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Environmentally benign catalytic technology for refining and petrochemical production

A recent review of related R&D activities in China

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1. Introduction

The more and more stringent requirement for environmental protection becomes now the major driving force for technological progress. The impact is significant for refining and petrochemical industry in China as well as in the world. Looking forward to 21st century, the technologies for waste treatment should be continuously improved, and meanwhile, the technologies of green processes should be developed. The technologies of green processes are demanded both for revamping the existing units and for designing new units during the capacity expansion of China's petrochemical industry in the next century.

A green process is a highly selective chemical process using green raw materials, catalysts, and solvents, producing green products. Since most of the petrochemical processes were developed in 1940–1950s, technological breakthrough based on entirely new scientific knowledge is necessary for developing green processes. Catalysis, the key element for many chemical processes, will still play an important role in the development of green chemistry and hence in the greening of chemical processes or clean production. Historical review reveals that technological breakthrough occurs generally through the discovery and application of new catalytic materials or new reactor engineering.

The R&D activity in China in the field of catalysis has come to a rapid development stage since 1980s, which results in a series of technological innovations [1–3]. A number of unique catalytic technologies have been invented and commercialized in China, such as deep catalytic cracking (DCC) for maximum production of gaseous olefins, distillate selective cracking accompanied by alkene polymerization (DSCAP), liquid phase selective hydrogenation for propene fraction using a single stage adiabatic reactor, medium pressure hydro-upgrading process for production of low sulfur and low aromatics diesel fuel (MHUG), etc. A variety of new catalysts has been developed and commercially applied in refining and petrochemical industry. Scientists in China from universities and research institutions of Chinese Academy of Sciences and industrial sectors have also made contributions to the basic research and applied basic research in different areas of catalysis, including those areas related to green chemistry. In recent years, a state key applied basic research project, "Catalytic Chemistry and Reaction Engineering for Developing Environmentally Friendly Refining and Petrochemical Technology", has been established and jointly supported by Natural Science Foundation of China (NSFC) and China Petrochemical Corporation (SINOPEC). The present paper reviews the recent work related to developing environmentally benign refining and petrochemical technology.

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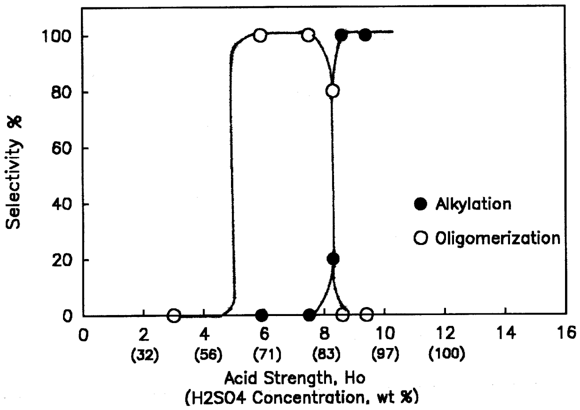

Fig. 1. Relationship between acid strength (H_2SO_4 concentration) and selectivity in the alkylation.

2. Alkylation of isobutane with butenes

Alkylation of isobutane with olefins is an important process in petroleum refining industry. The product, alkylate, is a valuable gasoline blending component with high octane number, low Reid vapor pressure (RVP), and no aromatics and olefins, and hence can be regarded as a clean-burning-paraffinic gasoline blending component. In current commercial practice, two kinds of liquid acids are used as catalysts for isobutane–butene alkylation, i.e., concentrated sulfuric acid and hydrofluoric acid. The disposition of spent sulfuric acid and the volatilization of hydrofluoric acid bring serious environmental concern. The challenge is obviously to develop effective solid acid catalysts for alkylation process. It is almost a worldwide effort for the researchers in the field of petroleum refining [4–6]. The requirement for a solid acid catalyst, which is effective for alkylation process, can be summarized as follows:

- High acid strength, as shown in Fig. 1.
- High density and homogeneous distribution of acid sites.
- Ability for catalyzing hydrogen transfer between C_8^+ carbonium ion and isobutane molecule.
- High surface area and large pore size.

