Reaction of Silver(I) Oxide with Nitrogen Monoxide

By **Shuichi Kagawa,* Hiroshi Furukawa, and Masakazu Iwamoto,** Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

The reaction of Ag_2O with NO has been studied in the range 333—473 K with flow and batch reactors. The reaction products are $Ag[NO_2]$, $Ag[NO_3]$, Ag, and NO_2. A change in the products with reaction times reveals that $[AgNO_2]$ is the primary product by reaction (i), $Ag_2O + NO \longrightarrow Ag[NO_2] + Ag$, and then decomposes to $Ag[NO_3]$ with the evolution of NO by reaction (ii), $2\,Ag[NO_2] \longrightarrow Ag[NO_3] + Ag + NO$. When $Ag[NO_2]$ is a starting material, reaction (iii), $Ag[NO_2] \longrightarrow Ag + NO_2$, occurs together with (ii). Reaction (i) occurs mainly at $\leqslant 353$ K and the reaction order with respect to [NO] is close to unity. Reactions (ii) and (iii) proceed at $\geqslant 353$ K and are inhibited by NO. At $\geqslant 453$ K in the flow system, $Ag[NO_3]$ reacts further with NO through (iv), $Ag[NO_3] + NO \longrightarrow Ag + 2NO_2$. In the static system, on the other hand, (iv) does not proceed. This difference is suggested to result from NO_2 inhibition of reaction (iv).

ALTHOUGH the catalytic decomposition of nitrogen-monoxide (NO) over noble metals or metal oxides has been studied by many workers,[1-3] little attention has been given to the reaction of the metal oxide itself with NO. To clarify and establish this reaction may be significant for the understanding of the decomposition of NO over metal oxides and would shed some light on the use of metal oxides as absorbents or adsorbents for NO. Among metal oxides, silver(I) oxide (Ag_2O) is specific in the reaction with NO to form the nitrate or nitrite, while many other oxides more or less promote the decomposition of NO. Oza[4] was the first to examine this reaction. The results, however, were insufficient in terms of the range of reaction temperatures, the conversion of Ag_2O, and especially the reaction mechanism. For example, he suggested that nitrate is the primary product and that nitrite is produced by the subsequent reaction of $Ag[NO_3]$ with NO, since both the amount of NO_2 and the proportion of nitrite to nitrate increased with reaction time. In contrast with this suggestion, the quantity of nitrate calculated from Table 2 in ref. 4 is not a monotonic function of the reaction time in spite of the constancy of the other experimental conditions and increases irregularly with time. What was judged as an increase in the proportion of nitrite to nitrate, might therefore, be an error in the measurements. The reaction mechanism is worth studying in more detail. In the present paper the reaction of Ag_2O with NO was investigated in the range 333—473 K.

EXPERIMENTAL

Materials.—Silver(I) oxide was precipitated from silver nitrate solution with sodium hydroxide, washed with water, and dried at 353 K for 76 h. Granules of 42—80 mesh were used for the reaction with NO. The salts $Ag[NO_2]$ and $Ag[NO_3]$ were commercial materials of guaranteed grade. Commercial He gas (>99.995%) and NO gas (>99% purity) were used as a diluant and a reactant, respectively. Nitrogen monoxide was purified before use in the following manner. The gas was first frozen at 77 K and pumped on. Less volatile components were removed by warming to the temperature of solid CO_2, and rejecting the residue. This fractionation was repeated five times.

Reaction Procedures.—Reaction of Ag_2O with NO was carried out in two ways, using flow and static systems.

