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Catalytic Technology for Selective Hydrogenation of Benzene to Cyclohexene



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Preface

Since 1990, China has carried out research on benzene selective hydrogenation catalyst and related basic theories and applications, and has resolved the key technology problems for benzene selective hydrogenation to cyclohexene in China. After 2010, China became the second country in the world to realize the industrialization of the catalytic technology for benzene selective hydrogenation to cyclohexene and held the proprietary intellectual property rights.

This book introduces the catalytic technologies of benzene selective hydrogenation to cyclohexene and its downstream products, the developing history and present status, and the innovative work conducted in China. Selective hydrogenation of benzene to cyclohexene is a complex heterogeneous catalytic system. It involves catalyst, catalytic process, key equipment, and a complete set of production facilities from laboratory to industrialization. Summarizing the research work systematically in the field of study and exploring the heterogeneous catalytic mechanism and the scientific essence of high yield and selectivity of cyclohexene are not only academically valuable, but also can promote technical progress of this research area.

This book reveals the objective laws, reaction mechanism, and scientific essence based on the experimental data, analysis, and characterization results and references, which will guide industrial production. The improved catalyst can enhance the selectivity and yield of cyclohexene with low resource consumption and environmental pollution. It is also valuable for peer specialists and technical workers.

The authors' division for this book is as follows: Liu Zhongyi is the Editor-in-Chief for Chaps. 1, 2, 7, and 10; Liu Shouchang is the Associate Editor for Chaps. 3–6; Li Zhongjun is for Chaps. 8 and 9. Liu Zhongyi and Liu Shouchang are also responsible for the ordination and review of the whole book.

This book is supported by the fund from the Ministry of Science and Technology and the National Natural Science Foundation. We also acknowledge the contribution of graduate students, enterprises, and related technical workers.

There may exist some mistakes due to our limited level and please criticize and point out the defects. We will be deeply grateful!

Zhengzhou, China
October 2016

Zhongyi Liu

Brief Introduction

Selective hydrogenation of benzene to prepare cyclohexene and its downstream products such as cyclohexanone, adipic acid, caprolactam, nylon 6, nylon 66, and bulk chemicals and high-value fine chemicals such as medicine, pesticides, essence, and spices are resource saving and environment friendly, and play an important role in national economic development. The main contents of this book involve the thermodynamics of benzene selective hydrogenation, heterogeneous catalytic kinetics, catalytic mechanism and scientific essence, catalyst of benzene selective hydrogenation, modulation on activity and selectivity of the catalyst, studies on deactivation and regeneration of the catalyst as well as the catalytic process, key equipment, and complete set of production facilities.

This book gives a lot of experimental data, analysis, and characterization maps and important references. It can provide the reference for the related professionals of advanced college and scientific research institutes, senior undergraduate, master's and doctoral graduate students as well as for the personnel of related enterprises where they engage in management or industrial production.

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Chapter 1

An Overview of the Catalytic Selective Hydrogenation Technologies of Benzene into Cyclohexene



Selective hydrogenation of benzene from the fossil and coal companies into cyclohexene and its downstream products including bulk chemicals of cyclohexanone, adipic acid, hexanolactam, nylon 6, nylon 66, and high value fine chemicals of medicine, pesticide, and perfumes are of great significance for the economic development. Compared with the traditional process of benzene, hydrogenation into cyclohexane is safe, resource saving, environmentally friendly, and has giant economic and social benefits for the selective hydrogenation of benzene into cyclohexene.

It has been a dream for a long time in history that selective hydrogenation of benzene into cyclohexene was considered very hard, especially in the field of industry. Many countries such as America, England, German, and Japan conducted universal researches from 1960 to 1990s. And Japan firstly realized the industrialization in 1989, and transfer the technology to China, in 1995 and 2005, respectively. However, they monopolized the catalysts preparation method.

After 1990s, Netherland, German, Italy, India, Sweden, Spain, Brazil, and China all continued the research work. In 2010, China, industrialized the whole technologies and broke out the abroad monopoly, becoming the second country in industrializing this technology and hold the proprietary intellectual property rights.

This chapter introduces selective hydrogenation of benzene into cyclohexene and its downstream products, foreign developing history and status in selective hydrogenation technologies of benzene, domestic research and progress on selective hydrogenation technologies of benzene, main technology index on selective hydrogenation of benzene over the world.