Research Institute of Petroleum Processing, China Petrochemical Corporation (SINOPEC), has been working actively on the project for developing solid acid catalysts and related process for alkylation. A number of solid superacids are developed and tested for alkylation reaction [7]. The alkylation of isobutane with butene under supercritical condition using a selected solid acid has been carried out in a fixed-bed reactor for 1400 h with high stability for catalyst activity and selectivity [8]. The catalyst stability is shown in Fig. 2. The product distribution is comparable with that of liquid acid alkylation process as shown in Fig. 3.

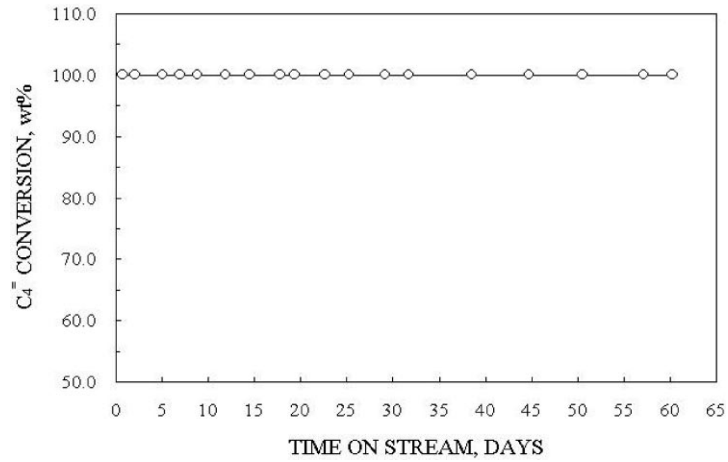

Fig. 2. Conversion of butene vs. time on stream during the lifetime test of solid acid catalyst under supercritical reaction condition.

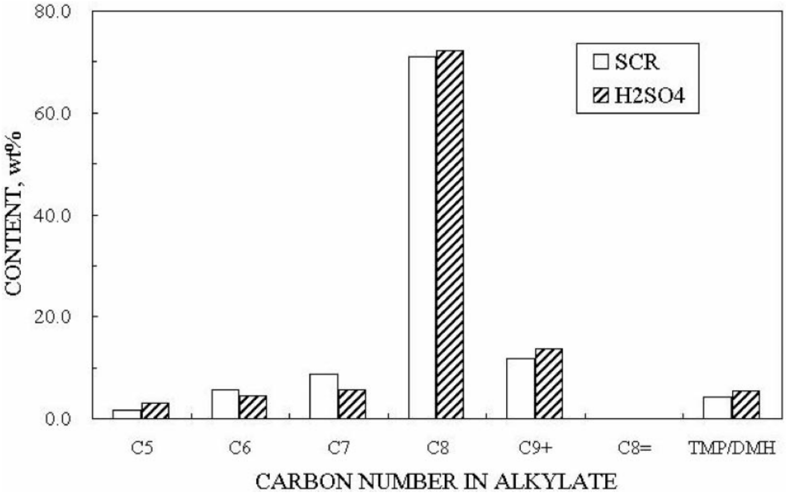

Fig. 3. Comparison of product distribution between solid acid and sulfuric acid alkylation.

3. Hydrodenitrogenation and hydrodesulfurization by transition metal nitrides

The strict specifications of transportation fuels force refiners to pursue approaches for deep desulfurization and denitrogenation of fuels. It is well known that the C–S bonding of some substituted dibenzothiophenes is very stable for currently used hydrodesulfurization catalysts and processes. Besides, the pre-sulfiding procedure commonly used for industrial hydrogenation processes may also cause environmental problems. Hence, much more efforts have been focused on developing new catalytic materials and related processes.

