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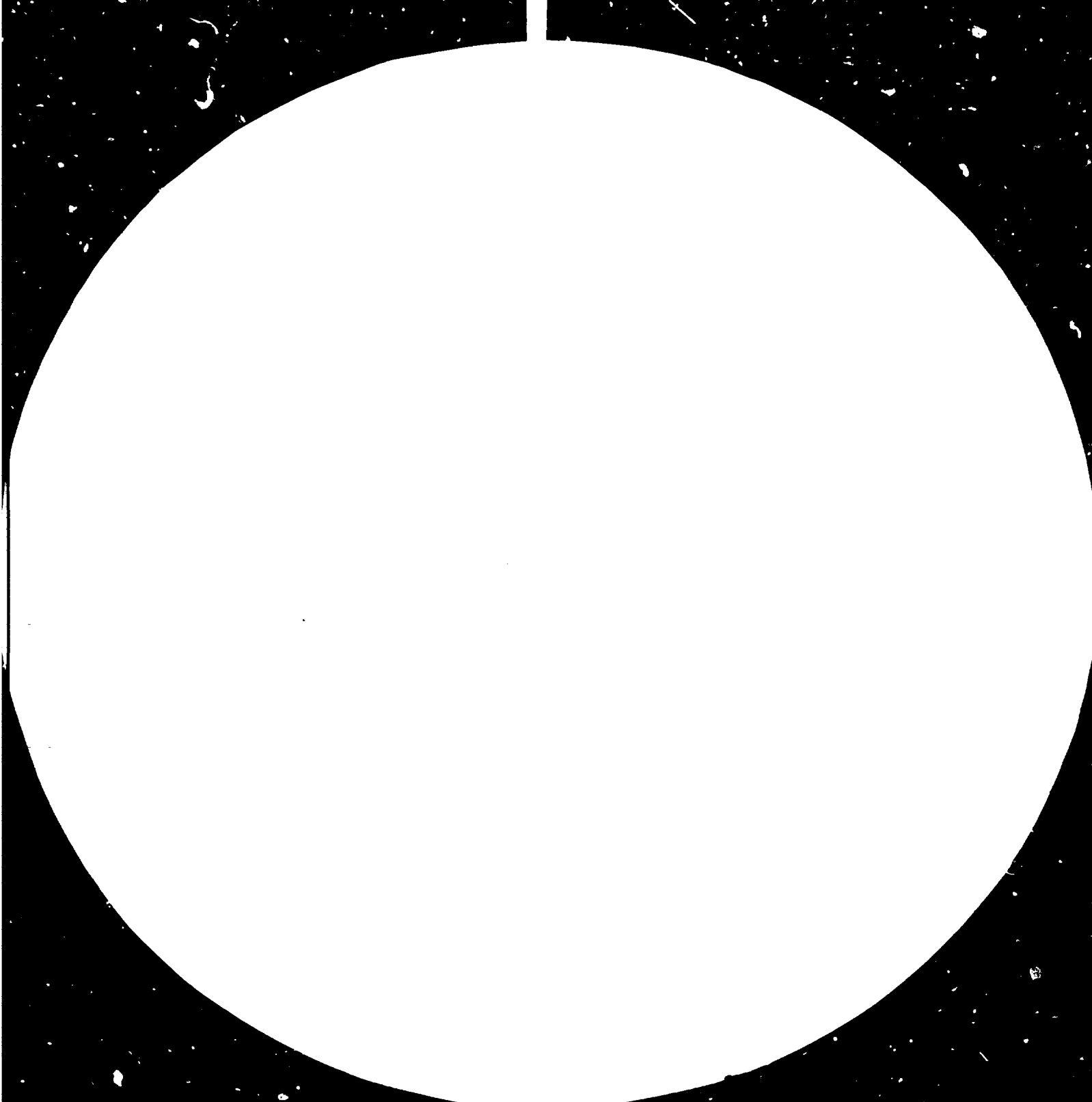
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DEVELOPMENTS IN CATALYSTS FOR WATER-
GAS SHIFT, METHANATION AND AMMONIA
SYNTHESIS IN CHINA*

