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Catalysis Today 51 (1999) 59–72

CATALYSIS TODAY

Research and development of catalytic processes for petroleum and natural gas conversions in the Dalian Institute of Chemical Physics

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Abstract

The Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences has a long history in the R&D of catalysts and catalytic processes for petroleum and natural gas conversions in China. In this paper, results and features of some commercialized petrochemical catalysts and processes as well as newly developed processes for natural gas conversion in the pilot-plant stage are described. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; Petrochemistry; Natural gas chemistry

1. Introduction

The Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS) is a comprehensive research institute which was founded in 1949 in a harbor city, Dalian of Liaoning Province, China. The main research areas of DICP include catalytic chemistry, engineering chemistry, chemical lasers, and molecular reaction dynamics and advanced analytical chemistry. Before 1963, DICP was an institute devoted mainly to the R&D of petroleum and petrochemical technologies based on the resources and demands of China, and was then called the Institute of Petroleum of the Chinese Academy of Sciences. Accordingly, DICP has a long history and a strong adherence in its research projects to the R&D of catalysts as well as catalytic processes for hydrocarbon conversion and for synthetic fuels with feedstocks from petroleum, coal, tar oils, shale oils and natural gas. In a span of nearly half a century, DICP has developed a great number of catalysts and catalytic processes which are commercialized for various applications in different industrial sectors of China. As examples of the R&D efforts to develop new catalytic technologies for the conversion of petroleum and natural gas resources to social demanding products, the results and features of some commercialized petrochemical processes as well as newly developed processes for natural gas conversion in the pilot-plant stage are described in this paper with emphasis on the key scientific and technological problems encountered and solved, and based mainly on the experiences of the authors.

2. Development of a hydrocracking process for middle-distillate production from VGO feedstocks of the Daqing crude of China

The R&D of hydrotreating and hydrocracking technologies have been carried out in China as early as the

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PII: S0920-5861(99)00008-5

1950s for producing liquid fuels from shale oil and coal tar feedstocks since there were only rather small quantities of crude oil resources in China at that time. Then, in 1960, with the discovery and exploitation of the large Daqing oil field in North-eastern China as well as several other smaller ones followed, the R&D of hydrocracking technologies were shifted to the manufacture of petroleum fractions.

In the early 1960s, a hydrocracking process was developed in the western countries for the production of high quality liquid fuel from heavy oil feedstocks. Comparing to the other refining processes, this process has the advantage of flexibility for the production of a variety of fuels such as high quality gasoline, naphtha, jet fuel and diesel fuel. Specifically, the ability to produce maximum middle distillate is a unique feature of the hydrocracking process. In China, large quantities of high quality jet fuel for air transportation and diesel for agriculture tractors and trucks are in great demand. Before the 1960s, middle distillate products were mainly imported from other countries.

The first hydrocracking unit in China with a capacity of 250 000 tons/year was built at the Daqing Petrochemical in 1967. This hydrocracking unit employed a single stage configuration with two different catalysts loaded in two separate beds of a single reactor. The catalysts, designated, respectively, as 219-A and 219-B, were developed by DICP, and both were constituted of NiS and WS_2 supported on an amorphous alumina–silica carrier. The 219-A catalyst, which was loaded on the upper section of the reactor had a higher hydrogenation activity so that it could remove a large part of the organic nitrogen compounds in the feed stocks, thus yielding low organic nitrogen content reactants together with the NH_3, which is less sensitive to the acid sites of catalyst for the 219-B catalyst in the lower section of the reactor to carry out the hydrocracking operation more efficiently since the 219-B catalyst was designed to possess higher acidity and was found to be more effective for the hydrocracking and hydroisomerization of the hydrocarbon reactants. The main purpose of these hydrocracking units was to produce maximum middle distillates with low pour points, and this goal was achieved satisfactorily throughout the performances of the unit for more than 20 years.

The feedstocks for this hydrocracking unit were mainly straight run VGO from the Daqing crude, and their properties are shown in Table 1. The hydrocracking data are listed in Table 2. We can see from the data in Table 2 that about 15–17 wt% gasoline, 34–40 wt% jet fuel and 10–22 wt% diesel fuel fractions could be obtained in the operation of this hydrocracking unit. Thus, the total amount of middle distillates, i.e., jet plus diesel fuel, reached 50–60 wt% of the total conversion. It is worth to point out that although the Daqing crude is high in paraffin content, the hydrocracking products contain rich amount of branched

Table 1
Feedstock properties for hydrocracker in the Daqing Petrochemical

Feed stock	I	II
Specific gravity, *d*(20/4)	0.8458	0.8479
Distillation (°C)		
IBP	251	222
10 vol%	319	314
50 vol%	379	367
90 vol%	439	448
EP	465	462
Nitrogen (ppm)	259	109
Alkaline nitrogen (ppm)	85	16
Sulfur (vol%)	0.173	0.180
Aniline point (°C)	–	96.8

Table 2
Typical performance data of the Daqing hydrocracking units for maximum middle distillate

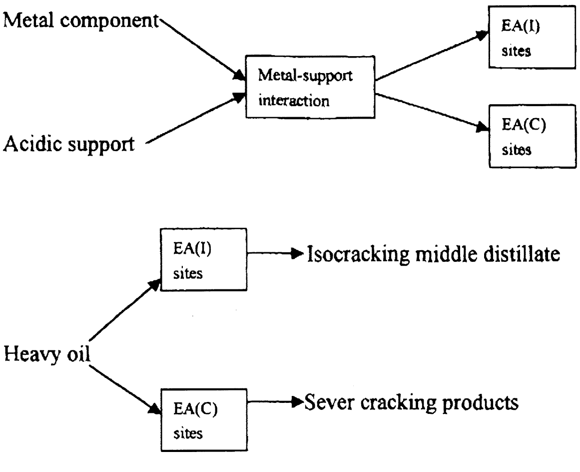
Feed stock	I	II
LHSV (h^{-1})	0.75	0.92
Pressure (kg/cm^2 gauge)	144	144
H_2/oil (vol)	1940	2000
Temperature (°C)		
Average	415	420
Maximum	430	440
Recycle hydrogen		
Purity (vol%)	82.5	85.5
H_2S (vol%)	0.23	0.35
NH_3 (ppm)	7.2	4.4
H_2 consumption (N M^3/tons)	231	237
Conversion (%)	69.9	76.0
Product data		
Specific gravity, *d*(20/4)	0.7759	0.7735
<130°C (wt%)	16.7	14.6
130–260°C (wt%)	34.0	40.4
260–320°C (wt%)	19.2	21.5
<320°C (wt%)	69.9	76.0
Jet fuel/gasoline (vol)	2.04	2.70

alkane owing to the high hydroisomerization activity of the 219 type catalysts so that the low-temperature properties (low freezing point or low pour point) of both the jet fuel and the diesel fuel were improved with a freezing point well below −60°C for the former, and a pour point of −35°C for the latter.