The preparation of the nitrides of transition metals is difficult and severe reaction conditions are usually required by the conventional methods. Moreover, the low surface area of the prepared nitrides limits their applications. A research group in Dalian Institute of Chemical Physics, Chinese Academy of Sciences, is very active in the study of high surface area nitrides. A number of supported or unsupported nitrides have been developed including monometallic nitrides and bimetallic nitrides, and their activities in hydrodesulfurization and hydrodenitrogenation have been studied [9–13]. The synthesis method is characterized in a temperature programmed reaction procedure and a rather mild reaction condition. If the starting material is MoO_3, the reaction proceeds through three stages with different heating rates in flowing ammonia, followed by a passivation step in a mixture of nitrogen with a small amount of oxygen to stabilize the formed nitride. The second metal of the bimetallic nitrides is introduced into the precursor by coprecipitation method. The final nitriding temperatures and surface areas of several synthesized nitrides are listed in Table 1 [10].

The activities of the nitrides listed in the table were tested for pyridine hydrodenitrogenation and compared with a commercial $CoMo/Al_2O_3$ catalyst, which was pre-sulfided before reaction. The comparison of the conversion level of pyridine (CON) and denitrogenation of pyridine (DEN, the percentage of nitrogen-free products) is shown in Fig. 4. Fig. 4 indicates that Ã-Mo_2N displays similar activity as the commercial sulfided catalyst, while all the bimetallic nitrides exhibit superior performance. In particular, CoMoN catalyst attains high levels of CON and DEN,

Table 1
The final nitriding temperatures and BET surface areas of synthesized nitrides

Nitrides	Final nitriding temperatures (K)	BET surface areas (m^2/g)
TiMoN	953	154
CoMoN	882	148
ZrMoN	973	132
CeMoN	938	130
Ã-Mo_2N	973	140

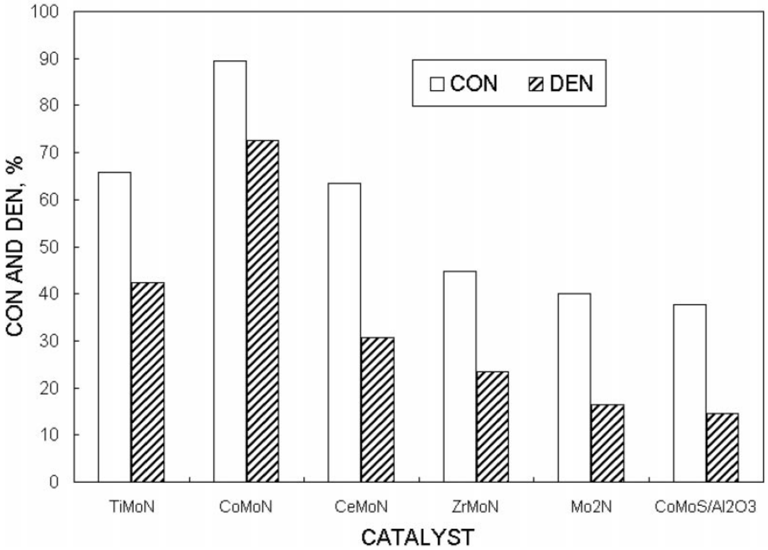

Fig. 4. The conversion (CON) and denitrogenation (DEN) of pyridine hydrodenitrogenation with various catalysts after 4 h on stream. Reaction temperature 573 K, $P_{H_2} = 3.0$ MPa.

89 and 72.5%, respectively, which are much higher than that of the sulfided CoMo/Al_2O_3 catalyst.