by

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ABSTRACT

This paper outline the major developments in catalysts for water-gas shift, methanation and ammonia synthesis since 1950's, especially in 1970's. The HT shift catalyst characterized by its low sulphur content is improved on its physical strength in reduced state. The thermostability of LT shift catalyst is increased, and the reduction property of this catalyst has been studied in detail. A novel methanation catalyst having both high activity and high stability has been developed by adding a special promotor and adopting a suitable manufacturing method. In the research of ammonia synthesis catalyst, the catalyst activity at low temperature has been increased successfully and the cause of this has been discussed on the basis of fundamental research data.

Along with progress of ammonia production and catalytic technique, the catalysts used in ammonia plants were developed continuously toward the direction of more variety, high efficiency and longevity for the last seventy years.⁽¹⁻⁴⁾ So far, ten categories or more of catalysts have been considered to be available for water-gas shift, methanation and ammonia synthesis (See Table 1).

Table 1. Main varieties of water-gas shift, methanation and ammonia synthesis catalysts

Shift catalyst:	Iron-chromium, Iron-molybdenum and cobalt-molybdenum systems, etc; Copper-zinc, copper-zinc-chromium and copper-zinc-aluminium systems, etc.
Methanation catalyst :	High and low nickel content types, pre-reduction type.
Ammonia synthesis catalyst :	Low temperature, medium temperature, heat resistance and pre-reduction types.

In our country, iron-chromium high temperature shift catalyst and iron-based ammonia synthesis catalyst have been produced since 1950's, and the copper-based low temperature shift catalyst and nickel-based methanation catalyst were developed in 1960's. Along with further

improvements of these catalysts sulphur resistance shift catalysts were developed in 1970's. The industrial applications manifest that these catalysts can satisfactorily meet the requirement of ammonia plants.

1. HT Shift Catalyst

The HT shift catalysts produced originally and used widely in our country were B104, B106 and B109 (See Table 2).

Table 2. Components and adaptable temperatures and pressures of B104, B106 and B109

Catalyst	Component	Adaptable Temp.(°C)	Adaptable Pressure
B104	Fe ₂ O ₃ Cr ₂ O ₃ MgO K ₂ O CaO SiO ₂ etc.	380-520	Atmospheric Pressure
B106	Fe ₂ O ₃ Cr ₂ O ₃ K ₂ O MgO CaO etc.	360-460	Atm. pressure or under Pressure
B109	Fe ₂ O ₃ Cr ₂ O ₃ K ₂ O etc.	320-450	-"-

The sulphur content of these catalysts is generally around 0.1 - 0.4 %. If the requirement of sulphur concentration in inlet gas of the subsequent units is below 1 ppm, the outlet gas from the high temperature converter should be purged about one week. In order to shorten the sulphur releasing time, catalyst B110 was developed in 1970's in our country. Its characteristics

are low sulphur content in its body, $S < 0.06\%$ (by weight); quickness in releasing of sulphur (usually to complete it within 2 days); and good strength in situ (catalyst side crush strength being maintained above 25 kg/cm. before and after reduction). Under normal condition, catalyst life can last more than two years.

The actual condition of sulphur release of catalyst B110 in a large-scale ammonia plant is shown in Figure 1, from which we find that the concentration of H_2S in the outlet gas is reduced to less than 1 ppm within 48 hours.