During the research and development of the hydrocracking catalysts and processes, some new concepts have been established on the base of the existing working rule of metal–acid bifunctional catalysts and the new results of our experiments. According to the carbonium-ion theory, catalytic cracking and isomerization of hydrocarbons follow the so-called β-scission rule under the action of the acidic sites of the catalyst. As a result of this β-scission mechanism, the hydrocarbon reactants are cracked mainly into lower molecular weight fragments associated with various extents of isomerization. It is also known that the isomerization activity is usually parallel to the cracking activity of the catalyst since both activities depend on the acid strength of the acidic sites. The higher isomerization we pursue, the more severe cracking will be resulted. This is the main reason why it is difficult to get high middle distillate yields in the catalytic cracking process. On the other hand, the thermal cracking process, which is known to follow a free-radical mechanism, facilitates cracking inside the molecule, and thus favors the production of middle distillates. However, only little isomerization is occurring in the thermal cracking process so that the low-temperature properties are poor for the thermal cracking products. Now, for the hydrocracking process which employs a bifunctional catalyst, the advantages of both the catalytic cracking process and thermal cracking process can be integrated, and middle distillate products with good low temperature properties can be obtained. Then, what are the principles or factors which govern the catalytic behavior of the bifunctional catalysts, which are seemingly different from those of the catalytic cracking catalysts? During our studying of bifunctional catalysts for the hydroconversion of hydrocarbons in 1964, we have carried out exploratory as well as explanatory research into these problems, and some interesting results have been summarized.

Our studies were commenced with the development of a bifunctional catalyst for the hydroisomerization of a kerosene fraction into a low freezing jet fuel. The catalyst was composed of WS_2–NiS supported on a fluorinated alumina. This catalyst was found to possess good activity and selectivity for the isomerization of middle distillate fractions. Moreover, we found that on this isomerization catalyst, hydrocracking by-products were also produced, and the product distribution of the cracked hydrocarbons was quite different from that predicted by the β-scission mechanism. These observations led us to initiate a systematic research of the combination effects of various kinds of metallic components and acidic supports on the cracking and isomerization activities and selectivity of the bifunctional catalysts [1,2]. On the basis of these investigations, we found it appropriate to propose that on the bifunctional catalysts with the result of interaction between metal and acid components, two different kinds of cracking sites were formed on the surface of the catalyst. One kind of cracking sites, which was designated as the EA(I) sites, causes the hydrocarbon reactants to undergo isomerization prior to cracking reactions, and the cracking products mainly consist of medium fragments. On the other hand, the second kind of cracking sites, designated as EA(C) sites, causes the hydrocarbons to crack to the light fragments according to the carbonium-ion mechanism. The difference of these two kinds of cracking sites can be illustrated by Scheme 1.

It was further proposed that the formation of these two different kinds of cracking sites depends on the nature of the metallic components as well as the acidic



Scheme 1.

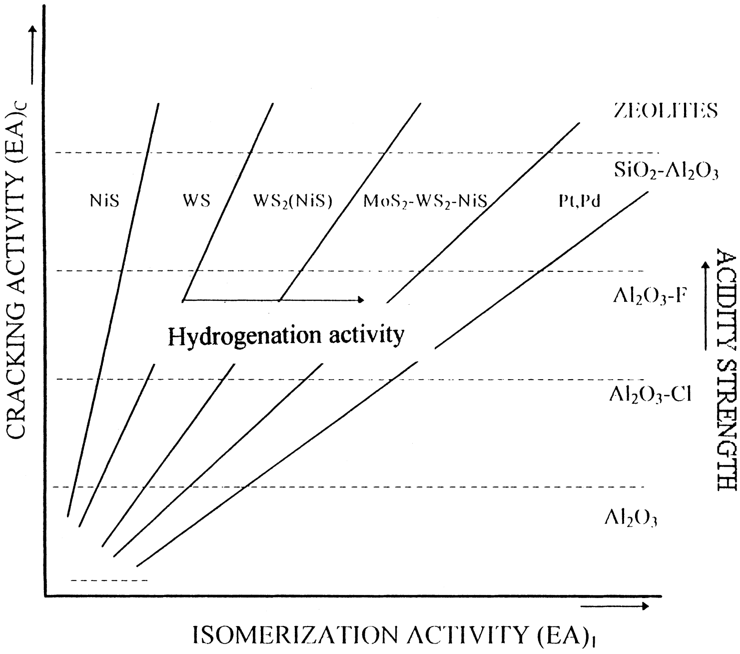


Fig. 1. A rough illustration of the dependence of the EA(I) and EA(C) activities on the properties of the bifunctional components.

supports. For example, the formation of the EA(I) sites is always associated with the combination of a metallic component with high hydrogenation activity such as platinum and palladium or WS_2–NiS, MoS–NiS, with the weak acidic support. On the other hand, the formation of the EA(C) sites resulted from the combination of a weak hydrogenation component, such as NiS or WS_2, with the strong acidic support. Thus, we can summarize the dependence of the relative activities of the EA(I) and EA(C) sites with various metallic components and acidic supports in a diagram as roughly shown in Fig. 1. We can anticipate from Fig. 1 that catalysts on the left lower corner, which are composed of weak hydrogenation metallic components and weak acidic supports, will have very low activities both in cracking and isomerization. On the other hand, catalysts on the top right corner will exhibit high activities for both cracking and isomerization, and favor the production of high octane-rating gasoline. Thus, we can estimate that hydrocracking catalysts favoring the production of middle distillate from heavy oil should be located in the region in Fig. 1 with higher hydrogenation activity and combine with a support of medium acidity.

