Kinetic Studies of Ammonia Formation over Fe and Mo Containing HZSM-5 Catalysts

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The direct reduction of nitrogen with hydrogen over iron and/or molybdenum containing HZSM-5 catalysts was carried out at different mole ratio of nitrogen and hydrogen. The effect of temperature from 575 K to 773 K was carried out on direct reduction of nitrogen with hydrogen. The loading of Fe and Mo on catalyst was varied from 1 to 10 % in order to explore the effect of the bimetallic combination in the presence of each other on ammonia synthesis. The rate of reduction of bimetallic catalyst with hydrogen in the process of preparation of reduced catalyst was determined. It was observed that the reduction of iron and molybdenum depends on their proportion loaded on H-ZSM-5. The rate of direct reduction of nitrogen over the catalyst by hydrogen has been determined. The results show that the rate of ammonia formation on reduced catalyst depends on the combination of the proportion of Fe and Mo in the catalyst.

Key words:
Kinetic studies, ammonia synthesis, supported catalyst, iron and molybdenum

Introduction

The commercial production of ammonia has been carried out by the Haber-Bosch process.[1] In this ammonia manufacturing process, iron is the main catalytic component;[2] it has strong activity over a long period and it is a low-cost catalyst. The rate of reaction of ammonia formation on catalyst surface depends on the rate of adsorption of nitrogen and hydrogen and their reaction on the catalyst surface, and consequently desorption of ammonia from the catalyst surface. The reaction is strongly influenced by the decreasing reaction rates at high ammonia concentration because of the strong interaction of ammonia with iron.[3] The most abundant intermediates on the catalyst surface are adsorbed nitrogen species. This is the intermediate inhibit the ammonia formation reaction.[4–6]

The sufficient reaction rates can be obtained at elevated temperatures around 650 K to 800 K, which for endothermic reasons requires work at high pressure, i. e. 140 bar.

The solubility of nitrogen and hydrogen in aqueous solution is very low. In order to increase the solubility of nitrogen and hydrogen in aqueous solution, the reaction in the aqueous phase is carried out at high pressure. However, in the gas phase the adsorption of gases increased by carrying reaction of reduction of nitrogen by hydrogen to ammonia at high pressure. With the increase in temperature, the reaction rate of nitrogen reduction increases, however, its solubility at high temperature in aqueous solution decreases. Thus, the rate of nitrogen reduction by hydrogen to ammonia depends on pressure and temperature. However, during the reaction the catalyst plays an important role in enhancing the reaction rate.

The formation of ammonia can be presented as

$$N_2 + 3\ H_2 \Leftrightarrow 2\ NH_3 \qquad (1)$$

It is an exothermic reaction in the presence of the catalyst, $\Delta H_{289\ K} = -45.7$ kJ mol^{-1}. The exact nature of the catalysts useful in the technical operation of the ammonia process has been described.[7–8] The thermodesorption mechanism of ammonia from ruthenium catalyst has been reported.[9] The adsorption behaviour of hydrogen and ammonia has been explored over Ni-doped CeO_2 and Ru/CeO_2 catalysts, respectively.[10] The activation of dinitrogen over alkali-nitrate-promoted caney ruthenium catalyst has been studied.[11] The kinetics of ammonia synthesis over ruthenium-based catalysts has been investigated.[12] The ammonia synthesis with barium-promoted iron-cobalt alloys supported on carbon has been reported.[13]

Thus, several attempts have been made by several investigators to overcome the limitations of ammonia synthesis. Several metals have been explored for the development of the best catalyst for ammonia synthesis at different temperatures and pressures. However, so far attempts at developing a catalyst useful for ammonia synthesis at ambient conditions have been unsuccessful. The major elements used for developing catalysts for ammonia synthesis are Ti, Zr, Ru, Mo, Fe, Ba, Ca, etc. Some other metal catalytic components were also used to promote the ammonia formation reaction. During the synthesis of ammonia, the different supports for Fe, Ru, catalytic component were carbon, MgO, Zeolite, etc. There are several reports on ammonia synthesis using iron and ruthenium catalysts with or without promoters. However, there are few studies using the combination of bimetallic catalysts. The reduction of the bimetallic catalyst in the presence of each other after loading on support is also an important quantity. Therefore, this paper studies the rate of ammonia formation over bimetallic Fe and Mo supported HZSM-5 catalysts at atmospheric pressure and high temperature.