1.1 Selective Hydrogenation of Benzene into Cyclohexene and Its Downstream Products

The technology of benzene selective hydrogenation into cyclohexene and its downstream products could be abbreviated as benzene selective hydrogenation technologies, including catalysts, catalytic processes of benzene selective hydrogenation into cyclohexene and its downstream products, key equipment, and devices. The stock of benzene from fossil and coal companies was catalytic selective hydrogenated into cyclohexene and its downstream products depending on the process, key equipment, and devices. Selective hydrogenation of benzene, namely partial hydrogenation or incomplete hydrogenation, is to hydrogenate the two double bonds in the ring to produce cyclohexene. The downstream chemicals of cyclohexene are involved in a large product chain because of the active double bond. Cyclohexene could be hydrated into cyclohexanol, which could be dehydrated into cyclohexanone, and oxidized into adipic acid directly. The hexanolactam obtained through the ammoximation of cyclohexanone, and rearrangement could be depolymerized into nylon 6. The adipic acid could also be used to prepare nylon 66 and polyesters through the co-polymerization with hexamethylenediamine and dihydric alcohols, respectively. Cyclohexene has been universally used in the field of high value fine chemicals production, such as medicine, pesticide, and perfume. Such compounds mentioned above have a wide market prospect.

From Fig. 1.1, the selective hydrogenation of benzene into cyclohexene is mainly to produce adipic acid (1), cyclohexanone (2), hexanolactam (3), nylon 6 (4), nylon 66 (5), and such staple chemicals.

It could be seen from Fig. 1.2: Cyclohexene could also be oxidized into cyclohexene oxide (1), which is the intermediate of medicines, pesticides, and polymers (2). Cyclohexene could be used to prepare the monomer of nylon 1212 cyclododecadiene (3) through metathesis, followed by oxidation. Phenylcyclohexane (5) could be formed from cyclohexene and benzene, and oxidized into phenylcyclohexane hydroperoxide (6), which could also be decomposed into phenol (7) and cyclohexanone (8). In addition, cyclohexene could be converted into cyclohexadiene (10)

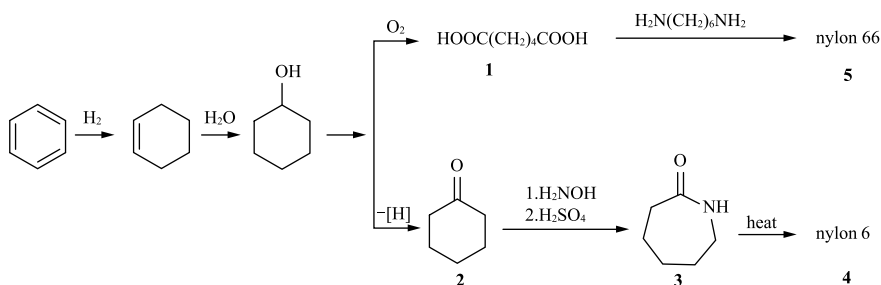


Fig. 1.1 Applied fields of benzene selective hydrogenation into cyclohexene and its downstream products in China

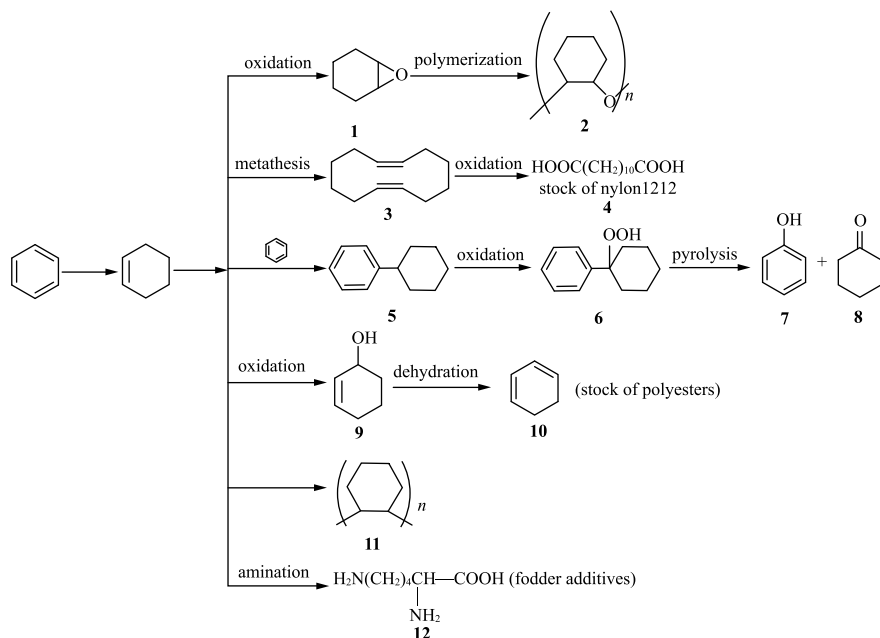


Fig. 1.2 Applied fields of cyclohexene and its downstream products in abroad [1]

through oxidation to cyclohexylene (**9**), followed by dehydration. Otherwise, cyclohexene could also be used to prepare α -amino type additive of L-lysine (**12**), perfume of civetone, rubber anti-aging agent of diphenol cyclohexane and fruit antiseptic [2]. These products development are almost vacancy in China, anyone exploited and launched successfully would be the technology and product support of Chinese middle and small-sized enterprises. It would be the new economic growth point.

