On the influence of oxygen on iron catalysts during ammonia synthesis and catalyst characterization

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Once again attention is brought to the sensitivity of iron catalysts to poisoning by sub ppm levels of oxygen and a procedure is suggested to evaluate the purity of the gas supply to a steady state flow reactor setup. It is demonstrated that extremely high gas purities are essential, in particular for studies of alkali promoted samples.

Keywords: Iron catalysts; ammonia synthesis; oxygen poisoning; potassium promoter

The poisoning effect of oxygen on ammonia synthesis catalysts has been discussed in numerous papers since the beginning of the century. A recent review is given in ref. [1]. The basic assumption behind the understanding of the effect of oxygen is that an equilibrium coverage of oxygen on the surface will be established after some time and that the oxygen will be converted to water in a narrow region at the inlet to the reactor. The equilibrium coverage will depend on the gas composition, the pressure and the temperature. The equilibration time resulting from changes in these parameters may be long, hours or even days. Observation of this time is the basis for the evaluation method suggested in this paper.

It was reported as early as 1926 [2] that potassium promoted catalysts are more sensitive to oxygen containing poisons than catalysts without alkali promoters. On this background it is unfortunate that many recent publications suffer from lack of sufficient information about any possible effects of poisons. However, many of the early papers underestimate the critical O_2 level, because the "pure" gas probably already contained several ppm of O_2 or H_2O [1]. A few ppm will not be too important under industrial conditions, that is, at more than 100 bar of preconverted gas and a temperature of around 400°C. For scientific studies we are concerned about sub ppm levels of oxygen containing impurities [1,3], so it is almost impossible to measure directly the actual values in the reactor with sufficient accuracy.

Table 1
Gas purity. Maximum values of oxygen containing impurities in ppm. Suppliers specifications

N60 99.9999%	Hydrogen	Nitrogen
O_2	0.1	0.1
H_2O	0.5	1
CO	0.01	0.1
CO_2	0.01	0.05

We have found that even the purest commercially available gases (99.9999%) require additional purification in order to ensure that the measured activity is relieved of any effects of oxygen. This is true in particular at low temperatures and low conversion [3]. Table 1 states the specifications of this type of gas. All oxygen containing species should be considered [4].

Figs. 1–3 illustrate the effect of a few ppm of oxygen on an industrial type ammonia catalyst under various conditions. The H_2/N_2 ratio was 3 for all experiments reported here and the inlet concentration of NH_3 was 0. The gas feed system was supplied with a self-designed purification unit.

Addition of O_2 was accomplished by mixing the 99.9999% gases with N_2 containing 32 ppm O_2. The number given in the following for the O_2 concentration is calculated from the flow ratio. The purification unit was bypassed during the poisoning experiment, so in addition to the calculated amount, the synthesis gas will contain the oxygen containing impurities present in the gases as supplied. Examples of the effect of such remaining impurities are shown in fig. 1. The declining slope continues for days indicating that the equilibrium oxygen coverage is large enough for it to be reached only very slowly, when the feed contains sub ppm levels of oxygen.

Fig. 2 demonstrates that at low pressure the effect of adding 1.6 ppm O_2 can be appreciable even at 450°C. The sample was a multiply promoted iron catalyst of the industrial type. The flow had to be rather large (of the order of 1

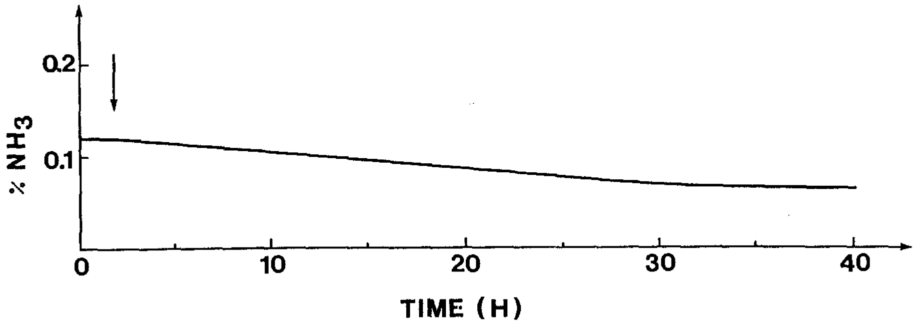

Fig. 1. Variation in NH_3 signal when the purification unit is bypassed (arrow). Gas quality: 99.9999%. Conditions: 350°C, ≈ 1.5 atm.