Experimental

Catalyst preparation

An iron chloride solution was prepared by dissolving a certain amount of iron chloride in acetone. An ammonium molybdate solution was prepared in dilute ammonia solution. The other metal salt solutions were prepared in aqueous solution. The supported catalysts were prepared by impregnating metal salt solution on porous solid support by incipient wetness technique. Metal salt solution impregnated in porous solid support was dried on water bath and then in oven at 363 K. The dried porous solid support catalysts were calcined in a muffle furnace at 573 K for preparation of reduced catalyst, and 773 K for preparation of oxide catalyst for 3 h in air at atmospheric pressure. Different atomic ratio's catalysts were prepared by impregnating different amounts of metal solution.

Catalyst characterization

The reduction of supported catalysts was carried out with temperature programmed desorption with hydrogen. The above-prepared catalysts were characterized for their surface area (using surface area analyzer, quantachrome, USA) and XRD pattern.

Reduction of nitrogen by hydrogen

The reduction of nitrogen by hydrogen over the different Fe-Mo supported catalysts was carried out in a quartz reactor ($D_i = 4$ mm $\cdot$ $H = 800$ mm, with at center $D_i = 8$ mm $\cdot$ $H = 100$ mm). Catalyst (m = 0.1 to 0.5 g) was placed at the centre of the reactor between two quartz wool plugs. The reactor was connected to a nitrogen and hydrogen flow setup. The controlled nitrogen and hydrogen flow rates were achieved with differential flow controllers or rotameters. The reduction of nitrogen ($n_{H_2/N_2} = 3 : 1$) using feed flow rate $F = 24.68 \cdot 10^{-7}$ and $F = 7.43 \cdot 10^{-7}$ mol s^{-1} at STP of hydrogen and nitrogen, respectively, was carried out at different temperatures. Ammonia synthesis runs under steady-state conditions at a maximum temperature of 773 K with Fe/H-ZSM-5, Mo/H-ZSM-5 and Fe-Mo/H-ZSM-5 catalysts. The outlet of gaseous mixture is bubbled through dilute hydrochloric acid. The formed ammonia was analyzed by acid base titration. The bubbled nitrogen and hydrogen mixture was used to analyze hydrogen by passing through a hydrogen analyzer in the presence of oxygen flow rate. The hydrogen conversion and ammonia synthesis was estimated with the titration value and hydrogen reading on a hydrogen analyzer.

Catalyst reduction

Catalyst reduction was carried out by hydrogen at different temperatures, i.e. the temperature was increased $\dot{T} = 10$ °C min^{-1}, until it reached the required temperature, and then kept constant until free from chloride. Thus, reduction of all the catalyst with hydrogen was carried out at 773 K. The liberated HCl during the reduction processes was determined with acid-base titration. The kinetics of reduction of catalyst was analyzed.

Result and discussion

The direct reduction of nitrogen by hydrogen over different catalysts was carried out at high temperature and pressure. However, high temperature and pressure increase economics of the process. It is important to explore the catalyst, which will give the result at different temperatures and atmospheric pressure. In view of the above aspect, the bimetallic catalysts of iron and molybdenum supported over HZSM-5 in individual or combined form were developed. The developed supported catalysts were reduced by hydrogen and used for the reduction of nitrogen by hydrogen at different temperatures and atmospheric pressure. The Fe (w = 2.5 %) / Mo (w = 18.8 %) / H-ZSM-5 catalyst was selected for different experimental parameter studies.

