Molecular sensing techniques for the characterization and design of new ammonia catalysts

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Abstract

The N–N stretching frequency of adsorbed dinitrogen on the actual (supported or promoted) Ru catalysts has been shown to be extremely sensitive to the electronic state of the active surface which is usually hard to detect even by XPS. The wavenumber was also a good index of the N_2 activation and ammonia synthesis on these Ru catalysts. Atomically adsorbed hydrogen and its effect on N_2 activation was also observed by FTIR. The addition of alkali promotes N_2 activation on Ru although it causes strong hydrogen poisoning. These various techniques have been discussed with regard to the development of the 'second generation ammonia catalyst'. © 1997 Elsevier Science B.V.

1. Introduction

The authors have devoted long years to the study of ruthenium catalysts for ammonia synthesis [1]. A well developed Ru catalyst has been shown to be more active than iron catalysts [2]. In 1992, the first commercial plant containing a ruthenium catalyst to produce ammonia was established in Canada. Many factors determine the rate of ammonia synthesis on the ruthenium catalyst, however, Ru had yet to be studied in detail compared with the iron catalyst [1].

For the ruthenium catalyst, the activity and the mechanisms are very much influenced by the support and promoter [2]. Thus, the kinetic features differ depending on the different Ru catalysts having different supports and promoters [3].

The mechanism behind ammonia synthesis on Ru has been proposed as follows [1,3]:

$$N_2 + 2*(= N_2(a) + *) \rightarrow 2N(a), \tag{1}$$

$$H_2 + 2* = 2H(a), \tag{2}$$

$$N(a) + 3H(a) = NH_3 + 4*. \tag{3}$$
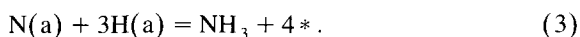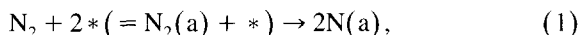
The dissociative adsorption of N_2 (through the short-lived N_2(a)) determines the rate of the synthesis (Eq. (1)), while strongly adsorbed hydrogen (Eq. (2)) blocks the vacant site (*) and retards Eq. (1) under the equilibrium of H_2 and the NH_3 produced. When the retardation index is described as $-z$ for the hydrogen atom and $-2y$ for the nitrogen atom,

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the rate of ammonia synthesis can be described as follows [3]:

$$R = kP_{N_2}\left(P_{NH_3}P_{H_2}^{-1.5}\right)^{-2y}\left(P_{H_2}\right)^{-z},\tag{4}$$

$$= kP_{N_2}P_{H_2}^{3y-z}P_{NH_3}^{-2y}.\tag{5}$$

FTIR techniques have been employed to characterize these mechanisms at the molecular level. Since the rate-determining step is the activation of dinitrogen (Eq. (1)), the nature of the precursor N_2(a) relates to the activity. Also, when the rate is controlled by H(a), it may cause the adsorption properties of N_2. Recently we have successfully observed both N_2(a) and H(a) [4–6].

In this paper, we would like to discuss how molecular sensing techniques used for characterization (especially the FTIR spectra of adsorbed molecules) are important in understanding the nature of the Ru catalyst for ammonia synthesis.

A comprehensive understanding will lead to the design of a better catalyst for ammonia synthesis. 2wt%Ru/Al$_2$O$_3$, 2wt%Ru–Cs$^+$/Al$_2$O$_3$ (Cs/Ru = 8 mol/mol), 2wt%Ru/MgO, and 2wt%Ru–Cs$^+$/MgO (Cs/Ru = 0.1 and 1 mol/mol) were used as model catalysts in this work.

2. Experimental

γ-Al$_2$O$_3$ (184 m^2/g) and MgO (90 m^2/g) were calcinated in air at 773 K for 5 h and then impregnated with Ru$_3$(CO)$_{12}$ in the stirred tetrahydrofuran solution at room temperature for 4 h. The solvent was evaporated at room temperature. Then, the samples were heated at 673 K under vacuum (ca. 10^{-6} Torr; 1 Torr = 133 Pa) for 2 h.

Cesium promoted samples were obtained by impregnating the prepared supported Ru catalysts with the CsNO$_3$ aqueous solution at ambient temperature for 4 h and drying at 373 K in air.

The dried samples were pressed to infrared disks (20 mm diameter, 20–50 mg), and then mounted in the center of the infrared cell with NaCl windows. The samples were heated under vacuum at the desired pretreatment temperatures and then treated with circulated He (200 Torr) with a liquid nitrogen trap for 12 h. The cesium nitrate in the samples was decomposed under H$_2$ atmosphere. The samples were

then evacuated at the same temperature for 1–2 h to remove the hydrogen. After pretreatment, the sample temperature was quickly controlled before measurement.