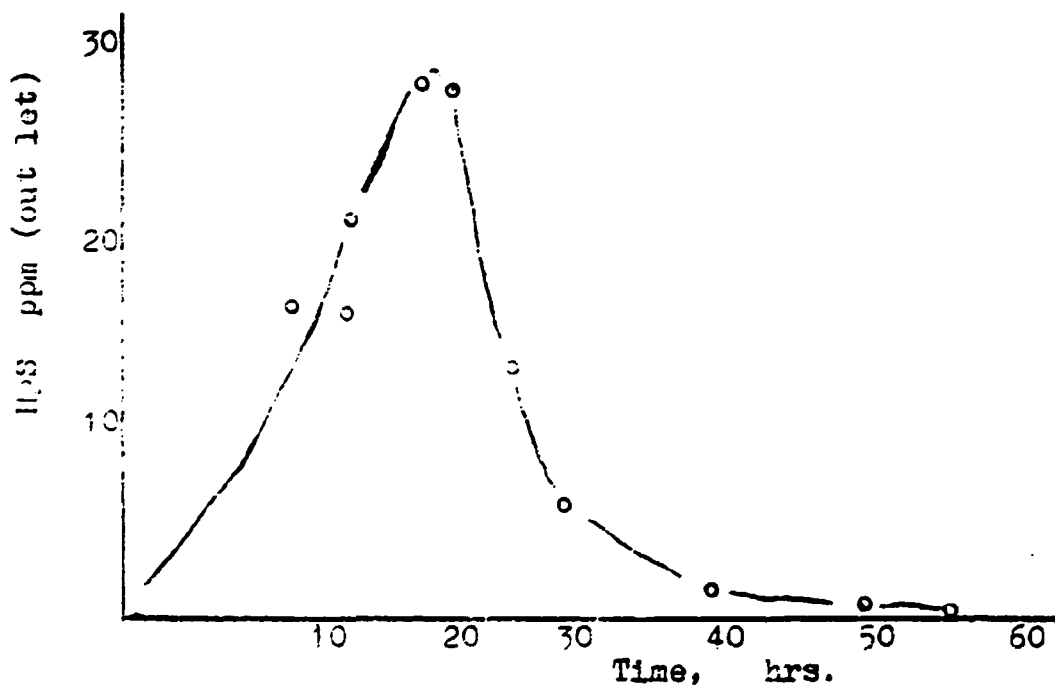


Fig. 1. Curve showing the releasing of sulphur from Catalyst B110 in a large-scale ammonia plant

It is apparent from our experiment that to raise temperature, steam/gas ratio and operating pressure

would shorten the time of sulphur release.

2. LT Shift Catalyst

In our country, catalyst B201 (copper-zinc-chromium system) was developed in 1965 and afterwards catalyst B202 (copper-zinc-aluminium system) was manufactured successfully for the purpose of avoiding chromium poison, expanding raw material source and reducing production cost. Operating data obtained from ammonia plants demonstrate that catalysts B201 and B 202 are good in activity and stability. The lives of both catalysts are usually more than two years. In order to prolong the catalyst life by improving its stability, we got another achievement in preparing catalyst B204 in 1970's with our ten years' experiences. The Chemical compositions of these catalysts are listed in Table 3.

The characteristics of catalyst B204 are as follows:
(1) The crystals of reduced copper are fine and stable (see Table 4); (2) its activity and stability are better than catalysts B201 and B202 and can compete with the same kind of superior catalyst in the international market; (3) it is good in mechanical strength; and (4) the degree of shrinkage of volume is small. According to customer's practice, the predicted life of catalyst B204 may be 3 years or more under normal operating condition.

Table 3. Compositions of LT shift catalysts in industrial production

Catalyst	CuO (%)	ZnO (%)	Cr ₂ O ₃ (%)	Al ₂ O ₃ (%)
B201	39.7	77.5	26.3	
B202	29.7	41.2		8.4
B204	37.3	38.0		8.6

Table 4. Copper crystallite data of LT shift catalyst

Catalyst	Cu crystallite size, Å	
	After Reduction	After heat resistance test
B204	70	80
L ^x	73	102

x Commercial catalyst in the international market.

