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The Oxidation of Ammonia

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I. INTRODUCTION: THERMOCHEMISTRY

The desired product of ammonia oxidation is NO according to the overall reaction

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 216.7 \text{ kcal/g mol heat evolved}$$

Depending on the selectivity of the reaction, a number of undesirable reactions also occur:

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O + 263.9 \text{ kcal/g mol evolved}$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O + 303.1 \text{ kcal/g mol evolved}$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O + 432.5 \text{ kcal/g mol evolved}$$

With a good catalytic reactor design, around 93–98% conversion of the feed ammonia to NO is possible. This high degree of selectivity can only be attained by minimizing the effects of loss-making reactions relative to the NO-forming reaction.

·MONIA OXIDATION BY OXYGEN

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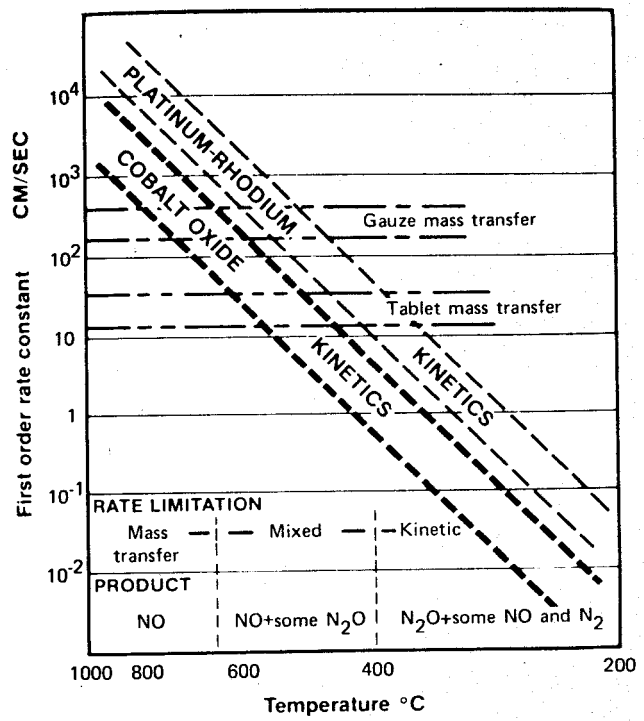

Fig. 1 Kinetic and mass transfer rates in NH_3 oxidation.

catalysts appear to be substantially less active (per unit surface area) than a metal such as platinum and are usually employed as high internal surface area tablets, whereas platinum is used as a fine wire gauze. This analysis indicates that the effect of catalyst poisoning is in essence the same for both precious metal and transition metal oxide catalysts. The result of poisoning is to reduce the activity of the catalyst by reducing its effective surface area. This reduction in surface area does not of itself alter the selectivity of the catalyst but, rather, because the ammonia partial pressure rises in contact with the surface, the selectivity falls as NH_3 reacts with NO to form N_2O or N_2. The commercial answer to this problem (apart from excluding poisons as much as possible) is to increase the temperature of the reaction, thereby increasing activity as much as possible.

B. Catalyst Temperature and Its Limitation

As was indicated above, a prudent choice of ammonia concentration in the mixed air-ammonia gas is given by:

II. HOMOGENEOUS AMMONIA OXIDATION BY OXYGEN

The uncontrolled homogeneous gas phase oxidation of ammonia is a relatively slow reaction with only a low selectivity toward NO. Data on this reaction are not detailed, but the lower inflammability limit of ammonia-air mixtures at 25°C appears to be about 15% in the pressure range 1–10 bar and diminishes as the initial temperature of the gas mixture increases. If C_{NH_3} is the mole fraction of NH_3 in the air-ammonia mixture having a temperature t_{mixed} (°C), then the lowe inflammable limit appears from the evidence to be given by $C_{NH_3} = 0.15 - 0.00011t_{mixed}$, suggesting that a burnt mixture temperature of around 1350°C is attained.