3. Researches on catalysts for the dehydrogenation as well as aromatization of alkane

3.1. *R&D of multicomponent catalysts for naphtha reforming*

In the 1970s, platinum reforming catalysts were gradually replaced worldwide by multicomponent catalysts which exhibited superior catalytic properties in many respects. Meanwhile, this new trend also affected the R&D of reforming catalysts in China.

Starting from 1972, researchers of DICP participated in a cooperative R&D program initiated by the Ministry of Petroleum of China for the research and development of multicomponent reforming catalysts. With great research efforts, a Pt–Ir–Ce/Al_2O_3 catalyst was successfully developed, which could give an aromatics yield of 56% from naphtha feedstocks containing less than 40% naphthene, while the aromatics yields in the refineries with monometallic Pt catalysts were <40% at that time. This newly developed multicomponent reforming catalyst was then commercialized, and was employed in catalytic reforming unit constructed in 1975 in the Dalian Refinery. The capacity of this reforming unit was 150 000 tons/year. This catalyst probably was the first one in commercial multicomponent reforming catalysts with rare-earth components. It was observed that, due to a stabilizing effect of the rare-earth component, this Pt–Ir–Ce/Al_2O_3 catalyst showed superior regeneration stability after very long operation time. It is worth to point out that the first batch of this commercial Pt–Ir–Ce/Al_2O_3 catalyst still showed very good catalytic activity after continuous operations for 15 years with regeneration cycles.

After accomplishing the cooperative R&D program of this multicomponent reforming catalyst, Lin and co-workers [3–8] in DICP continued their systematic studies of highly dispersed multicomponent catalysts such as the Pt–Ir, Pt–Re and Pt–Sn systems, and the progresses achieved in these studies have helped DICP to open up new prospects in the fruitful developments of new catalysts and processes for dehydrogenation of long chain alkanes and lower alkanes, and for Fischer–Tropsch synthesis (Ru–Fe catalysts) and ethanol synthesis from syngas (Rh–Mn catalysts).

3.2. *Studies of catalysts prepared by the impregnation of complex compound for the dehydrogenation of long-chain paraffin*

Long-chain normal olefins are essential starting materials for the production of alkylbenzenes (LAB), which are the raw materials for the production of synthetic detergents. The long-chain normal olefins are produced by dehydrogenation of long-chain normal paraffins in the presence of highly dispersed multicomponent metallic catalysts mainly comprised of Pt and Sn on Al_2O_3 supports. This dehydrogenation process is one of the new and important catalytic technologies following the development of the multicomponent catalytic reforming process. At present more than 30 installations have been put into operation all over the world.

In 1975, Lin and his co-workers initiated the R&D of catalysts for the dehydrogenation of long-chain paraffins in DICP, and they found that the catalytic properties of the catalysts depended on the method of preparation. For example, they noted that the stability of the catalysts could be greatly enhanced if a complex impregnation method was employed [9–11]. Consequently, systematic studies were carried out to probe the preparation parameters and their influence on the structure of the catalysts as well as the correlation of these factors to its catalytic properties.

For this purpose, three kinds of Pt–Sn/Al_2O_3 catalysts were prepared according to different procedures. The first one was prepared by the conventional co-impregnation method designated as the Pt–Sn(I) catalyst. The second kind of catalysts were prepared with incorporating the synthetic complexes inorganic solvent of $[(CH_3)_4N]_2\cdot[Pt(SnCl_3)_2Cl_2]$, $[(C_2H_5)_4N]_4\cdot[Pt_3Sn_8Cl_{20}]$ and $[(CH_3)_4N]_3\cdot[Pt(SnCl_3)_5]$, respectively, onto the alumina supports with the Pt/Sn ratios being 1:2, 3:8 and 1:5, respectively. These catalysts were designated as Pt–Sn(II) type. The third kind of catalysts was prepared by impregnating the alumina support with a solution containing a Pt–Sn complex with a given Pt/Sn ratio, which was designated as Pt–Sn(III) type. These different kinds of catalysts were examined by H_2 adsorption, ethylene titration of adsorbed H_2, Mössbauer spectroscopy, electron-microscopy and XRD determinations, etc. It was interesting to find that, irrespective of the preparation method, the Pt components can be reduced to metallic Pt with crystallite sizes of 1.0–3.0 nm, whilst the Sn component can only be reduced to lower oxidation states. From the characterization results, it was also possible to differentiate between two types of Pt active sites on the Pt–Sn/Al_2O_3 catalysts. The first type of Pt active sites, designated as the M_1 sites, were mainly Pt crystallites located on the surface of the γ-Al_2O_3 support, while the second type of Pt active sites, the M_2 sites, were visualized to be Pt clusters intimately linked to the boundaries of the Sn oxides. By measuring the amounts of H_2 adsorbed at different temperatures and by ethylene titration of the adsorbed H_2 [10], it is possible to quantitatively determine the concentration of the M_2 sites. From the result of experiments over Pt catalyst and Pt–Sn bi-component catalysts, it is found that H_2 uptake on Pt surface are accessible to adsorb ethylene at 20°C, while only a part of adsorbed H_2 can react with ethylene to form ethane, we denoted the active sites which adsorbed the available hydrogen for the hydrogenation of ethylene as M_1 sites and those which are unable to react with ethylene as M_2 sites. From the ratio of M_1 or M_2 sites with the total H_2 uptake by Pt surface, the value of M_1/Pt and M_2/Pt can be calculated. The most significant finding of these