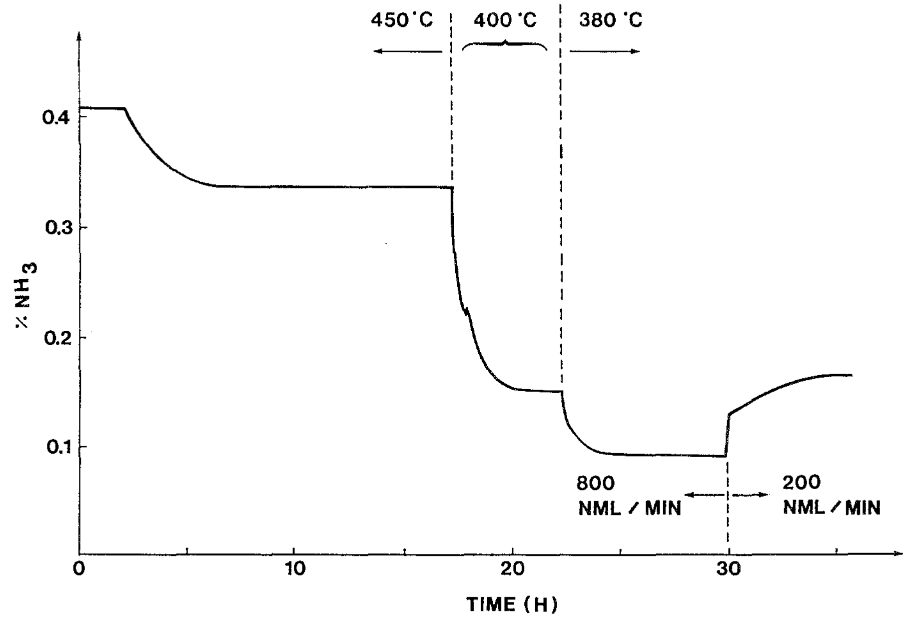

Fig. 2. Variation in NH_3 signal when 1.6 ppm of oxygen is added (time = 2 h) to the gas at 450°C, ≈ 2 atm. The effect of changes in the temperature or the flow is also demonstrated. The notch at the first cooling step is caused by the correction of an accidental undercooling of the reactor (a few degrees).

ℓ/min/g) in order to get a conversion lower than the gas equilibrium value. Since we were using a tubular plug flow reactor containing small (0.1–0.15 mm) catalyst particles, this resulted in a significant pressure drop over the length of the bed.

The change in the exit concentration from 4150 to 3430 ppm of NH_3 is more important than it may look at a first glance, since the conversion is close to equilibrium. It actually corresponds to a change of a factor of 2 in the rate constant [4]. This does not mean that half of the surface is blocked by O_2. The important point here is the change in the coverage of free sites, $\Theta\text{-}*$, since the rate is proportional to $\Theta\text{-}*^2$. If the coverages of all reacting surface species are lowered in the same proportion, then the rate will drop by a factor of 4, when $\Theta_{O\text{-}*} = 0.5$. However, the balance between the coverages could well be more complicated.

Fig. 2 also shows the variations in the NH_3 signal, when the temperature or the gas flow is changed. The increasing activity after the decrease in the flow demonstrates that the catalyst is less sensitive to poisoning at higher conversions [3], but it recovers only very slowly.