Flow system. The reaction was performed in a flow reactor with a fixed bed at atmospheric pressure. The reactor, a Pyrex tube of 8-mm internal diameter and 200-mm length, was mounted vertically in an electric furnace. The temperature of the reactor was regulated within ± 1 K using an electronic temperature controller. About 1 g of sample was loaded into the reactor, purged with helium at room temperature, and then heated to the fixed temperature. A mixture of 4 vol. % NO and 96 vol. % He was diverted to flow through the reactor at a constant flow rate of 36 $cm^3\ min^{-1}$, unless otherwise stated. After the prescribed time of reaction the solid sample was cooled to room temperature in a helium atmosphere for 10 min and analyzed by the method described later. The effluent gas was determined at intervals during the reaction by gas chromatography using Porapak Q for N_2O and molecular sieve 5Å for O_2, N_2, and NO. Nitrogen dioxide was detected in the present work, but its amount could not be accurately measured as reported by Stricker and Meinel.[5]

Static system. Aliquots of the samples were allowed to react in a batch reactor. The uptake of NO could be followed exactly as a function of time by measuring the pressure decrease using a mercury manometer. The apparatus was the same as that used in volumetric measurements of adsorption.[6] About 1 g of sample was loaded into the reactor, degassed at a reaction temperature for 30 min, and exposed to a NO atmosphere of a fixed pressure for the prescribed time. The sample was then evacuated for 10 min and quenched to room temperature *in vacuo*.

Analyses of the Solid Phase.—The solid reaction products were identified by *X*-ray powder diffraction and their composition was determined by conventional chemical analyses. The former was carried out on a Rigaku Geigerflex 2034 using nickel-monochromatized Cu-K_α radiation. By comparison with ref. 7, the diffraction patterns were assigned to Ag_2O, $Ag[NO_2]$, $Ag[NO_3]$, and Ag. In the last case the solid residue was shaken in water (250 cm^3) for 24 h. Thereafter, the amounts of Ag^+ and $[NO_2]^-$ were measured by Mohr's method and iodimetry, respectively, and the quantity of $[NO_3]^-$ was calculated from the difference between those of Ag^+ and $[NO_2]^-$.† The solubilities of $Ag[NO_3]$ and $Ag[NO_2]$ at 298 K are 70.7 and 0.414 g

---

† The amounts of $[NO_2]^-$ and $[NO_3]^-$ thus obtained were in fair agreement with those determined by the spectroscopic method of Bhatty and Townshend.[8] In the present work, the simpler volumetric method described in the text was adopted.

in 100 g of saturated aqueous solution, respectively.[9] Silver(I) oxide and Ag are only negligibly soluble.[9] It was confirmed that the amounts of nitrate and nitrite could be determined with a relative error of ±2% by these methods.

RESULTS AND DISCUSSION

Reaction of Ag_2O *with* NO *at Various Temperatures.*—Silver(I) oxide reacted with NO at $\geqslant 333$ K. The results in the flow system are shown in Figure 1(*a*). The degree of conversion of NO, which was defined by the ratio of the flow rate of NO at the outlet to that at the inlet, was relatively high at first but decreased gradually to <10% after a few hours. In the range of 353—423 K no product such as N_2, O_2, and N_2O and only a trace amount of NO_2 was detected in the exit gas. Clearly, a substantial amount of NO was sorbed by the Ag_2O. At 473 K the consumption of NO was accompanied simultaneously by the evolution of a significant amount of NO_2. The initial rate of NO consumed was in the order $473 > 423 \simeq 353 > 393$ K.

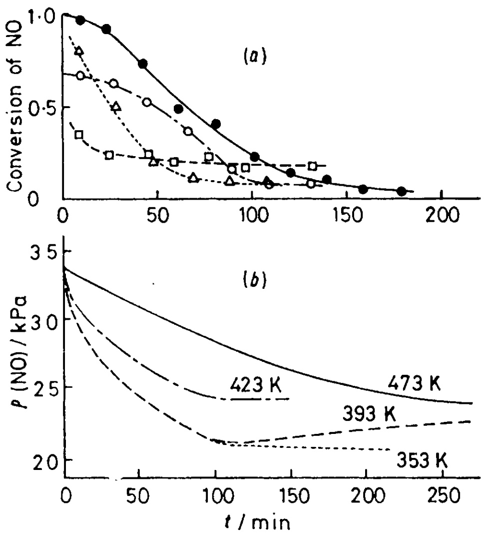


FIGURE 1 Reaction of Ag_2O with NO at 353 (△), 393 (□), 423 (○), and 473 K (●) in the flow (*a*) and static systems (*b*)