Approaches to cyclohexene contained cyclohexanol dehydration, halocyclohexane dehalogenation, and Birch reduction in previous time. However, these methods had a complicated process, high energy consumption, low yield, and high cost, so the cyclohexene was limited in production and narrowed in fabricating high value and fine chemicals. It was reported that the Chinese annual demand of cyclohexene in 2010, was more than 700,000 tons, while the production was less than 30,000 tons, which limited the development and utilization of downstream stocks [3]. The successful development of benzene selective hydrogenation into cyclohexene broke out the technical bottleneck and build the base for the downstream products.

Selective hydrogenation of benzene into cyclohexene could be dated back to 100 years ago. In 1901, it was well known that benzene could be selectively hydrogenated into cyclohexene, but it was easier into cyclohexane due to the relative stability of benzene. Thus, it had still been a dream for the selective hydrogenation of benzene into cyclohexene [4]. Up to 1972, this process was made giant progress by Drinkard from Dupont company. The yield of cyclohexene could up to 30%

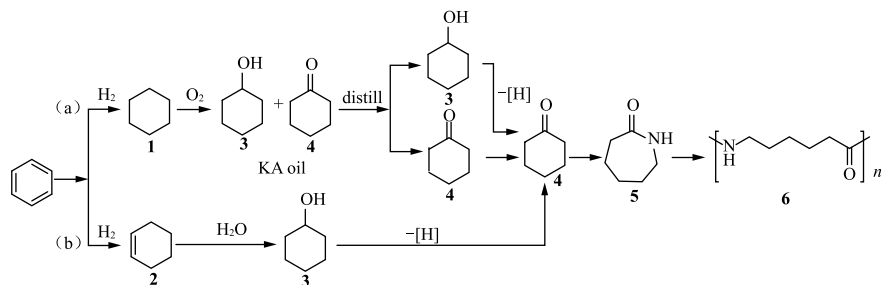


Fig. 1.3 Comparison of benzene total hydrogenation with selective hydrogenation into cyclohexene

with the catalysis of Ru catalyst, alkaline solution, and additives under 177 °C and 7.0 MPa. Then a large number of patents were applied by other chemical companies. The system of benzene selective hydrogenation was described in detail by many researchers especially Odenbrand. In 1970s, the Japanese companies including Mitsubishi, Toray, Sumitomo, and Mitsui prepared series of Ru-supported catalysts, the yield, and selectivity of cyclohexene were enhanced. The technical of benzene selective hydrogenation system was innovated by Asahi Chemical Industry Co., Ltd., and it was industrialized in the end of 1980s. In 2010, China, industrialized the whole technologies and broke out the abroad monopoly, becoming the second country in industrializing this technology and hold the proprietary intellectual property rights.

Figure 1.3 shows the comparison of benzene total hydrogenation with selective hydrogenation into cyclohexene.

In traditional benzene hydrogenation process (a), benzene is fully hydrogenated into cyclohexane (1) on Raney nickel catalyst, then cyclohexane is oxidized to cyclohexanol (3) and cyclohexanone (4) mixtures (KA oil). Cyclohexanol (3) could be obtained through the decomposition of KA oil under alkaline conditions, followed by waste base separation and distillation. Cyclohexanone (4) could also be obtained through the dehydrogenation of cyclohexanol. And KA oil could be oxidized into adipic acid with nitric acid. But the oxidation of cyclohexane belongs to the radical reaction, there exists safety hazards although this reaction could be controlled by inhibitor. The single-pass conversion of cyclohexane was controlled as 3–5%, because there are serious accidents happening occasionally in the world. This route has the disadvantages of long procedure, multistage, high energy consumption, and low yield. In addition, a large amount of wastewater and gas would be produced during manufacture, the utilization of carbon atom is around 85%, which could lead to resource waste and environmental pollution.

In benzene selective hydrogenation route (b), the selective hydrogenation into cyclohexene avoids the cyclohexane oxidation, which promotes safety production. Otherwise, the by-product of cyclohexane could be fully utilized. The production process of downstream stocks, including cyclohexanone (4), caprolactam (5), nylon 6 (6) and nylon 66 from benzene, would be shortened through the hydration of cyclohexene into cyclohexanol (3) and dehydration of cyclohexanol into cyclohexanone (4). The utilization of carbon atom of this new route is 100%, and the hydrogen

consumption could be saved about 1/3. Thus, this is a giant technical innovation to traditional benzene fully-hydrogenation.