For hydrodesulfurization, it was reported [14] that the activities of unsupported Ã-Mo_2N for a coal-derived feed is twofold that of a commercial Ni–Mo/Al_2O_3 catalyst. Based on the synthesis method described above and further control of the particle size, Mo nitrides with high surface area can be prepared. Activities of prepared nitrides with different surface areas for thiophene hydrodesulfurization (HDS) and cyclohexene hydrogenation (HYD) have been tested simultaneously [9]. The results demonstrated in Fig. 5

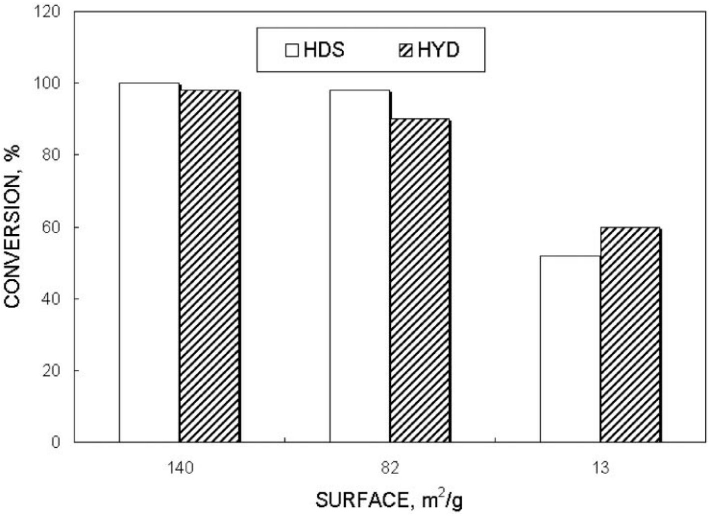

Fig. 5. Effects of surface area on the conversion of thiophene HDS and cyclohexene HYD at 573 K, LHSV = 18 h^{-1}, $P_{H_2} = 3$ MPa.

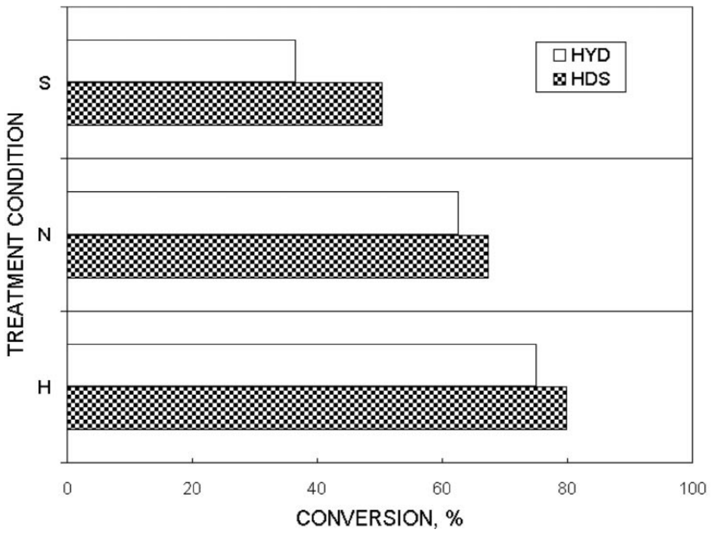

Fig. 6. Conversion of thiophene and cyclohexene over Mo_2N-6 subjected to different pre-treatment conditions: (N) without pretreatment; (S) pre-sulfidated and (H) pre-reduced.

show that high surface area is important in enhancing activities of nitrides for both hydrodesulfurization and hydrogenation. The pre-treatment of the catalysts before testing is also critical for their performance. Fig. 6 indicates that pre-reduction by hydrogen is much more effective comparing with pre-sulfidation. It means that the application of nitride catalyst favors environmental protection.

