RECENT PROGRESS IN ELUCIDATING THE MECHANISM OF HETEROGENEOUS
CATALYSIS

Kenzi Tamaru

Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku,
Tokyo, Japan

Abstract — The mechanism of the decomposition of ammonia on a
tungsten surface and the Fischer-Tropsch synthesis over a Ru
catalyst have been elucidated by following the full dynamic
behavior of each of the adsorbed species under working condi-
tions. In both cases the properties of the catalyst surfaces
in their working state are remarkably different from those of
the clean surfaces. The importance of such dynamic approach
under working conditions has been emphasized for elucidating
the mechanism of heterogeneous catalysis.

INTRODUCTION

The mechanisms of reactions in heterogeneous catalysis have been studied in
various manners by means of many kinds of instruments and techniques. Since
in heterogeneous catalysis the reaction system consists of reactants and
catalyst, one of the approaches to the study of mechanism has been the use of
well-characterized catalysts. Thus, surfaces with known density of steps or
kinks on the surface or with characteristic electronic structures have been
investigated. Another approach has been the study of the characteristic
behavior of reactants with time. Thus, the kinetics of the overall reaction
have been examined under various reaction conditions by following the changes
in the concentrations of reactants and products with time. The results have
been interpreted on the basis of assumptions, most commonly, those of the
Langmuir-Hinshelwood mechanism or the Eley-Rideal mechanism. Labelled com-
pounds have also been employed to obtain deeper insights into catalytic reac-
tions. Chemisorption of each of the reactants and products have also been
studied.

In all these approaches the catalyst is treated as existing in a "black-box"
of which only the entrance and the exit are studied. Because the insides of
the "black-box" are not looked at, that is, the catalyst is not examined in
its working state, many controversial fundamental problems have remained
unsolved.

Under the reaction conditions, some of the reactants, products, intermediates
or other species are usually adsorbed on the catalyst surface, and the
properties of the catalyst surface sites are considerably influenced by the
presence of such adsorbed species. The heat of adsorption and the electron
accepting or donating properties or work function of the surface, for example,
are generally affected by both the nature and amount of the adsorbed species.
In some cases, such as catalysis by alloys, the composition of the catalyst
at the surface is not only different from that of the bulk, but also altered
by the chemisorption as the Auger techniques has revealed in many cases.

The extent of adsorption on a catalyst surface during the course of reaction
cannot be estimated from separate adsorption measurements for each of the
reactants and products. The nature and extent of adsorption in the working
state is not only dependent upon the interactions among the surface species
such as the formation of surface complexes, but also upon the position of the
rate-determining step, because this largely determines the chemical potential
of the reaction intermediates.

Under these circumstances, one of the most important things to measure in

saturated with nitrogen, NH_3 and ND_3 should decompose at the same rate, as all the hydrogen should be split off to form hydrogen molecules prior to the nitrogen desorption process. Accordingly, the kinetic isotope effect must be explained by some other reaction mechanism, for instance, by assuming that NH(a) saturates the surface. However, the experiments of Frankenburger and Holder make this improbable.

In particular, if a hydrogen containing species such as NH(a) participates in the rate-determining step, and the partial equilibrium between hydrogen and ammonia, such as

$$NH_3 = NH_x(a) + (3-x)/2 \cdot H_2(g)$$
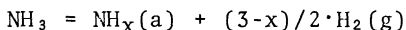
is realized, the rate of the overall reaction should be dependent upon the hydrogen pressure, as in the case of the Temkin-Pyzhev mechanism unless the amount of the $NH_x(a)$ species stays constant under various hydrogen pressures as in the case of saturated adsorption. Thus, even in the case of such a simple catalytic reaction we still had many possibilities to investigate.

Under these circumstances the author measured adsorption by a volumetric method under the reaction conditions using a closed circulating system and a tungsten powder catalyst of large surface area which was carefully reduced by hydrogen (11). Recently similar experiments were repeated in more detail employing a tungsten foil and a single crystal surface, the cleanliness of their surfaces being constantly checked by Auger electron spectroscopy. The amount of chemisorption was also studied by flash-desorption as well as the Auger techniques and both previous and new results, under higher and lower pressures of ammonia, respectively, resulted in similar conclusions as to the reaction mechanism.