By comparison in Table 1.1, the utilization efficiency of benzene and water of traditional benzene fully-hydrogenation is 76.5% and 75.3%, while the selective hydrogenation is 100% and 96.2%, respectively. The consumption of hydrogen, water, and electricity, and the production of wastewater, waste gas, and waste solid could be decreased by about 32%, 41%, 50%, 85%, 86%, and 55%, respectively. The cost of preparing one ton products could be reduced by about 1,000–1,500 RMB.

Take the Chinese universally applied benzene (100,000 t/a) selective hydrogenation into cyclohexene as an example, the yearly consumption of benzene, water, and electricity could be saved about 8,300 t, 1,030,000 t, 2.82×10^7 kW·h. The wastewater, gas, and solid could be decreased by about 253,000 t, 1.01×10^9 Nm³ and 24,000 t, respectively. And another 21,400 t cyclohexane could be produced.

Thus, the generalization and application of benzene selective hydrogenation technologies have not only economic benefit, but also social benefit in safety production, natural resource and ecological environment protection, pollution release and working condition improvement.

1.2 Foreign Developing History and Status in Catalytic Selective Hydrogenation Technologies of Benzene

In 1934, Horiuti and Polanyi developed the stepwise hydrogenation mechanism, benzene was hydrogenated into cyclohexane via the intermediates of cyclohexadiene and cyclohexene [5].

In 1957, Anderson firstly adopted a nickel membrane to catalyze the hydrogenation of benzene and detected the cyclohexene [6]. Cyclohexadiene is very active and would transform into cyclohexene as soon as it is produced, so researchers can't detect cyclohexadiene in hydrogenation products. But it could be detected in the products of benzene dehydrogenation products. In the following days, researchers reported the existence of cyclohexene under the low conversion of benzene catalyzed by Ru catalysts. And the Horiuti–Polanyi mechanism was generally accepted by researchers. Thus, it stimulated the interests of business circles and the academic community for the possibility of benzene selective hydrogenation into cyclohexene, though the selectivity and yield was not high.

In 1963, Hartog utilized ruthenium black catalysts to catalyze the hydrogenation of benzene in the water solution of aliphatic alcohol (50 wt.%) under room temperature and atmosphere, the yield of cyclohexene was only 2%. The selective hydrogenation of benzene into cyclohexene was beginning to made progress [7–9].

In 1972, the selective hydrogenation of benzene into cyclohexene was achieved breaking progress by Drinkard from Dupont company. The yield of cyclohexene could reach up to 30% with the catalysis of RuCl₃ under 450 K, 7 MPa H₂, and the

Table 1.1 Comparison of two processes for prepare cyclohexanone (60,000 t/a)

Entry	Class (unit)	Traditional fully hydrogenation			Selective hydrogenation		
		Consumption/t	Time/h	Yearly/8000 h	Consumption/t	Time/h	Yearly/8000 h
1	Stock	Benzene /t	7.65	61,200	0.962	7.215	57,720
2		H ₂ /Nm ³	7,500	6 × 10 ⁷	680	5,100	4.08 × 10 ⁷
3	Product	C ₆ H ₁₀ O/t	7.5	6 × 10 ⁴	1.005	7.5	6 × 10 ⁴
4		C ₆ H ₁₂ /t	—	—	0.215	1.6	1.28 × 10 ⁴
5	Energy consumption	Water/t	189	1.51 × 10 ⁶	14.9	112	8.96 × 10 ⁵
6		Electric /(kW·h)	4,215	3.37 × 10 ⁷	280	2,100	1.68 × 10 ⁷
7		Steam/t	31.5	2.52 × 10 ⁵	5.8	43.5	3.48 × 10 ⁵
8	Three wastes	Water/t	22.2	1.78 × 10 ⁵	0.43	3.24	2.59 × 10 ⁵
9		Gas/Nm ³	88,370	7.07 × 10 ⁸	1,680	12,600	1.01 × 10 ⁸
10		Solid/kg	3.31	26,480	0.2	1.5	12,000
11	Water utilization efficiency/%		75.3		96.2		

reaction systems including benzene, basic aqueous solution, and additives of ZnCl_2 , TiCl_4 , and carbonyl cobalt [10, 11].

In 1974 and 1975, the selective hydrogenation of benzene into cyclohexene with the catalysis of Ru-supported catalysts in weak acidic water solution was conducted by Johnson and Nowack, from Philips petroleum company. It was considered that the ions of iron, nickel, and chromium that were corroded from the surface of the steel reactor could promote the selectivity [12–14].

