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Advances in China's refining and petrochemical catalysts

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Abstract

Advances in China's refining and petrochemical catalysts, especially the catalysts that are related and developed by the China Petrochemical Corporation, the largest petrochemical enterprise group in China, are briefly introduced focusing on the catalysts for catalytic cracking, hydroprocessing, reforming, commodity organic chemicals, polyolefins, hydrogen production, etc. Prospects for China's catalytic technologies and catalysts in the field of the refining and petrochemical industries around the turn of the next century are given.

Keywords: China; Refining; Petrochemicals

1. Introduction

The past 10 years have marked a very rapid growth of China's refining and petrochemical industry, which will become one of the pillar industries of the national economy in the near future. China Petrochemical Corporation (SINOPEC) accounted for 87% of total amount of crude oil processed and 85% of total amount of ethylene produced in China. The China Petrochemical Corporation is a colossal enterprise group with dozens of subordinate enterprises and institutions concerned with production, sales, scientific research, design and construction, as well as foreign trade, information, finance, and education, etc. Its operations include 22 giant plants and 13 large plants for oil refining, petrochemical, synthetic fiber and chemical fertilizer production. The rapid growth of China's economy stimulates the demand for petroleum products and petrochemicals. Statistics show that 61 300 million dollars was spent in the period 1986–1994 for importing 47.78 MM t of petroleum products, 28.74 MM t of synthetic resin and plastics, 5.64 MM t of synthetic fibers, 0.95 MM t of synthetic rubber, and 15.67 MM t of 20 commodity quantity organic raw materials. Catalytic technologies and related catalysts for producing the above mentioned imported products are very important. Meanwhile, the crude oil resources in China are limited and the supply of petroleum products falls short of demand. As a whole domestic crude oil tends to be heavy in nature and the crude oil from most of its oil fields is heavy crude containing 6–10 wt% of naphtha boiling below 180°C, 20–24 wt% of middle distillates boiling at 180–350°C, and 40–50 wt% of vacuum residue. The development of corresponding technologies and catalysts is also an important issue for the nation's economy.

Since most of the processes in petroleum refining and petrochemicals are catalytic processes, a key factor in the development of petroleum refining and petrochemical industry is catalytic technology and related catalysts.

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Tremendous efforts have been made on the catalysts and catalytic technologies by petroleum refining and petrochemical companies in the world. SINOPEC, cooperating with the Academy of Sciences and universities, has devoted much effort to the development and commercial applications of new catalysts and catalytic technologies. More than 100 different catalysts have been developed since the foundation of SINOPEC, with a quality and cost of the catalysts competitive with those of foreign companies. Of the total amount of different kinds of catalysts used in China's refining and petrochemical units, more than 80% now used have been developed and produced domestically and some of the catalysts and technologies are exported or licensed to foreign countries. The R&D efforts are mainly focused on catalysts for refining, such as catalytic cracking, hydroprocessing, reforming, etc., the production of commodity organic raw materials and polyolefins, fertilizer production, and hydrogen production. Some of these will be discussed below.

1.1. Catalytic cracking catalysts

The conventional catalytic cracking processes are mainly used for gasoline and LCO production. Since the foundation of SINOPEC, the major challenges facing China's refining industry have been the conversion of vacuum residue and the upgrading of petroleum products. Residue catalytic cracking processes were developed with heat removal in the regenerator, and residue catalytic cracking processes with two-stage regenerators of licensed foreign technological design were also put into operation. A series of residue cracking catalysts based on different types of high silica Y zeolites were developed and manufactured. The first commercialized residue cracking catalyst in China is ZCM-7. The catalyst consists of an ultra-stable Y zeolite with a commercial name of DASY and a semi-synthetic matrix. The selectivity and activity of ZCM-7 well satisfies the requirement of residue cracking units.