At the reaction temperatures the adsorption of nitrogen from gaseous ammonia, releasing all the hydrogen, took place rapidly at first, and then slowed down to approach its saturation value, whereas nitrogen desorption took place slowly at first and then more rapidly till finally reaching its steady rate. $\theta_N=1$ was defined as the nitrogen coverage where one N-atom is allotted to every surface tungsten atom. Almost all the hydrogen atoms desorbed at the moment of ammonia adsorption, no appreciable amount of hydrogen being left adsorbed on the surface above 600°C.

The rate of nitrogen uptake from ammonia onto the surface, V_{in}, and the rate of nitrogen desorption from the surface to form nitrogen, V_{out}, are expressed as the number of N-atoms which get onto or come off from the surface per second per surface tungsten atoms. (Fig. 1)
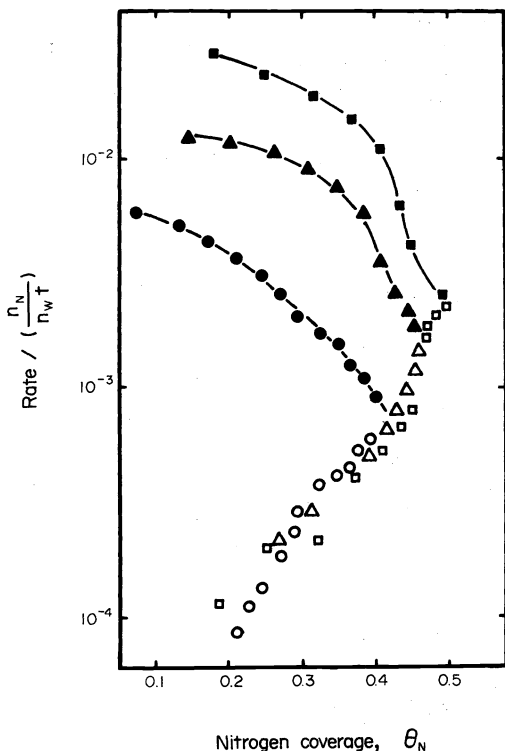

Fig. 1. Rates of NH_3 uptake and N_2 desorption plotted against nitrogen coverage on W.
$T = 1073$ K, P_{NH_3},
$(\bullet, O)$ 1.7×10^{-6} Pa,
$(\blacktriangle, \triangle)$ 5.1×10^{-6} Pa,
$(\blacksquare, \square)$ 9.8×10^{-6} Pa.

$(\bullet, \blacktriangle, \blacksquare)$ $V_{IN} = -\dfrac{dn_{NH_3(g)}}{n_W dt}$

$= \dfrac{dn_{N(a)}}{n_W dt} + V_{OUT}$

$(O, \triangle, \square)$ $V_{OUT} = \dfrac{2 \dfrac{dn_{N_2(g)}}{n_W dt}}{}$

The rate of consumption of ammonia (V_{in}) decreases considerably with increase in nitrogen coverage, and, with the same nitrogen coverage, V_{in} increases in proportion to ammonia pressure. On the other hand, the rate of production of molecular nitrogen (V_{out}) mainly depends upon nitrogen uptake and increases markedly with increasing nitrogen uptake. The intersection of the two curves gives the balancing point between the supply and consumption of surface nitrogen, where a steady-state of the overall reaction is realized, nitrogen coverage staying unchanged with time.

The rate of ammonia decomposition measured by nitrogen production and the amount of nitrogen atoms adsorbed on the surface during the course of the reaction were studied. As to the adsorption of hydrogen-containing species, the flash desorption experiments indicate that above 600°C virtually no hydrogen atoms stay on the surface in any form in the steady-state of the reaction. It was also demonstrated that no changes in the rate of nitrogen production and also in nitrogen uptake took place on addition of hydrogen.

The amount of adsorbed nitrogen is markedly more than that of adsorption equilibrium with ambient nitrogen gas (where $\theta_N=0.5$ corresponds to its saturation), which demonstrates that the nitrogen desorption process is a rate-determining step.

When the ammonia pressure becomes higher, nitrogen uptake during the reaction increases markedly so that nitrogen atoms penetrate into the bulk of the tungsten and form multilayers of surface nitride.