Reduction of catalysts

During ammonia synthesis, hydrogen is required in excess concentration in comparison with nitrogen. During this process if metal oxide is used, it is reduced to its metallic state. The reduced metallic catalyst component is used for ammonia synthesis. Thus, either before or during the process, metallic catalyst component is reduced to metallic state. Even in reduced metallic state, ammonia synthesis by reduction of nitrogen with hydrogen at ambient conditions could not take place. Therefore, the direct reduction of nitrogen with hydrogen at high temperature and pressure was carried out. The reduction of metallic component alone or in combination with each other is important in order to study the reduction behaviour of iron and molybdenum during preparation of reduced catalyst. Thus, this study deals with the reduction of the metallic component with hydrogen, and direct reduction of nitrogen with hydrogen.

The results of reduction of mixed metal supported catalysts are shown in Fig. 1. It is observed that the effect of molybdenum content on reduction of bimetallic catalyst containing iron in combination is very important. During the reduction of iron and molybdenum to their metallic state, the liberated hydrochloric acid was measured. In the reduction process, the HCl evolved is more when molybdenum ($w = 0.5$ to 5 %) fraction increases in presence of iron ($w = 5$ %) in combination of bimetallic catalyst. After, $w = 5$ % of Mo and $w = 5$ % Fe, with the increase in w/% of Mo, the evolved HCl is less in comparison with that of $w = 5$ % of each Fe and Mo. In presence of $w = 2.5$ % Fe and $w = 18.8$ % Mo, the evolved HCl is less than that of $w = 5$ % of each Fe and Mo, and $w = 5$ t % and $w = 12$ % Fe and Mo, respectively. These results indicate that the combination of Fe and Mo in % is essential in the reduction process. However, the reduction of iron in absence of Mo is very slow. Thus, the presence of Mo in combination with iron in bimetallic catalyst enhances the reduction rate of iron. The single component molybdenum catalyst, Mo/H-ZSM-5, reduces faster than that of iron catalysts. Table 1 shows the initial rate of reduction of bimetallic Mo + Fe/H-ZSM-5 catalysts, the initial rate of reduction bimetallic catalyst to metallic state is increased with increase in $w = 0.5$ to 5 % of molybdenum. Table 1 indicates the reduction rate of iron and molybdenum in presence of each other, which indicates reduction reaction by hydrogen on iron and molybdenum bimetallic catalyst depends on their proportion, which could accelerate ammonia formation reaction on bimetallic catalyst. Although, Mo ($w = 5$ %) + Fe ($w = 5$ t%)/H-ZSM-5 catalyst is having higher reduction rate among the given catalysts in Figure 1, Mo ($w = 18.8$ %) + Fe ($w = 2.5$ %)/H-ZSM-5 has been used for further investigation in the ammonia formation process.

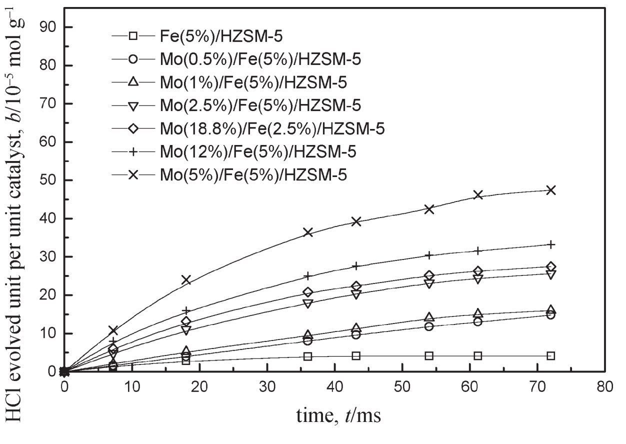

Fig. 1 – *The plot of HCl evolved vs time during the reduction of iron and molybdenum salt to their reduced metallic supported catalysts $T = 773$ K, $H_2 = 7.5 \cdot 10^{-6}$ mol s^{-1}, catalyst amount $m = 0.5$ g*