Fig. 3 shows the effects of 8 ppm of O_2 at 90 atm. The slow response and the negative curvature in the initial stage of the poisoning are a consequence of the kinetics of NH_3 synthesis (inhibition by NH_3).

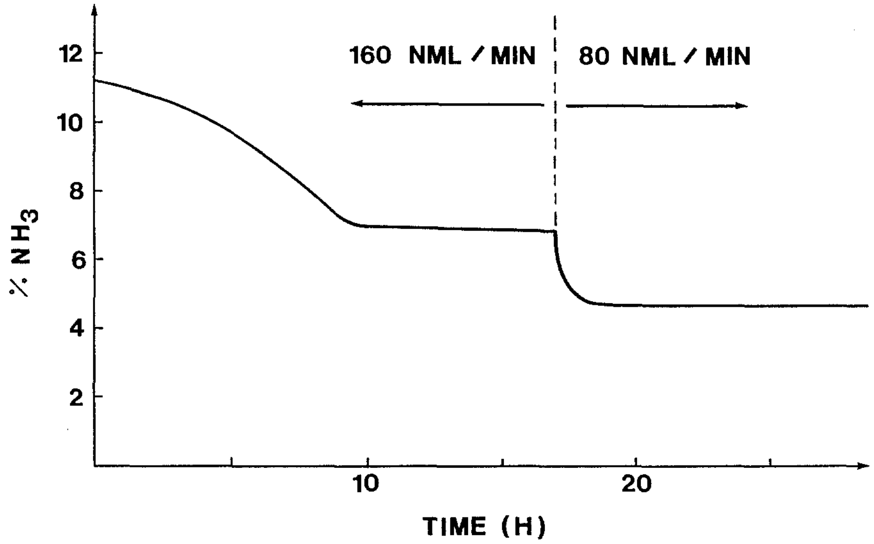

Fig. 3. Variation in NH_3 signal when 8 ppm of oxygen is added (time 0) to the gas at 410°C, 90 bar.

The difference between catalysts with and without potassium is illustrated in table 2. A large amount of the catalyst of the K free type was loaded into the reactor in order to get a conversion which was inside the range found for the K promoted sample. The time allowed for stabilization of the NH_3 signal during poisoning was increased accordingly to be on the safe side. It is obvious that the effect of O_2 is more serious for the catalyst containing potassium. The rate constant decreases a factor of 5, while for the K free catalyst it only drops 20% below the non-poisoned value.

The figures suggest a method to check whether the purity of the gas supply is good enough. It is very simple if a continuous NH_3 detection system and a good temperature control are available.

(1) Run the synthesis under stable conditions at 400°C, 1 atm.

(2) Cool down fast at constant rate to 300°C. Temperature oscillations should be avoided.

(3) Observe the NH_3 signal for several hours. It should be constant once the new conditions have been established.

Table 2
Effect of O_2 on catalysts with and without K at 90 bar and 410°C. Exit concentrations of NH_3 (in %)