As has been shown, the mechanism of the decomposition of ammonia on tungsten was studied by measuring the rate of the overall reaction and the dynamic behaviors of the adsorbed nitrogen during the course of ammonia decomposition using a clean tungsten surface. The results demonstrated that the reaction proceeds through the mechanism of "dynamic balance" between two consecutive rate-determining steps; the supply of surface nitrogen atoms from ammonia and its consumption by formation of nitrogen molecules. The amount of nitrogen uptake during the reaction is determined by this "dynamic balance". In this sense the nitrogen adsorbed in the working condition is not in equilibrium with ammonia and hydrogen as in the case of the Temkin-Pyzhev mechanism, and this is the reason why ambient hydrogen does not influence the nitrogen uptake and also the rate of the overall reaction.

When we introduced ND_3 instead of NH_3, the amount of nitrogen uptake in the steady-state of the reaction was less than that for NH_3 as is shown in Fig. 2.
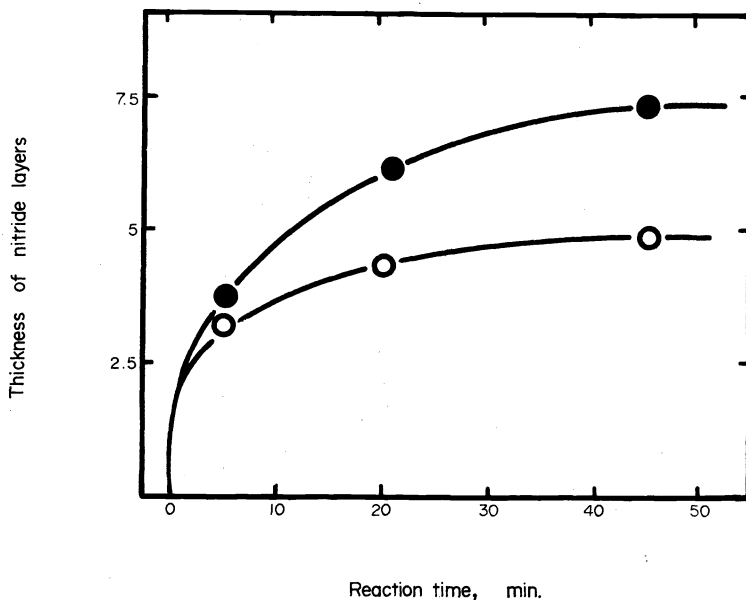

Reaction time, min.

Fig. 2. Thickness of nitride layers formed during NH_3 and ND_3
         decomposition on W.
P_{NH_3,ND_3} = 28 Pa, T = 1023 K.   ● : NH_3,   ○ : ND_3 (99%D).

order to elucidate the mechanism of a heterogeneous reaction are the proper-
ties of the catalyst surface in the working state. The amount of adsorption
and the nature and structure of each of the surface species under the reac-
tion conditions should be examined and the rate of reaction of each should be
compared with the rate of the overall reaction. The full dynamic behavior of
each of the species should be followed under working conditions. Even if
some surface species in its working state is observed, it does not follow
that it is a reaction intermediate through which the overall reaction pro-
ceeds, neither is the most abundant adsorbed species necessarily associated
with the reaction intermediate. The behavior of each adsorbed species under
the reaction conditions should be used to determine the reaction mechanism.
Non-stationary state treatments may also be effectively applied for this
purpose. Such a dynamic treatment of the surface species which we initiated
some years ago is the effective approach which leads to the elucidation of
the real reaction mechanism in terms of reaction path (1).

The behavior of adsorbed species on the catalyst surface at reaction condi-
tions may be studied in various manners: volumetric methods may be employed
to estimate adsorption from a material balance and the behavior as well as
the amount of the adsorbed species under reaction conditions may be examined.
The spectrophotometric techniques such as infrared techniques and the elec-
tron spectroscopic methods are also effectively applied not only to identify
the adsorbed species, but also to follow their dynamic behavior under reac-
tion conditions.

Isotope techniques are also applicable with both volumetric and infrared
methods. In the steady-state of the reaction the reactants may be replaced
by their labelled compounds and the behavior of each of the adsorbed (label-
led) species and, also, the products may be followed in time, thus elucidat-
ing the dynamic behavior of each adsorbed species as well as the reaction
path of overall reaction. In the steady-state of the reaction one of the
reactants may be quickly removed from the ambient gas and the dynamic behav-
ior of each of the adsorbed species as well as the ambient gas may be followed
with time.