In 1988, a catalyst designated as CHZ-1 and based on the SRNY zeolite was commercially produced and tested. For this work, a new approach to the preparation of the high silica Y zeolite, SRNY, was developed on the basis of a study of the hydrothermal chemistry of the [HY + $RE(OH)_3$ + SiO_2] system [1–3]; a rare earth hydroxide and SiO_2 species were deposited on the surface of NaY zeolite, followed by ammonium exchange and hydrothermal calcination. It is believed that the existence of RE species in SRNY plays a role in stabilizing the framework aluminum of zeolite. Hence, the CHZ-1 catalyst based on SRNY zeolite displays high activity, selectivity, and extremely high hydrothermal stability in commercial application. The catalyst also possesses high vanadium tolerance because the SRNY zeolite has a RE species incorporated in a high silica Y zeolite.

The physico-chemical properties of cracking catalysts ZCM-7, CHZ-1, and CRC-1 (a REY based catalyst used for both VGO cracking and residue blended VGO cracking) are listed in Table 1.

In recent years, the catalytic cracking process is increasingly used for olefin production. A series of unique technologies and related catalysts have been developed by SINOPEC, such as DCC (deep catalytic cracking), MGG (maximum gas plus gasoline), and MIO (maximum *iso*-olefins). The success of these technologies lies in creating a new route, other than steam cracking, for selectively producing light olefins

Table 1
The physico-chemical properties of catalytic cracking catalysts

	CRC-1	ZCM-7	CHZ-1
Chemical composition (wt%)			
Al_2O_3	50.0	45.0	40.4
Na_2O	0.1	0.2	0.2
RE_2O_3	2.7	0.9	1.8
Surface area (m^2/g)	225	198	306
Pore volume (ml/g)	0.3	0.3	0.2
Apparent bulk density (g/ml)	0.75	0.60	0.62
Attrition index [a]	3.0	1.6	1.7
MAT (800°C/4 h)	77	64	64

[a] The attrition index is defined and measured by a method developed by SINOPEC.

from heavier feeds at mild temperatures by modifying the conventional FCC process and utilizing new catalysts, and is providing a good basis for integration of refinery with petrochemical plant.

Deep catalytic cracking is a process for the maximal production of gaseous alkenes from vacuum gas oil [4,5]. The process scheme is similar to that of a conventional fluid catalytic cracking unit. The innovation involves certain changes in the proprietary catalyst, the process conditions and the construction of the reactor system. The proprietary catalyst, which is based on a MFI type zeolite ZRP [6], exhibits extremely high activity and stability under severe hydrothermal conditions, as well as good selective cracking activity and low hydrogen transfer activity which maximize alkene production. The highest yields of propylene, *iso*-butene, and *iso*-amylene can reach 23.7, 7.4, and 6.8 wt% (feed basis), respectively. Two operating modes can be effected in the DCC process: the DCC-I mode for maximum propene production and DCC-II mode for maximum *iso*-butylene plus *iso*-amylene production. Both the DCC-I and DCC-II processes have been commercialized successfully.

The development of MGG technology, using AGO blended with vacuum residue as feedstock, and its proprietary catalyst, RMG, is aimed at optimising the yields of light olefins and gasoline and using heavier distillates as feedstocks. The RMG catalyst is a delicately formulated shape selective catalyst with carefully designed porosity and appropriate acidity distribution. With the RMG catalyst, gaseous olefins and high quality gasoline can be produced in rather high yield under mild operating conditions comparing with those of the DCC process. A commercial test was performed in 1993, giving a doubled yield of LPG, while maintaining the same yield of high quality gasoline compared with a conventional FCC process.

For meeting the increasing demand of *iso*-olefins, another innovation of SINOPEC is MIO technology and its related catalyst. The catalyst for the MIO process possesses good shape selectivity and isomerization activity, as well as low hydrogen transfer activity. The results of a commercial test of the MIO technology in 1995 showed that the yield of C_4 and C_5 *iso*-olefins attains a level of 10.3 wt% while the MON of gasoline increases by 2 units compared with the conventional FCC process.

