Catalysis Letters 24 (1994) 197–210

The mechanism of the poisoning of ammonia synthesis catalysts by oxygenates O_2, CO and H_2O: an in situ method for active surface determination

K.C. Waugh

Department of Chemistry, University of Manchester, Institute of Science and Technology, PO Box 88, Manchester M60 1QD, UK

D. Butler and B.E. Hayden

Department of Chemistry, University of Southampton, Highfield, Southampton SO9 5NH, UK

Received 2 July 1993; accepted 14 October 1993

The effect of adding an oxygenated poison (O_2, CO or H_2O) to a hydrogen/nitrogen stream producing ammonia over a triply promoted (K_2O, CaO, Al_2O_3) commercial catalyst is not unsurprisingly rapidly to poison the catalyst. However, immediately the oxygenated poison reacts with the catalyst and before total poisoning has occurred, which in these experiments took $\sim$ 10 min, there was an explosive release of ammonia producing concentrations in the gas phase in excess of the equilibrium value. This is thought to be due to a convulsive reorganisation of the surface of the catalyst in forming regions of an oxide overlayer, resulting in the expulsion of the standing surface nitrogen atom coverage as ammonia. However, in contradistinction to the observation of complete poisoning of the triply promoted catalyst shortly after switching the water (2.9%) into the hydrogen/nitrogen stream, when polycrystalline iron was used as the catalyst, after the initial pulse of ammonia was observed, the small quantity of water (2.9%) in the hydrogen/nitrogen stream resulted in an increased rate ($\sim \times 3$) of ammonia synthesis which declined only slightly over the twenty minute duration of the experiment. The difference in behaviour between the triply promoted catalyst and the polycrystalline iron is thought to be due to the relative ease of reduction of the latter, so that submonolayer quantities of oxide can be stabilised on the surface of the polycrystalline iron. The promoting effect of this oxide overlayer is either structural or electronic; no distinction can be made from these experiments. The technique of injecting either O_2 or CO into a hydrogen/nitrogen stream which is producing ammonia over promoted catalysts in quantities insufficient to cause complete poisoning and measuring the oxygen coverage of the catalyst to a measured decrease in the ammonia synthesis rate, appears to be a ready, in situ method for the determination of the active catalyst area.

Keywords: Poisoning; ammonia synthesis; active surface determination

1. Introduction

The basic components of all commercial ammonia synthesis catalysts are iron (~ 97%) and the two promoters, alumina (2–3%) and potassium (1–2%). A considerable body of work by Ertl and co-workers has shown the mode of action of the potassium promoter to be electronic; donation of an electron from the potassium to the iron lowers the work function of the iron. This allows a greater degree of electron donation from the iron into the anti-bonding orbitals of the adsorbed molecular nitrogen, thereby increasing the molecular nitrogen/iron bond strength (and surface coverage) and facilitating dissociative nitrogen adsorption by weakening the nitrogen/nitrogen bond strength [1].

The role of the alumina promoter has long been considered to be structural. It is thought to be located at the grain boundaries of the iron crystallites where it inhibits sintering and active area loss [2]. Consequent to this, the alumina should in effect decorate the iron surface and indeed Ertl and co-workers have published that the free iron area of a reduced, multiply promoted commercial catalyst is only 15% of the total area, the remainder being occupied by promoters [3].

Recently, however, Somorjai and co-workers have suggested that the adventitious water treatment of the iron during reduction results in its migration over the alumina, encapsulating it; it is also claimed that in this water treatment the iron is restructured, restructuring the (110) and the (100) faces to the most active (111) face [4]. In this case, therefore, the alumina promoter would not decorate the surface and the free iron area would equal the external area.

The initial purpose of this work was to try to resolve this dichoteny by measuring, in situ, during ammonia synthesis the area which was active in the reaction. This would be done by measuring the amount of oxygen required to stop the reaction, assuming that total cessation occurred at monolayer coverage by the oxygen atoms. A subsidiary objective was to elucidate the nature of the poisoning by monitoring the rate of ammonia production at sub-monolayer coverages of the oxygen atoms. The poisons used are oxygen, carbon monoxide and water which have been shown to be reversible poisons and to be identical in their mode of action [5,6]. Two iron catalysts were used: (i) unpromoted polycrystalline iron and (ii) a triply promoted (CaO, K_2O, Al_2O_3) commercial catalyst.

2. Experimental

THE APPARATUS

The multipurpose microreactor used in these experiments has been described in detail previously [7]. Briefly, it is a singly tubular reactor (15 cm long, 0.64 cm i.d.) connected in tandem to a thermal conductivity detector or mass spectrometer (VG SX 200), the latter being controlled and interrogated by computer. The tubular reactor is housed in a metal block which can be cooled to 77 K by pumping liquid nitrogen through it. The temperature of this reactor can also be raised linearly with time from 77 to 900 K using a Newtronics controller. Among the many in situ capabilities available to this configuration, those used in this study are total area measurements and isothermal rate measurements.