In such a manner we have successfully elucidated the mechanisms of many kinds
of catalytic reactions, for instance, the decomposition of formic acid or
alcohol on alumina and zinc oxide (2), the hydrogenation of olefins (3), the
water gas shift reaction (4) and the H_2-D_2 exchange reaction over zinc oxide
(5) and so forth (6).

In this report some results which we have obtained recently are explained;
namely about the decomposition of ammonia over a tungsten surface as an
example of a fundamental catalytic reaction and also about the Fischer-
Tropsch synthesis over a Ru catalyst as an example of a more complex reaction.
In both cases the properties of the catalyst surfaces in their working state
are remarkably different from those of the clean surfaces.

DECOMPOSITION OF AMMONIA ON TUNGSTEN SURFACES

The decomposition of ammonia on tungsten has been widely studied by many
investigators as one of the most fundamental catalytic reactions. Hinshelwood
and Burk (7) reported that the reaction is zero order, the rate being inde-
pendent of the pressures of ammonia, hydrogen and nitrogen. The overall reac-
tion does not exactly obey the zero order kinetics, but the initial rate of
the reaction, at least, seems to be independent of ammonia pressures.

The zero order kinetics may be interpreted as indicating that the catalyst
sites are saturated with ammonia molecules. However, Frankenburger and
Holder (8) found that when ammonia was brought into contact with a tungsten
surface, hydrogen formation took place even at 150°C. At 250°C, more than
one molecule of hydrogen desorbed per adsorbed ammonia molecule, but no
nitrogen molecules were formed.

Accordingly, at the usual reaction temperatures of more than 600°C, it is
improbable that the surface is saturated by adsorbed molecular ammonia. It
is more plausible to assume that the catalyst surface is fully covered by
chemisorbed nitrogen, its desorption being the rate-determining step.

It is of interest to mention that Jungers and Taylor (9), and Barrer (10)
studied the kinetic isotope effect in ammonia decomposition by than ND_3. If
the rate-determining step is the desorption of nitrogen from a surface

The kinetic isotope effect in the decomposition of NH_3 and ND_3 is accordingly reasonably explained by the reaction mechanism. The kinetic isotope effect comes from the different rates of supply of adsorbed nitrogen from NH_3 and ND_3. NH_3 and ND_3 give different amounts of nitrogen adsorbed in the steady-state of the decomposition. It is interesting to note that in this case practically no hydrogen is being adsorbed on the catalyst surface during the course of the reaction and the hydrogen pressure does not influence either the rate of the reaction or the nitrogen uptake in its working state but nevertheless, an isotope effect arises. As has been demonstrated, it is a kinetic, and not a thermodynamic, isotope effect (12).

As I explained so far under these circumstances it should be obvious that the properties of the surface should be studied in the working state of the catalyst. The study of chemisorption of each of the reactants in many cases has little to do with the elucidation of the mechanism of catalytic reactions.

FISCHER-TROPSCH SYNTHESIS OVER A Ru/SiO_2 CATALYST

It is generally accepted that Ru/SiO_2 is a good catalyst for synthesizing straight-chain hydrocarbons from CO and H_2 (13). During the course of the reaction at 150°C at CO and H_2 pressures of one atmosphere or less, it has been demonstrated by infrared spectroscopy (14) and volumetric measurements that the greater part of the Ru surface is covered by chemisorbed CO in addition to a small number of hydrocarbon species.

The hydrocarbon chains grow with time their amount being estimated by volumetric and infrared adsorption measurements, while their average chain length is estimated by the infrared adsorption ratio of $CH_3(a)$ and $CH_2(a)$ of the hydrocarbon species. Since the band position for methyl and methylene groups of the adsorbed hydrocarbons are exactly identical to those observed in liquid aliphatic hydrocarbons, linear growth of the hydrocarbon chain species is also indicated.