The mixing of ammonia and air is frequently far from perfect. It is therefore prudent to operate with an adequate safety margin below the lower inflammable limit, typically

$$C_{NH_3,\ design} \not> 0.13 - 0.00011t_{mixed}$$

III. THE HETEROGENEOUS AMMONIA OXIDATION

A. General Principles

A large number of transition metal oxides and transition metals cataly this reaction, and several have been employed industrially. Indeed there is a broad general similarity in their behaviors (Fig. 1). At low operation temperatures, selectivity of the oxidation reaction produces good yields of N_2O and N_2; at high temperatures good yields of NO are obtained, while at intermediate temperature a mixture of NO, N_2, and N_2O is produced. Correspondingly, at low temperatures the rate of conversion of ammonia is kinetically limited, relatively hig concentrations of NH_3, NO, and O_2 occurring in contact with the cata lyst. At high temperatures all catalysts have their ammonia oxidation rates limited by the velocity of diffusional access of ammonia to their surface through the "gas film."

The catalyst surface is subjected to only a very small partial pressure of ammonia and a reduced oxygen partial pressure. There is evidence that the heterogeneous catalyzed reaction between NH_3 and NO leading to the formation of N_2O or of N_2 is enhanced by the simultaneous presence of appreciable partial pressures of both NH_3 and NO Much of the improved selectivity of catalysts such as platinum, iron, and cobalt oxides toward NO at high temperatures thus appears to be a result of their operating far into the gas film diffusion-limited mode at high temperatures, with consequent reduced loss of the NO because of low NH_3 partial pressures in contact with the surface. The oxide

$$C_{NH_3} \not> 0.13 - 0.00011t_{mixed}$$

Now the oxidation of ammonia to form NO with about 95% selectivity results in a temperature rise of some 70°C per 1% ammonia oxidized in the absence of heat losses from the gas mixture. For a horizontal catalyst bed placed over an insulated tube plate, loss of heat is primarily by radiation to the inlet cone of the reactor; under these circumstances the final gas temperature leaving the catalyst bed is roughly

$$t_{cat} = \left(t_{mixed} + 7000C_{NH_3} - \frac{20,000}{G}\right) °C$$

where G is the superficial gas rate into the catalyst bed in N $m^3/hr\ m^2$ (where N refers to 1 bar absolute and 20°C).

Now, as the objective is to operate the catalyst in the gas film ammonia diffusion-limited regime, the convective heat transfer rate from the catalyst to the gas stream is also gas film limited. The catalyst temperature, to a first approximation, is therefore equal to the gas exit temperature from the bed *at all levels in the bed*, including the inlet, provided that the catalyst is adequately active. However, the nature of the catalyst often limits its permissible operating temperature. Cobalt oxide catalysts, for optimum activity, must operate in the Co_3O_4 form. Consideration of the equilibrium $Co_3O_4 \rightleftharpoons 3CoO + 1/2O_2$ over the catalyst suggests that

$$t_{cat} \not> 930 - 1000C_{NH_3}$$

(which gives roughly a 50°C safety margin to allow for fluctations in C_{NH_3}).

At high gas rates it will be seen (Fig. 2) that the Co_3O_4 decomposition limit is some 1.5% ammonia *below* that set by the practical homogeneous lower inflammability limit. In practice, Co_3O_4 catalysts are constrained to operate with C_{NH_3} not greater than 0.105.

The precious metal platinum-rhodium catalysts also suffer from an upper constraint on temperature, though this is less well defined and is associated with the economic consequences of too rapid a catalyst loss. As the rate of platinum loss rises very rapidly above 940°C, C_{NH_3} is, in effect, limited to not greater than 0.12 (Fig. 3).

C. Optimum Operation Conditions for Burners

Most industrial burners use 90% Pt–10% Rh gauzes constructed from a square mesh of 0.076-mm-diameter wire and having about 1000 apertures per square centimeter. Less frequently 95% Pt–5% Rh gauzes ar