The yield and selectivity of cyclohexene were both enhanced by Mitsubishi Chem. Ind., Toray Ind., Sumitomo Chem. Co., and Mitsui Petrochem. Ind., through the support studies ranging from general Al_2O_3 , SiO_2 to other oxides, hydroxides, zeolites, rare earth oxides, and insoluble salts in combination with salt additives during 1975 and 1977 [15–23].

From 1980 to 1983, the selective hydrogenation of benzene into cyclohexene on Ru catalysts in steel autoclave was researched by Odenbrand. The catalysts, reaction systems, and mechanisms were described well. The Ru particles with the diameter range of 3–30 μm could be obtained through in-situ reduction of Ru hydroxides (the sodium hydroxide was added into RuCl_3 solution). The Ru catalyst and hydrogen were distributed in the emulsion of benzene and water. Ru particles, benzene, and hydrogen were, respectively, distributed in the water phase, oil drop with the diameter range of 0.05–0.12 mm and bubble with the diameter range of 0.1–0.8 mm. The limited mass transfer of hydrogen was one of the reasons for the high yield of cyclohexene. Two independent routes were assumed for benzene hydrogenation: Step-by-step hydrogenation to produce cyclohexane via cyclohexene, and one-step direct hydrogenation to produce cyclohexane. These metals which could partly poison Ru could block the active center which was helpful for one-step direct hydrogenation of benzene, thus cyclohexene selectivity is increased. They also thought the drop of ions of Fe, Cr, and Ni from the corroded inner wall of the equipment was one of the reasons for high cyclohexene selectivity [24–27].

From 1984 to 1987, the Ru catalyst without using additives was prepared by Niwa through “chemical mixture method”, and the catalytic performance could be matched with the Ru-supported catalysts in cooperation with additives. The chemical mixture method is also called sol–gel method, the complexes of RuCl_3 with ethanol and tetraethoxysilane (or aluminum tri-sec-butoxide) were used to prepare the Ru/SiO_2 (or $\text{Ru/Al}_2\text{O}_3$) catalyst. The diameter of Ru microcrystalline was smaller than 20 Å, the specific area could reach up to 850 m^2/g , and these catalysts also had a micropore structure ($d_{\text{pore}} < 2 \text{ nm}$). It was considered the Ru element in the catalyst was mixed with Si (or Al) in the status of the molecule. The high distribution of Ru and the strong interaction between Ru and support were the reason for the high yield of cyclohexene [28–30].

It has been considered that the selective hydrogenation of benzene into cyclohexene is very difficult for industrialization. From 1985 to 1990, the Asahi Kasei Company developed the catalytic technology for high selective hydrogenation of benzene. The company also had several technological innovations including preparation of special Ru particles (the diameter of microcrystalline was less than 20 nm) contained catalysts with *ex-situ* method, the introduction of zinc salts ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)

to control the pH between 4 and 6.5, the addition of distribution agent to avoid the coalescence and adhesion of catalyst particles. The distribution agent could be the oxides, hydroxide or hydrous oxides of Zr, Hf, Ti, Nb, Cr, Fe, Co, Al, Ga, and Si that with the particles of 0.005–10 μm . The reaction system contained four phases of gas (H_2), oil, water, and solid (catalyst), which was a relatively comprehensive multiphase catalytic system. The reaction occurred in the water phase, the reactant and product transferred in different phases through dissolution, diffusion, and extraction, during which the diffusion process played an important role in enhancing the selectivity of cyclohexene. The zinc complexes could stabilize cyclohexene, avoiding further hydrogenation into cyclohexane. In 1988, the Asahi Kasei Company found a 60,000 t/a device on Mizushima for the production of cyclohexanone from cyclohexene through benzene selective hydrogenation. This device was put into operation in 1989, which indicates the first realization of the production of cyclohexene and its downstream products through benzene selective hydrogenation [31–34].

Before 1990s, the catalytic technical for benzene selective hydrogenation mostly existed in the type of patents, and the key technologies for catalyst preparation were in the status of confidentiality and blockage. After 1990s, many countries carried out such researches and the representatives were Netherland, Germany, Italy, India, Switzerland, Spain, Brazil, and China.