Although the hydrocarbon chain grows up to a length of 30 carbon atoms at 150°C, the strong infrared absorption due to the adsorbed CO does not change much, which indicates that the hydrocarbon grows on a limited part of the Ru surface the greater part of which remains occupied by adsorbed CO. On the basis of the total amount of hydrocarbons on the catalyst surface and the estimated chain length, the number of hydrocarbon chains on the Ru surface may be calculated. The number actually corresponds to adsorption on a small percentage of the metal surface.

When the Ru catalyst with such adsorbed species is treated by hydrogen at 150°C, the hydrocarbon species are hydrogenated to form mainly methane, following a first order decrease in adsorbed hydrocarbon amount and thus exhibiting uniform reactivity for hydrogen. The hydrogenation of adsorbed hydrocarbons occurs much more readily than the hydrogenation of adsorbed CO.

When the Ru catalyst with such adsorbed species is evacuated at 150°C, it is interesting to note that shortening of hydrocarbon chains occurs readily. The evacuated gas consisted of a large quantity of CO as expected, but in addition there was a substantial amount of H_2. Furthermore, no hydrocarbons were detected. This pointed to the occurrence of rapid dehydrogenation with concomitant formation of surface carbide on that part of the surface previously occupied by CO.

These findings demonstrate that in the absence of gaseous CO the activation of hydrogen or other reactions such as carburization and hydrogenation occur readily. These processes occur on the Ru sites free of adsorbed CO. In stark contrast to this, in the presence of CO the activation of hydrogen or other reactions are markedly inhibited by adsorbed CO and only a limited part of the surface can contribute to the surface reaction. The overall rate of the the Fischer-Tropsch synthesis is negative order as to the pressure of CO, which also indicates inhibition by adsorbed CO.

A typical example which shows the marked effect of adsorbed CO is the following: If a mixture of D_2 and paraffin is passed over the Ru catalyst at 150°C, almost all the paraffin is converted to methane at a very fast rate. However, if we employ the mixture in the presence of CO at the same temperature, no methane is formed and indeed not even exchange between D_2 and paraffin hydrogen takes place. The mixture of D_2 and paraffin simply appears unchanged at the exit of the reactor. From this it is evident that the presence of CO actually has great influence on the behavior of the catalyst surface and,

consequently, all the information about the catalyst surface in the absence
of CO will have very little to do with the elucidation of the mechanism of
the Fischer-Tropsch synthesis. What are always most important are the proper-
ties of the catalyst surface in the working state.

Kinetic and isotopic studies using ^{13}C with a larger amount of Ru catalyst
revealed that some part of the adsorbed hydrocarbon species is a reaction
intermediate for the Fischer-Tropsch synthesis. After the accumulation of
^{13}C hydrocarbon species by $^{13}CO + H_2$ reaction at 150°C, $^{12}CO + H_2$ gas was
substituted for the $^{13}CO + H_2$ gas. A rapid exchange reaction between adsorb-
ed CO and gaseous CO occurred, but ^{13}C content in the initial hydrocarbon
products could be well extrapolated to 100%, which demonstrates that the reac-
tion products come from the adsorbed hydrocarbon species. When ^{13}C was
deposited over the catalyst surface by means of the reaction: $^{13}CO \longrightarrow$
$^{13}C + ^{13}CO_2$, and $^{12}CO + H_2$ was subsequently introduced, ^{13}C content in the
initial hydrocarbon products could also be well extrapolated to 100%, which
revealed that the hydrocarbon products may be produced from the dissociated
carbon without CO insertion.

On a reduced Ru/SiO$_2$ catalyst three adsorbed CO species were observed by
infrared spectroscopy at room temperature. The main band at about 2050 cm^{-1}
is assigned to linear CO(a) (Ru-CO), two weak bands at 2146 cm^{-1} and 2085 cm^{-1}
(sh) to twin CO(a) (Ru$<^{CO}_{CO}$)(15) and broad band between 1900 cm^{-1} and 1700 cm^{-1}
to bridge CO(a) (Ru$_2$CO).

The adsorbed twin CO(a) was very weakly held and diminished by evacuation or
hydrogenation even at room temperature. After carbon was deposited by the
reaction, $2CO(g) \longrightarrow C(a) + CO_2(g)$, at above 150°C on reduced Ru/SiO$_2$, IR
measurements of CO adsorbed at room temperature indicates that the amount of
adsorbed twin CO(a) decreased markedly and the amount of adsorbed linear
CO(a) increased. After twin CO(a) disappeared linear CO(a) decreased slowly
and the band shifted to lower frequency by subsequent carbon deposition.