It is well known that suitable reduction of LT shift catalyst which may give full play to the activity of catalyst is very important. In order to facilitate customers to master the reduction property of catalyst B204, its reduction nature has been studied in our laboratory. The result of investigation is shown in

Figure 2. The investigation indicates that under constant low temperature and low H₂ concentration, the reduction displays three stages - induction period, acceleration period and deceleration period. It also indicates that the lower the temperature and H₂ concentration, the longer the induction period. The rate of reduction is obvious at 150-160°C and is hastened over 200°C, and it is advisable to add hydrogen gradually into inert gas stream to perform reduction at 175-190°C. A good result is obtained from the reduction data by adopting the following relation. This shows that reduction has its self-catalyzed property. Thus, the activation energy of reduction is calculated as 10.2 Kcal/g mol.

$$\frac{d\theta}{dt} = k\theta (1-\theta)$$

where, θ = degree of reduction; t = time,
 k = specific rate constant

In 1960's the development of sulphur resistant cobalt molybdate shift catalyst opened a new way to convert high sulphur content feed gas directly. Since 1970's the operating temperature of this kind of catalyst has extended to a range of 200-475°C without upper limitation of sulphur content. In 1970's, both sulphur resistant iron molybdate and cobalt molybdate shift catalysts were developed in our country.

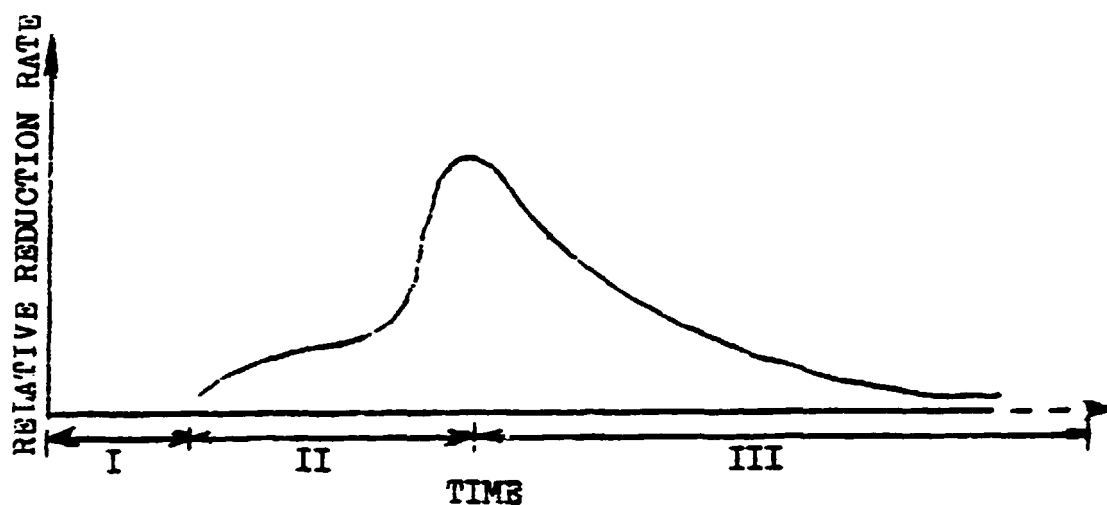


Fig. 2-1 Variation of reduction rate with time
 I - induction period
 II - acceleration period
 III - deceleration period