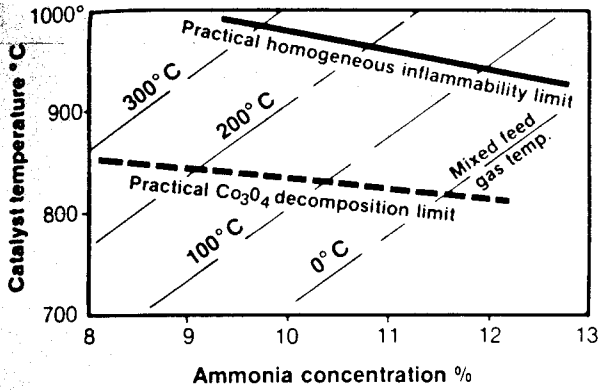

Fig. 2 Practical temperature and NH_3 content limitations for a Co_3O_4 ammonia oxidation catalyst.

employed, which are somewhat cheaper. In low-pressure plants with a low gas loading, 0.06-mm-diameter gauzes are often used. The precious metal catalysts are much less sensitive to poisons than the nonprecious metals, though, as was indicated above, the latter may, under very poison-free conditions, be arranged to give selectivities virtually identical to those of the precious metal catalysts. This section therefore considers primarily Pt–Rh gauzes, though qualitatively a very similar type of analysis can be applied to metal oxide catalysts

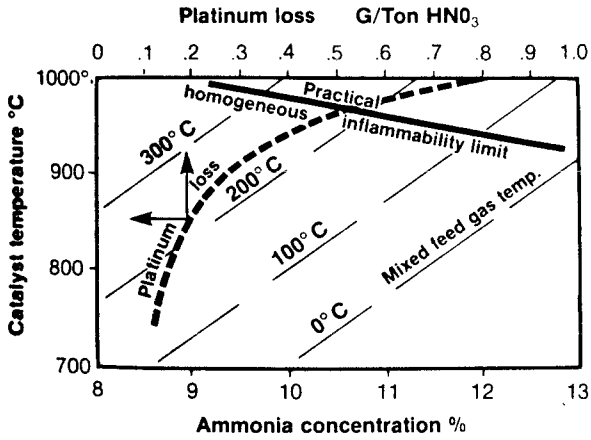

Fig. 3 Practical temperature and NH_3 content limitations for a platinum-rhodium ammonia oxidation catalyst.

and references are made to these were appropriate. The objective is to design and operate the oxidation reactors so as to maintain optimum selectivity for NO production.

It was indicated above that the first cause of lack of selectivity is conversion to N_2 and N_2O at the inlet to the reactor as a result of too low a catalyst activity relative to the gas film-limited mass transfer of NH_3. New gauzes suffer from this defect, which, however, disappears over a period of time as the wire surfaces roughen by recrystallization, thereby enhancing the catalytic activity.

New evidence (particularly on Co_3O_4 catalyst, as well as on Pt–Rh) suggests that the loss-forming N_2 and N_2O reactions are one order higher in the partial pressure of ammonia at the catalyst surface than the desired NO-forming reaction. Thus direct selectivity loss due to the initial reaction of ammonia is proportional to $(P_{NH_3cat}$, or the direct fractional loss of NH_3 reacted is $k_1P_{NH_3cat}$, where k_1 is the ratio of the rate constant for loss-making reactions divided by the rate constant for the NO production reaction.

Now the reaction rate of ammonia at the surface is proportional to $(P_{NH_3})_{cat}A$, where A is the activity of the catalyst. This rate is also equal to the gas film transfer coefficient k_g multiplied by the partial pressure driving force:

$$k_g[C_{NH_3}P - (P_{NH_3})_{cat}] \simeq k_gC_{NH_3}P$$

as $(P_{NH_3})_{cat}$ is small. Now $k_g \propto DM^{0.5}$, where D is the diffusion constant, M is the mass flow rate, and P is the total pressure. Hence as $D \propto 1/P$,

$$k_gC_{NH_3}P \propto M^{0.5}C_{NH_3}$$

$$\propto A(P_{NH_3})_{cat}$$

where A is the catalyst activity assuming a first-order dependence of NH_3 oxidation rate to form NO on the ammonia partial pressure, or

$$(P_{NH_3})_{cat} \propto (1/A)M^{0.5}C_{NH_3}$$

The fractional loss due to NH_3 reacting to give $N_2 + N_2O$ is thus proportional to $k_1(1/A)M^{0.5}C_{NH_3}$.