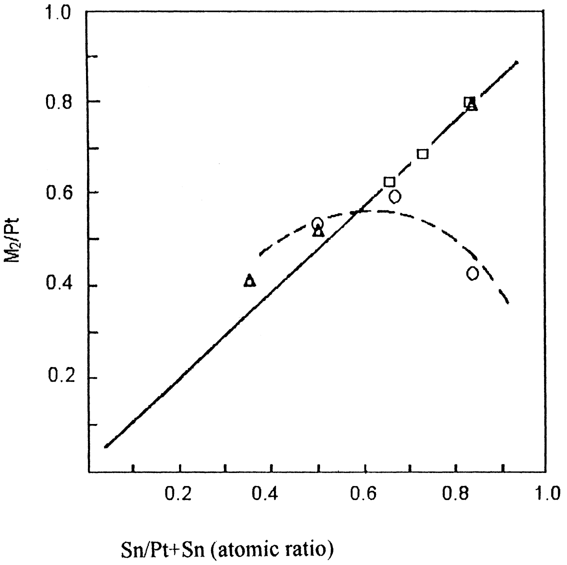


Fig. 2. Relationship between M_2/Pt and Sn/Pt+Sn of various catalysts: (○) catalyst prepared by method I; (□) catalyst prepared by method II; (△) catalyst prepared by method III.

studies was that when the catalysts were prepared by complex incorporation, the concentration of the M_2 sites was proportional to the content of the Sn component, while no such correlation existed for the conventionally impregnated catalysts (Fig. 2). Another striking observation was that the significantly enhanced selectivity and operation stability of the catalysts prepared by the complex methods were closely related to the role of the M_2 sites.

On the basis of the Pt–Sn/Al_2O_3 studies, the model of the formation of the M_1 and M_2 sites for highly dispersed bimetallic catalysts have been further verified by means of high-resolution electron-microscopy, scanning electron microscopy, Mössbauer spectroscopy, EXAFS and XANES. The catalyst systems were extended to Pt–Fe/Al_2O_3 and Ru–Fe/Al_2O_3 [12–16]. It could be concluded from the results of Mössbauer spectroscopy, XANES and EXAFS for the Pt–Sn/Al_2O_3 and Pt–Fe/Al_2O_3 catalysts that, after reduction, the second component of the catalysts, such as SnO and FeO, form a highly dispersed two-dimensional layer on the surface of the alumina support; Pt metallic crystallites then are distributed on the surface of the metal oxide layer. In other words, a "sandwich" structure of metal–metal oxide–alumina was formed. The existence of this structure was confirmed by high resolution electron-microscopy measurements which showed very clear surface crystalline rows of the Pt metal particles, and that the measured lattice distance was 0.23 Å corresponding to the lattice parameter of the Pt(1 1 1) plane. On the other hand, no alloy lattice was observed. Further investigations have shown that if the Pt crystallites were located on top of the promoter oxide surface and the sandwich structure was formed, then the catalyst would exhibit superior catalytic reactivity. In contrast, if the Pt crystallites were situated on the Al_2O_3 surface, the catalytic properties of the catalyst were similar to those of the mono-component Pt catalysts.

In fact, when the content of the promoter oxide was less than 1 wt%, its coverage on the Al_2O_3 surface was less than 10% of a mono-layer dispersion. Under such circumstance, it has been found that for a catalyst with the metallic loading less than 1 wt%, only method II or III, the Pt crystallites could be guaranteed to locate on top of the promoter oxide surface and sandwich structures could be formed. A comparison of the reaction performances of the commercially manufactured catalysts by the complex method and by the conventional procedure is shown in Table 3. The results indicate that the catalysts prepared by the complex method have better stability than that prepared by conventional method selectivity for the dehydrogenation of long-chain paraffins.

3.3. *The role of Sn in Pt–Sn catalysts for the resistance of coke formation*

As a part of the systematic study of Pt–Sn catalysts in DICP, the effects of Sn addition, and the Sn/Pt ratio on carbon deposition on Pt and Pt–Sn catalysts were investigated by using an in situ thermogravimetric (TG) method [17]. It was found that the amount of accumulated carbon increased rapidly at the initial stage of the reaction, and then increased gradually with a lower rate. The rate of carbon deposition over the Pt/Al_2O_3 catalyst was higher than that over the Pt–Sn/Al_2O_3 catalyst at the initial stage of the reaction. This means that Sn plays a role of suppressing carbon accumulation on Pt–Sn/Al_2O_3 catalysts. In order to investigate the coverage of active sites with carbonaceous deposits, H_2 chemisorption was performed with coked Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts [18]. The

Table 3
Comparison of catalytic performance between conventional commercial catalyst and catalyst prepared by complex method for long-chain normal paraffin dehydrogenation

Catalyst	Pt–Sn/Al_2O_3 (complex method)	Pt–Sn/Al_2O_3 (conventional)
Operation time (days)	69	34
Initial temperature (°C)	477	476
Final temperature (°C)	480	481
Temperature increment (°C)	3	5
Temperature increment rate (°C/day)	0.057	0.147
Carbon deposition (wt% of catalyst)	1.8	3.1
Alkylbenzene yield (tons/day)	181.5	181.3
Yield of normal olefins (tons/day)	124.7	124.6
Selectivity (%)	90–92	90
Tons of olefins/kg catalyst	9.7	5.4

Reaction conditions: H_2 pressure 0.16–0.2 MPa; LHSV 30 h^{-1}; H_2/alkanes (mole) 6.

ratio of hydrogen uptake on the coked catalyst to that of the fresh catalyst was used to characterize the percentage of exposed metal (θ_m). By plotting the percentage (θ_m) against the amount of deposited carbon on the catalyst (Fig. 3), it appears that a small amount of the coke deposited reduce greatly the exposure of active sites on both the Pt and the Pt–Sn catalysts. However, when the carbon content reaches ca. 0.25 wt% of the catalysts, the rate of carbon deposition decreases and the active surface could be maintained at a constant level. About 10 wt% of the metals remained uncovered by coke on the Pt/Al_2O_3 catalyst, while this number became 35 wt% for the Pt–Sn/Al_2O_3 catalyst. These results strongly demonstrates that the Pt–Sn/Al_2O_3 catalyst was capable of tolerating more carbon on the catalyst [19].