The oxygen poisoning experiments were simply achieved by switching flows from the hydrogen/nitrogen mixture (3 : 1, 25 cm^3 min^{-1}, 1 bar) to one into which oxygen (1%) had been bled. The pulsed oxygen and carbon monoxide poisoning experiments were achieved by sweeping out a calibrated loop of a pneumatic sample valve with the hydrogen/nitrogen stream. The water poisoning experiments were achieved by switching the hydrogen/nitrogen flow (3 : 1, 25 cm^3 min^{-1}, 1 bar) from a by-pass to a U-tube containing a molecular sieve saturated with water held isothermally at 300 K. This produced a hydrogen/nitrogen stream containing 2.9% atmosphere of water.

3. Materials

3.1. THE CATALYSTS

Two catalysts were used in this study. They were polycrystalline iron and a triply promoted (K_2O, CaO, Al_2O_3) commercial ammonia synthesis catalyst.

Iron oxide was first prepared by ammoniacal precipitation from an iron(III) nitrate solution (BDH AnalaR). The precipitate was repeatedly filtered and re-slurried until the ammonium nitrate concentration fell below 0.01% w/w (measured by conductivity). This material was then dried in air at 430 K for 18 h. X-ray fluorescence showed the oxide so produced to contain Al, Ca, Si, Ti, V, Mn, Co, Ni, K, Mg and Cr, while inductively coupled plasma emission showed that, of these, only Si, Ni and Cr were present at greater than 100 ppm at 0.03, 0.11 and 0.24% w/w respectively.

The iron oxide was crushed and sieved to 300–425 μm and loaded (2.4325 g) into the microreactor where it was reduced in a hydrogen/nitrogen (3 : 1) stream (25 cm^3 min^{-1}, 1 bar, 753 K, 16 h). The water partial pressure was monitored continuously on the mass spectrometer during reduction; its value fell to the background level after 1 h. The surface area of this polycrystalline iron so prepared was 1.5 m^2 g^{-1}, measured, in situ, on the reduced material.

The commercial catalyst used was prepared in the conventional manner by fusing magnetite with alumina (~ 3% by weight), calcium oxide (~ 2% by weight) and potash (~ 2% by weight) in an electric furnace at 1800 K. The exact composition of this catalyst is not given for commercial reasons but its composition lies in the range normally used industrially. As with the polycrystalline iron oxide, it was crushed and sieved to 300–425 μm, loaded into the microreactor where it was reduced in the hydrogen/nitrogen (3 : 1) stream (25 cm^3 min^{-1}, 1 bar, 753 K, 16 h).

In this case the water signal monitored continuously on the mass spectrometer, did not return to its background level until 10 h after the start of the hydrogen/nitrogen flow (cf. 1 h for twice the weight of iron oxide).

3.2. THE GASES

The hydrogen/nitrogen (3 : 1) mixture was supplied by Electrochem Ltd. Its quoted purity was 99.9999%. The helium, nitrogen, hydrogen and ammonia calibration gases were supplied by Air Products Ltd and were also of 99.9999% purity. All gases were passed over a desiccant and oxygen trap before use.

4. Results and discussion

4.1. OXYGEN POISONING OF A TRIPLY PROMOTED CATALYST

Fig. 1 shows the effect of switching flows from a hydrogen/nitrogen stream (3 : 1, 25 cm^3 min^{-1}, 1 bar) which was producing ammonia at 723 K over a triply promoted commercial ammonia synthesis catalyst (0.953 g, 7.2 m^2 g^{-1}) to a hydrogen/nitrogen stream (3 : 1, 25 cm^3 min^{-1}, 1 bar) containing oxygen (1%). In the figure, in the time regime of 0–1000 s the hydrogen/nitrogen stream is changed from passing over the catalyst to a bypass and then back again. The difference in height is a measure of the ammonia partial pressure; it is 0.08 atm. The switch to the hydrogen/nitrogen stream containing the 1% oxygen is made at 1087 s. After ~ 90 s (the dead time of the system) there is a massive transient pulse of ammonia which reaches a peak value of $\sim 5 \times 10^{-3}$ atm which is more than twice the equilibrium value of 2.3×10^{-3} atm; ammonia production then falls to zero (complete poison-