There are, however, further causes of NH_3 loss. The decomposition of NO to form N_2 and O_2 proceeds heterogeneously on the catalyst with the result that if an excessive depth of catalyst (number of gauzes) is

employed, then NO already formed is decomposed. This appears to be a second-order reaction in P_{NO} such that the fractional loss due to this process is given by

$$k_2 C_{NH_3} P^2 M^{-1} AV$$

where k_2 is the rate constant for this process, A is the catalyst activity, and V is the catalyst quantity per unit gas flux M.

Finally there are circumstances where an inadequate quantity of catalyst is employed for a given gas flux M, with the result that ammonia slips through the catalyst bed to subsequently react with NO, and thereby both are lost. The stoichiometry indicates that 2.5 molecules of combined nitrogen are lost per 1 NH_3 molecule slipping through the gauze (1 NH_3 and 1.5 NO). In order to calculate this loss only the gas film transfer performance of the catalyst bed need be considered. The ammonia slip fraction is given by the expression

$$\frac{C_{NH_3,\ exit}}{C_{NH_3,\ inlet}} = e^{-B_3(V/M^{1/2})}$$

where $B_3M^{1/2}$ is the relevant gas film rate constant.

The total loss now becomes, when expressed as a fraction of the entering NH_3,

$$k_1 C_{NH_3} A^{-1} M^{1/2} + k_2 C_{NH_3} P^2 M^{-1} AV + 2.5e^{-B_3 V M^{-1/2}}$$

With gauzes $B_3VM^{-1/2}$ is normally chosen to be at least 5.5 so that the last term is no more than 0.01 (i.e., 1% loss). Hence $V \propto M^{1/2}$. A rough guide for selecting the number of gauzes is therefore

$$\text{number of gauzes} \propto \sqrt{M}$$

The very small diameter (0.07 mm) wires the gauze, coupled with their close spacing, result in a very high gas film mass transfer coefficient per gauze.

The superficial area of a gauze (fresh wire) of about 1.5 cm^2 per square centimeter of gauze area for a single gauze coupled with a very high gas film mass transfer coefficient (about 200 cm/sec; see Fig. 1) results in a very shallow packed bed having a high gas film efficiency for contacting ammonia with the wire. A bed 3 wires deep ≅ 0.2 mm gives a product $k_g a \cong (200)(3)(1.5) = 900$ cm^2/sec per square centimeter of gauze superficial area. By contrast, a nonprecious metal catalyst formed into 3-mm tablets has a superficial area of about 3 cm^2 per square centimeter for a single layer of tablets, but with a gas film

transfer coefficient of only about 20 cm/sec (see Fig. 1). A similar gas film contacting efficiency can only be obtained with a similar $k_g a$ at the same superficial gas loading on the catalyst bed. Thus the number of tablet layers required = (900)/(3)(20) = 15, or a bed depth of about 4.5 cm.

With V thus related to M, the remaining two loss terms mean that

$$M^{1/2}A^{-1} + (\text{const.})P^2M^{-1/2}A$$

must be minimized. In practice, A cannot readily be varied (except by changing temperature), so that the designer or plant operator has the job of minimizing

$$M^{1/2} + (\text{const.})P^2M^{-1/2}$$

A rough guide for selecting M, as the second term rapidly increases with P, is taking M proportionate to $P^{1.5}$. Typically $M \cong 200P^{1.5}$ N m^3/hr ft^2, where P is in bar; hence V is proportional to the number of gauzes, $P^{0.75}$. Typically the number of gauzes is about $4P^{0.75}$.

The commercial optimum number of gauzes is ill defined, depending on a variety of factors, as can be seen from the following table:

Pressure (bar)	Typical number of gauzes
1	3–5
4	6–8
5	7–10
8–10	20–30

High-pressure burners thus operate with both a high gas loading per unit section of gauze and a large number of gauzes. Figure 4 diagrammatically represents typical figures for the three loss terms showing how they contribute to the burner efficiency.

D. Effect of Poisons

Virtually any involatile material which may be deposited on the catalyst acts as a poison. Typical materials are iron oxide (rust), calcium silicate or silica, and calcium phosphate, which may be found in the air entering the plant and which may not be entirely removed if the filters are not well maintained or adequately designed. Temporary poisons such as SO_2 and phosphate may also affect the catalyst. Nonprecious metal catalysts are particularly sensitive to all poisons.