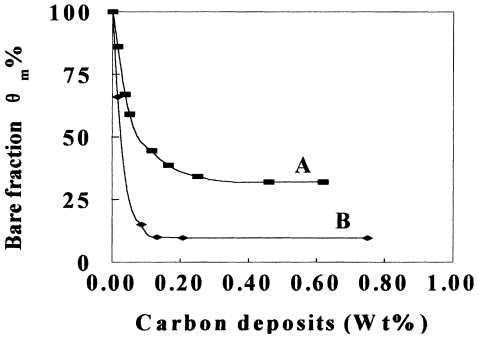


Fig. 3. Relation between total bare fraction of metal surface and carbon deposits (wt%) on the catalysts (A) Pt–Sn/γ-Al_2O_3 and (B) Pt/γ-Al_2O_3.

4. Development of a process for the utilization of low concentration ethylene in FCC off gas for the production of ethylbenzene

Alkylbenzenes are important basic chemicals for the production of polymers, detergents, pharmaceuticals, perfumes, etc. Usually, alkylbenzenes, such as ethylbenzene, are produced by alkylation of benzene with olefins and catalyzed by acidic catalysts such as HF or $AlCl_3$. However, these two commonly used acidic catalysts are corrosive materials, and also present environmental problems. Accordingly, the seeking of acidic solids, such as synthetic zeolites, to replace HF or $AlCl_3$ for the alkylation of benzene have attracted the attention of many researchers.

In DICP, several research projects on the R&D of new zeolite catalysts for various benzene or toluene alkylation processes have been carried out. These include the alkylation of benzene with ethylene and long chain olefin of C_{10}–C_{14} to produce ethylbenzene [20] and linear alkylbenzenes (LAB) [21], respectively. Alkylation of toluene with ethylene to produce para-ethyl-toluene [22] as well as side-chain alkylation of toluene with methanol to produce ethylbenzene [23] have also been investigated. Among all these studies, a breakthrough is the development of a commercial process for the production of ethylbenzene by the alkylation of benzene on a zeolite catalyst with low concentration ethylene in the FCC off gas [24].

Fluid catalytic cracking (FCC) is one of the largest and basic processes in petroleum refineries all over the world. In China, FCC units are essential for nearly all refineries, and the total FCC capacity has attained 56 Mt/a in 1996 with 1.68 Mt/a of off gas as by-products, which are usually consumed as fuels in the refineries. However, since there are about 10–30 vol% of ethylene in the FCC off gas, more valuable chemicals, such as ethylbenzene, can be produced if the ethylene can be utilized as the raw material. The main difficulty in the utilization of this low concentration ethylene for the production of ethylbenzene lies in the fact that there are also considerable amounts of H_2S, CO_2 and H_2O present in the off gas, which deteriorate the catalytic properties of the alkylation catalysts. Certain patents have claimed the development of processes for the utilization of low concentration ethylene in the off gas to produce ethylbenzene in the presence of different catalysts such as BF_3, $AlCl_3$ and ZSM-5 zeolite [25–27]. However, in all these processes, the off gas has to be pretreated for the removal of the H_2S, CO_2, O_2 and H_2O to concentrations of the ppm level before entering the alkylation reactor.

Starting from 1985, researchers in DICP, collaborating with engineers of Refinery no. 2 of the SINOPEC Fushun Petrochemical, have successfully developed a zeolitic catalyst, designated as the 3884 catalyst, which can catalyze the alkylation of benzene with low concentration ethylene of the FCC off gas without the necessity of any pretreatment of the off gas [28,29]. The 3884 catalyst is a pentasil type zeolite with high-silica content prepared by a special technique of co-crystallization, and incorporated with a rare-earth element as promoter. This catalyst has been proved to possess the unique properties of high activity, high thermal stability, high tolerance to feedstock impurities, and long durability. Preparation of the 3884 catalyst has been scaled-up from laboratory scale first to semi-commercial scale, and finally to commercial scale, and the duplication during the scaling-up was satisfactory, as can be seen from a comparison of the basic data for the catalysts prepared in the laboratory and in the commercial installation (Table 4).

Table 4
Basic properties of the high silica content zeolite catalyst for the alkylation of benzene with FCC off gas

	Laboratory scale	Commercial scale
Modifying element (wt%)	1.65	1.55
Na_2O (wt%)	0.0058	0.0023
n-Hexane adsorption (wt%)	5.92	6.63
Cyclohexane adsorption (wt%)	3.48	4.53
Mechanical strength (kg/cm)[a]	15.2	26.0
Surface area (m^2/g)	315	320

[a] Radial strength of cyclindrical pellet with ϕ 1.7×10 mm.

After pilot plant unit tests and semi-commercial run in a 500 t/a unit, a commercial unit of 30 kt/a was constructed which was started up successfully in 1993. Since then, this commercial unit is running satisfactorily. Under reaction conditions of 300–450°C, 0.5–1.2 MPa, ethylene WHSV 0.4–1.5 h^{-1}, and a mole ratio of benzene to ethylene of 4–7, the conversion of ethylene is higher than 95%, and ethylbenzene selectivity exceeds 99%. Performance data during the test-run period of the commercial unit are shown in Table 5.

Table 5
Data from test-run performance of the commercial unit for the alkylation of benzene with FCC off gas[a]

	SOR[b]	MOR[c]	EOR[d]
Ethylene conversion (%)	99.85	98.78	92.52
Ethylbenzene (EB) selectivity (%)	–	>99	>99
Benzene consumption (tons/tons EB)	–	0.765	0.761
Ethylene consumption (tons/tons EB)	–	0.269	0.275
Overall energy consumption (kg FOE/tons EB)	<400	400	410
Aromatics in tail gas (wt%)	0.03	0.06	0.07
Purity of EB (wt%)	>99.6	>99.6	>99.6

[a] Typical composition of the feeding dry gas (vol%): H_2 14.00, O_2 1.06, N_2 11.00, CO 0.75, CO_2 1.07, CH_4 32.09, C_2H_4 19.19, C_2H_6 19.77, C_3H_6 0.59 and C_3H_8 0.15. The H_2O content was 1300 ppm, and the H_2S content was 3000 mg/m^3.