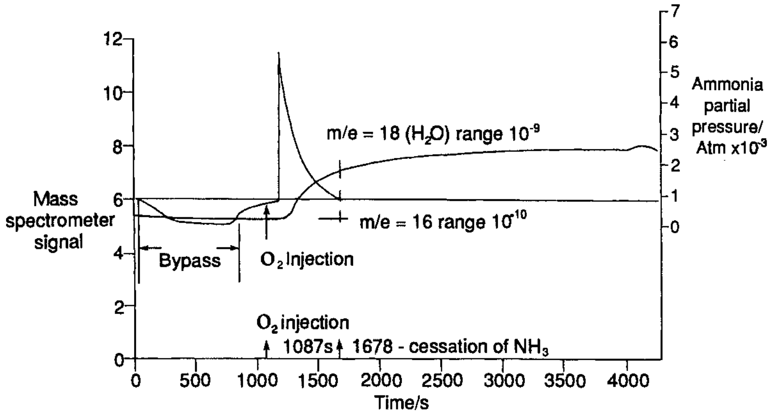

Fig. 1. The poisoning of a triply promoted catalyst by switching oxygen (1%) into the hydrogen/nitrogen stream.

ing) at 1678 s. (The apparent increased value in the steady state rate of ammonia synthesis after 1678 s is due to the ammonia being monitored on the $m/e = 16$ signal on the mass spectrometer. The $m/e = 16$ signal is also a significant fraction of the oxygen peak and so the ammonia baseline has been displaced upon the addition of oxygen to the hydrogen/nitrogen stream.) One final point to note from fig. 1 is that ~ 190 s after the initial increase in the rate of ammonia synthesis water begins to be formed, its rate of production rising continuously for the remainder of the experiment.

Several points can be made from this experiment relating to: (i) the oxygen coverage required for complete poisoning of the rate of ammonia synthesis, (ii) the origin of the transient increase in the rate of ammonia synthesis upon the addition of oxygen to the hydrogen/nitrogen feed and (iii) the nitrogen atom coverage of the iron at a measured rate of ammonia synthesis. However, it must be emphasized at the outset that whereas the addition of 1% of oxygen to the H_2/N_2 feed causes a transient increase in the rate of ammonia synthesis it ultimately (after ~ 6 min) causes the complete poisoning of the catalyst. This total but reversible poisoning effect of oxygen has been attested to in many papers, dating from Almquist and Black in 1926 to the present [6,8–12].

4.1.1. Oxygen coverage at complete poisoning of the rate of ammonia synthesis

The oxygen coverage at complete poisoning at the rate of ammonia synthesis can be readily calculated from fig. 1. It is the total oxygen flowed to poisoning minus the water evolved up to that time. Its value is 9.7×10^{19} oxygen atoms g^{-1}. The total surface area of the catalyst measured, in situ, by nitrogen adsorption at $-196°C$ is $7.2\ m^2\ g^{-1}$ on which basis this corresponds to an oxygen atom coverage of 1.35×10^{15} atoms cm^{-2} or an area per oxygen atom of 7.4 $Å^2$. This oxygen atom coverage is roughly the same as the average surface population of iron atoms ($\sim 1.2 \times 10^{15}$ atoms cm^{-2}) on the three low index faces of iron. Therefore, it might be concluded that all of the external catalytic area is iron. This would agree with the contention of Somorjai and co-workers [4] that the adventitious high temperature water treatment of the iron occasioned during reduction results in the migration of the iron over the alumina promoter. However, it is at odds with our previous conclusion that the lowered turnover number (by a factor of 2) of an industrial catalyst at 1 bar relative to polycrystalline iron was due to the promoters decorating roughly 50% of the catalyst [13]. This degree of decoration is in accord with the values quoted by Schlögl and co-workers [2,14]. On that basis, then, two monolayers of oxide are required completely to poison the rate of ammonia synthesis, suggesting that some of the oxygen migrates below the surface during adsorption, and a complete oxide overlayer is not produced until two monolayers of oxygen atoms are adsorbed. What is certain though is that bulk Fe_3O_4 is not formed.

The catalyst was allowed to run in the hydrogen/nitrogen stream containing the oxygen (1%) for a total of 150 min after which the flow was switched back to the pure hydrogen/nitrogen stream. On regeneration the steady state activity had fallen to 0.07% atm of ammonia but the total surface area had also fallen by a compensatory amount to 6.5 m^2 g^{-1}. Indeed, in these oxygen poisoning experiments it was always found that the total surface area fell on regeneration after extended oxygen poisoning but that the activity/total surface area ratio was constant as shown in table 1.