TABLE 1

Reaction of Ag_2O with NO

Run no.	Reaction conditions T/K	t/min	Amount of NO consumed (mol) [a]	Amount (mol) of product in solid phase [a] Ag[NO_2]	Ag[NO_3]	$\frac{Ag[NO_3]}{Ag[NO_2] + Ag[NO_3]}$
(*a*) Flow system [b]						
1	333	70		0.009	0.001	0.10
2	353	140		0.149	0.028	0.16
3	373	150		0.134	0.139	0.51
4	393	150		0.004	0.155	0.97
5	423	170		0.003	0.209	0.99
6 [b]	453	180		0	0.132	1.00
7	473	150		0	0.022	1.00
(*b*) Static system [c]						
8	353	210	0.316	0.316	0	0
9	373	310	0.350	0.308	0.042	0.06
10	393	293	0.268	0.053	0.215	0.80
11	423	150	0.233	0	0.235	1.00
12	443	150	0.215	0	0.215	1.00
13	473	160	0.176	0	0.196	1.00

[a] Expressed as moles per mol of $AgO_{0.5}$ loaded. [b] The partial pressure of NO in the feed gas was 4.00 kPa in these runs except for run 6 in which it was 20.3 kPa. [b] The initial pressure of NO was 33.3 kPa.

If the only process occurring was sorption of NO and no evolution of other gases occurred during the reaction, the reaction of Ag_2O with NO could be followed by measuring the pressure of NO as a function of time in the static system. Typical results are depicted in Figure 1(*b*). At 393 K the pressure of NO varied specifically with reaction time; the decrease in pressure stopped at 110 min and then the pressure increased. Furthermore, in contrast to the flow system, little NO_2 was detected at 353—473 K and the rate of consumption of NO was lower at the higher temperature. These facts suggest that the reaction mechanisms are complicated and depend on both the reaction temperature and the type of reactor.

The *X*-ray diffraction patterns of the solid products indicated the formation of Ag[NO_2], Ag[NO_3], and Ag through the reaction of Ag_2O with NO. The amounts of Ag[NO_2] and Ag[NO_3] produced as determined by the chemical analyses are summarized in Table 1. In the static system the total amount of Ag[NO_2] and Ag[NO_3] was in good agreement with the amount of NO consumed within experimental error, while in the flow system the last values were difficult to measure. The proportion of the amount of Ag[NO_3] to that of Ag[NO_3] + Ag[NO_2] increased from 0 to 1 with temperature in both systems. As shown in Figure 2, this proportion varied rapidly at 373—393 K. The scatter of values at 353—393 K is probably due to the dependence of the product distribution on the reaction time as mentioned later.

In Table 1, it is to be noted also that after reaction at 453 or 473 K in the flow system the amount of Ag[NO_3] produced was much lower and Ag[NO_2] was not observed. In these runs the solid phase was practically all Ag metal and a substantial amount of NO_2 was produced. It is clear that Ag_2O was decomposed or reduced to Ag by NO at these temperatures. In the static system, on the other hand, $Ag[NO_3]$ was stable even at 473 K. This phenomenon will be discussed again in a later section.