4. Hydrogenation of organic compounds by amorphous alloys

The hydrogenation of a number of organic compounds in industry is performed in discontinuously operated batch reactors using Raney nickel catalysts. Those processes are usually ineffective and may have problems in waste treatment. For developing continuous processes, highly active and selective catalysts are the prerequisite. Amorphous alloys, especially Ni-based amorphous alloys, have been extensively studied in China due to their superior catalytic activity and selectivity. However, the low surface area and poor thermal stability of the amorphous alloys prepared by rapid quenching method limit their application as practical catalysts. A novel skeletal Ni–P amorphous alloy (R–Ni–P) has been invented [15]. Its preparation procedure is characterized in alkali leaching of an amorphous Ni–P–Al alloy obtained by the rapid quenching method. Comparing with a regular Ni–P amorphous alloy, the surface area of R–Ni–P has been increased by nearly two orders of magnitude and the thermal stability has been enhanced by 80°C. Their performance in the liquid phase hydrogenation of hexanedinitrile to 1,6-hexanediamine, which is an important intermediate in the production of nylon-6,6, is compared in Fig. 7. The results show that both TOF value and selectivity of R–Ni–P are almost same as those of Ni–P owing to their similar amorphous structures, however, the activity of R–Ni–P is about 50 times higher than that of Ni–P, which can be ascribed to the significantly higher surface area as shown in Table 2.

For developing fixed bed hydrogenation process to substitute batch reactor process, research efforts have been further focused on the preparation of supported amorphous catalysts [16]. By using chemical reducing method, several supported amorphous alloy catalysts have been prepared and their properties are compared with Ni–P and R–Ni–P amorphous alloys in Table 2. The high surface areas and crystallization temperatures of supported amorphous alloy catalysts Ni–P/SiO_2 and Ni–B/SiO_2 listed in Table 2 assure their high catalytic activity and stability, compar-

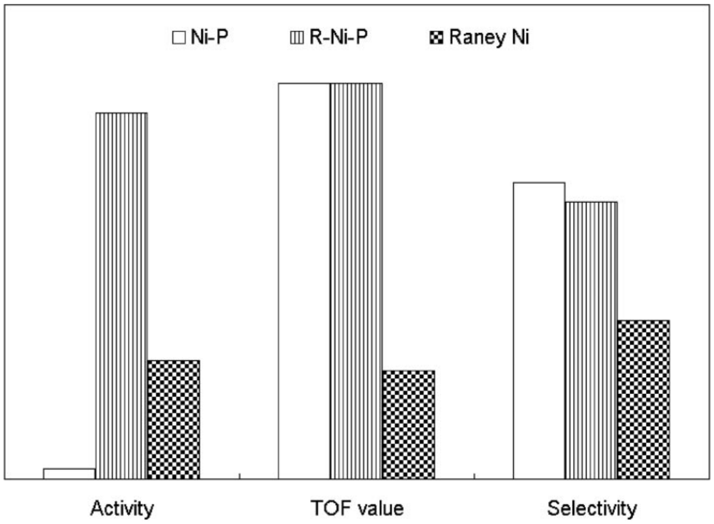

Fig. 7. Catalytic activity (mmol H_2/hg_{Ni}), selectivity, and TOF value of the as-prepared R–Ni–P and Ni–P amorphous alloy catalysts as well as Raney Ni during the liquid phase hydrogenation of hexanedinitrile (HDN) to 1,6-hexanediamine. Reaction conditions: $T = 350\,K$, $P_{H_2} = 4.0\,MPa$, EtOH/HDN (v/v, 3:1).

Table 2
Properties of the as-prepared supported Ni-based amorphous catalysts

Samples	Ni loading (wt.%)[a]	Composition (atomic ratio)	S_{BET} (m^2/g)	S_{Ni} (m^2/g)	T_C (K)
Ni–P	–	$Ni_{88}P_{12}$	1.2	0.8	593
R–Ni–P	–	$Ni_{68}Al_{25}P_{14}$	87	58.0	671
Ni–P/SiO_2	3.0	$Ni_{86}P_{14}$	187	25.0	713
Ni–B/SiO_2	10.0	$Ni_{76}B_{24}$	156	22.5	610
Ni–Co–B	–	$Ni_{32}Co_{32}P_{36}$	7.5	6.8	653

[a] Weight percentage.

ing with supported Ni catalysts and industrially used Pd/C catalyst in the hydrogenation of cyclopentadiene to cyclopentene and liquid phase hydrogenation of 4-carboxyl benzaldehyde. The results are shown, respectively, in Table 3 and Fig. 8. In addition, it is noticeable that Ni–B/SiO_2 amorphous catalyst exhibits higher sulfur resistance than the corresponding Ni/SiO_2 catalyst as shown in Table 4.