[b] SOR denotes "start of run". In SOR, only single-pass operation was carried out, i.e., diethylbenzenes and propylbenzenes were not recycled for trans-alkylation reactions.

[c] MOR denotes "middle of run".

[d] EOR denotes "end of run".

Table 6
Characteristics of the high silica content zeolite catalyst after regeneration in the commercial unit of benzene alkylation

	Position of catalyst in the reactor				
	Section 1	Section 2	Section 3	Section 4	Section 5
Coke deposited (wt%)	0.2	0.2	0.1	0.1	0.1
n-Hexane adsorption (wt%)[a]	6.04	6.18	6.45	6.57	6.60
Cyclohexane adsorption (wt%)[a]	3.56	4.36	4.47	4.50	4.48
Surface area (m^2/g)	302	310	308	313	320

[a] Saturate adsorption at 25°C under the partial pressure of adsorption of 20 mm Hg.

The test-run period of the commercial unit lasted for 215 days. It can be seen from Table 5 that due to coke formation, the activity of the catalyst decreased gradually. However, the activity could be restored completely after regeneration of the catalyst by burning off the coke. Basic data of the 3884 catalyst after regeneration in the commercial unit are listed in Table 6.

Presently, several commercial units utilizing the technology of this process are planned to be constructed in other refineries of China.

5. Development of a new process for the conversion of syngas to lower olefins via dimethylether (syngas via DME to olefins, or the SDTO process)

Recently in DICP, Cai et al. [30–33] have successfully developed a new process for the conversion of syngas to lower olefins via the formation of dimethylether (DME) as an intermediate compound, and this process was designated as the SDTO process (syngas via DME to olefins). In this process, bifunctional metal (Cu, Zn, etc.)-zeolite catalysts have been developed, which can convert syngas very selectively to DME with high CO conversion, since this reaction is far more favorable thermodynamically than methanol synthesis from syngas. Furthermore, compared with the methanol to olefin (MTO) process, the SDTO process converts syngas directly to DME, which is also a reaction intermediate of the MTO process, and thus exhibits greater efficiency than the MTO process since the latter process has to first produce methanol from syngas, and then convert methanol to DME. Other special features of the SDTO process include: (1) the development of a SAPO-34 type molecular sieve catalyst for the conversion of DME to lower olefins with an ethylene selectivity as high as 50–60%, which is remarkably higher than that obtained with the conventional ZSM-5 type zeolites; (2) a fluidized bed reactor is utilized in the second stage for the conversion of DME to lower olefins so that no water addition is needed during the reaction, and smooth operation can be achieved.

The first stage of the SDTO process is the conversion of syngas to DME. This stage can in fact be regarded as an independent process since DME itself is a versatile chemical raw material which is widely employed in the preparation of drugs, dyestuffs, pesticides, cosmetics, etc. Recently, it has been proposed that DME can be used as an environmentally friendly substitute for diesel fuel.

At present, DME is produced mainly from the dehydration of methanol, while the direct synthesis of DME from syngas is still in a developing stage. The catalysts commonly used for the direct synthesis of DME from syngas are composite catalysts comprised of Cu–Zn type methanol synthesis catalysts and γ-Al_2O_3. These composite catalysts, however, exhibit rather low DME selectivity and single-pass CO conversion, both close to 70%. Furthermore, the initial reaction temperature is also rather high (250–270°), which is unfavorable for the stability of the catalyst as well as for the conversion of the reaction, since this reaction is strongly exothermic, and CO conversion will be diminished when the reaction temperatures are higher than 240°C. Accordingly, new catalyst systems for the synthesis of DME directly from syngas have been developed in DICP. Zeolites are used as the catalyst supports, which have a much stronger acidity than γ-Al_2O_3, and the regular pore structure of the zeolite can also diminish the formation of coke. Also, the Cu–Zn components of the conventional methanol synthesis catalyst were modified with transition metals

Table 7
Performance of DICP catalysts for the direct synthesis of DME from syngas

Catalyst	Temperature (°C)	CO conversion (%)	Carbon efficiency (%)	DME selectivity (%)
Cu–Zn/zeolite	260	86.4	64.0	94.0
Cu–Zn–Mn–W/zeolite(1)	240	90.0	64.9	95.8
Cu–Zn–Mn–W/zeolite(2)	230	95.1	64.7	93.8
Cu–Zn–Mn–W/zeolite(3)	220	94.4	70.6	95.5

to enhance the activity so that the initial reaction temperature can be effectively lowered. Two types of novel catalysts, the SD217 type (Cu–Zn/zeolite) and the SD219 type (Cu–Zn/zeolite promoted with Mn and W oxides), have been successfully developed [34–36]. In the SD217 type catalyst, a zeolite with the mordenite structure is employed as the acidic support, while combination of Cu and Zn are used as the hydrogenation component. For the SD219 type catalyst, the support is a ZSM-5 zeolite, while the hydrogenation components are Cu–Zn oxides with tungsten and manganese oxides as promoters. Typical performance data of these two types of catalysts are shown in Table 7.

It can be seen from Table 7 that while the SD217 catalyst possesses satisfactory activity and selectivity at a higher temperature of 260°C, the SD219 catalysts exhibit good reactivity at temperatures as low as 220–240°C. It is worth to point out that besides their superior activity and selectivity, the SD219 catalysts also show activities for the hydrogenation of CO_2. One of the features of the SD219 type catalysts associated with this CO_2 hydrogenation property is that they exhibit better tolerance for the deteriorating effect of small amount of CO_2 in the feedgas. Thus, according to published data of analogous studies [37], when the feedgas contained 5.0 wt% of CO_2, the CO conversion decreased 13 wt%, and the DME selectivity decreased 27 wt%. However, with the same 5.0 wt% CO_2 in the feedgas, the CO conversion decreased by only ca. 5 wt%, while the DME selectivity increased slightly over the SD219 catalysts.

