Tamaru's model for ammonia decomposition over titanium oxynitride

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Abstract

Titanium oxynitride TiN_xO_y was prepared by reaction of titania with flowing ammonia between 890 and 1120 K. Optimized operating conditions led to specific surface areas ranging from 58 to 87 m^2 g^{-1}. Kinetics of catalytic ammonia decomposition at 900 K showed that titanium oxynitrides presented a tungsten (or iron)-type behaviour at low hydrogen pressure and a Temkin–Pyzhev behaviour characteristic of platinum, at higher hydrogen pressures. These two behaviours enter the general model of Tamaru for ammonia decomposition. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ammonia decomposition; Titanium nitride; Hydrogen effect; Tamaru's model

1. Introduction

Transition metal nitrides or carbides are non-stoichiometric materials [1–3] and have been claimed to present metallic properties [4,5]. Temperature programmed synthesis [6–9], in flowing ammonia over metal oxide precursors, have been shown to be efficient in providing transition metal nitrides with high specific surface areas. Synthesis of nitrides probably go through ammonia decomposition, providing reducing and nitriding species such as $^{\cdot}H$, $^{\cdot}NH$, $^{\cdot}NH_2$. Kinetics of ammonia decomposition was conducted in the present paper to evidence both the metallic properties of titanium oxynitride as well as the model of Tamaru [10] for this reaction.

Tamaru [10] has shown that published data about catalytic synthesis and decomposition of ammonia could be classified into two classes, depending on temperature or reactant pressure.

1.1. Low hydrogen pressure and high temperature working catalysts

In these experimental conditions, catalysts obey a rate law such as:

$$r = \frac{kKP_{NH_3}}{1 + KP_{NH_3}} \tag{1}$$

mathematically equivalent to [11,12]:

$$r = k'P_{NH_3}^{\alpha} \tag{2}$$

where k, K and k' are constants. This rate equation is not dependent on hydrogen pressure and has been found to apply over tungsten

metal. Tamaru has shown that Eq. (1) does not result from a Langmuir–Hinshelwood sequence, but rather from a dynamic balance between production and desorption of chemisorbed nitrogen atoms $*N$ considered as the most abundant reaction intermediates (*mari*) as defined by Boudart and Djéga-Mariadassou [11,12]. All other species are present at the surface at much inferior concentration levels. The *mari* is mathematically defined when the balance of surface species is made:

$$[L] = [*] + [*N] + [*H] + [*NH] + [*NH_2] + [*NH_3] \qquad (3)$$

where $[L]$ is the density of sites, $*$ is a free active site, whereas $*N$, $*H$, $*NH$, $*NH_2$ and $*NH_3$ are surface adsorbed species. If $*N$ is the *mari*, the other species can be neglected and the balance can be simplified as:

$$[L] = [*] + [*N] \qquad (4)$$

It must be noted that the *mari* is not necessarily the most abundant surface species, since the surface may be covered by species that do not take part in the reaction.

1.2. High hydrogen pressure and low temperature active catalysts

In this case, a Temkin–Pyzhev rate law is observed:

$$r = k \left\{ \frac{P_{NH_3}^2}{P_{H_2}^3} \right\}^\alpha \qquad (5)$$

where k and α are constants. The rate determining step (rds) is the desorption of adsorbed nitrogen atom, a quasi-equilibrium now existing between chemisorbed nitrogen and ammonia, and dihydrogen in the gas phase. In these conditions, dihydrogen acts as an inhibitor of the reaction. The present work describes the activation of a titanium oxynitride and its catalytic activity in the decomposition of ammonia at atmospheric pressure, in the general framework

defined by Tamaru [10] and Boudart and Djéga-Mariadassou [11,12].

2. Experimental

After nitridation the titanium nitride was either passivated by flowing 1 vol.% O_2/He to avoid its strong oxidation when contacting air (pyrrophoricity), or stored in the reactor without contacting air. As passivated titanium nitride contain oxygen, it was called titanium 'oxynitride'.

Temperature programmed desorption (TPD) experiments of preadsorbed species on oxynitrides were carried out in vacuum with a quadrupole mass spectrometer as detector (Riber QS 200) at the outlet of the reactor. The TPD heating rate between room temperature and 970 K was 18 K min^{-1}.

Catalytic decomposition of ammonia was carried out in a conventional dynamic differential microreactor, at atmospheric pressure, between 880 and 940 K. Initial partial pressures varied between 3.8 and 22.3 Torr (1 Torr = 133 Pa) for ammonia and 6.2 and 27.6 Torr for dihydrogen. A constant total flow rate was maintained at 10 l h^{-1}. Partial pressures were provided by dilution of reactants with helium. Sample weights were in the range between 30 to 185 10^{-3} g. In order to determine Arrhenius activation energy and pre-exponential factor, each temperature step was maintained for 90 min in order to get a steady state of the system. No deactivation of the catalysts was observed.