The spectra were taken by an FTIR spectrometer (Japan Spectroscopic, Model FT/IR5300) which was equipped with a triglycine sulphate (TGS) detector. The spectrometer was placed on a movable table to position the infrared beam to the center of the sample.

Commercial grade N_2, H_2, and He were purified through a reduced active copper catalyst (473 K) connected to a liquid nitrogen trap. One gram of the catalyst was used to measure the rate of ammonia synthesis in the flow system at 588 K under atmospheric pressure of $N_2 + 3H_2$. The catalysts were reduced with hydrogen at 623 K before use for ammonia synthesis.

3. Results and discussion

3.1. Rate of ammonia synthesis and wavenumber of adsorbed dinitrogen on 2 wt% Ru catalysts

The rate of ammonia synthesis on the catalysts was measured at 588 K under $N_2 + 3H_2 = 101$ kPa and shown in Fig. 1. The activities of the Ru catalysts range in the order of the basicity of their supports or promoters with supports as follows: Al$_2$O$_3$ < MgO < Cs$^+$/Al$_2$O$_3$ (Cs/Ru = 8 mol/mol) < Cs$^+$/MgO (Cs/Ru = 0.1 mol/mol) < Cs$^+$/MgO (Cs/Ru = 1.0 mol/mol).

On the other hand, FTIR measurements of N_2(a) were carried out and it was found that when 50 Torr of N_2 was introduced onto the five Ru catalysts, sharp peaks attributed to the adsorbed dinitrogen could be observed. The wavenumbers are shown in Fig. 1. The peaks for Ru/MgO and Ru–Cs$^+$/MgO (Cs/Ru = 0.1 mol/mol) had shoulders at higher frequencies, which are also shown in the figure (two points are shown for each sample). The wavenumbers of the N–N stretching frequencies are all lower than that of the free molecule (2331 cm^{-1}). This means that the N_2 molecule is activated (N–N stretching is loosened) on the Ru metal surface. The extent of the looseness (wavenumber shift from that of the free molecule) ranges in the order of basicity
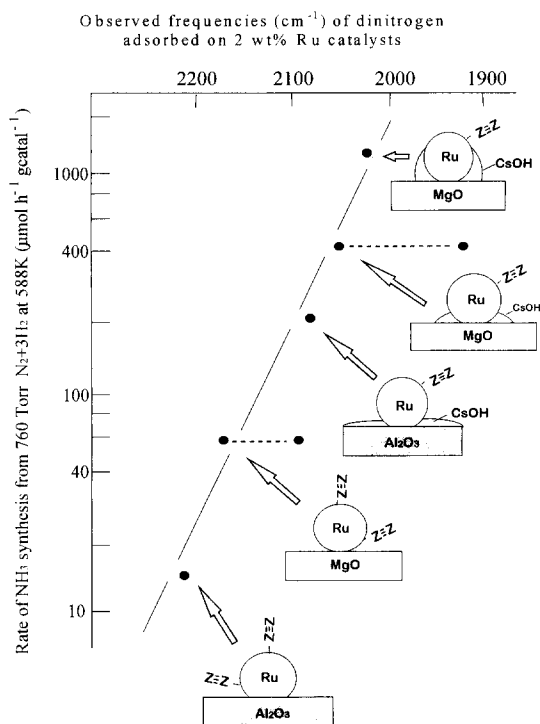
Fig. 1. Rate of ammonia synthesis on 5 Ru catalysts under $N_2 + 3H_2 = 101$ kPa and at 588 K and the observed frequency of adsorbed dinitrogen on the same catalysts at 298 K.

(or the electron donation property) of the support (or the promoter–support combination).

The rate-determining step of ammonia synthesis is the dissociation of dinitrogen on the ruthenium surface (the same as on the iron surface). If the first interaction between N_2 and Ru atom is the end-on type adsorbed state, Ru metals with a high electron concentration can donate more electrons back to the anti-bonding state of dinitrogen to weaken the N–N bond. Such a Ru surface thus must be more active for ammonia synthesis. Adsorbed dinitrogen should not be observed by FTIR at a reaction temperature of 588 K because of the low concentration, it must be the short lived intermediate. Thus, the FTIR spectra of adsorbed dinitrogen were shown to be successful to tell the degree of electron-donation from the support and/or the promoter and can be a measure of the catalyst activity. Here the effects of hydrogen and ammonia were covered because no kinetic measurement was done, which will be shown in the next section.