From 1992 to 1993, Struijk et al. conducted the selective hydrogenation of benzene into cyclohexene in the catalytic system of Ru catalysts and ZnSO_4 solution under 423 K and 5 MPa H_2 . The content of the research including the effect of catalyst preparation and characterization, process parameters such as temperature, pressure, stirring speed, catalyst amount, Ru microcrystalline size, salt additives, pH, and water/benzene ratio on the selectivity and yield of cyclohexene. And the major conclusions were obtained as follows:

The hydrophilicity of catalyst is very important and the diffusion control leads to the high selectivity and yield of cyclohexene. As the hydrophilic catalyst is surrounded by a film of backwater membrane, the hydrogen controlled by such backwater layer has two important performances. One is to decrease the reaction rate of each elemental step of benzene hydrogenation, leading to the enhancement of cyclohexene selectivity. The other is to inhibit the inner diffusion of cyclohexene and the further hydrogenation into cyclohexane. The diffusion of benzene and cyclohexene that was controlled by the backwater layer also has two functions. On one hand, the dissolution difference between benzene and cyclohexene in water (benzene: 125 mol/ m^3 and cyclohexene: 21 mol/ m^3) and the distribution of benzene and cyclohexene leads to the concentration difference on the hydrophilic surface; on the other hand, as soon as the cyclohexene produces, it is more difficult for adsorption than desorption. In addition, when cyclohexene desorbs and dissolves in the oil phase, the cyclohexane only forms after prolonged collision and contact. Thus, with the formation of backwater and the increase in mass transfer resistance, the relatively high selectivity of cyclohexene could be observed. And this conclusion is also supported through the calculation of Wheeler-Weisz group ($\eta\phi^2$) and Carberry number (Ca). The better hydrophilicity and thicker backwater film could be contributing to the higher selectivity of cyclohexane [35].

The inorganic or organic additives could make the hydrophobicity of catalyst particles surface transfer into hydrophilicity, leading to the formation of a layer of backwater film around the catalyst. Otherwise, the strongest active centers on the Ru catalyst surface could be selectively covered, which would be a benefit for reducing the adsorption enthalpy of benzene and cyclohexene and enhancing the desorption rate. The salts as additives should have sufficiently strong adsorption on the Ru catalyst surface, but the equilibrium coverage should be suitable, or the catalytic activity would reduce sharply. Moreover, the metal cation is difficult to be reduced under such hydrogenation conditions and would be the toxicant of Ru catalyst. In theory, the coverage percentage of salt should be adjusted to such a degree that the physical process of substance migration is the rate-determining step [36].

The factors of temperature, hydrogen pressure, stirring speed, catalyst amount, Ru microcrystalline size, salt additives, pH, and water/benzene volume ratio have an effect on the yield and selectivity of cyclohexene. For the adsorption of cyclohexene need to be activated, while the hydrogenation of cyclohexene needn't, the appropriate high temperature (150–160 °C) is favorable for promoting the selectivity of cyclohexene. The selective hydrogenation of benzene should proceed under suitable high hydrogen pressure (4–5 MPa). The relatively high stirring speed could eliminate the external diffusion restriction of benzene and hydrogen in the interface of oil–water and gas–water, and accelerate the mass transfer. The mass ratio of catalyst to distribution agent is 1:5, the total percentage of solids in the slurry is 3–5%, or the cyclohexene would be further hydrogenated into cyclohexane. The Ru microcrystalline, pH, and water/benzene volume ratio should be around 5 nm, 5.5–6.5, and 2–3, respectively [35, 36].

In 1996, the gaseous reaction kinetics of benzene hydrogenated into cyclohexene over Ru/La₂O₃ was conducted by Döbert in the alkaline solution containing ZnCl₂. It was considered that the cyclohexane only produces during the continuous hydrogenation of benzene, the conversion rate of benzene and cyclohexene were, respectively, independent on the partial pressure of benzene and cyclohexene. So it could be concluded that the adsorption and hydrogenation of benzene and cyclohexene occurred over different active sites [37].

During 1996 and 2001, the conclusions obtained by Milone, Hronec, and Ronchin from benzene selective hydrogenated into cyclohexene were as follows:

Milone et al. adopted the relatively low temperature (333 K) and high-pressure autoclave with teflon lining to release the diffusion and the metal ion pollution from the reactor surface. The effects of reaction condition, RuCl₃ precursor, chloridion, and catalyst pretreatment on yield and selectivity of cyclohexene were also investigated over Ru/Al₂O₃ in the presence of water. The diffusion controlling between hydrogen and liquid could be eliminated by increasing the stirring speed. But the calculation results of $\eta\varphi^2$ and Ca indicated the selectivity of cyclohexene was almost independent on hydrogen diffusion. In the range of all benzene conversion, the ignorance ($Ca(H_2) = 0.08$) and non-ignorance ($Ca(H_2) = 0.30$) of hydrogen diffusion to the selectivity of cyclohexene was the same to all catalysts, which was not similar to the Netherland researchers. The benzene hydrogenation occurs under the kinetic controlling and strong mass transfer restriction. Although the mass controlling is