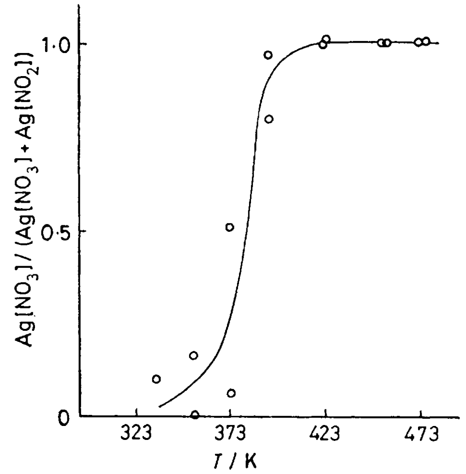


FIGURE 2 Effect of reaction temperature on product distribution

In conclusion, the reaction products from Ag_2O and NO altered remarkably with temperature, *i.e.* the main products at 333—373, 393—423, and 453—473 K were, respectively, $Ag[NO_2]$ + Ag, $Ag[NO_3]$ + Ag, and $Ag[NO_3]$ + Ag (static system) or only Ag (flow system).

The change of the solid product distribution with reaction time was studied with the static system at 393 K, since at this temperature the pressure of NO behaved specifically as shown in Figure 1(*b*). The results are depicted in Figure 3, where $P(NO)^i$ represents the initial pressure of NO. Silver nitrite was a main product in the early stages, but its amount decreased with time after reaching a maximum at 110 min. Whilst there was little $Ag[NO_3]$ produced at first, its amount increased sigmoidally to attain a constant value after 300 min. The amount of NO consumed, which was in fair agreement with that of $Ag[NO_2]$ + $Ag[NO_3]$, reached a maximum at 110 min and then decreased hand in hand with the decrease in $Ag[NO_2]$. The final amount of NO consumed was close to that of $Ag[NO_3]$ formed or half the initial Ag_2O. These results suggested that $Ag[NO_2]$ was produced at first by the reaction of Ag_2O with NO and then converted into $Ag[NO_3]$ accompanied by the evolution of NO as in equations (1) and (2). The

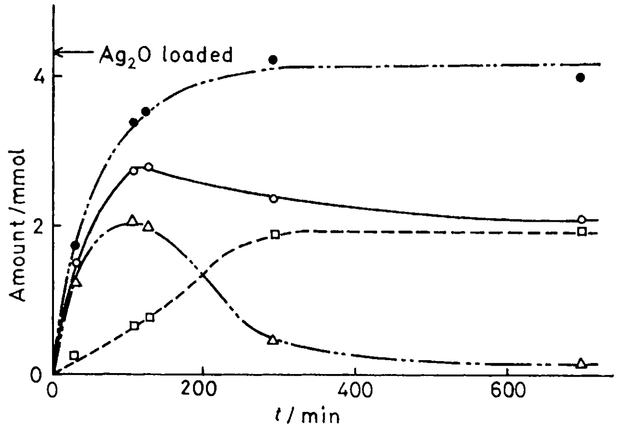


FIGURE 3 Reaction of Ag_2O with NO at 393 K and $P(NO)^i$ = 33.3 kPa in the static system. The values for Ag_2O (●) and NO (○) represent the consumed amounts, while those for $Ag[NO_2]$ (△) and $Ag[NO_3]$ (□) are the produced amounts

$$Ag_2O + NO \longrightarrow Ag[NO_2] + Ag \qquad (1)$$

$$2\,Ag[NO_2] \longrightarrow Ag[NO_3] + Ag + NO \qquad (2)$$

amounts of Ag_2O consumed, estimated on the basis of these equations, are depicted in Figure 3 by closed circles. After 300 min this amount was roughly in agreement with that of the initial Ag_2O loaded and there was no further reaction. The change in the proportion of $Ag[NO_3]$ in Figure 2 probably results from the fact that at <373 K reaction (1) mainly occurs and above this temperature (2) becomes possible.