1.2. Hydroprocessing catalysts

The major Chinese crude oils have a low sulfur content, but a high nitrogen content. Hence, hydrodenitrogenation (HDN) processes are required for fuel production. A high activity tungsten–nickel hydrodenitrogenation catalyst with a commercial name RN-1 used at relatively low pressure has been developed [7,8]. The selection of tungsten as the active component for RN-1 is based not only on its performance, but also on the abundant resources of this element in China. The incorporation of fluoride into the catalyst plays a role in inhibiting coke formation at the start of the run and in substantially enhancing the HDN activity. The preparation conditions of the catalyst are carefully controlled to avoid the formation of nickel aluminate spinel and to form the active phase of HDN. Nowadays, the RN-1 catalyst is widely used in commercial units for hydrotreating coker gas oil, coker gasoline, light cycle oil from residue catalytic cracking, lube feedstock, etc. The catalyst has also been exported to and applied in foreign countries. New generations of hydrodenitrogenation catalysts, RN-10 and RN-100, have been developed for further enhancing HDN activity by improving the properties of the γ-Al_2O_3 including the pore distribution, and also the shape of the extrudates. Under the following reaction conditions, hydrogen partial pressure = 3.0 MPa; space velocity = 2.0 h^{-1}, hydrogen to oil volume ratio = 350; and reaction temperature 320°C, the relative denitrogenation abilities (%) for RN-1, RN-10, and RN-100 are 1, 1.14, and 1.29, respectively.

Table 2
The product yield and quality of a commercial MHUG process

Light naphtha (< 65°C) (wt%)	3.8
Heavy naphtha (65–165°C) (wt%)	17.7
Density (20°C) (g/ml)	0.7387
Refractive index (N_D^{20})	1.4139
N+2A (wt%)	63.05
Middle distillate-1 (165–290°C) (wt%)	39.5
Density (20°C) (g/ml)	0.8111
Pour point (°C)	−44
Sulfur (ppm)	11
Nitrogen (ppm)	< 1
Aromatics (vol%) (FIA)	17.1
Cetane index	49.4
Middle distillate-2 (290–350°C) (wt%)	20.33
Density (20°C) (g/ml)	0.8013
Pour point (°C)	+14
Sulfur (ppm)	15
Aromatics (vol%) (FIA)	6.9
Cetane index	> 70
Tail oil (> 350°C) (wt%)	18.6
Density (20°C) (g/ml)	0.8056
Sulfur (ppm)	25
Nitrogen (ppm)	< 2
BMCI	3.55

In order to reduce the investment and operation costs of high pressure (15 MPa) hydrocracking, a medium pressure (7.0–8.0 MPa) hydro-upgrading (MHUG) technology and the appropriate catalysts have been commercialized in a 120000 tons per year unit for improving the quality of middle distillates and increasing the yield of reforming feedstock [9]. Two catalysts, RN-1 and RT-5, are used in one reactor or separately in two reactors in series. The catalyst RT-5 is a zeolite containing a hydrocracking catalyst which is highly selective for middle distillate production. The product distribution and quality of the products from a commercial unit are listed in Table 2. This unit processed a feedstock of 50/50 (weight) mixture of LCO/LVGO with a conversion level of 33.5 vol% under reaction conditions of: weighted average reactor temperature (reactor 1/reactor 2) 352/356°C, hydrogen partial pressure 6.11 MPa, space velocity (reactor 1/reactor 2) 1.59/3.00 h^{-1}, hydrogen to oil volume ratio 969.

Several series of hydrocracking catalysts [11] have also developed and have been used commercially for producing middle distillate, such as those designated as 3824, 3901, 3903, 3882, 3912, FRC-2, etc., and naphtha, such as 3325, 3905, 4321, etc. The success of these hydrocracking catalysts is based on extensive R&D work concerning USY zeolite, hydrophobic zeolite UHPY, SSY and beta zeolite, as well as alumina and silica–alumina supports with large pore structures. In particular, lower or medium pressure (6.0–8.0 Mpa) hydrocracking techniques have been developed; one is a mild hydrocracking catalyst and process (MHC) for preparing steam cracking feedstock VGO [10] and another is medium pressure hydrocracking catalyst and process (MPHC) for producing naphtha and middle distillates from light VGO (end point < 429°C).