3. Results and discussion

3.1. Activation of titanium oxynitrides

TPD of samples showed that ammonia and water were totally evolved at 960 K. Hydrogen did not desorb easily, even after several TPD up to 1300 K. No desorption of dioxygen was

observed. Nevertheless, nitrogen desorbed at high temperature (1110 K), in a higher ratio with respect to hydrogen than that corresponding to ammonia stoichiometry, showing that the oxynitrides could decompose at high temperature.

As a consequence, a standard pretreatment of the oxynitride was processed at 950 K, first in the nitriding mixture, then in helium at the same temperature before catalytic runs.

3.2. Catalytic decomposition of ammonia

In the first case, no dihydrogen was added in the initial reaction feed. Fig. 1 shows that the order α of reaction with respect to ammonia is positive and the rate law obeys Eq. (2). The apparent activation energy was determined to be 139 kJ mol^{-1} and the pre-exponential factor was found to be 6.96×10^{24}.

In the second case, dihydrogen was added to the reaction mixture. In these conditions, Fig. 1 shows that the order with respect to dihydrogen β is negative and the rate law obeys Eq. (5).

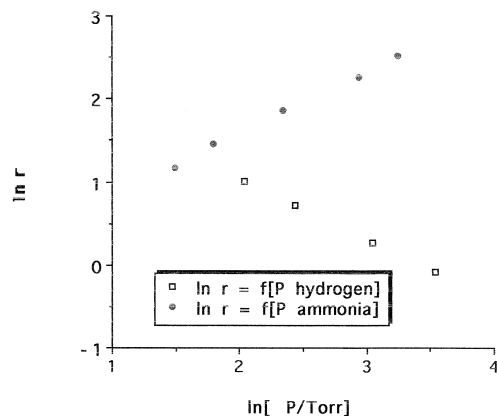As a summary, it appears that the order β with respect to H_2 varied from zero without

Fig. 1. Order determination plots ($r/10^{-17}$ molecules NH$_3$ g^{-1} s^{-1}). ● $r = k'P_{NH_3}^\alpha$ (Eq. (2)); no dihydrogen in the initial feed; positive order with respect to ammonia ($\alpha = 0.75$ at 921 K). □ $r = k'P_{NH_3}^\alpha P_{H_2}^\beta$ (Eq. (5)) with $P_{NH_3} = 9.6$ Torr. Negative order with respect to dihydrogen introduced in the feed: $\beta = -0.73$ at 921 K.

adding hydrogen in the feed, to a negative value when H_2 is initially introduced in the feed. So it appears that the titanium oxynitride behaves like transition metals in ammonia decomposition. As it will be presented hereafter in the general framework of Tamaru's model, the two corresponding rate laws (Eqs. (1) and (2)) can be treated, according to Boudart and Djéga-Mariadassou [11,12], as two-step reactions.

At *low hydrogen pressure*, that is when no dihydrogen is added in the reaction feed, concentration of H_2 is not sufficient to permit step (6) to go back and $*NH_2$ does not rehydrogenate into NH$_3$. As dihydrogen does not play a kinetic role (Eq. (1)), the following two-step sequence can be considered: each step is one-way and far from equilibrium:

$$NH_3 + 2* \overset{k_1}{\to} *NH_2 + *H \tag{6}$$
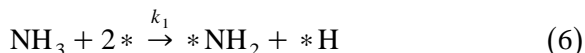
unspecified steps kinetically non-significant

$$2*N \overset{k_2}{\to} N_2 + 2* \tag{7}$$

where $*N$ is the *mari*. Step (7) represents the desorption of adsorbed nitrogen as dinitrogen. Therefore, application of the quasi-steady state approximation [11,12] leads to:

$$r = r_1 = r_2 = k_1 P_{NH_3} [*]^2 [L]^{-1}$$

$$= k_2 [*N]^2 [L]^{-1} \tag{8}$$

The justification of $[L]^{-1}$ is discussed in Refs. [11,12]: the rate is proportional to the probability of finding two '$*$' or two '$*N$' side by side, and not only to $[*N]^2$. Hence:

$$\frac{[*]}{[*N]} = \sqrt{\frac{k_2}{k_1 P_{NH_3}}} \tag{9}$$

and

$$[L] = [*] + [*N] = [*N]\left(1 + \frac{[*]}{[*N]}\right) \tag{10}$$

hence

$$[*N] = [L] \frac{\sqrt{\frac{k_1}{k_2} P_{NH_3}}}{1 + \sqrt{\frac{k_1}{k_2} P_{NH_3}}} \qquad (11)$$

The overall rate is then:

$$r = k_2 [L] \left\{ \frac{\sqrt{\frac{k_1}{k_2} P_{NH_3}}}{1 + \sqrt{\frac{k_1}{k_2} P_{NH_3}}} \right\}^2 \qquad (12)$$

Eq. (12) is formally identical to Eq. (1) [11,12]:

$$r = \frac{kK P_{NH_3}}{1 + K P_{NH_3}}$$

with $k \equiv k_2[L]$ and $K \equiv k_1/k_2$.