On the basis of a continuous durability test of 2000 h for a SD219 catalyst, a pilot plant was constructed in the Qingpu Chemical Factory of Shanghai for a scale-up performance of the catalyst. A fixed-bed tubular reactor system containing one tube of i.d. 40 and 4000 mm in length was employed, and the pellet size of the catalyst was ϕ 5×6~7 mm. The feedgas was a semi-water-gas produced by the gasification of coal containing 42.43 vol% H_2, 23.21 vol% CO, 11.59 vol% CO_2 and 21.54 wt% N_2, respectively. Under 3.4–3.7 MPa, 240±5°C and GHSV 1000 h^{-1}, the pilot plant test had been operated continuously and smoothly for 1000 h, with a CO single-pass conversion of 75–78 wt% and a DME selectivity of 95% (Fig. 4). Evaluation of the pilot plant data showed that 190–200 g of DME were yielded for each standard cubic meter of syngas. Also, it can been seen from Fig. 4 that the stability of the SD219 catalyst was good, and the results proved that this process has a potential for scaling-up to a commercial process.

The second stage of the SDTO process is the conversion of DME formed in the first stage to lower olefins. The key problem in the development of this second stage is the R&D of an appropriate catalyst

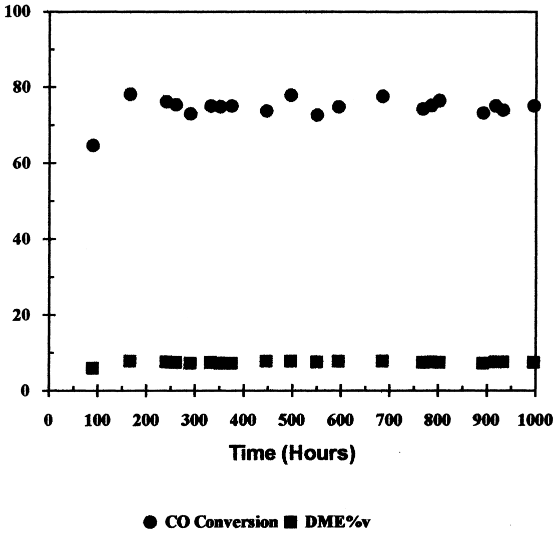


Fig. 4. Pilot plant performance over a Cu–Zn–Mn–W/zeolite catalyst for the direct synthesis of DME from syngas.

with good catalytic properties to be used in fluidized-bed operation.

In earlier studies on the conversion of methanol or DME to lower olefins, pentasil type zeolites, and mainly ZSM-5 type, were used as the catalysts. However, the ethylene selectivity is not satisfactory with these catalysts, which were mainly used in fixed bed reactor system. Furthermore, a large amount of water (as high as 70%) has to be added to the feedstocks to remove the heat evolved by the reactions. In DICP, as early as in the late 1980s, investigations have been conducted on the conversion of methanol to lower olefins over catalysts SAPO-34 molecular sieve [38,39] which was first developed by Union Carbide of the United States [40,41].

In the SDTO process, a SAPO-34 type catalyst, designated as DO123, has been developed for the conversion of DME to lower olefins with good performance in a fluidized-bed reactor system. One of the features of the DO123 catalyst lies in that the molecular sieve is synthesized with a new method different from the conventional procedure. Usually, the SAPO-34 type molecular sieve is synthesized by using tetra-ethyl-hydroxyl-amine (TEAOH) as the template agent. However, TEAOH is an expensive reagent, and this will bring a high cost for the production of the zeolite catalysts. In DICP, Liu and coworkers [42–45] developed new routes for the synthesis of the SAPO type zeolites by employing triethylamine or certain diamines as the template which are much cheaper than TEAOH. It has been estimated that SAPO type molecular sieve synthesized with templates of these cheap amines can reduce the cost to 20% of that prepared via TEAOH template.

In order to optimize the synthetic conditions of the DO123 catalyst, the process of crystallization can be monitored by means of IR, NH_3-TPD, SEM and MAS-NMR techniques so that the properties of the catalysts such as the number and strength of the acid sites, the contents of the Si, Al and P elements, the crystal size and the pore size, etc., can be controlled. Consequently, the selectivity for ethylene formation can be remarkably enhanced, and the formation of alkanes, especially the propane, can be suppressed.

Finally, by incorporating appropriate binders to the SAPO-34 type molecular sieve synthesized according to the DICP technology, the DO123 catalyst has been prepared into microspheres with good mechanical as well as abrasive-resistant properties. This catalyst was then tested with a bench-scale fluidized-bed reactor of a size of ϕ 20×500 mm, and at ambient pressure, 550°C, WHSV of 5–7 h^{-1}, and linear velocity of 12–15 cm/s. The conversion of DME was 100%, and the selectivities to C_2^{2-}, $C_2^{2-}-C_3^{2-}$ olefins and $C_2^{2-}-C_4^{2-}$ olefins were 50–60%, 85% and 90%, respectively. Methanol was also used as the feedstock for a test, and nearly identical results were obtained as with the DME feedstock (Table 8). This shows that both DME and methanol can be used as the feedstock for the production of lower olefins over the DO123 catalyst. It has also been found from the bench-scale operations that coke deposited on the DO123 catalyst could be removed easily by burning in air at 600°C for 10 min. 100 regeneration cycles were carried out, and the reactivity of the catalyst did not change apparently. All these results indicate that the DO123 catalyst has not only good activity and selectivity for the conversion of DME or methanol to lower olefins, but also the advantage of easiness in regeneration, high stability under hydrothermal conditions, and no need of water addition during the reaction operations.

Table 8
Performance of SAPO-34 type catalyst for olefin production with different feed components in a fluidized-bed bench-scale reactor[a]

Feed	Products (wt%)			
	C_2H_4	C_3H_6	$C_2^{2-}-C_3^{2-}$	$C_2^{2-}-C_4^{2-}$
Methanol[b]	62.79	22.34	85.13	89.57
DME+H_2O[c]	62.80	22.65	85.45	90.23
DME[d]	59.35	24.22	83.57	88.32

[a] Reaction temperature 550°C, products collected at 10 min after reaction started, and at 100% conversion.

