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Recent advances in R and D of commercial catalysts for acrylonitrile synthesis, styrene production and toluene disproportionation processes

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Abstract

This paper reports the progresses in R and D and commercial application of the industrial catalysts, developed and produced by SRIPT for acrylonitrile, styrene and toluene disproportionation processes.

The research works of developing a unique method of catalyst preparation, adding proper amount of sodium ions to the Mo–Bi oxides system to improve catalytic activity and attrition resistance, and adding bromine ions to increase acrylonitrile selectivity have been conducted. The new catalyst for acrylonitrile production, MB-96, has been successfully used in a plant of 25 000 t/a with an acrylonitrile yield of 82 mol%.

In the development of the catalysts for ethylbenzene dehydrogenation, the studies on the structure of active phase and the effects of potassium and cerium as promoters show that under reaction conditions potassium mainly promotes the electronic exchange between Fe^{2+} and Fe^{3+} ions, while cerium improves the stability of Fe–K phase. The new catalyst, GS-05, has been successfully used in an ethylbenzene dehydrogenation plant of 60 000 t/a with an ethylbenzene conversion of 65–66 wt% and a styrene selectivity higher than 96 wt%.

In the development of the catalysts for toluene disproportionation and transalkylation, the studies on improving the synthesis of mordenite, coke formation behavior of catalyst and modifying surface acidity have been done. The new catalyst HAT-095 has been successfully used in a plant of 1 007 000 t/a with a reaction temperature of only 634 K under a high space velocity of $1.44\ h^{-1}$ and a high conversion of 45 mol%, showing high activity and high stability.

Keywords: Commercial catalyst; Acrylonitrile; Styrene; Toluene disproportionation

1. Introduction

Catalysis has made major contributions to many areas of petrochemical industry. Before a catalyst is commercialized, applied research and development, which are indispensable, are carried out in the laboratory and pilot plant of Shanghai Research Institute of Petrochemical Technology (SRIPT).

In recent years, a series of catalysts for important petrochemicals such as acrylonitrile, styrene, benzene and xylenes, have been developed by SRIPT. According to the respective development features of these catalysts, some important applied fundamental research conducted in laboratories and engineering scaling-up of the catalysts and corresponding processes in model or pilot plant for development are selectively described in this paper. The outstanding performance of the catalysts produced by SRIPT in

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large commercial plants to replace their foreign counterparts are also briefly introduced.

2. R and D of important petrochemical catalysts

2.1. *Catalyst for acrylonitrile production by propylene ammoxidation*

The R and D of acrylonitrile catalyst began in the early 1960s. Since then, a lot of applied research works for multi-component metal oxide catalysts based on Mo–Bi–Fe system were conducted, including the research of catalyst on formulation, main active phase, preparation, cation lattice defect, redox property, role of bi-valent or tri-valent metal as promoter, etc. Following is a brief introduction to the major features of the R and D of acrylonitrile catalyst. Patents relating to the catalysts were authorized in China, USA and Europe [1–6].

A unique method of preparing acrylonitrile catalyst for fluidized bed reactor has been developed [1]. Under particular conditions, a stable water solution of bismuth molybdate is prepared, then the solution, which will not precipitate within 48 h, is mixed with other components to form a slurry. The slurry is heated, spray-dried and calcined in a conventional way to form the desired catalyst. Because there is no precipitate in the mixed solution, good mixing of catalyst components and easy conveyance of slurry in continuous production are ensured, and the catalyst prepared in this way has higher activity.

The catalysts, using the same catalyst components, the same preparation conditions and different molybdates (e.g. bismuth molybdate) used as key phase are prepared. The corresponding catalytic activities of the catalysts were evaluated and are shown in Table 1.

Table 1 shows that the catalyst prepared by use of γ-bismuth molybdate solution has higher activity than the catalysts made from α-bismuth molybdate solution or α-bismuth molybdate precipitate.

Through the research on the role of alkali metal as a promoter, it was found that proper addition of sodium, which had been widely considered as a detrimental component in propylene ammoxidation, not only increases acrylonitrile yield, but also improves attrition-resistance, an important property in a commercial fluidized bed reactor.

Table 1
Effects of different bismuth molybdates used in preparation on the activity of the resulting catalyst

Molybdate	Yield of acrylonitrile (mol%)
α-Bismuth molybdate solution	75.9
α-Bismuth molybdate precipitate	75.6
γ-Bismuth molybdate solution	77.8

Activity evaluation conditions – I.D. of fluidized bed reactor: 38 mm; reaction temperature: 708 K; reaction pressure: 0.085 MPa (G); $C_3^{=}$: NH_3 : air = 1 : 1.2 : 10 (mol).