It does not correspond to a Langmuir–Hinshelwood mechanism, and also behaves mathematically like Eq. (2) [11,12].

To achieve a complete description of the metallic behaviour of the titanium oxynitride, it is interesting to compare the present results with those of Löffler and Schmidt [13,14] (over Fe). The linearized expression of Eq. (1) gives the values presented in Table 1. It can be seen that pre-exponential factors are of the same order of magnitude.

At *a higher hydrogen pressure*, rehydrogenation of nitrided adsorbed species in ammonia can occur. According to Tamaru's model, the following two-step sequence can then be assumed to take into account the inhibitor effect of dihydrogen.

$$2NH_3 + 2* \quad \overset{K_1}{\rightleftharpoons} \quad 2*N + 3H_2 \qquad (13)$$

$$2*N \quad \overset{k_2}{\longrightarrow} \quad N_2 + 2* \qquad (14)$$
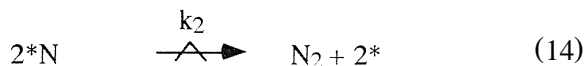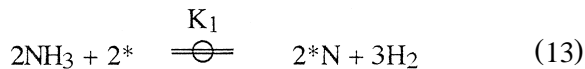
Step (13) is now quasi-equilibrated; it is not an elementary step, but it represents a sum of quasi-equilibrated steps leading to the formation of the *mari* $*N$. Step (14) is far from equilibrium; it is the rds and the rate equation becomes:

$$r = k_2 [L] \frac{K_1 P_{NH_3}^2}{\left(\sqrt{K_1 P_{NH_3}^2} + P_{H_2}^{3/2} \right)^2} \qquad (15)$$

Eq. (15) is formally equivalent to:

$$r = k_{exp} P_{NH_3}^{\alpha} P_{H_2}^{\beta} \qquad (16)$$

From experimental data it was found that:

$$r = 2.15 \times 10^{29} \exp\left(\frac{-214\,852}{RT} \right) P_{NH_3}^{\alpha} P_{H_2}^{\beta}$$

molecules g^{-1} s^{-1}. $\qquad (17)$

This data can be compared to the equation given by Löffler and Schmidt [13,14] over plat-

Table 1
Comparison between constant values: $k_1' = k_1[L]$, $k_2' = k_2[L]$ and K

TiN$_x$O$_y$ (880 ≤ T ≤ 940 K) present work	Fe (600 ≤ T ≤ 1250 K) [13,14]
P_{NH_3} = 4 to 23 Torr	P_{NH_3} = 0.05 to 1 Torr
$K = 1.58 \times 10^{-10} \exp(145\,464/RT)$	$K = 6.70 \times 10^{-9} \exp(145\,464/RT)$
$k_1' = 1.89 \times 10^{20} \exp(-162\,184/RT)$	$k_1' = 1.05 \times 10^{20} \exp(-41\,800/RT)$
$k_2' = 0.60 \times 10^{30} \exp(-307\,648/RT)^a$	$k_2' = 1.57 \times 10^{28} \exp(-207\,328/RT)^a$

Pressure: in Torr.
Energy: in joules.
[a]Refs. [13,14], $K \equiv k_1/k_2$.

inum which presents a Temkin–Pyzhev type behaviour:

$$r = 1.0 \times 10^{24} \exp\left(\frac{-133\,760}{RT} \right) P_{NH_3} P_{H_2}^{-3/2}$$

(energy in joules)

formally equivalent to Eq. (5):

$$r = k \left\langle \frac{P_{NH_3}^2}{P_{H_2}^3} \right\rangle^{\alpha}$$

As a conclusion, it can be seen that titanium oxynitride clearly shows, in presence of dihydrogen in the reaction feed, a behaviour near from that of platinum. In contrast, at low hydrogen pressure, that is when no dihydrogen is added in the initial feed, it behaves like tungsten or iron. These results are in agreement with the model of Tamaru [10] from which it appears that the adsorption of ammonia—the first step of the preceding 'two-step sequences'—can be near or far from equilibrium. The *mari*—∗N—remains the same in both cases.

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