4.1.2. *The origin of the transient increase in the rate of ammonia synthesis upon the addition of oxygen (1%) to the hydrogen/nitrogen stream*

The surprising thing about the observation of a transient increase in the rate of ammonia synthesis upon the injection of an oxygenated poison e.g. O_2, CO (section 4.2) or H_2O (section 4.3) reported in this paper is that it is not unique. In a remarkable paper published in 1934, Ussatschew and co-workers pulsed CO, CO_2, O_2 and SO_2 into a hydrogen/nitrogen stream which was producing ammonia at ambient pressure and published traces identical to the figures produced here [10]. After a transient increase in the rate to values exceeding equilibrium after the injection of the poison, the rate then fell to below its initial steady state value (after ~ 10 min), recovering to its initial steady state value in all cases except where SO_2 was used as the poison [10]. Schlögl also reported on the transient increase in the rate of ammonia synthesis upon the addition of oxygen to the hydrogen/nitrogen stream [14]. The result, therefore, is real and not an artefact of our experimental method as had been suggested by one of the referees.

Schlögl suggested that the effect is due to local heating resulting from the formation of the oxide overlayer [14]. However, the sharpness of the onset of the transient would argue against this.

Two other possibilities exist. One is that the oxygen causes reconstruction of the iron surface to the most active (111) face as has been suggested by Somorjai and co-workers [4]. Two facts argue against this. These are (i) the surface is supposed to have been reconstructed completely to this face due to adventitious water treatment during reduction [4] and (ii) were the reconstruction during reduction incomplete and the oxygen (1%) in H_2/N_2 merely producing total reconstruction to the (111) face, nevertheless the ammonia synthesis partial pressure could never exceed its equilibrium value as is observed here and previously [10].

The second possibility is that the oxygen causes displasive desorption of the adsorbed ammonia. However, since by the arguments outlined in section 4.1.1 complete poisoning occurs at the formation of one or two monolayers of the oxide,

Table 1
Relationship between the catalyst total surface area and ammonia synthesis activity

Total surface area (m^2 g^{-1})	Activity (%NH_3 g^{-1})	Activity/total surface area
7.9	0.094	0.012
7.2	0.084	0.012
6.5	0.071	0.011

all of the adsorbed nitrogen atoms must therefore have been removed from the surface as ammonia. The effect, therefore, could be electronic in which sub monolayer quantities of co-adsorbed oxygen weaken the iron–nitrogen bond, raise the energy minimum in the ammonia potential energy diagram and so increase the rate of ammonia synthesis. Kishi and Roberts have claimed that the increase in the nitrogen [15] binding energy when chemisorbed on iron occasioned by co-adsorbed oxygen results from a draining of the bonding electron density of the nitrogen atom to the iron by the more electronegative oxygen atom. The nitrogen atom/iron bond is, therefore, weaker. Here again, however, the effect could never result in an ammonia partial pressure in excess of equilibrium. The water poisoning experiments (section 4.3) add further insights on this debate.

4.1.3. The standing nitrogen atom coverage of the iron during ammonia synthesis at 1 bar

The standing nitrogen atom coverage of the iron can be obtained from these experiments on the assumption that the formation of the oxide overlayer removes all of the chemisorbed nitrogen atoms as ammonia. (Further experiments should ensure the validity of this assumption and that no molecular nitrogen is desorbed.) The total amount of ammonia in the transient peak is 1.38×10^{19} molecules. If all of the external surface area is active this would correspond to a coverage of 2×10^{14} N atoms cm^{-2}. If only 50% of the external area is iron then the coverage is 4×10^{14} N atoms cm^{-2}.

4.1.4. Measurement of the active iron area by pulsed oxygen experiments

Fig. 2 shows the effect of pulsing oxygen (8.8×10^{18} molecules) into a hydrogen/nitrogen stream (3 : 1, 30 cm^3 min^{-1}) which was producing ammonia at 723 K over a triply promoted commercial ammonia synthesis catalyst (0.5 g,

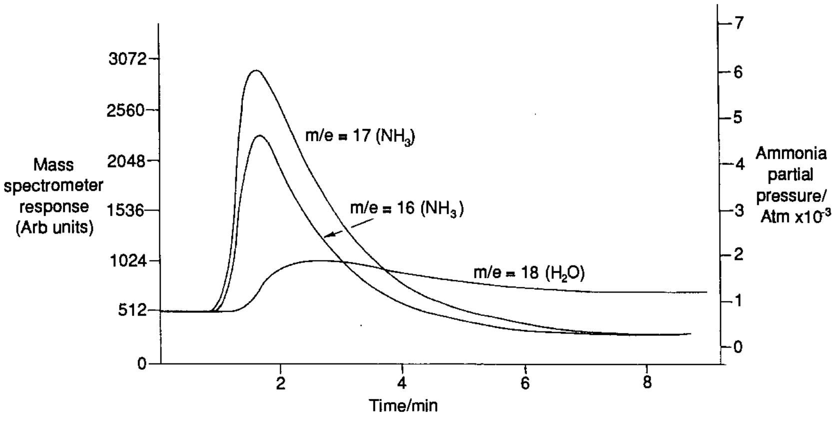

Fig. 2. The effect of pulsing oxygen (8.8×10^{18}) molecules into a hydrogen/nitrogen stream which is producing ammonia over a triply promoted commercial ammonia synthesis catalyst.