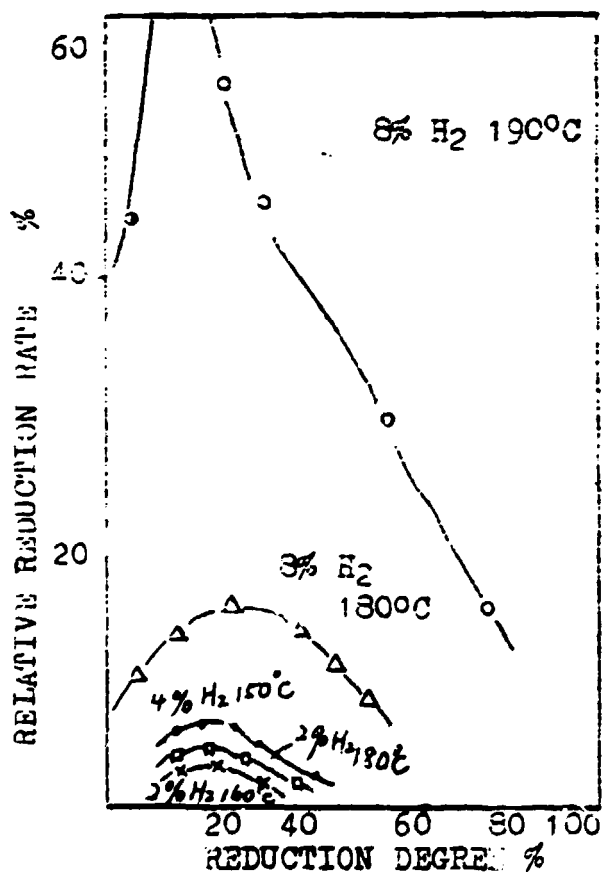


Fig. 2-2 Variation of reduction rate with reduction degree

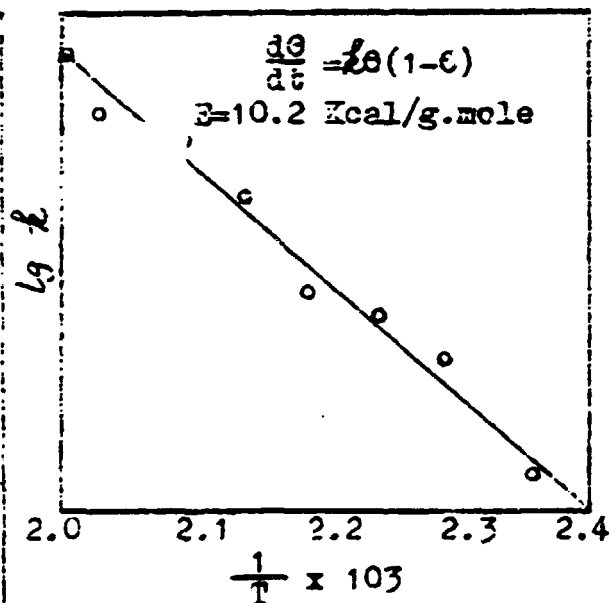


Fig. 2-3 Variation of reduction rate constant with temperature
 θ - reduction degree
 k - specific rate constant
 t - reduction time
 E - activation energy

3. Methanation Catalyst

Methanation catalyst J101, which is widely used in synthesis gas purification process characterized by employing LT shift-methanation, was developed in 1966 in our country. To further improve the catalyst thermostability, catalysts J104 (cement as support) and J105 (Al_2O_3 as support) were produced successfully in the last few years.

J105 is similar to other commercial catalysts in active constituent (Ni) and support, but is a novel methanation catalyst having both high activity and thermostability because of adding a special promotor and adopting a suitable manufacturing method. Table 5 shows its experimental results as compared with other methanation catalysts being used in large scale plants.

Table 5. Comparison of experimental results of methanation catalysts

Catalysts	Q-1	Q-2	R	V	U	J104	J105 x
initial activity							
$\cdot 10^{-4}, x$	7.5	9.0	8.0	6.0	5.2	9.0	9.0
after overheating							
	5.5	7.5	7.4	6.0	5.8	9.0	9.0

$$= SV \cdot 1g \frac{\text{INLET } (CO_2)}{\text{outlet } (CO_2)} \text{ hr}^{-1}$$

An effect on the activity of J105 by pressure and temperature is shown in Figure 3.

x Q-1, Q-2, R, V, U are commercial catalysts in international market.

It is shown by practice in ammonia plants that J105 is rather adaptable to high space velocity, over-heating and carry-over of liquid. Under normal condition, the predicted life of J105 may last more than five years.