Table 1 – *Initial rate of evolution of HCl during reduction of Fe and Mo supported HZSM-5 catalyst and their surface area.*

Catalyst	Initial rate of HCl evolution, r/mol g^{-1} s^{-1}	Surface area m^2 g^{-1}
Fe(5 %)/HZSM-5	$1.88 \cdot 10^{-9}$	384.5
Mo(0.5 %) + Fe(5 %)/HZSM-5	$2.22 \cdot 10^{-9}$	375.3
Mo(1.0 %) + Fe(5 %)/HZSM-5	$2.78 \cdot 10^{-9}$	368.4
Mo(2.5 %) + Fe(5 %)/HZSM-5	$6.67 \cdot 10^{-9}$	365.5
Mo(5 %) + Fe(5 %)/HZSM-5	$15.00 \cdot 10^{-9}$	334.8
Mo(12 %) + Fe(5 %)/HZSM-5	$11.11 \cdot 10^{-9}$	303.8
Mo(18.8 %) + Fe(2.5 %)/HZSM-5	$8.33 \cdot 10^{-9}$	251.1

Catalyst characterization

During reduction of metallic catalytic component to their metallic state, the changes in surface area and XRD pattern are studied. The surface area of reduced catalyst was determined (Table 1). It was found that there is variation in the surface of catalyst with the variation of loading of metal ion. The catalyst were characterized for XRD patterns, these presentation is given in Fig. 2. Observed intensity vs 2θ values for the reduced Mo + Fe/H-ZSM-5 catalysts were given in Fig. 2. However, Mo ($w = 18.8$ %) + Fe ($w = 2.5$ %)/H-ZSM-5 catalyst was used for the direct reduction of nitrogen by hydrogen.

Reduction of nitrogen by hydrogen to ammonia

The direct reduction of nitrogen with hydrogen was carried out with hydrogen at different temperatures over reduced catalyst. The formation of ammonia with respect to time was measured. Fig. 3 shows plot of ammonia formation with respect to time at different temperatures 573, 673 and 773 K at constant flow rate of nitrogen and hydrogen with a fixed amount of catalyst Mo (18.8%) + Fe (2.5 %)/H-ZSM-5. The plot of ammonia formation with respect to time is linear.