14.7 m^2 g^{-1}). (The oxygen pulse was produced by sweeping out a calibrated loop of the pneumatic sample valve with the hydrogen/nitrogen stream.) The figure shows the characteristic pulse in the ammonia concentration to a value (~ 0.6% atm) exceeding equilibrium (0.23% atm) upon the adsorption of the oxygen. After about 7 min the rate of ammonia synthesis has fallen to ~ 40% of its original value at which point the oxygen atom coverage of the iron (oxygen injected – water produced) is 24.6×10^{18} oxygen atoms g^{-1}. Somorjai and co-workers have shown that the rate of ammonia synthesis is proportional to the free iron area [16]. On this basis, assuming the oxygen atoms to be completely dispersed and to be adsorbed on top of the surface iron atoms occupying an area of 8 Å^2, the poisoned area i.e. 1.97×10^4 cm^2 g^{-1} which is 60% of the active area, the measured rate being only 40% of the original value. The active area is, therefore, 3.3×10^4 cm^2 g^{-1} or only 22% of the external area.

This method of pulsing submonolayer quantities of poison and determining their coverage at measured reduction in the rate of ammonia synthesis affords considerable promise as a means of determining, in situ, the active iron area of the operating catalyst. The fact that the coverage of the poison and the ammonia rate measurement are determined 6 min after the injection of the poison means that the poison will not have been accumulated at the front end of the catalyst bed but will have been distributed throughout the bed by hydrogen reduction of the oxide and by water decomposition. The method, therefore, should be reasonably accurate. Regardless of the inaccuracies, e.g. the possibility of multilayer adsorption of the oxygen which, were it to occur, would render the present result to be an overestimate, the value obtained here clearly shows that at 1 atm total pressure under ammonia synthesis conditions the promoters decorate the external surface of the catalyst.

4.2. CARBON MONOXIDE POISONING OF THE RATE OF AMMONIA SYNTHESIS ON A TRIPLY PROMOTED COMMERCIAL CATALYST

Fig. 3 shows the result of pulsing carbon monoxide (8.8×10^8 molecules) into a hydrogen/nitrogen stream (3 : 1, 1 bar, 30 cm^3 min^{-1}) which was producing ammonia (0.09% atm) at 723 K over a triply promoted commercial catalyst (0.5 g, 14.7 m^2 g^{-1}). The effect is the same as that produced on pulsing oxygen, namely a transient increase in the rate of ammonia synthesis followed by a decrease in the rate to a minimum value which is only 65% of the initial steady state value. The figure is included mainly to show the detailed equivalence of all oxygenated poisons.

An interesting point to note from fig. 3 is the ease with which the carbon monoxide dissociates on the iron surface, evidenced by the rapid increase in methane formation some time before the oxygen adsorption produces a transient increase in the rate of ammonia synthesis.

The pulsing of carbon monoxide can also be used to determine the active iron area by measuring the oxygen coverage at a given reduced rate of ammonia syn-

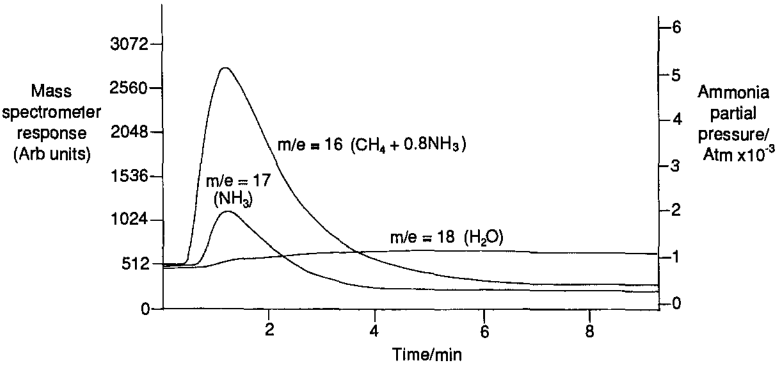

Fig. 3. Carbon monoxide poisoning of ammonia synthesis produced on a triply promoted commercial catalyst.

thesis. The oxygen atom coverage at 65% of the original rate is 16×10^{18} atoms cm^{-2}. As in section 4.1.4, taking 8 $Å^2$ for the area per oxygen atom this corresponds to an area of 1.28×10^4 cm^2 g^{-1} which is blocked and constitutes 35% of the active area. The total active area then is 3.66×10^4 cm^2 g^{-1} or 25% of the total area. This is in reasonably good agreement with the pulsed oxygen poisoning experiments and again shows that the promoters decorate the surface of a triply promoted commercial catalyst when producing ammonia at 1 bar.