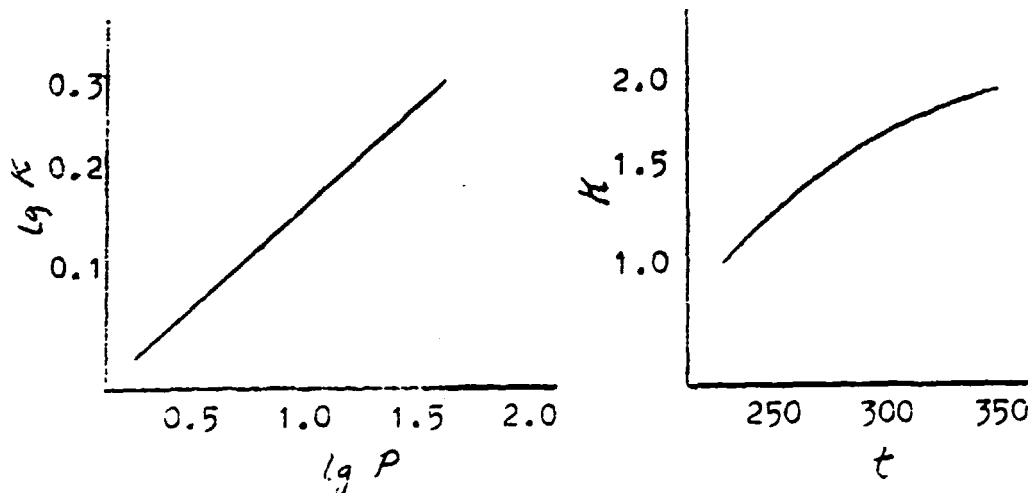


Fig 3. Effect on activity of J105 by pressure and temperature

κ = relative activity;

p = pressure kg/cm^2

t = inlet gas temperature, $^{\circ}\text{C}$.

4. Ammonia synthesis Catalyst

Ammonia synthesis catalyst has been produced in our country since the first period of 1950's. A great amount of catalysts A102, A104, A106, A109 and A110, etc. have been adopted by ammonia synthesis plants and the activities of these catalysts have been improved one after another. At present, the last three have been widely used. In addition, pre-reduced and spherical catalysts are also in production. The dates put into production

of these catalysts are as follows:

Catalysts:	A102	A 104	A106	A109	A110
Time of production:	1953	1956	1958	1971	1977

Table 6 shows the characteristics of main catalysts.

Table 6. Characteristics of main catalysts of our country

Catalysts	Reducing temp. (°C.)			Operating Temp. °C
	Evident	Rapid	max.	
A106	370-385	450-475	525	395-560
A109	330-340	400-430	500-510	380-530
A110	300-350	400	500	360-510
A110-1	300-350	400	500	350-510

Our fundamental research work indicates that with variations in catalyst promoters and their contents, the main phases of oxidized state are identical, but the lattice parameters are different (see Table 7). The larger the deviation of the lattice parameter of the main phase in the catalyst from that of raw magnetite, the better the catalyst activity. This not only signifies the effect of the improvement of promoter distribution on the lattice parameter of magnetite, but also implies that the defective structure in oxidized form might be favourable for raising the energy state of - Fe in reduced form, thus causing the improvement of catalyst activity. Besides these, from Table 7 we can see that A109 and A110 are provided with more FeO

which may be the cause of easy reducing of these two catalysts.

Table 7. Main phase and Its Lattice Parameter Deviation of Series "A" Catalysts in Oxidized Form

Sample	A102	A106	A109	A110
Main phase	Magnetite	Magnetite	Magnetite	Magnetite
Deviation of lattice parameter (Å)	-0.001	+0.004	+0.009	+0.013
Phases in small amounts		FeO Δ^{xx}	α -Fe ₂ O ₃ , FeO $\Delta\Delta$	α -Fe ₂ O ₃ FeO $\Delta\Delta\Delta$

x Lattice parameter deviation = Lattice parameter of main-phase in catalyst - lattice parameter of raw magnetite

xx The more of Δ represents more the quantity.

Table 8 shows some physicochemical data of several catalysts in reduced form. The result of studying A110 indicates that the excellent activity of A110 seems to be in relation to the uniform distribution of potassium which is favourable for the activation of α -Fe.