beneficial for the cyclohexene selectivity under high benzene conversion, the formation of cyclohexene couldn't be attributed to the substrate transfer. The Ru could be completely reduced under the hydrogen atmosphere, and the surface of the catalyst could be covered with a layer of hydrogen, leading to improving cyclohexene selectivity. However, no effect is observed when the catalyst is pretreated under the hydrogen atmosphere. The precursor of the Ru component with Cl^- is better than that without Cl^- for preparation of the catalyst. Firstly, the residue Cl^- could modify the electronic structure of Ru to form $\text{Ru}(\delta^+)$ species. Secondly, the existence of Cl^- could take up the strongest active sites of Ru, which is disadvantageous for the one-step hydrogenation of benzene into cyclohexane. Thirdly, the Cl^- anchored on the catalyst surface could bond with water through hydrogen bonding, promoting the interaction strength between water and catalyst surface and the hydrophilicity of catalyst. The function of water has the following two sides. On one hand, water has stronger adsorbability than benzene on the hydrophilic surface, so the water could easily replace the formed cyclohexene through competing adsorption. On the other hand, the water could bond with intermediate cyclohexene through hydrogen bonding, reducing the adsorbability of cyclohexene, thus the cyclohexene could be easily produced on the Ru active site absorbed with water molecule [38].

The nonpolar activated carbon and polar anionic cross-linked polymers was selected by Hronec as support for the preparation of Ru/C and Ru/ACLP catalysts. The effect of support polarity, water, and zinc salt additives on cyclohexene selectivity was conducted in aclave with glass lining under 100–110 °C and 1.5 MPa hydrogen. And the obtained conclusions are as follows: the polar support could promote the selectivity of cyclohexene and the Ru/ACLP is better than Ru/C under the conversion of 42–47%. Water can not only form a suitable chemical environment around Ru particles but also enhance the accessibility of metal particles distributed in hydrophilic polymers [39].

Ronchin et al. used 1 L PTFE-lined high-pressure reactor to study the effect of mass transfer, carrier and alkaline additive on cyclohexene selectivity and yield based on supported and unsupported Ru catalyst, under the reaction conditions of 150 °C, 5 MPa hydrogen pressure and 0.6 mol/L ZnSO_4 solution. Main conclusions were that, as to unsupported Ru catalyst, gas–liquid mass transfer resistance was not the control step when stirring rate was above 1000 r/min, and the reaction order of hydrogen was above one. Apparent activation energy was 19 kJ/mol for 130–150 °C, which was so small and meant that the reaction was limited by external diffusion or internal diffusion, but the relation between catalyst selectivity and the value of $\eta\varphi^2$ and Ca of benzene and hydrogen was not found. So, benzene selective hydrogenation was partly controlled by external and internal diffusion of benzene and hydrogen, while catalyst activity and selectivity depended strongly on the preparation procedure, especially on the properties of alkali and alkaline-earth metal hydroxides used for catalyst precursor preparation. Turnover frequency (TOF) of benzene increased with the increasing of molecular weight of hydroxides in the same group. Based on double isothermal line method, they studied the reversible chemical absorption formed between Ru atom exposed on the catalyst surface, and hydrogen molecule poorly bonded on the catalyst surface. The amount of hydrogen on the catalyst surface

by poor chemical absorption depended on the property of alkali during precipitation. It was the above amount of hydrogen that affected catalyst activity and selectivity [40, 41]. As to supported Ru catalyst, the reaction order of hydrogen was zero, and the reaction rate was not affected by hydrogen pressure. Catalyst selectivity was mainly affected by the nature of the carrier and the interaction between metal and carrier. The carrier with the best hydrophilicity gave the best results. With the best catalyst of Ru/ZrO₂ and the best precipitant of KOH, cyclohexene selectivity and yield was 80% and 41%, respectively. Strongly chemical absorbed hydrogen was linked to the exposed metal atom, while poorly chemical absorbed hydrogen was linked to highly unsaturated active center, which had relation with initial reaction rate. Catalysts containing TiO₂ and Fe₂O₃ gave very low hydrogen and high selectivity, which may be explained by that strong metal-support interaction reduced the absorption ability of catalyst surface to hydrogen. For the same group of alkali used for catalyst preparation, the initial reaction rate increased with the increasing of amount of reversible absorbed hydrogen. The $\eta\phi^2$ and *Ca* of catalyst had the same behavior using IA metal hydroxide as precipitant; catalyst activity using IIA metal hydroxide as precipitant was lower than that using IA metal hydroxide, but both have similar selectivity. The aging time during catalyst preparation became much longer, initial activity of catalyst became much lower because the reaction rate was reduced, but initial selectivity and cyclohexene yield aroused. Turnover frequency of benzene increased with the increasing of molecular weight of hydroxide in the same group, so alkali can be used as additive or modifier. When catalyst was treated by pure water, benzene hydrogenation reaction rate was fast with a low cyclohexene selectivity, while treated by NaOH, reaction order of cyclohexene hydrogenation reduced from 1.5–2 to 1, and hydrohexene selectivity increased obviously. This could be explained from the saturation effect of NaOH-absorbed active center, increasing of average diameter of catalyst and diameter of catalyst microcrystal. Catalyst activity reduced obviously when it is treated with N₂H₂ or HCOOH [42].