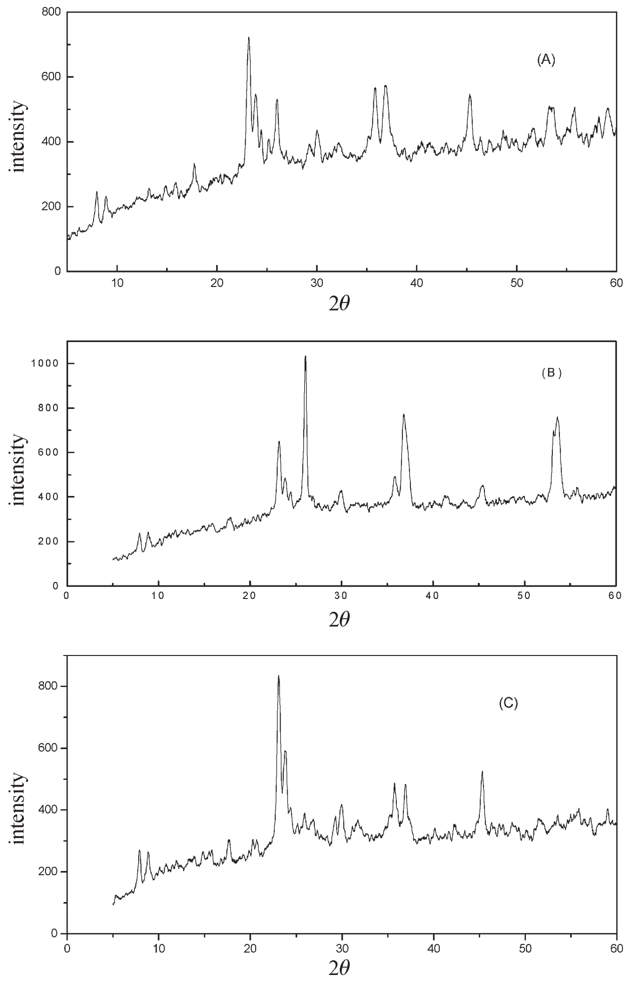

Fig. 2 – *XRD pattern of some supported catalyst*

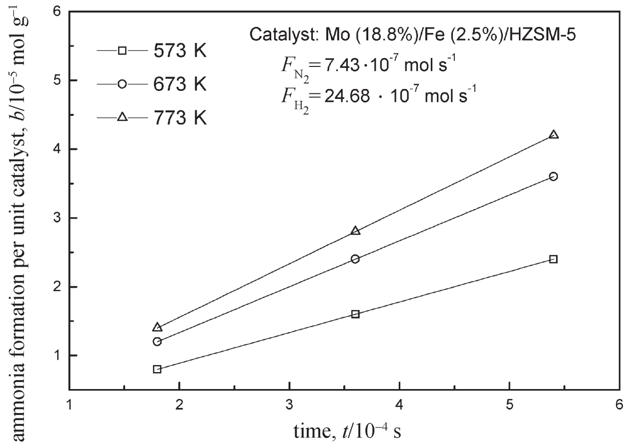

Fig. 3 – *The relation between ammonia formation and time at different temperatures, $F_{H_2} = 24.68 \cdot 10^{-7}$ and $F_{N_2} = 7.43 \cdot 10^{-7}$ mol s^{-1}, Catalyst = Mo (18.8 %) + Fe (2.5 %)/H-ZSM-5*

Effect of temperature

The rate of formation of ammonia was plotted against temperature (Fig. 4). The result shows that the rate of ammonia formation increases with the increase in temperature. Thus, the results indicate that the rate of ammonia formation favours with increases in temperature.

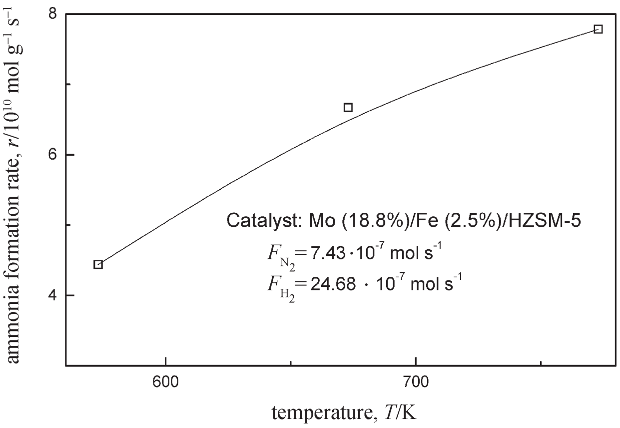

Fig. 4 – *The dependency of rate of ammonia formation at different temperatures. Catalyst = Mo (18.8) + Fe (2.5)/H-ZSM-5, $F_{H_2} = 24.68 \cdot 10^{-7}$ and $F_{N_2} = 7.43 \cdot 10^{-7}$ mol s^{-1}*

Effect of molybdenum loading

The rate of ammonia formation depends on the catalytic component used in the catalyst preparation. Therefore, the catalytic component variation of Mo loading was studied. Fig. 5 shows the plot of the rate of ammonia formation with respect to molybdenum loading. The loading of molybdenum was varied from $w = 0$ to 2.5 wt % in presence of iron ($w = 2.5$ %). The rate of ammonia formation increases with increase in molybdenum loading. Thus, the presence of molybdenum with iron in the catalyst enhances the rate of ammonia formation. The results of the ammonia formation rate (Fig. 5) over these catalysts agree with the rate of reduction of iron and molybdenum catalyst in presence of each other (Fig. 1).