Table 8. Physico-Chemical Data of Series "A" Catalysts

Catalysts	Bulk density (kg/l)	Surface Area (m ² /g)	Alkali Surface (m ² /g)	Specific pore Volume (ml/g)
A106	2.7-3.0	14	4.6	0.10
A109	2.7-2.9	13	4,7	0.09
A110	2.8	13	5.2	0.13

A110 is a kind of catalyst having high activity at low temperature, good reducibility, ⁽⁵⁾ thermostability and mechanical strength. Its activity at low temperature is superior to other commercial catalysts of the same kind as shown in Fig. 4. As the catalyst body contains 3-5 ppm of water soluble anhydride (calculated as chlorine ion), it completely satisfies the requirement of large-scale ammonia plants.

The investigation of intrinsic kinetics of ammonia synthesis reaction on catalyst A110 was carried out under the operating conditions similar to those of commercial ammonia plants. ⁽⁶⁾ The outcome of the treatment of experimental data through computer proves that the modified expression of Temkin-Pyzhev equation is valid for intrinsic kinetics of ammonia synthesis on A110. To take the value of 0.5 for kinetic parameter is suitable and the activation energy measured is 40-45 Kcal/g mol. It is clear from Figure 4 that A110 has a higher catalytic activity, especially in the lower temperature range, in comparison with other commercial catalysts.

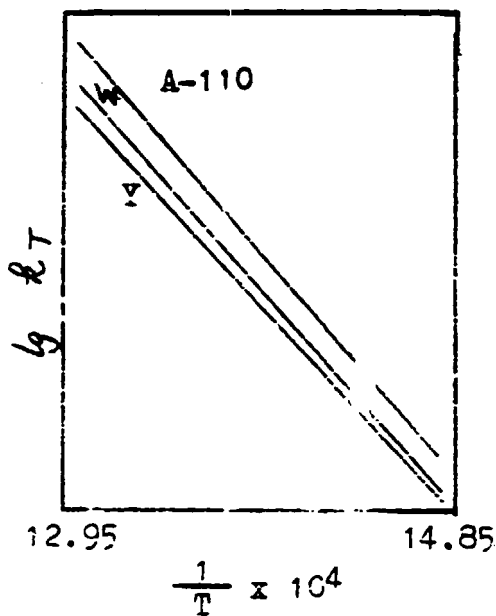


Fig. 4. Variation of reaction rate constant against temperature

T - temperature ($^{\circ}$ K)
 k_T - reaction rate constant at temperature T
W, Y - other commercial catalysts

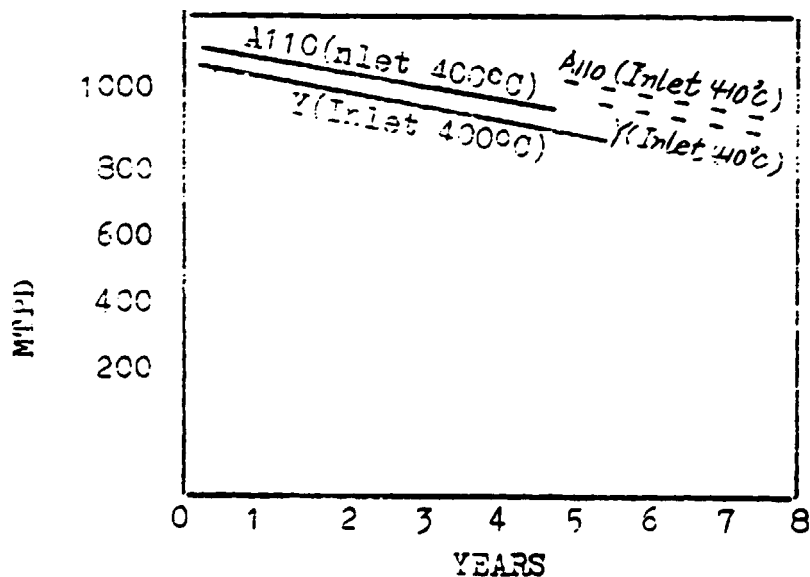


Fig. 5. Catalyst life calculated with computer

Al10 can meet the demand of catalyst life expected by users. From Figure 5, it can be predicted that the life of Al10 may last more than five years under normal operating conditions in the large-scale ammonia plants

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