As an example of the MHC catalyst application, Shengli VGO was processed through a single-stage reactor with a hydrorefining catalyst and a MHC catalyst in series under a pressure of 7.75 MPa in a unit with a capacity of 220000 t/a. The conversion to a distillate with an end point of less than 350°C was 38.6 wt%. The converted fractions were high quality naphtha and diesel. The unconverted fraction (> 350°C, 61.8%) can be used as a feedstock for steam cracking. The yields of ethylene, propene and butadiene obtained by using the feedstock in a steam cracker were 26.3, 16.6, and 5.3 wt% respectively, higher than those obtained from Shengli Naphtha and AGO.

As an example of the MPHC catalyst application, Nanyan light VGO (end point 429°C) was processed through a single-stage reactor with a hydrofining catalyst and a MPHC catalyst in series under a pressure of 7.6 MPa in a unit with a capacity of 250000 t/a. The following product yield (feed basis) was obtained:

C_4:	6.2 wt%
< 65°C:	8.1 wt% (MON 73)
65–180°C:	26.5 wt% (aromatics potentiality 40 wt%)
180–350°C:	39.2 wt% (cetane number > 70)

> 350°C (unconverted): 21.4 wt% (BMCI 8)

1.3. Naphtha catalytic reforming catalysts

For naphtha catalytic reforming for octane enhancement and aromatic production, two major technologies, i.e. a fixed bed reactor combined with semi-regeneration and a moving bed reactor combined with continuous regeneration, are widely used in the world. SINOPEC has developed two series of reforming catalysts for the corresponding technologies (see Table 3) [12–14].

Compared with a competitor's catalysts, SINOPEC's reforming catalysts possess the following advantages: high purity γ-Al_2O_3 support with highly concentrated pore distribution improving both the activity and stability of the catalyst; better crush strength, for semi-regenerative catalysts; higher performance of Pt–Re catalyst series with low platinum content. The above advantages for both fixed bed catalysts and moving bed catalysts have been commercially proved in a number of reforming units.

The high stability of SINOPEC's reforming catalysts is attributed to the better thermal stability of the alumina support and the higher stability of the platinum crystallites. The stability of the platinum crystallites, which is a critical parameter for the performance of reforming catalysts, depends on the preparation procedure and on the properties of support. Table 4 compares the stability of the Pt crystallites of SINOPEC's catalysts with those of a competitor's catalysts, A and B.

Table 4
A comparison of the stability of the platinum crystallites of various reforming catalysts

	Pt (wt%)	Re (wt%)	Re/Pt (wt)	Cl (wt%)	Average diameter of Pt crystallites after thermal treatment [a] (nm)
Re/Pt(wt) = 1					
3932	0.24	0.26	1.08	1.49	2.6
CB-6	0.30	0.28	0.93	1.17	4.8
A	0.30	0.31	1.03	1.04	22.1
Re/Pt(wt) > 1					
3933	0.21	0.45	2.15	1.27	4.0
CB-7	0.21	0.43	2.05	1.29	5.1
B	0.21	0.43	2.05	1.17	23.7

[a] Thermal treatment conditions: flowing hydrogen, 700°C.

Table 3
Reforming catalysts developed by SINOPEC

	Metallic component (wt%)		Relative stability	Year of commercialization	Feed requirement, S (ppm)
	Pt	Re or Sn			
For fixed bed					
3741-2	0.52			1884	< 1
CB-6	0.30	0.27(Re)	1.0	1986	< 0.5
CB-7	0.21	0.42(Re)	1.5	1990	< 0.5
3932	0.25	0.25(Re)	1.0	1995	< 0.5
3933	0.21	0.46(Re)	> 1.5	1995	< 0.5
CB-5	0.40	0.30(Re)		1985	< 0.5
CB-8	0.15	0.30(Re)		1990	< 0.2
For moving bed					
3861-I	0.37	0.30(Sn)		1990	< 0.5
GCR-10	0.29	(Sn)		1994	< 0.5

The better stability of the size of the platinum crystallites explains the better activity and stability of SINOPEC's reforming catalysts in industrial application.