When sodium is added to the acrylonitrile catalyst containing multi-metal oxides such as $K_{0.1}Ni_{2.5}Co_{4.5}Fe_3Bi_1P_{0.5}Mo_{12}O_x$, it can be in a form of any of its decomposable compounds added to ammonium molybdate and nitrate solution. Sodium can also be added to an ammonia-stable silica gel support, but the SiO_2/Na_2O ratio (wt%) of the silica gel must be in the range 200–400. The effects of the sodium amount on acrylonitrile yield and catalyst attrition loss were examined [2]. The results are shown in Table 2.

It is very interesting and important to learn from Table 2 that the addition of a proper amount of sodium to a multi-component acrylonitrile catalyst increases both its catalytic activity and attrition-resistance, while an excess of sodium significantly decreases catalytic activity. Besides, it was found that the catalyst, prepared by adding halogen anion of strong acidity, exhibits a strikingly improved selectivity without the problem of instability caused by halogen volatilization.

Adding halogens to multi-metal oxide catalyst significantly decreases the formation of CO and CO_2 during propylene ammoxidation, and therefore increases the selectivity of acrylonitrile [6]. However, the ammonium salts often used as raw materials in catalyst preparation yield volatile halogenated ammo-

Table 2
Effects of sodium amount on catalytic activity and catalyst attrition loss

Na:Bi, atomic ratio	Acrylonitrile yield (mol%)	Catalyst attrition loss (wt%)
0:1	77.4	7.92
0.3:1	79.8	2.00
0.8:1	73.9	–

Activity evaluation conditions are the same as those of Table 1, except the reaction pressure is atmospheric.

Table 3
Effects of different halides on yield and selectivity of acrylonitrile

Halogen/Bi, atomic ratio	Selectivity of acrylonitrile (mol%)	Yield of acrylonitrile (mol%)	Yield of CO+CO_2 (mol%)
No halogen	81.5	76.0	12.0
Br:Bi=0.1:1	83.5	77.8	8.5
I:Bi=0.15:1	83.2	77.0	8.4
Cl:Bi=0.15:1	82.7	76.1	7.9

Activity evaluation conditions are the same as those of Table 1.

nium by combining with halogen anions during catalyst calcination, and then the halogen is removed from the catalyst. A special preparation method has been invented to avoid the loss of halogen. First, a catalyst precursor without halogen is made. The precursor is impregnated with a water solution of halide like KBr, KI or KCl, and then dried, calcined to the desired catalyst. The effects of different halides on the yield and selectivity of acrylonitrile are shown in Table 3.

The data in Table 3 show that halogens, especially Br, are advantageous to decreasing CO and CO_2, and increasing selectivity of acrylonitrile.

Obviously, in improving acrylonitrile selectivity, it is also important to select a proper anion besides the adjustment of metal cation components.

As a result of improvement for several generations, catalyst MB-82 has been used in acrylonitrile plants of 5000–10 000 t/a in China since 1985. The acrylonitrile yield of MB-82 reached 76–77 mol% in a 25 000 t/a plant in 1991. A new generation catalyst of MB-86, was tested in a ϕ600 mm reactor and a commercial reactor of 7000 t/a in 1989 and 1990, respectively. In 1992, MB-86 was commercialized in an imported acrylonitrile plant of 25 000 t/a, with yield higher than 80 mol%.

In 1994 and 1996, catalyst MB-86 was successfully employed in two imported plants, each of 50 000 t/a. Acrylonitrile yield in both plants reached higher than 80 mol%.

Based on applied fundamental research and continuous improvement, the newest generation catalyst in MB series, MB-96, has been used in a 25 000 t/a plant successfully since October 1997. The acrylonitrile yield reaches 82 mol%, which is 2% higher than MB-86' under the same operating conditions.

2.2. *Catalyst for styrene by ethylbenzene dehydrogenation*

Catalysts of a GS series and corresponding process technology for styrene from ethylbenzene by negative-pressure adiabatic dehydrogenation have been developed by SRIPT recently. The GS-05 catalyst based on Fe–K–Ce–Mo oxide system shows high conversion, high selectivity, high mechanical strength and good stability.

Muhler et al. [7] found out the presence of $KFeO_2$ under the reaction condition by XRD and suggested that the active phase might be some kind of ternary Fe–K oxides, but some controversy and doubt still exist.