The effect of a poison is to substantially reduce the activity of the catalyst at the inlet of the bed. As this is the catalyst on which

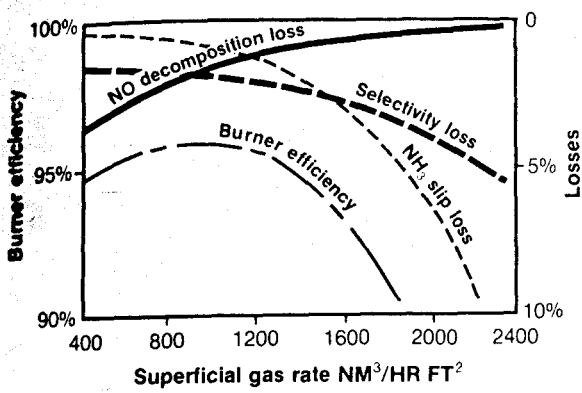

Fig. 4 Typical variation of Pt–Rh gauze burner efficiency with superficial gas rate, showing the origins of the losses in conversion.

most of the ammonia is oxidized, the fall of activity A causes a very significant loss in selectivity due to increase in the term $k_1 C_{NH_3} A^{-1} M^{1/2}$.

With platinum-rhodium gauzes operating normally at lower temperatures (say, below 800°C) an irreversible decline in activity can also be occasioned by such poisons, as the influence of the loss in activity can be to slow the kinetic processes relative to the gas diffusional mass transfer process with the result that the top of the catalyst bed is no longer fully diffusion limited. Its temperature then falls locally below the adiabatic temperatures for the reaction—a visible phenomenon, as the poisoned patch becomes duller. The lower temperature is also associated with a somewhat higher oxygen partial pressure in contact with the catalyst. This combination then stabilizes the presence of rhodium oxide at the catalyst surface which rapidly accumulates there by diffusing as metal from the bulk of the wire.

Rhodium oxide has a low activity relative to metallic platinum, with the result that the catalyst activity of the top gauzes dives rapidly and irreversibly downward. Recovery is only possible if the gauzes are pickled to remove the original poisons and the rhodium oxide reduced, for instance, by operating the gauze at a higher temperature.

The significant feature of the above is that inlet gauzes which have lost activity and selectivity due to poisoning must be removed from the plant, or at least covered with fresh, more active gauzes. Inlet gauzes which have merely lost activity owing to mechanical disintegration are much less of a menace, as the metal that is left remains active and selective.

With a particulate oxide catalyst, such as cobalt oxide, the bad effects of a poisoned top layer of catalyst can be mitigated with the plant

on-line, provided that a system of rakes is installed which can turn over the bed of particles and bury the poisoned top layer.

E. Other Loss-Making Processes

As was explained above, when relatively cold catalyst is in contact with the NH_3-air mixture, the reaction is selective toward N_2 and N_2O. Some loss therefore occurs where the catalyst is cooled by contact with the outside support structures of the reactor (for instance, the flanges which hold the gauzes). Loss also occurs if the reactor structure is itself a catalyst. Thus the inlet cone and gas distribution system above the catalyst bed may become so heated by radiation from the bed that the rust layer on the steel may act as a catalyst. In order to reduce this effect, the inlet cone is seldom insulated on the outside and chromium- or aluminum-containing steels are employed which, by presenting chromium and aluminum oxide faces to the mixed gas, have a reduced catalytic activity.

The homogeneous reaction between ammonia and product NO is also a cause for loss. This reaction is not, however, particularly fast, and even with the longer contact times occurring when using packed beds of nonprecious metal oxide catalysts (times of about 0.01–0.05 sec) there is little evidence of loss due to this reaction. With the much smaller contact times when employing gauze stacks (0.0001–0.001 sec), the effect should be entirely negligible. This reaction does, however, take place in the relatively long residence time below the catalyst bed, where it is no doubt also heterogeneously catalyzed by hot metal surfac