1.4. Catalysts for commodity organic chemicals

1.4.1. Acrylonitrile catalyst [15]

The R&D work on the technology for producing acrylonitrile (AN) by the ammoxidation of propylene has been carried out in China for

30 years. Since acrylonitrile is an essential raw material for producing polyacrylonitrile fiber and other synthetic polymers, SINOPEC has paid great attention to the catalyst research and has developed techniques for producing acrylonitrile, including catalyst, reactor and post-processing technology. The commercial application of this technology has shown that its performance is comparable to the best technology in the world.

The catalyst is composed of several metal oxides (such as Mo, Bi, Fe, Na, P) on SiO_2 support. Unique preparation techniques have been developed to achieve a synergetic effect among the different catalyst components; this is critical for making a catalyst with high activity, high selectivity, and high attrition resistance. The commercial results show that the AN per pass yield is 81%, with high purity and good stability. The physical and chemical properties and catalytic performance of the catalyst are as follows:

Attrition loss (wt%):	< 4
Bulk density (g/ml):	0.88–1.02
Agglomerates:	none
Distribution of particle size (*m*%):	
< 20 mesh	100
> 90 mesh	0–25
< 44 mesh	30–50
AN yield per pass (%):	80–81
Acetonitrile yield per pass (%):	2–3
HCN yield per pass (%):	5–6
Air ratio:	9.5
Ammonia ratio:	1.15
AN purity (%):	99.65

A series of AN catalysts has been developed. Recently, a newly developed example displays better performance in ammonia conversion ($>$ 98 wt%). Thus, the ammonia recovery unit in the post-processing section can be eliminated and the flow scheme for producing AN can be significantly simplified.

1.4.2. EO silver catalyst [16]

EO or EG as an essential raw material for producing polyester fibers – the first major synthetic fiber in China has been greatly concerned. SINOPEC paid great attention to the EO production. A new generation EO catalyst with major improvements has been developed and commercialized.

The catalyst is prepared by an immersion method with silver and other promoters on a unique Al_2O_3 carrier. The specially manufactured carrier has an appropriate pore size distribution (especially pore sizes between 30–50 μm), a large enough pore volume and pore channels, and also a large surface area; this leads to a decrease of the diffusion resistance of reactants and products, an ease release of reaction heat, and a catalyst with high selectivity and high stability. Commercial application has shown that the YS-5 type catalyst reaches a selectivity of 81% and has a service life of 3 years. The selectivity of the YS-6 type catalyst reaches 83%.

Some typical properties and performance data of the catalyst are as follows:

Surface area:	~ 1 m^2/g
Packing density:	0.50–0.70 g/ml
Silver content:	13–20%
Operation pressure:	1.0–2.5 MPa
Reaction temperature:	230–260°C
Space velocity (h^{-1}):	3000–8000
Productivity (g EO/h^{-1}):	≤ 300

1.4.3. Ethylbenzene / styrene catalysts

A unique ethylbenzene production catalyst based on a zeolite, which is a co-crystallization product of ZSM-5 and ZSM-11, has been developed for benzene alkylation using dilute ethylene from FCC off gas [17]. The features of the catalyst are: high activity, high selectivity, long service life and an impurity tolerance, e.g. to sulfur and water. The total sulfur content and propylene content in feedstock can be up to 6000 mg/ml and 0.7% (vol), respectively.

The process has been successfully commercialized in a unit with a capacity of 30000 t/a using FCC off gas as feedstock without any pretreatment. It gives an ethylene conversion of

> 95% and an EB selectivity > 99% with the trans-alkylation process included in the flow scheme.