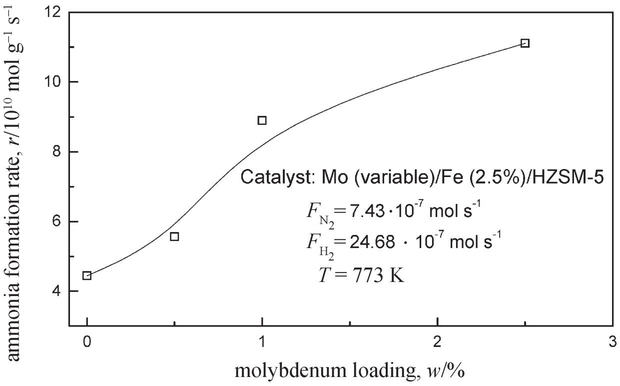

Fig. 5 – *The plot of rate of ammonia formation vs molybdenum loading, Catalyst = Mo (variable) + Fe (2.5)/H-ZSM-5, $T = 773$ K, $F_{H_2} = 24.68 \cdot 10^{-7}$ and $F_{N_2} = 7.43 \cdot 10^{-7}$ mol s^{-1}*

Effect of hydrogen flow rate

During direct reduction of nitrogen by hydrogen in the presence of reduced metallic catalyst was studied by using excess hydrogen, which is required for ammonia synthesis. Therefore, the essential role of hydrogen in ammonia synthesis was investigated. The ammonia formation rate with respect to hydrogen flow rate is plotted in Fig. 6. The results show the ammonia formation rate is enhanced with the increase in hydrogen flow rate in the initial stage, however, after a certain flow rate, it decreases in the studied range (1 to $7.5 \cdot 10^{-6}$ mol s^{-1} at STP).

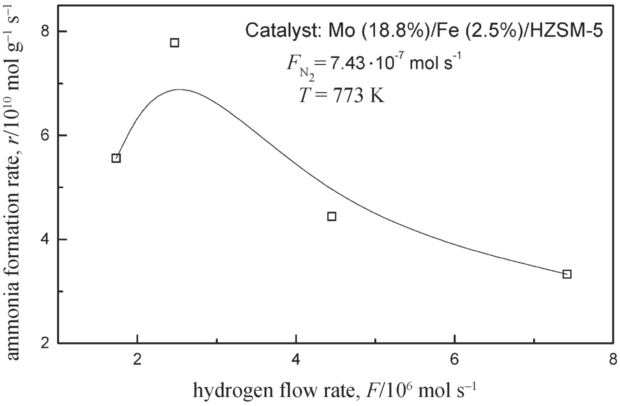

Fig. 6 – *The dependency of rate of ammonia formation on hydrogen mole flow rate, Catalyst = Mo (18.8) + Fe (2.5)/H-ZSM-5, $F_{N_2} = 7.43 \cdot 10^{-7}$ mol s^{-1} and T = 773 K*

Effect of Fe and Mo loading on catalyst

The catalytic component Fe and Mo are essential during ammonia formation by direct reduction of nitrogen by hydrogen. Therefore, variation of Fe and Mo loading over H-ZSM-5 was carried out. The catalysts were used for direct reduction of nitrogen by hydrogen to ammonia. The ammonia formation rate is plotted against the Fe and Mo loading on catalyst in Fig. 7. The result shows that the rate of ammonia formation over catalyst increases with respect to loading of Fe and Mo on catalyst in the studied range 1 to 10 %. The results show the proportion of Fe and Mo is essential in the ammonia formation reaction. The rate of reduction of Fe and Mo catalyst is also dependent on their proportion loaded on the H-ZSM-5 (Fig. 1). The same trend is observed in direct reduction of nitrogen by hydrogen (Fig. 7). Thus, results conclude that ammonia formation over bimetallic Fe and Mo catalysts depend on their loaded proportion.