The dispersion of the amorphous alloy on support, the interaction between amorphous alloy and support, and hence the stabilizing effect of support on amorphous alloy were discussed in detail [16]. The sur-

Table 3
Selective hydrogenation of cyclopentadiene (CPD) to cyclopentene (CPE) at ambient pressure and 393 K in a fixed bed

Catalyst	H_2:CPD (molar ratio)	LHSV (h^{-1})[a]	Conversion (%)	Selectivity (%)	Lifetime (h)
5% Ni–B/SiO_2	1.4	12	100	96	>1000
5% Ni/SiO_2	2.0	12	100	80	–
5% Ni/Al_2O_3	2.0	12	100	50	–
0.5% Pd/C	3.0	2	<100	45	–

[a] Liquid velocity.

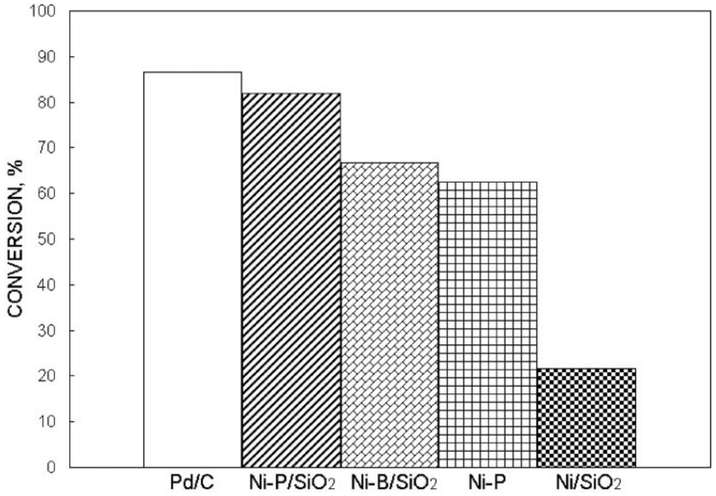

Fig. 8. The conversion of 4-carboxyl benzaldehyde (4CBA) over different catalysts in liquid phase hydrogenation. Reaction conditions: $T = 551\,\mathrm{K}$, $P_{\mathrm{H}_2} = 6.8\,\mathrm{MPa}$, 4CBA/TA (w/w, 2000 ppm).

Table 4
Benzene hydrogenation at ambient pressure in a fixed bed

Catalyst	LHSV (h^{-1})[a]	H_2/benzene	*T* (K)	Solvent	Conversion (%)	Selectivity (%)	Sulfur resistance (ppm)
15% NiB/SiO_2	2–3	2–3	423	Benzene	100	100	2000
15% Ni/SiO_2	2–3	2–3	423	Benzene	85	100	500

[a] Liquid velocity.

face electronic state of amorphous alloys has been studied by carefully designed XPS experiments [17]. By comparing with the electron binding energies of the pure Ni, B and P, the XPS spectra demonstrated that boron donated electron to nickel in Ni–B alloy, resulting in electron-enrichment of elemental Ni and electron-deficient elemental B, while no significant electron transfer between Ni and P in N–P alloy was observed. The results possibly explain the different catalytic behaviors of Ni–P and Ni–B amorphous alloy catalysts including hydrogenation activity and sulfur resistance ability based on following model, in which boron adsorbed sulfur reversibly prior to nickel, protecting active Ni sites from the sulfur poisoning.