4.3. WATER POISONING OF THE RATE OF AMMONIA SYNTHESIS ON A TRIPLY PROMOTED COMMERCIAL CATALYST

Fig. 4. shows the sequence of events which occurred upon switching water (2.9%) into and out of a hydrogen/nitrogen stream (3 : 1, 1 bar, 25 cm^3 min^{-1})

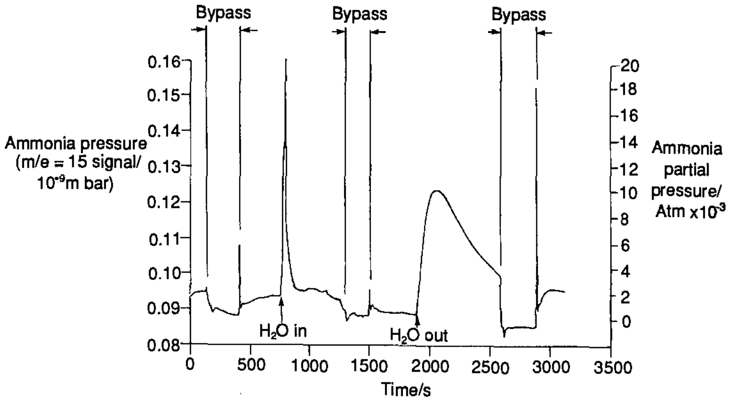

Fig. 4. The effect of switching water (2.9%) into and out of a hydrogen/nitrogen stream which was producing ammonia on a triply promoted commercial catalyst at 753 K.

which was producing ammonia on a triply promoted iron catalyst (0.9556 g, 12 $m^2 g^{-1}$) at 753 K. The effect is qualitatively the same as that produced when oxygen on carbon monoxide is used as the poison. Shortly after the water is switched into the hydrogen/nitrogen stream (within the dead time of the system) a sharp pulse of ammonia is observed to values greater than equilibrium, identical to that seen when oxygen or carbon monoxide is used as the poison, again demonstrating the equivalence of all oxygenated poisons.

Total poisoning of the catalyst occurs ~ 17 min after the introduction of the water to the hydrogen/nitrogen stream. The net total flow of oxygen on to the catalyst up to this point corresponds to two monolayers of oxide. This obviously is an overestimate of the oxygen coverage of the catalyst since it takes no account of the reduction of the oxide by the hydrogen which figs. 1, 2 and 3 have shown to occur. Clearly, however, no bulk Fe_3O_4 could have been formed as has been suggested by one of the referees.

The most remarkable occurrence is observed shortly after switching the water out of the hydrogen/nitrogen stream when a second but less sharp pulse in the rate of ammonia synthesis is again observed. The ammonia concentration produced is again in excess of equilibrium after which the value decays to the original steady state value.

The fact and shape of this second pulse of ammonia upon regeneration of the catalyst are important indicators of the mechanism of the poisoning. The initial explosive evolution of ammonia to concentration levels in excess of equilibrium upon the addition of water to the H_2/N_2 stream cannot be catalytic and must result from a convulsive reconstruction of the surface of the operating catalyst to some form of oxide overlayer. This results in the expulsion of the surface hydrogen atom/nitrogen atom overlayer as ammonia and traps the dissolved nitrogen in the bulk. When the water is switched out of the hydrogen/nitrogen stream the surface oxide overlayer is reduced, less quickly than it had been oxidised, and so the ammonia pulse shape is wider but nevertheless again a convulsive reorganisation occurs with the release now of the subsurface nitrogen as ammonia.

4.4. WATER POISONING OF THE RATE OF AMMONIA SYNTHESIS ON POLYCRYSTALLINE IRON

Fig. 5a shows the effect of switching water into and out of a hydrogen/nitrogen (3 : 1, 1 bar, 25 $cm^3 min^{-1}$) stream which was producing ammonia over polycrystalline iron (2.4325 g, 1.5 $m^2 g^{-1}$) at 716 K. As with adding water to triply promoted catalyst which was synthesising ammonia (section 4.3) so here immediately the water reacts with the iron surface there is an explosive evolution of ammonia. Because the iron has such a low surface area the concentration of ammonia during this explosive release never exceeds the equilibrium value.