A series of iron catalysts for styrene production incorporating with rare-earth and other metal oxides as promoters for ethylbenzene dehydrogenation has been developed [18]. The catalysts are characterized by high activity, high selectivity, and high stability at lower reaction temperatures and water ratios. One catalyst of this series, GS-05, was used in 1994 in a unit with a capacity of 60 000 t/a in the Yanshan Petrochemical Company. Compared with a catalyst imported from a foreign company, the GS-05 catalyst exhibited a yield increase of 1–2% and a styrene output increase of 4%, while the operation temperature was 10°C lower than that for the imported catalyst. The commercial results are summarized as follows:

Temperature (°C):	545–612 (1st stage); 566–617 (2nd stage)
Pressure (MPa):	0.067–0.079
Space velocity (h^{-1}):	0.5
Conversion of EB (%):	60–61
Selectivity (%):	> 95

1.4.4. Catalysts for aromatics production

There is a serious shortage of benzene and xylene in China. One important and effective way to balance the demand and supply of aromatics is toluene disproportionation and C_9 trans-alkylation to produce benzene and xylene [19]. SINOPEC has developed a series of high-silica mordenite catalysts using alumina as binder which have high activity (the initial reaction temperature is 360°C), high selectivity, good regeneration performance and good stability (run length of more than 1 year and service life more than 3 years). The high-silica mordenite is prepared by a proprietary method using inorganic raw materials. One catalyst, ZA94, has been used in an aromatics unit with a capacity of a million t/a in the Yangtze Petrochemical Company, with the following commercial results:

Temperature (°C):	360–405
Pressure (MPa):	3.0
LHSV (h^{-1}):	1.01
Total conversion (C_7 A + C_9 A):	44.2%
Yield (benzene + xylene):	40.8%
Selectivity (benzene + C_8 A):	97.03%

A xylene isomerization catalyst (coded SKI) has been developed which is used to convert the ethylbenzene, *o*-xylene, *m*-xylene of C_8 mixed aromatics into *p*-xylene used in the production of polyesters. The catalyst is composed of Pt on a specific mordenite component with Al_2O_3 as binder, it is characterized by moderate acid strength and a concentrated pore distribution in the range of mesopores to improve the selectivity, suppress the coke formation. One of the SKI series catalysts, SKI-300, has been used in a commercial unit of the Yanshan Petrochemical company for more than 10 years. The latest catalyst, SKI-500, has been used in the Tianjin Petrochemical Company to replace an imported catalyst and shows better performance compared with the imported one. After the replacement of the imported catalyst with SKI-500 catalyst, for each metric ton of feedstock, the *p*-xylene output is 30 kg higher (xylene yield is 0.364% higher), the operation temperature is 20°C lower, the space velocity is 10.6% higher, and the H_2/HC ratio is 31.2% lower.

1.4.5. Strong acidic ion-exchange resin catalyst for bisphenol A (BPA) production[20,21]

In China, strongly acidic ion-exchange resin catalysts of different specifications have been used in various reactions such as hydration, etherification, condensation, etc., to produce *tert*-butyl alcohol, *iso*-propyl alcohol, MTBE, TAME, and MIBK, etc. Recently, a newly developed resin catalyst has been used to produce BPA with much better performance than conventional resin catalysts. The new resin catalyst has high selectivity and high activity. The process using this catalyst has been commercialized.

During the development of this new resin catalyst, the research efforts were focused on the selection of a third monomer, a pore agent and a benzene ring passivator. The key factor in the preparation of the new resin catalyst is to incorporate the acidic functional groups into the inner pores of resin and to strengthen the interaction between the acidic functional groups and the resin, hence the stability and the application temperature (up to 160–180°C) of the resin catalyst are improved.

In the reaction of acetone with phenol in the presence of the new resin catalyst to produce bisphenol-A, the selectivity to BPA is higher than 99%, and the once-through conversion of acetone is higher than 50%. The reaction is performed in a specially designed reactor: a catalytic stripping reactor which combines reaction with inert gas stripping in a multistage reactor, thus maximizing the conversion level and simultaneously achieving the highest selectivity. The total acetone conversion is nearly 100%. The recovery of acetone is unnecessary, and hence the flow scheme is much simplified.

Comparing with the traditional BPA process using hydrochloric acid or gaseous hydrogen chloride as catalyst, the new process, combined with the new catalyst, can be regarded as a breakthrough in BPA technology.