[b] WHSV of methanol 6.45 h^{-1}, linear velocity of the reactants 15.21 cm/s.

[c] WHSV of DME 4.64 h^{-1}, linear velocity of reactants 15.21 cm/s.

[d] WHSV of DME 7.16 h^{-1}, linear velocity of reactants 11.75 cm/s.

The molecular sieve was then prepared in a autoclave of 1 M^3 capacity under commercial production conditions, and the DO123 catalyst so produced was put into scale-up test in a pilot plant fluidized-bed reactor system (ϕ 100×1000 mm), which was connected in series with the ‘‘syngas to DME’’ fixed-bed reactor mentioned above. The fluidized-bed reactor was an up-flow dense bed type with a capacity of 15–25 tons/year. The DME feedstock for the second stage reaction came from the concentrated product of the

Table 9
Pilot plant performance data over the SAPO-34 type catalyst for the production of olefins from DME

Product distribution (wt%)	550°C	560°C
CH_4	5.04	5.56
C_2H_4	50.32	53.48
C_2H_6	1.89	1.68
C_3H_6	30.69	28.96
C_3H_8	3.39	3.35
C_4H_8	8.07	6.38
C_2^{2-}–C_3^{2-}	81.80	82.44
C_2^{2-}–C_4^{2-}	89.68	89.32
Conversion (%)	98.10	99.27

first stage with a concentration greater than 98 wt%. The DO123 catalyst was operated in this pilot plant under different reaction conditions for process studies, and a total of 1500 cycles of regeneration were carried out on the same batch of catalyst. Characterization have been done on the catalyst after the operations, and no remarkable changes on its physico-chemical properties had been detected. Data from the pilot plant performances showed that there was a good duplication of the pilot plant results with that of the bench-scale tests (Table 9). Estimations from material-balance indicated that for the production of a ton of lower olefins (constituting 0.533 ton of ethylene, 0.340 ton of propylene and 0.118 ton of butenes), 1.880 tons of DME or 2.615 tons of methanol have to be consumed.

The SDTO process is now undergoing feasibility studies for the construction of a demonstration plant with a capacity of 3000 tons/year.

6. Development of a new catalyst for the gas-phase direct synthesis of ethanol from syngas

Ethanol is an important basic chemical which is consumed in a great quantity by various industries in China. Ethanol can be produced by processes based on the hydroformulation of methanol or on the hydration of ethylene. In China, however, ethanol is produced mainly via the fermentation process using foodstuffs as the raw materials, which often suffer from shortage in supply. On the other hand, direct conversion of syngas into ethanol with coal or natural gas as the starting materials has been assessed to be a more appropriate route in China since there are rich resources of coal and natural gas in this country. Based on such considerations, researchers in DICP initiated a R&D project in 1990 for the production of ethanol directly from syngas.

It has been reported that for the direct gas-phase synthesis of ethanol from syngas, supported rhodium are the most promising catalysts [46]. However, the rhodium loading of the catalysts reported were generally in the range 4–5 wt%, which imply that the primary investment for the commercialization of this process will be too high. Thus, one of the chief goals of the DICP project is to seek new and effective supported catalysts with low rhodium loading.

After laborious R&D work [47,48], including screening of catalysts, basic studies and characterization of the catalysts, as well as process development, promising results have been achieved. A 1 wt% Rh catalyst with silica as the supporting material and lithium and manganese oxides as promoters has been found to be a satisfactory catalyst. Reaction tests of the catalyst have been performed first in a microreactor system, and then scaled up to a single-tube bench scale reactor system of 200 ml catalyst and with tail-gas recycling [49]. Results from bench scale operations indicated that the low-rhodium catalyst exhibited high activity and selectivity for the production of C_{2+} oxygenates from syngas. At a pressure of 6.0 MPa, a temperature of 310°C, GHSV of 40 000 ml/g cat h, and H_2/CO mole ratio of 2:1, the space–time yield (STY) of C_{2+} oxygenates reached 290 mg/g cat h. The product distribution of the C_{2+}-oxygenated compounds is shown in Table 10.

Table 10
Product distribution of C_{2+}-oxygenates from the bench-scale performance (wt%)

CH_3CHO	C_2H_5OH	C_3H_7OH	$C_2H_5COOCH_3$	$C_2H_5COOC_2H_5$	C_4H_9OH	CH_3COOH
19.2	34.8	3.8	4.0	4.5	3.0	30.7

Catalyst: Rh–Mn/SiO_2 (Rh content 1 wt%).
Reaction conditions: 310°C, 6.0 MPa, H_2/CO=2, SV=43 000 l/kg cat h.

It can be seen from Table 10 that in the C_{2+}-oxygenate products, ethanol, acetic acid and acetaldehyde were the main constituents which are all valuable chemicals. However, since ethanol is the most desired product for the process, the selectivity to ethanol can be maximized by loading a copper catalyst in the lower section of the same tubular reactor, which can hydrogenate the other C_2-oxygenates into ethanol. This modified technology has also been successfully developed in the bench-scale investigations, and a selectivity of 92% for ethanol has been achieved. Furthermore, a durability test of continuous operation for 1000 h had been carried out, and the activity and selectivity of the catalyst were practically unchanged during the test.

On the basis of the bench-scale performance, a pilot plant installation was designed and constructed in Sichuan Province, a province well known for its richness in natural gas. The pilot plant comprised a multitubular reactor of 30 l catalyst volume, a tail-gas recycling compressor, and distillation columns for product separation. The raw syngas feedstock is supplied by a steam-reforming converter of a commercial methanol plant, which utilizes natural gas as the starting material. A syngas purification technology has been successfully developed for the removal of sulfur and carbonyl impurities for ensuring a good durability of the catalyst. Operation results demonstrated that scaling-up of the process is successful, and provided data for the designing of a demonstration plant, e.g., of 1000–3000 tons/year capacity.

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