The structure of the active phase and the role of potassium and cerium as promoters incorporated in this iron-based catalyst were investigated by means of high temperature XRD and in situ Mösbaure spectroscopy. The results indicate that under reaction conditions of 893 K and in the presence of steam, the main active phase is Fe_3O_4 without existence of $KFeO_2$, and the role of potassium is to promote electron exchange between Fe^{2+} and Fe^{3+} ions [8,9].

Ethylbenzene dehydrogenation on the potassium-promoted iron oxide containing different contents of cerium oxide was investigated. It was found that the addition of cerium to the Fe–K system decreases the hyperfine magnetic fields for Fe^{3+} ions, because cerium ions partially occupy the positions near neighbor and the next near neighbor to Fe^{3+} ions. In addition, the presence of cerium enhances the stability of Fe–K phase and the reducibility of Fe oxide to Fe_3O_4 under the reaction conditions [10].

In recent years, a new catalyst has been developed by adding MgO and other oxides of metals chosen from IB-VIIIB or IIIA-VA families to Fe–K–Ce–Mo system. The new catalyst shows high activity and high selectivity. At a reaction temperature of 893 K, the ethylbenzene conversion is 73.5–74.6 wt% and selectivity 95–96 wt%. Besides, absence of steam for 20 min during reaction operation brought no effect on activity and selectivity. This indicates that the catalyst has a high ability of self-regeneration [11].

To ensure successful commercialization of catalyst GS-05 in a largescaled plant, we built a 1000 t/a pilot plant, developed a unique adiabatic, vacuum ethylbenzene dehydrogenation process with an adiabatic

Table 4
Performance of catalyst GS-05 in a styrene plant of 60 000 t/a and a pilot plant of 1000 t/a

Catalyst	Plant	LHSV (1/h)	Steam/EB (wt)	Pressure in reactor II inlet/outlet (MPa) (A)	Reaction temperature (K) inlet/outlet		Conversion (wt%)	Selectivity (wt%)
					Reactor I	Reactor II		
GS-05	60 000 t/a plant	0.507	1.30	0.060/0.054	898/824	898/853	65.6	96.1
Original catalyst		0.470	1.37	0.056/0.046	896/824	897/858	63.3	95.8
GS-05	Pilot plant	0.470	1.49	0.070/0.056	618/525	622/559	63.0	96.0

Reactor I – the first reactor; reactor II – the second reactor.

and radial fixed bed reactor. Through pilot test, the data and process parameters were obtained, and kinetic model was established for the optimum operating conditions in industrial application.

In 1994, based on the pilot plant test of 1000 t/a, catalyst GS-05 was successfully commercialized in a styrene plant of 60 000 t/a to replace an imported catalyst. The performances of catalyst GS-05 are given in Table 4.

Under the reaction conditions of a temperature of 893–898 K, a pressure in the second reactor of 0.06 MPa (A) and a water/EB ratio of 1.30 (wt%), the conversion of ethylbenzene reached 65–66 wt% and the selectivity of styrene exceeded 96 wt%. The results showed that under the same reaction conditions GS-05 shows a conversion 2 wt% higher and a selectivity also higher than those of the original catalyst.

A new generation catalyst GS-06B has been successfully used in a 60 000 t/a ethylbenzene dehydrogenation plant since July 1997. The catalytic activity of GS-06B is 1 wt% higher than that of GS-05.

2.3. *Catalyst for toluene disproportionation and transalkylation*

Toluene disproportionation and transalkylation using toluene and C_9 aromatics are important processes for the production of benzene and xylenes. In the early 1980s, a UOP patent indicated that a TA catalyst family was developed for this reaction [12]. A catalytic composite of improved selectivity and a method of manufacture is reported. The catalytic composite is characterized by a method of preparation which comprises subjecting a mordenite–alumina to an aqueous ammoniacal treatment at a pH of at least about 9.5; calcining the resulting mordenite to an aqueous solution containing a boron salt; and calcining the resulting mordenite alumina to provide said catalytic composite. The performance of the TA-4 catalyst, which exhibits superior ability for the transalkylation with a low aromatic ring loss of 0.56 mol%, is also reported.

The ZA catalysts have been successfully commercialized in five commercial plants as a result of applied fundamental research for more than 20 years at SRIPT.