1.5. Olefin polymerization catalysts

Due to the well-known importance of polyolefin and the key role of catalysts in this production, research and development of olefin polymerization catalysts has been carried out in China for over 40 years. Big progress has been made in the R&D of these catalysts. Some new catalysts for polyethylene (PE) and polypropylene (PP) have been developed and commercialized, especially the polypropylene N catalyst.

Unlike the previous ball-milled $MgCl_4/TiCl_4$/ester supported catalysts, the N catalyst is an unsupported catalyst prepared by coprecipitating the titanium and magnesium compounds [22]. The catalyst does not show any diffraction peak of $MgCl_2$ in its XRD pattern, indicating that it is different from the $MgCl_2$ supported $TiCl_4$ catalyst. Especially due to appropriate incorporation of internal and external electron-donors, the catalyst possesses high activity (30–50 Kg pp/g cat for mass polymerization or 12–16 Kg pp/g cat for slurry polymerization), and high stereospecificity (polymer isotacticity $> 98\%$). Polymer bulk density is 0.43–0.47 g/cm^3, and polymer particle morphology is good, with a narrow particle size distribution. (The percentage of the polymer particles with particle size in the range of 20–80 mesh is more than 96%.) The resin product has a high crystallization temperature and high crystallization speed. It possesses good mechanical properties, high melt strength, good antioxidation, antiradiation and aging properties (the storage period is up to several years without added stabilizer). The commercial application proves that the quality and specification of the catalyst come up to the world advanced standard. Recently it is found that the catalyst also can be used in PE production.

1.6. Catalysts for hydrogen production and shift catalysts

Because of the market demand of H_2 and ammonia, a variety of catalysts used for the production of H_2 and NH_3 have been developed and applied in China. Following catalysts are recently been commercialized.

1.6.1. Naphtha steam reforming catalysts for H_2 production [23]

A new catalyst with $NiO–K_2O$ as the main components and a rare earth as the promoter has been developed. Using light oil (< 210°C) feedstock, the catalyst is characterized by its large operation flexibility with high space velocity, its better resistance to carbon deposit (see Table 5), its good reduction ability at lower temperature, and its good regeneration ability, its high stability, its lower loss rate of potassium, its high mechanical strength, and its long service life

Table 5
Carbon deposit and reduction ratio of catalyst after one year of operation

Height of converter bed (m)	Z409 catalyst		An imported catalyst	
	C.D.[a] (%)	R.R.[b] (%)	C.D. (%)	R.R. (%)
0–1	8.64	49.0	9.53	49.0
1–2	4.22	77.1	10.65	71.2
2–3	1.26	77.4	1.68	71.9
3–4	1.11		1.31	
4–5	0.89		0.71	
5–6	0.50		0.50	

[a] C.D.% = amount of carbon deposit in catalyst.
[b] R.R.% = Ni(metal)/ΣNi (total) wt% in catalyst.

(1–4 years). Commercial application in over 20 converters proves the better performances of the catalyst compared with 6 imported catalysts from 4 foreign companies.

1.6.2. Oil field gas steam reforming catalyst for the H_2 production [24]

A new catalyst with high strength, high activity and high hydrothermal stability has been developed for H_2 production by oil field gas steam reforming. A high quality ceramics prepared under high temperature is used as carrier, and this makes the catalyst highly stable. The surface of the catalyst is modified by rare-earth oxide to give the active phase long-term stability. Commercial application proves that the catalyst has good reduction ability and high activity on occasions of frequent shut-down and start-up. The chemical composition and operation condition of the catalyst are as follows:

NiO (*m*%): 11–12
Re_2O_3 (*m*%): < 2
Pressure (MPa): 2.1–2.3
Inlet temperature (°C): 500
Outlet temperature (°C): 700–800
LHSV, h^{-1}: 0.65–1.29
Water/carbon ratio: 3.2–6.0

1.6.3. Sulfur tolerant shift catalysts [25]

Coal and residue oil are popularly used in China as feedstocks for producing NH_3. A sulfur resistant catalyst used in a wide temperature range and over a wide sulfur concentration has been developed and applied commercially. Co and Mo are the main active components for the catalyst and Ti is used as the promoter; the latter improves the conversion and activity of the catalyst, especially at low temperatures and low sulfur concentrations.