	Without O_2	8 ppm O_2
with K	9.6	5.2
without K	7.4	6.9

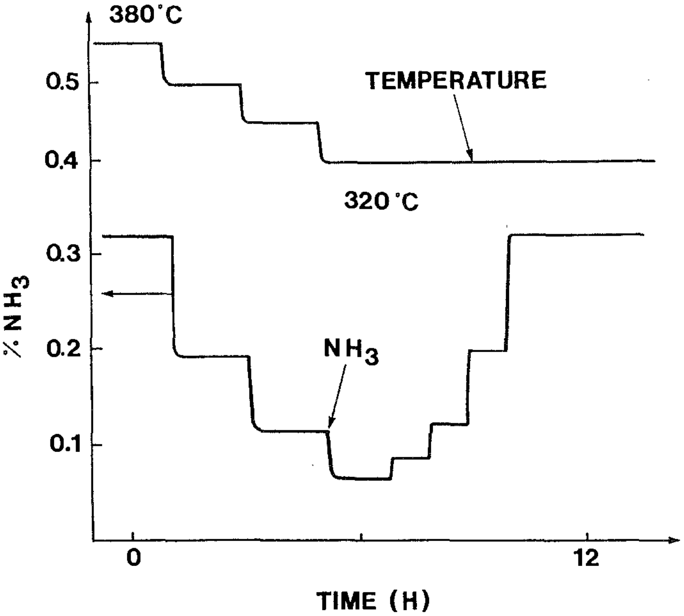

Fig. 4. Response of the NH_3 signal to a series of temperature ramps followed by flow ramps when the gas is very pure. Pressure ≈ 1 atm.

The flow should be large enough to keep the conversion below equilibrium, at least at 300°C but preferable also at 400°C. The test can of course be done at higher pressures but the larger amount of gas contained by the reactor introduces appreciable time delays, which can be inconvenient for this purpose.

If investigations under non-synthesis conditions are planned, then the observation time at 300°C should be of at least the same length as the duration of such experiments, and the flow should be comparable or larger. If, for example, the aim is to perform a temperature programmed desorption experiment, it is advisable to test the carrier gas supply by mixing an appropriate amount into the synthesis gas.

An increase in the flow will reveal some of the same features as the temperature drop, but in this case the sign of the effect may depend on the source of the impurity. If the contamination is caused by a leak in front of the reactor then the O_2 content will decrease with increasing flow. This will result in an increasing slope of the NH_3 signal after the flow is increased, while a constant O_2 concentration gives the opposite effect as demonstrated in figs. 1–3.

Fig. 4 demonstrates that it is possible to get a rather instantaneous response of the NH_3 signal to the change in flow or temperature, if the gas is properly purified. There is no slope of the NH_3 signal once the temperature has stabilized. Note the sharpness of the steps caused by the flow changes.

A very high level of oxygen in the gas may also result in fast responses, but in that case the activity would be very low, and the O_2 concentration should be measurable.

The type of response to O_2 described here is observed for conventional alumina promoted iron catalysts, but for other samples the interpretation may be less straightforward. A decreasing NH_3 signal will of course be observed, if the catalyst is losing activity permanently. However, this should be easily distinguished from the effect of contamination. For instance, if the deactivation is a result of sintering it will get worse if the temperature is increased, contrary to what is the case for O_2 poisoning. The possibility of more subtle reversible effects, such as surface reconstructions, is more difficult to handle. Independent ways of observing these effects are needed. One can for example study an industrial catalyst in the same reactor before and after the experiment in question. Any joints (upstream of the catalyst bed), which were opened when replacing the catalyst, should be carefully leak tested. The size of the leaks to be concerned about is quite small, so it may be impossible to localize them even with a sensitive hydrogen detector unless the setup is pressurized to at least 10 atm.

An interesting question was asked by one of the referees of this paper: can the methodology to determine the purity of the synthesis gas be applied to other reactions? There is no general answer to this question. It will have to be decided separately for each process *and* catalyst. The fact that the method works for the industrial ammonia catalyst relies critically on the following three facts:

(1) the stability of said catalyst,

(2) the reversibility of the poisoning,

(3) the fact that the critical O_2 concentrations are so small that (at space velocities appropriate for activity evaluation) the time needed in order to reach an equilibrium coverage is long enough to be separated from other time constants involved in the process.

Conclusion

We have demonstrated the importance of working with extremely pure gases in studies of NH_3 synthesis catalysts. A procedure to evaluate the gas quality is suggested.

Finally, we would like to suggest that a distinction between the reversible surface oxygen and the more permanent oxygen present in the promoter phases should be attempted. Thus we would define the "poison" as the oxygen which is not present during synthesis of well purified gas at high pressure (100 atm or more), temperature ($> 400°C$) and conversion ($> 50\%$ of equilibrium). Starting from these conditions, the effect of any oxygen in the gas can be evaluated using a procedure similar to the one suggested here.

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