Y catalyst. The reaction was interrupted by evacuation at reaction temperature (broken line). Curve d is for NiO.

ical activity profile is shown in Fig. 1d. The initial decline in activity was much more rapid than that for Ni–Y, but a steady state was reached. Regeneration by evacuation at 370°C resulted in a more active catalyst. The activity of the regenerated catalyst also declined with time, but reached a higher stable value as was previously reported (13). Such increase in activity on regeneration continued through the third cycle. An attempt to measure CO chemisorption on NiO at 0°C was unsuccessful as no detectable adsorption (<0.5 × 10^{-5} mole of CO/g NiO) was found for the fresh or deactivated catalyst.

These results clearly demonstrated that the CO chemisorption capacity has no relationship to the oxidation activity of Ni–Y. This may be due to the possibility that both catalytically active and inactive Ni ions adsorb CO. While this cannot be excluded conclusively, it is unlikely that the two types of Ni ions adsorb CO with the same stoichiometry and strength such that the same isotherm was observed. A more likely explanation is that while CO chemisorption is due to accessible isolated Ni ions, the catalytic activity is due to some other sites which are present in a relatively small concentration, and which may or may not adsorb CO. These active sites can well be small clusters of Ni ions bonded to each other through oxygen or hydroxyl linkages (7, 14), or small crystallites of NiO. Small Ni ion clusters were reported to be much more active than isolated Ni ions (14). Our observation also suggested that NiO is more active on a per mole of Ni basis. Thus, although results of our chemical analyses suggested that the ion exchange of Na and Ni ions was stoichiometric to within 5%, and the pH of the exchange solution (5) made it unlikely that significant exchange was due to protons, there could be enough Ni ion clustering to account for the activity. This is consistent with the variation up to a factor of 2 in activity among different batches of our catalyst.

The observed deactivation has been established to be an intrinsic property of the reaction. The decrease in CO_2 production was not due to physical transient of the reactor because, as shown in Fig. 1c, deactivation continued even if the reaction was interrupted by evacuation at reaction temperature. The different deactivation kinetics between Ni–Y and NiO also supported this. Pretreating the Ni–Y catalyst with pure O_2 up to 370°C, with pure CO_2, with pure CO, or with a mixture of CO_2 and O_2 at reaction temperature for a few hours did not result in a deactivated catalyst. These excluded the possibility that deactivation was due to impurities in the feed stream, formation or growth of NiO crystallites, product inhibition, or migration of Ni ions into inaccessible sites. That simple evacuation regenerated the catalyst also excluded coking.

That deactivation was only observed in the presence of the reactant mixture sug-

gests that it is probably due to the formation of an intermediate via a competitive pathway that desorbs very slowly and effectively blocks the active site. The fact that the deactivation rate was much decreased at 0°C when the reaction rate was also much reduced supports this. However, the nature of this deactivating species is unknown except that it is some carbon–oxygen complexes. An attempt to obtain its stoichiometry by analyzing the gas composition during regeneration was complicated by desorption from the zeolite. This carbon–oxygen complex is decomposed on evacuation at elevated temperature. The decomposition is an activated process. By measuring the extent of recovery of lost activity as a function of evacuation time and temperature (over the range 320 to 380°C), and by assumption of a first-order process for regeneration, an activation energy of 76 kJ/mole was obtained which is perhaps the activation energy for the decomposition of the complex.

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