The main active component of ZA catalysts is mordenite, a synthetic zeolite. The tests of the activity of the catalysts prepared by changing the silica/alumina ratio, the conditions of crystallization and calcination, etc., and investigation of acidic property and pore structure of the catalyst were conducted. The highlight of preparation was the direct synthesis of high-silica mordenite with a SiO_2/Al_2O_3 ratio of 15–30 in the presence of NH_3, by use of water glass and a salt of aluminum as raw materials. The directly synthesized mordenite showed a high activity and good stability as compared with those of de-aluminated mordenite with the same silica/alumina ratio. The results are given in Table 5.

To maintain the activity after 400 h to be the same as the initial one, the directly synthesized mordenite catalyst needs a temperature increase of 34 K lesser than that of dealuminated mordenite. The directly synthesized mordenite keeps a high selectivity while the dealuminated mordenite decreases the selectivity by 3.6 mol%.

It has been recognized that alumina contained in the catalyst as a binder has nothing to do with the catalytic activity. However, the important role, which alumina plays in the coke formation behavior of mordenite catalyst in toluene disproportionation and transalkylation reaction, was revealed by the studies by measure-

Table 5
Reaction results obtained by use of two kinds of mordenite catalysts

Mordenite catalyst (SiO_2/Al_2O_3 23)	Reaction time (h)	Reaction temperature, initial/end (K)	Reaction activity, B+X (wt%)	Selectivity initial/end (mol%)
Directly synthesized mordenite	1–400	663/685	40.0	95.9/96.2
De-aluminated mordenite	1–410	663/719	39.1	97.8/94.3

Reaction conditions: reaction pressure 3.0 MPa, LHSV 0.9 1/h, H_2/hydrocarbon 8:1 (mol), toluene/C_9A=65/35 (wt%).

ment of pore size distribution of the catalyst before and after reaction. The location of coke formation on the catalyst and relation between pore structure, coke formation and catalytic performance were elucidated. The distributions of pore diameters before and after the reaction indicated that the coke deposited mainly in the secondary pores composed of alumina binder and the outer surface of mordenite crystals. The size and pore volume of the secondary pores affect much the coke formation and catalytic performance [13].

The study of IR and TPD of adsorbed pyridine indicated that there are Lewis acid sites only on the surface of γ-Al_2O_3 and that the coordination structure of hydroxy groups is different due to the difference in preparation conditions, even though the crystal phase of γ-Al_2O_3 is the same. Meanwhile, the study also showed that alumina modifies acidic properties on the catalyst surface. Perhaps the modification of the acidic properties could be attributed to some interaction between alumina and mordenite. For this reason, by modifying the surface property of alumina, we can prepare mordenite catalyst with middle or weak Brønsted acid sites active for the reaction of toluene disproportionation.

Catalyst ZA-3 was commercialized in 1987 in an imported disproportionation plant of 125 000 t/a. Catalyst ZA-90 and ZA-92 were commercialized in June and August, 1994, in imported aromatic plants of 210 000 and 398 000 t/a, respectively. The commercial operation showed that catalyst ZA-92 had high activity and high selectivity. Catalyst ZA-94, which was used in a large aromatic plant of 1 007 000 t/a in April, 1995, showed a selectivity higher than 96.5 mol% at an initial reaction temperature of only 641 K and a space velocity of 1.2–1.4 h^{-1} to attain total conversion 43–44 mol%.

The newest generation HAT-095 catalyst, has been successfully used in a toluene disproportionation and transalkylation plant of 125 000 t/a since June 1996. The catalyst showed excellent catalytic performance in more than a year's operation. At a high space-velocity of 1.44 h^{-1}, the total conversion is 45 mol%, with a selectivity of 96 mol%, and an initial reaction temperature of only 634 K. HAT-095 was also successfully used in a 1 007 000 t/a plant in September 1997. The replacement of catalyst by HAT-095 brought about an increase in the plant capacity by 22% without reactor revamping and catalyst inventory increasing.

3. Summary

Having worked for China's petrochemical industry for 37 years, we have realized the importance of strengthening the fundamental research of applied catalysis in the laboratory and the pilot plant. In order to guide the synthetic design of industrial catalyst, the applied fundamental research must include the structure characterization and exploration of the relations between the component and structure of catalyst and the performance of the catalyst. In addition, research of catalyst reaction engineering should be emphasized and combined with catalysis research. The engineering problems encountered in scaling-up as to whether the catalyst suits an industrial catalytic reactor must be solved before commercialization. In a word, we must pay attention to conducting the necessary pilot test of catalysts and processes for industrial catalyst development, and to improving the properties and performance of catalyst in a constant, generation-by-generation manner.

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