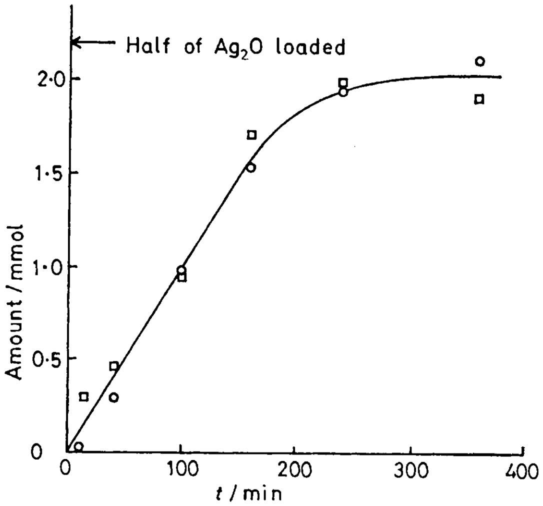


FIGURE 4 Reaction of Ag_2O with NO at 473 K and $P(NO)^i$ = 33.3 kPa in the static system. The values for $Ag(NO_3)$ (□) and NO (○) represent, respectively, the produced and consumed amounts

The effect of the pressure of NO on reaction (1) at 353 K in the static system is expressed by the equation, $r_0 = 7.50 \times 10^{-5} [P(NO)^i]^{1.1}$, where r_0 is the average rate of NO consumption in $cm^3\ min^{-1}$ up to 5% conversion of Ag_2O. The reaction order with respect to [NO] was close to unity, suggesting that adsorption of NO is the rate-determining step. The rate equation as a function of the conversion of Ag_2O, however, could not be determined because of the complexity of the reaction.

The change of the products with reaction time was also investigated at 473 K (Figure 4). Both the amounts of NO consumed and $Ag[NO_3]$ produced increased monotonically with time and then reached plateau values. In the gas phase there was no product except a trace amount of NO_2. In the solid phase only Ag_2O, $Ag[NO_3]$, and Ag were always observed.

Apparently, the amount of NO consumed was in fair agreement with that of Ag[NO_3] produced and the final quantity of the latter agreed approximately with half the Ag_2O loaded. These facts indicate a reaction stoicheiometry of $2\ Ag_2O + NO \longrightarrow Ag[NO_3] + 3\ Ag$, *i.e.* a combination of equations (1) and (2). Thus, reaction (1) is considered to be immediately followed by (2) at such high temperatures.

Reaction of Ag[NO_2] *under Various Pressures of* NO.—As mentioned above, the reactions of Ag_2O with NO proceeds *via* the path $Ag_2O \longrightarrow Ag[NO_2] \longrightarrow Ag[NO_3]$ ($\longrightarrow$ Ag). In order to investigate this path in more detail the reaction of Ag[NO_2] was studied under various pressures of NO. The results in the static system are summarized in Table 2, where P^f designates the final pressure of the gas phase which contained both NO and NO_2. The *X*-ray diffraction patterns of the solid residue showed the production of Ag[NO_3] and Ag, where the latter was the only product insoluble in water. Thus the contents of Ag[NO_2], Ag[NO_3], and Ag in the solid residue could be determined by chemical analyses.

TABLE 2

Thermal decomposition of Ag[NO_2] in the static system

Run no.	Reaction conditions T/K	 t/h	 $P(NO)^i$/kPa	 P^f/kPa	Content (mol) [a] after reaction Ag[NO_2]	 Ag[NO_3]	 Ag	Amount (mol) [a] of Ag[NO_2] consumed by reaction (2)	 (3)
14	393	6	0	3.15 [b]	0.521	0.170	0.310	0.340	0.140
15	393	6	6.27	8.13 [b]	0.670	0.085	0.216	0.170	0.131
16	393	6	13.7	14.3 [b]	0.843	0.029	0.128	0.058	0.099
17	393	6	31.5	31.5	0.998	0	0	0	0
18	453	3	0	12.4 [b]	0.210	0.276	0.547	0.552	0.271
19	453	3	32.5	40.8 [b]	0.366	0.249	0.430	0.498	0.181
20	453	3	0	0 [c]	0	0	1.000	0	1.00

[a] Expressed as moles per mol of Ag[NO_2] loaded. [b] Both NO and NO_2 gas were produced. [c] This experiment was performed under degassing.