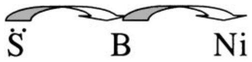

Table 5
The comparison of magnetic-stabilized reactor using amorphous alloy catalyst with batch reactor using Raney Ni catalyst in caprolactam hydrofinishing

	Batch reactor	Magnetic-stabilizing fluidized reactor
Catalyst	Raney nickel	Ni-based amorphous alloy
Pressure of hydrogen (Mpa)	0.7	1.0
Temperature (K)	368	363
Hydrogen/feed (v/v) ratio	–	100
Catalyst/feed (w/w) ratio	1/2000	–
LHSV (h^{-1})	–	16
PM value of the product	2000	5500

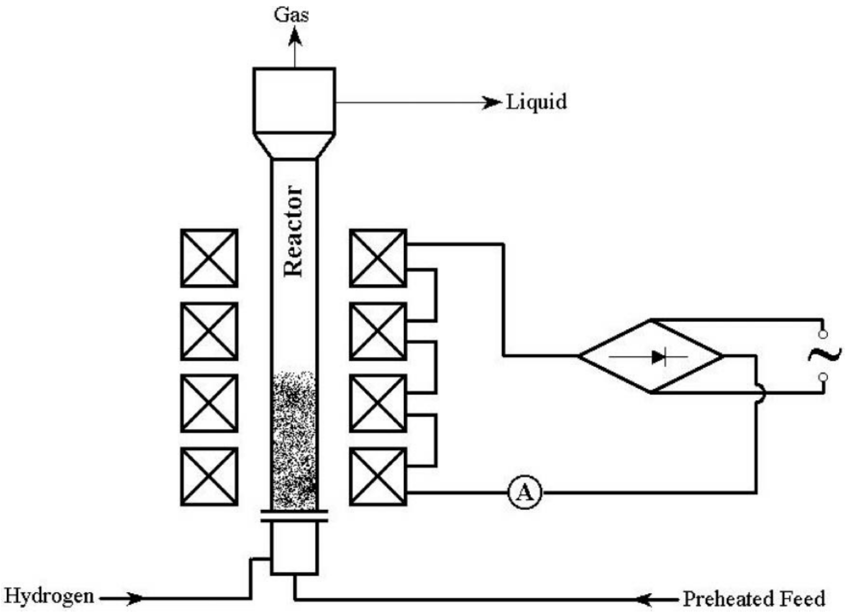

Fig. 9. The magnetic stabilized fluidized reactor.

Research Institute of Petroleum Processing, SINOPEC, has developed a series of amorphous alloys used for olefin hydrogenation, aromatics saturation, reformate hydrofinishing, caprolactam hydrogenation, etc. [18–24]. A unique magnetic stabilized fluidized reactor with Ni-based amorphous alloy catalysts, as shown in Fig. 9, has been developed for hydrogenation of organic compounds [21,23,24]. For the hydrofinishing of caprolactam, comparing with the conventional technology based on a batch reactor using Raney nickel as catalyst, the new reactor system using highly active amorphous alloy catalyst is characterized in not only high efficiency in hydrogenation, but also a highly efficient continuous flowing system with low catalyst consumption. The comparison is shown in Table 5. The bench scale test for the new reaction system has been successfully performed.

5. Selective oxidation of hydrocarbons

The oxidation of hydrocarbons is an important reaction for the production of many petrochemicals. The clean production of oxygen-containing compounds heavily depends on the selectivity of the reaction. It is well known that the development of titanium silicalite (TS-1) catalyst has greatly enhanced the selectivity of oxidation reactions for producing hydroquinone, propylene epoxide, cyclohexanoneoxime, etc. The solid TS-1 catalyst is usually used in liquid phase reactants to catalyze the reaction. Hence, small crystallite especially nanometer crystallite of titanium silicalite should be more effective in catalyzing the oxidation reaction using hydroperoxide. A unique in situ planting method has been developed to grow isolated nanometer crystallites of titanium silicalite on the surface of a support [25–27]. The catalyst prepared exhibits excellent performance in epoxidation of propylene with hydroperoxide. Under a reaction condition of 0.7 MPa, 333 K, and time length 1.5 h, the conversion and utilization of hydroperoxide are 94.7 and 96.3%, respectively, and the selectivity for PO achieves 88.5%. For the conventionally synthesized TS-1 catalyst the utilization of hydroperoxide is only 89.8% under the same reaction condition.