Table 1
Kinetic expression of NH_3 synthesis under 101 kPa total pressure over 0.5 g of 3 wt% Ru catalyst at 588 K

Catalyst	Cs/Ru (mol/mol)	Reaction order in		
		N_2	H_2	NH_3
Ru/MgO	0	0.90	−0.33	−0.34
Ru–Cs$^+$/MgO	1.0	0.97	−0.78	−0.28

3.2. Hydrogen inhibition against ammonia synthesis on the Ru surface

The reaction order with respect to ammonia was obtained by changing the total flow rate. The N_2 (or H_2) order was obtained by keeping the H_2 (or N_2) pressure constant and by compensating NH_3 order contributions. The results are shown in Table 1. Contrary to the iron catalyst, the hydrogen orders are negative (see Eqs. (4) and (5)). The typical orders for iron catalysts are 1.0 for nitrogen, 1.5 for hydrogen, and −0.75 for ammonia ($y = 0.375$ and $z = 0$). Cs$^+$ promoted Ru/MgO is more active, but has high negative value of hydrogen order. If we analyze this result in the manner of Eqs. (4) and (5), the nitrogen retardation indexes y are 0.17 and 0.14 and the hydrogen retardation indexes z are 0.84 and 1.20 for Ru/MgO and Ru–Cs$^+$/MgO, respectively. Thus, the nitrogen retardation order is iron > Ru/MgO > Ru–Cs$^+$/MgO and the hydrogen retardation order is iron ≪ Ru/MgO < Ru–Cs$^+$MgO.

Industrially, ammonia must be produced under high pressure because of the equilibrium constraint. The negative order in hydrogen means that the reaction rate is not high enough at high pressure. Hydrogen seems to be more strongly adsorbed on Ru–Cs$^+$/MgO than on Ru/MgO. The rate-determining N_2 activation process is inhibited by the strong adsorption of hydrogen.

67 kPa of H_2 was introduced at 293 K on to the

Table 2
FTIR wavenumber of adsorbed hydrogen on Ru catalysts at 293 K

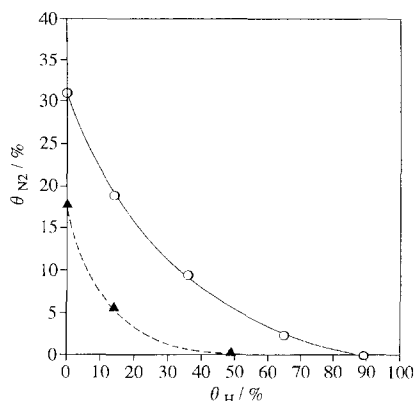| Catalyst	Cs$^+$/Ru (mol/mol)	Wavenumber (cm^{-1})	
		on-top	three-hold
2wt%Rh/MgO	0	1717s	1120m, 933m
2wt%Ru–Cs$^+$/MgO	2.0	1781s	1233m, 940m

Fig. 2. Amount of chemisorbed dinitrogen as a function of preadsorbed hydrogen atoms on Ru/MgO (solid line) and on Ru–Cs$^+$/MgO (dotted line). Both are identified by FTIR and estimated quantitatively by GC. N$_2$ was introduced at 183 K and evacuated at the same temperature for 5 min.

Ru catalysts. The observed wavenumbers are shown and identified as hydrogen atom as in Table 2. Since the wavenumber of Ru–H on Ru–Cs$^+$/MgO is higher than that on Ru/MgO, hydrogen must be strongly adsorbed on the former. This result is in accordance with the above kinetic results.

Adsorbed N$_2$ observable by FTIR was found to be decreased by introducing hydrogen at 183 K. The estimated chemisorbed amount of N$_2$ is shown as a function of the amount of adsorbed hydrogen in Fig. 2.

It is seen that Cs$^+$ promoted Ru/MgO inhibits N$_2$ adsorption more strongly. These FTIR measurement was not done under the reaction temperature, but the results reflect the performance under the reaction.

3.3. Possibilities and problems of the molecular-sensing characterization for new ammonia catalyst design

Modern surface science techniques such as EELS, XPS, TPD, LEED devoted much on the understanding the catalyst surface especially through the single crystal work. Of course these are important, but sometimes it differs much from the real catalyst which is supported and promoted.

The real catalyst can be easily studied by FTIR, EXAFS, and XPS. FTIR seems to be more powerful than the others. The electronic state of Ru surface was once studied by XPS, however, the extents of BE shift were not remarkable [7]. N–N frequencies by FTIR instead showed a remarkable difference in several catalysts here. The N$_2$(a) and H(a) interaction was also observable by FTIR because it can be observed among the gaseous reactants. XPS may give such information but only for the strongly adsorbed species. EXAFS is only effective for a model catalyst with a small size metal cluster.

The relation between a reaction and the active site-nature is called 'the mechanism'. A study to relate the active site-nature and chemical nature of the catalyst may be called 'the surface characterization'. A detailed study of 'the mechanism' only judges the effectiveness of 'the surface characterization'. The ammonia catalyst is now being improved. A meaningful surface characterization should help the design of new catalyst. One of the conclusions to help the design is that alkali promotes N$_2$ activation but suffers from strong hydrogen inhibition.

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