The decomposition of Ag[NO_2] at 393 K became more difficult with increasing NO pressure. At 453 K, even at $P(NO)^i \neq 0$, the decomposition proceeded appreciably but the rate was considerably less than that at $P(NO)^i = 0$. When the batch reactor was degassed continuously Ag[NO_2] was almost completely converted into Ag within 3 h. Similar results were also obtained in the flow system.

If the decomposition of Ag[NO_2] proceeds *via* only reaction (2), the amounts of Ag[NO_3] and Ag produced in the static system should be equal, since Ag[NO_3] does not react further as shown in Figure 4. Nevertheless, in all the runs of Table 2 the amounts of Ag produced were much more than that of Ag[NO_3] produced. As described above, a substantial amount of NO_2 was detected together with NO in these runs. Since the decomposition of Ag[NO_2] is the only path for the creation of NO_2, it is concluded that the decomposition of Ag[NO_2] proceeds *via* two paths, *i.e.* reactions (2) and (3). The decomposition and the reaction with NO of

$$Ag[NO_2] \longrightarrow Ag + NO_2 \qquad (3)$$

Ag[NO_2] were reported previously by Oza *et al.*[10] who suggested such reactions as (3) and $Ag[NO_2] + NO \longrightarrow Ag[NO_3] + \frac{1}{2}N_2$, but in the present work the latter reaction was excluded because of the absence of N_2. The amounts of Ag[NO_2] consumed by reactions (2) and (3) are presented in the last column of Table 2, demonstrating that both these reactions are inhibited by NO. On the other hand, it was established that NO_2 does not affect the decomposition of Ag[NO_2].

One fact remains difficult to interpret, as elucidated by a comparison of Table 2 with Figure 4. As pointed out above, reactions (2) and (3) occur depending on the NO pressure. In contrast, in Figure 4 little NO_2 is formed and only reaction (2) proceeds. A possible explanation for this difference would be that the reactivity of Ag[NO_2] alone is distinct from that of Ag[NO_2] produced by the reaction of Ag_2O with NO.

Reaction of Ag[NO_3] *with* NO.—In order to clarify the difference between the product distributions in the static and flow systems after the reaction of Ag_2O with NO at higher temperatures, the reaction of Ag[NO_3] with NO was investigated. The results are summarized in Table 3. In the static system, neither decomposition nor reduction of Ag[NO_3] was observed at 473 K independently of the presence (run 24) or absence (run 25) of NO, in agreement with the results in Figure 4. In the flow system at $P(NO)^i = 0$ and 453 K, Ag[NO_3] also did not react. This would be expected since the decomposition temperature of Ag[NO_3] is 713 K.[11] On the other hand, in run 21, where Ag[NO_3] was exposed to a NO atmosphere in the flow system, Ag and NO_2 were formed. The fact that the gaseous product was NO_2 alone suggests reaction (4).

TABLE 3

Reaction of Ag[NO_3] with NO

Run no.	Reaction conditions T/K	 t/h	 $\frac{P(NO)^i}{kPa}$	 $\frac{P^f}{kPa}$	Content (mol) [a] after reaction Ag[NO_2]	 Ag[NO_3]	 Ag
(*a*) Flow system							
21	453	3	20.3		0	0.817	0.191
22	453	3	0		0	1.000	0
23	453	3	17.6 [b]		0	1.000	0
(*b*) Static system							
24	473	10	34.9	34.9 [c]	0	0.998	0
25	473	8	0	0	0	1.000	0

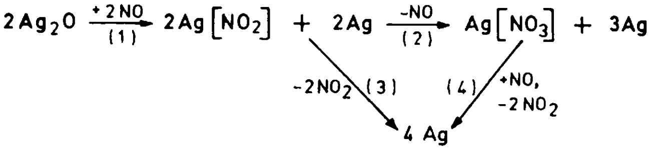
[a] Expressed as moles per mol of Ag[NO_3] loaded. [b] The feed gas consisted of 17.6 kPa NO and 2.67 kPa NO_2. [c] A trace amount of NO_2 was included after reaction.