Again as with the triply promoted catalyst so here with the polycrystalline iron a second pulse of ammonia of somewhat longer duration than the first is observed

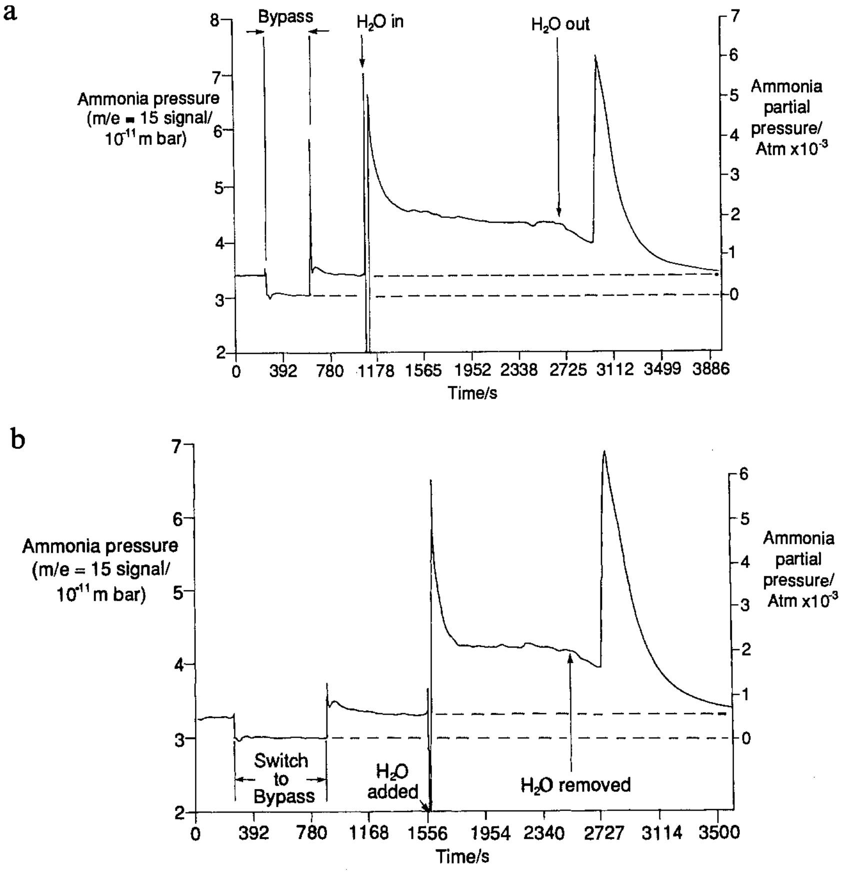

Fig. 5. (a), (b) The effect of switching water (2.9%) into and out of a hydrogen/nitrogen stream which was producing ammonia over polycrystalline iron at 716 K.

on switching the water out of the hydrogen/nitrogen feed, the pulse decaying asymptotically to the initial steady state value. What is distinctly different here though is that after the initial pulse has decayed down to a steady state value, roughly three times the original steady state value, this high water promoted rate is maintained (with a slight decline with increasing time) for a further 21 min. The effect is completely reproducible as can be seen from fig. 5b which is produced under identical conditions while fig. 6 shows the result of raising the temperature to 740 K. The fact that the water promoted effect was not observed with the triply promoted catalyst where ammonia partial pressures were ~ 10 times higher than those produced over polycrystalline iron shows that the water promoted state is not an artefact of the experiment in which the water displaces ammonia from the walls of the mass spectrometer.

That ammonia continues to be formed (at an accelerated rate) is testament to the fact that the oxygen coverage of the reconstructed polycrystalline iron is sub-

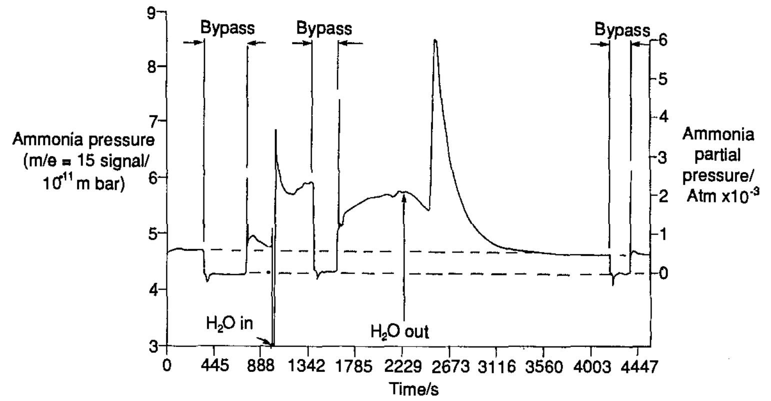

Fig. 6. The effect of switching water (2.9%) into and out of a hydrogen/nitrogen stream which was producing ammonia over polycrystalline iron at 740 K.

monolayer–monolayer coverage would produce complete poisoning. The difference in behaviour between the triply promoted catalyst and polycrystalline iron probably derives from their different reduction kinetics. The activation energy for the reduction of the triply promoted catalyst is higher than that of polycrystalline iron, evidenced by the fact that it took 20 times longer to reduce the same weight of the triply promoted catalyst at the same temperature than it did to reduce the polycrystalline iron.