The lattice oxygen atoms of composite oxides such as VPO, the oxides of vanadium and phosphorus, can be used to selectively catalyze the oxidation of hydrocarbons. However, the selectivity of the reaction, such as butane oxidation to produce *cis*-butenedioic anhydride, greatly depends on the availability of

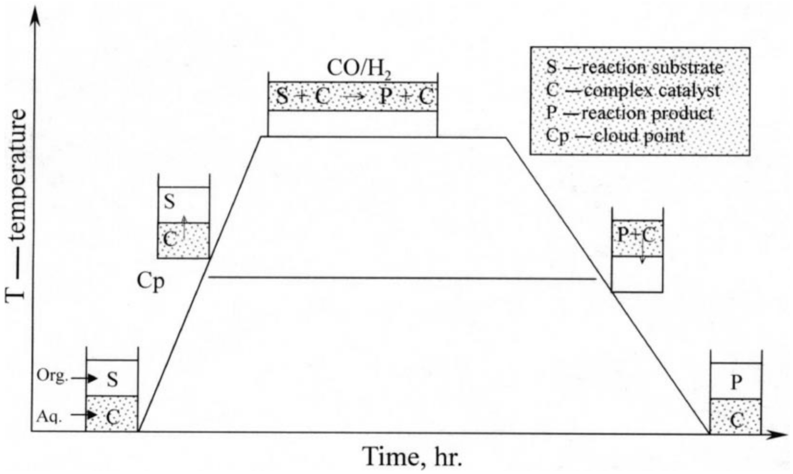

Fig. 10. The concept of thermoregulated phase transfer catalysis.

lattice oxygen on the surface. Ultrafine VPO particles have been prepared through a supercritical drying process followed by surface modification, and used to catalyze butane oxidation [28–30]. The selectivity for *cis*-butenedioic anhydride attains a level as high as 89% (the conversion of butane is 34%). Meanwhile, fine particles of VPO have also been prepared by a high strength milling method and tested for the same reaction. A compromise between conversion and selectivity has been achieved by using the catalyst: when the selectivity for *cis*-butenedioic anhydride is 84%, the conversion of butane is 60%, or, when the former is 70%, the later is 87%.

6. Hydroformylation of olefins

More than 90% of the processes for hydroformylation of long chain olefins so far in industry are still using traditional cobalt catalysts. Those processes are not efficient enough and easy to cause environmental problems. Worldwide research efforts in this field are concentrated in aqueous/organic bi-phase catalytic system and related ligand catalysts.

A unique thermoregulated phase transfer method and catalyst have been developed for aqueous/organic bi-phase hydroformylaiton of long chain olefins [31–34]. The concept of thermoregulated phase transfer catalysis can be illustrated by Fig. 10.

A series of ligands with different structures has been synthesized and their cloud points have been determined and correlated with the structure. The performance of the corresponding rhodium complexes has been tested for 1-dodecene hydroformylation. The conversion and aldehyde yield attain levels of higher than 95 and 90%, respectively. The catalysts are easy to be separated and re-used.

The hydroformylation of 1-dodecene has also been catalyzed by a water-soluble rhodium complex, $RhCl(CO)(TPPTS)_2$, in the presence of different surfactants and alcoholic solvents [35–38]. In the formula, TPPTS stands for $P(m\text{-}C_6H_4SO_3Na)_3$. The results show that hydroformylation reaction in bi-phase catalytic system occurs in the interface of aqueous/organic phases. The formation of micelle promotes the reaction and favors the linear aldehyde products. The interaction between the active rhodium anion species and cationic terminal of surfactant is the key for the enrichment of rhodium catalyst in the interlayer and the enhancement of reaction rate.

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