We wondered why reaction (4) did not progress in the static system under a NO atmosphere as it did in the

$$Ag[NO_3] + NO \longrightarrow Ag + 2\ NO_2\ (\text{or } N_2O_4) \quad (4)$$

flow system. There was no possibility that NO hindered the reaction as in the decomposition of $Ag[NO_2]$. Thus the effect of NO_2 was tested in run 23. A small amount of NO_2 mixed in the feed gas obviously inhibited the reaction of $Ag[NO_3]$ and NO. Conclusively, in the case of the static system, a trace amount of NO_2 would be formed immediately after the start of the reaction, be adsorbed on to the $Ag[NO_3]$, and prevent the subsequent reaction. In the case of the flow system (run 21) the elimination of NO_2 from the sample surface would be achieved by the carrier gas and enable the reaction of $Ag[NO_3]$ and NO to proceed. This is the reason for the fact that in the reaction of Ag_2O with NO at higher temperatures the final products in the static or flow system are $Ag[NO_3]$ and Ag or Ag alone, respectively. A further discussion might lead to the mechanism that the NO + $Ag[NO_3]$ reaction proceeds by O-atom abstraction by NO giving NO_2, and leaving $Ag[NO_2]$ which then decomposes to Ag and NO_2. In this case, NO_2 might inhibit the earlier stage of the consecutive reaction.

Conclusions.—It has been shown that the reaction of Ag_2O with NO produces Ag and NO_2 as final products. The reaction paths, however, are relatively complicated and change remarkably with reaction conditions. The paths are summarized as follows. As a matter of course, reactions (1) and (4) require the presence of NO. Reaction (3) occurs only when $Ag[NO_2]$ is used as a starting material. The dependence of the rate of reaction (1) on the NO pressure in the early stages of reaction was approximately first order. In contrast, a higher pressure of NO hinders the progress of reactions (2) and (3).



Nitrogen dioxide inhibits reaction (4) but hardly affects (3). The above specific properties of Ag_2O may lead to its use as an absorbent or an oxidizing agent for NO.

[8/442 *Received*, 10*th March*, 1978]

REFERENCES

[1] E. R. S. Winter, *J. Catalysis*, 1971, **22**, 158.
[2] A. Amirnazmi, J. E. Benson, and M. Boudart, *J. Catalysis*, 1973, **30**, 55.
[3] J. W. Hightower and D. A. van Leirsburg, 'The Catalytic Chemistry of Nitrogen Oxides,' eds. R. L. Klimsch and J. G. Larson, Plenum, London, 1975, p. 63.
[4] T. M. Oza, *Indian J. Chem.*, 1965, **3**, 100.
[5] W. Stricker and H. Meinel, *Combustion and Flame*, 1977, **29**, 95.
[6] W. G. Frankenburg, *J. Amer. Chem. Soc.*, 1944, **66**, 1827.
[7] 'Powder Diffraction File,' Joint Committee on Powder Diffraction Standards, Pennsylvania, 1972, File no. 12-793 (Ag_2O), 6-0349 ($Ag[NO_2]$), 6-0363 ($Ag[NO_3]$), and 4-0783 (Ag).
[8] M. K. Bhatty and A. Townshend, *Analyt. Chim. Acta*, 1971, **56**, 55.
[9] W. F. Linke, 'Solubilities of Inorganic and Metal Organic Compounds,' 4th edn., ed. A. Seidell, van Nostrand, New York, 1958, vol. 1.
[10] T. M. Oza, V. T. Oza, and R. H. Thaker, *J. Chem. Soc.*, 1955, 2457.
[11] M. Windholz, 'The Merck Index,' 9th edn., Merck & Co. Inc., Rahway, N.J., U.S.A., 1976, p. 1101.