This submonolayer quantity of oxygen on the surface of the iron may have caused a more general reconstruction to the (111) surface (the most active face). Alternatively, its effect may have been electronic, weakening the iron nitrogen bond and thereby facilitating the kinetics. These experiments cannot distinguish between the two propositions. The most direct method for doing this would be to set up the water promoted state, lower the temperature rapidly to ambient under the gas mixture, switch flows to helium and programme the temperature to 800 K to desorb the nitrogen. This will be the most direct means of determining if the co-adsorbed oxygen atoms weaken the iron–nitrogen atom bond.

5. Conclusions

(1) The oxygenated poisons O_2, CO and H_2O all act equivalently in their mode of action of poisoning a triply promoted commercial ammonia synthesis catalyst. Prior to complete poisoning of the catalyst, submonolayer quantities of the oxygenated poison appear to cause a convulsive reconstruction of the surface which produces an explosive release of the adsorbed nitrogen and hydrogen atoms as ammonia to concentrations greater than equilibrium. The effect is therefore not "catalytic" in the normally accepted sense of being equilibrium limited.

(2) Whereas all oxygenates, O_2, CO or H_2O rapidly poison a triply promoted commercial catalyst, water (i.e. submonolayer quantities of surface oxygen) does promote a steady state rate of ammonia synthesis ~ 3 times higher than that obtained in its absence on polycrystalline iron. Monolayer coverage of the polycrystalline iron by oxygen (complete poisoning) is not achieved in the timescale (~ 21 min) of this experiment due to the ease of reduction of the polycrystalline iron. This suggests that, were it possible to find an additive which would significantly lower the activation energy for the reduction of a triply promoted catalyst, then the addition of small quantities of an oxygenate to the hydrogen / nitrogen feed could lead to an increased rate of ammonia synthesis.

(3) The promoters (K_2O, CaO, Al_2O_3) decorate the external surface of a triply promoted commercial catalyst when operating at 1 bar to such an extent that $< 50\%$ of the total surface area is active.

(4) The technique of injecting either O_2 or CO, in quantities insufficient to cause complete poisoning, into the hydrogen / nitrogen stream which is producing ammonia over promoted iron catalyst and measuring the oxygen coverage to a measured reduction in the rate of ammonia synthesis, appears to be an accurate and ready technique for the in situ determination of the active area of an operating catalyst.

Acknowledgement

The experiments reported in this paper were conducted in the research laboratories of ICI Katalco R T and E, Billingham. One of us, DAB, would like to thank Katalco R T and E for support in the form of a CASE Award.

References

[1] G. Ertl, in: *Catalytic Ammonia Synthesis*, ed. J.R. Jennings (Plenum Press, New York, 1991) p. 128, and references therein.

[2] W. Mahdi, J. Schutze, G. Weinberg, R. Schoonmaker, R. Schlögl and G. Ertl, Catal. Lett. 11 (1991) 19.

[3] G. Ertl and N. Thiele, Appl. Surf. Sci. 3 (1979) 99.

[4] D.R. Strongin, S.R. Bare and G.A. Somorjai, J. Catal. 103 (1987) 289.

[5] A. Nielsen, in: *An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia* (Gjellerup, Copenhagen, 1968).

[6] C. Bokhoven, *Proc. 2nd Radioisotope Conf.*, Oxford 1954, p. 53.

[7] K.C. Waugh, Appl. Catal. 43 (1988) 315.

[8] J.A. Almquist and C.A. Black, J. Am. Chem. Soc. 48 (1926) 2814.

[9] P.H. Emmett and S. Brunauer, J. Am. Chem. Soc. 52 (1930) 2682.

[10] P.W. Ussatschew, W.J. Tarakanowa and W.A. Komarov, Z. Elektrochem. 40 (1934) 647.

[11] P.E. Hojlund Nielsen, in: *Catalytic Ammonia Synthesis: Fundamentals and Practice*, ed. J.R. Jennings (Plenum Press, New York, 1991) p. 253.

[12] B. Fastrup and H. Nygard Nielsen, Catal. Lett. 14 (1992) 233.

[13] K.C. Waugh, D. Butler and B.E. Hayden, Topics in Catalysis 1 (1994), in press.
[14] R. Schlögl, Topics in Catalysis, to be published.
[15] K. Kishi and M.W. Roberts, Surf. Sci. 62 (1977) 252.
[16] S.R. Bare, D.R. Strongin and G.A. Somorjai, J. Phys. Chem. 90 (1986) 4726.