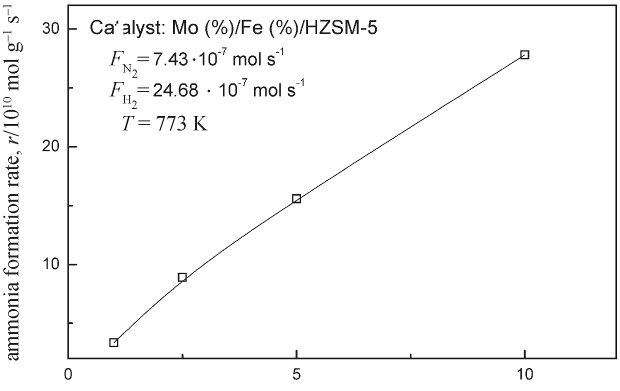

Fig. 7 – *The plot of ammonia formation rate vs loading of Fe and Mo over catalyst, Catalyst = Mo (%) + Fe (%)/H-ZSM-5, $F_{H_2} = 24.68 \cdot 10^{-7}$ and $F_{N_2} = 7.43 \cdot 10^{-7}$ mol s^{-1} and T = 773 K*

Effect of different metal combination with iron

In order to check the combination of bimetallic catalysts for ammonia formation, other than Fe and Mo combination, Cu, Pd and Pt metals were used in combination with Fe or Mo. The metallic catalytic components in the ammonia synthesis were used in reduced form. Noble metals also play an important role in hydrogen adsorption and desorption. Therefore, the effect of Cu, Pd and Pt in presence of Fe or Mo on the ammonia formation was investigated. Table 2 shows the result of bimetallic catalyst for the formation of ammonia. The combinations of Cu, Pt and Pd with molybdenum or iron for ammonia formation catalysts are found to be effective in bimetallic catalyst.

Table 2 – *The formation of ammonia over different catalysts*

Catalyst	Temperature T/K	Rate of NH_3 formation r/mol g^{-1} s^{-1}
Mo(3 %) + Pt(1 %)/HZSM-5	723	$7.58 \cdot 10^{-10}$
Fe(2.5 %) + Pd(0.2 %)/HZSM-5	773	$6.6 \cdot 10^{-10}$
Fe(2.5 %) + Pd(15 %)/HZSM-5	773	$10.0 \cdot 10^{-10}$
Fe(0.87 %) + Cu(3 %)/HZSM-5	773	$4.44 \cdot 10^{-10}$

Conclusions

Direct reduction of nitrogen by hydrogen to ammonia over Fe and Mo containing catalysts has been studied. The result of individual catalyst Fe/H-ZSM-5 and Mo/H-ZSM-5 shows that the combined effect of Fe and Mo for the synthesis of ammonia is promoted with their combination. It is observed that the study of the reduction process is also important to understand ammonia formation. The reduction of bimetallic catalyst combination in their fraction (%) proportion of Fe and Mo in certain accelerates the rate of reduction

The similar behaviour was observed in the direct reduction of nitrogen by hydrogen to ammonia over these bimetallic catalysts.

Nomenclature

b – amount of substance per unit mass of catalyst, mol g^{-1}

D_i – inner diameter, mm

F – mole flow rate, mol s^{-1}

H – height, mm

ΔH – reaction enthalpy, kJ mol^{-1}

m – mass, g

n – mole ratio, n_{H_2}/n_{N_2}

r – reaction rate, mol g^{-1} s^{-1}

t – time, s

T – temperature, K, °C

$\dot{T}$ – rate of temperature change, °C min^{-1}

w – mass fraction, %

θ – Bragg angle, °

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