The catalyst has been used successfully in a semi-commercial trial in the Wulumuqi plant for one year. The results show that the temperature range for the catalyst activity is 230–500°C, and the process can be put into operation on the occasion of sulfur concentration > 150 ppm. The performance of the catalyst is superior to that of imported catalysts.

2. Prospects

As one of the main industries, China's petrochemical industry will continue to engage in great development. The Chinese government has set up a two-stage development strategic goal. The first stage is to increase the crude runs to 200 million t/a and the ethylene output to 5 million t/a by the year 2000; the second stage is to boost the crude processing capacity to 300–350 million t/a and ethylene output to 8–10 million t/a by the year 2010.

SINOPEC will put more emphasis on the research and development of catalysts and catalysis. In the predicted near future, the catalysts mentioned above will continue to be the focus of R&D. We will plan the R&D program of catalyst development according to the principle of exploring, developing, commercializing and licensing in series.

The continuous technology advancement includes improving the performance of catalysts, developing more environmental friendly catalysts, expanding the variety, upgrading a new generation and also augmenting manufacturing techniques and engineering, to save raw materials, to decrease the utility consumption and production costs. As an example, a series of MB-86, MB-90 and MB-93 the catalyst for acrylonitrile production with the ever improving performance has been developed, and has been and will be commercialized in China. Continuous improvements to existing technologies will continue to constitute the major advances in catalytic technologies.

The discontinuous technology development will be focused on innovation. A number of directed basic research projects have been carried out, especially in the field of new catalytic materials, homogeneous catalysts and metallocene catalysts.

Research on new catalytic materials will provide the basis for inventing new catalysts. Nonzeolite molecular sieves, pillared clays, solid superacids, heteropolyacids, amorphous alloys, ultrafine alloys and oxides, etc. are being extensively investigated in China. Some technological discontinuity will undoubtedly occur in this field.

Metallocene catalyst research and development has been carried out and promising preliminary results has been achieved; a catalyst for production of syndyotactic polypropylene has been developed and a more effective manufacturing technique for preparing the methyaluminoxane (MAO) promoter has been succeeded, breakthrough in this field probably will come soon.

Homogeneous transition metal-based catalysis plays an essential role in the manufacture of basic chemicals, intermediate chemicals and fine chemicals. Research is now being carried out in the areas of hydroformylation, carbonylation, oxidation and oligomerization, etc. Aqueous phase transition metal homogeneous catalysts and supported liquid phase (or an aqueous phase) catalyst with the advantage to overcome the difficulty of separation of the reactant with homogeneous catalyst is now being explored. Several homogeneous catalysts with better separation performance with reactants have been developed.

The integration of catalysis with separation process, such as catalytic distillation and catalytic inorganic membranes, is expected to open up new technical routes in petrochemical and fine petrochemical manufacturing.

Studies on catalytic inorganic membranes, a rapidly growing field of industrial catalytic research in China, are being carried out on the processes of dehydrogenation, hydrogenation and oxidation of hydrocarbons. The catalytic distillation routes to produce MTBE and TAME have been commercialized in China. The production of EB and cumene by a catalytic distillation process has also been studied with good progress.

The integration of catalysis with chemical reaction engineering principles is being widely studied. A completely new catalytic stripping reactor has been commercialized in the BPA process with nearly 100 percent conversion of acetone; the brand new internal structure of acrylonitrile ammonoxidation reactor has enabled an increase in the yield of AN by quite a few percentage points to be achieved; the super-short resident time reactor and super quick gas–solid contact techniques have been introduced in catalytic cracking and hydrocarbon oxidation processes with the features of utmost utilization of the reactive potentials of the catalysts and this will form the technological breakthrough to the process.

With all the above research activities going on in China, it is expected that more innovations in refining and petrochemical catalytic technologies will emerge in the near future.

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