Although the system is complex with, under various conditions, three sorts of
CO bands varying in intensity, these results would suggest that the dissocia-
tion of CO molecules occur at twin CO(a) sites to deposit carbon atoms such
that the Ru atoms at these sites can no longer adsorb two CO molecules at
once.

After the dissociation of CO the dissociated carbon species are hydrogenated
by H$_2$ gas and removed from this site to form mainly methane under mild condi-
tions. Then the adsorbed twin CO(a) reappears as was shown in the adsorption
experiment at room temperature. The same phenomena were observed when the
H$_2$-CO reaction formed hydrocarbon species. After the initial decrease of
twin CO(a) and increase of linear CO(a), linear CO(a) also decreased very
slowly with accompanying accumulation of the hydrocarbon species. These
facts suggest that the dissociation of CO and growth of adsorbed hydrocarbon
species occur more easily on weakly held high frequency CO(a) sites, espe-
cially twin CO(a) sites, than strongly held low frequency CO(a) sites. Such
a conclusion is in agreement with the findings of some workers who have
studied Fischer-Tropsch reaction on supported group VIII metals (16).

CONCLUSIONS

The importance of adsorption measurements during the course of catalytic
reaction has been emphasized and the reactivity of adsorbed species and the
properties of catalyst surfaces in the working state were examined in the
case of the decomposition of ammonia on tungsten surface and the Fischer-
Tropsch synthesis over Ru/SiO$_2$ catalyst.

REFERENCES

1. K. Tamaru, Bull. Chem. Soc. Jpn., 31, 666 (1958); Adv. Catal., 15, 65
   (1964); Dynamic Heterogeneous Catalysis, Academic Press, London (1978).
2. Y. Noto, K. Fukuda, T. Onishi and K. Tamaru, Trans. Faraday Soc., 63,
   2300, 3081 (1967); K. Fukuda, Y. Noto, T. Onishi and K. Tamaru, Trans.
   Faraday Soc., 65, 2215 (1969).
3. S. Naito, Y. Sakurai, H. Shimizu, T. Onishi and K. Tamaru, Bull. Chem.
   Soc. Jpn., 43, 2274 (1970).
4. A. Ueno, T. Yamamoto, T. Onishi and K. Tamaru, Bull. Chem. Soc. Jpn., 42,
   3040 (1969); A. Ueno, T. Onishi and K. Tamaru, Trans. Faraday Soc., 66,
   756 (1970).
5. S. Naito, H. Shimizu, E. Hagiwara, T. Onishi and K. Tamaru, Bull. Chem.

     Soc. Jpn., 43, 974 (1970); Trans. Faraday Soc., 67, 1529 (1971).
 6. A. Ueno, T. Onishi and K. Tamaru, Trans. Faraday Soc., 67, 3585 (1971);
     M. Takagi, T. Kawai, M. Soma, T. Onishi and K. Tamaru, J. Catal., 50,
     441 (1977).
 7. C. N. Hinshelwood and R. E. Burk, J. Chem. Soc., 127, 1105 (1925).
 8. W. Frankenburger and A. Holder, Trans. Faraday Soc., 28, 229 (1932).
 9. J. C. Jungers and H. S. Taylor, J. Am. Chem. Soc., 57, 679 (1935).
10. R. M. Barrer, Trans. Faraday Soc., 32, 490 (1936).
11. K. Tamaru, Trans. Faraday Soc., 57, 1410 (1961).
12. H. Shindo, C. Egawa, T. Onishi and K. Tamaru, Z. Naturforsch., 34a, 96
     (1979).
13. D. L. King, J. Catal., 51, 386 (1978).
14. R. A. Dalla Betta and M. Shelef, J. Catal., 48, 111 (1977); J. G. Ekerdt
     and A. T. Bell, J. Catal., 58, 170 (1979).
15. R. A. Dalla Betta, J. Phys. Chem., 79, 2519 (1979).
16 D. L. King, Symposium on Advances in Fischer-Tropsch Chemistry, Anaheim
     meeting, 482 (1978).