During 1997 and 2000, the influence of organic additives and support on the yield and selectivity of cyclohexene was studied by Suryawanshi and Mallat. It was discovered that the additive of monoethanolamine (MEA) was better than zinc sulfate, because the latter would lead to the acidity of the reaction system and the pollution of reboiler. Among the supports of Al₂O₃, ZrO₂, TiO₂, and Nb₂O₃, Al₂O₃ was the best [43]. The selectivity of cyclohexene could be promoted by mixing appropriate organic or inorganic compounds with reactants [44].

From 2003 to 2005, the Ru/Al₂O₃ catalysts were prepared by Mazzieri from RuCl₃ and hydrochloride solution with different concentrations using the impregnation method. And the catalysts were characterized with FT-IR, TPR, and so on, and the conclusions were obtained as follows:

The aftertreatment of catalysts including calcination and reduction after calcination all could not remove the chloride ion, but it could be decreased sharply by washing with NH₄OH. The electronic state of Ru species including Ru⁰, RuCl₃, Ru oxides, and Ru oxychlorides could be affected by the treatment methods. The Ru species would also influence the catalytic activity and selectivity, and the catalyst with the highest chloride amount had the best selectivity of cyclohexene. Because

the chloride ion could keep Ru in the status of electron deficiency through modifying the electronic property, leading to the decrease of cyclohexene adsorption. The basic sites of Al_2O_3 could induce the hydrolysis products of RuCl_3 , such as ruthenium oxychloride, ruthenium hydroxide, co-precipitate on Al_2O_3 . It would affect the distribution of Ru, but it had no effect on catalytic performance [45–47].

From 2003 to 2010, Estevam, da-Silva, da-Costa, and Rodrigues researched the supported catalysts, and the conclusions were obtained as follows:

The Ru–Fe/ TiO_2 and Ru–Fe/ SiO_2 catalysts were prepared by Estevam and da-Silva with co-impregnation method. And the impact of the support structure and Fe additives on catalytic activity was studied. It was proved by XRD, oxygen chemisorption, and TPD that the reducibility and distribution of Ru depended on the support structure. And the influence of Fe on Ru species and its relationship with catalytic activity was also revealed. The Ru supported on SiO_2 was easier to be reduced than that on TiO_2 , the addition of Fe could promote this process. The addition of Fe could also enhance the distribution and oxidation of Ru. Although this effect was more obvious on SiO_2 , it would not influence the stability of Ru/ TiO_2 . In summary, Ru–Fe/ TiO_2 had higher cyclohexene selectivity than Ru–Fe/ SiO_2 [48, 49]. While the impact of preparation condition (calcination temperature and reduction) on the catalytic performance of Ru/ CeO_2 was investigated by da-Costa, and it was proved that Ru/ CeO_2 was a good catalytic system under TiCl_3 solution. The catalyst reduced directly would have better activity, cyclohexene selectivity, and yield than that reduced after calcination [50]. The support natural property of Al_2O_3 and Nb_2O_5 on the activity of Ru catalysts that with different particle sizes and specific areas were researched by Rodrigues. It was found that the support natural property had no effect on cyclohexene selectivity. However, the decrease in particle size and specific area could promote the yield and selectivity of cyclohexene [51].

In 2011, a very simple catalysis system only containing Ru/ Al_2O_3 and ionic liquid solution (ppm) were reported by Schwab. The characterization results of XPS revealed that the chemical adsorption of ionic liquid didn't lead to the electronic state (binding energy) change of Ru. So the reason for lowering activation should be attributed to the group effect of a second metal or ligand influence on the kinetic interference of benzene hydrogenation. The anion of ionic liquid would interact strongly with Ru center, blocking active sites and changing the geometrical arrangement of active sites. Thus, the active sites for benzene hydrogenation into cyclohexane were diluted or decreased. It was a new ligand effect and could be treated as the decrease of adsorption enthalpy of hydrogen. In general, the adsorption enthalpy of water on Ru would decrease to half in the presence of hydrogen. The coverage of hydrogen would also be decreased in the existence of an ionic liquid, which could promote the hydrophilicity of catalyst and inhibit excessive hydrogenation of benzene [52].

After 1990s, many countries were engaged in the catalyst research for benzene selective hydrogenation into cyclohexene. On one hand, the catalysts with high activity and selectivity were wished to be developed, on the other hand, the catalytic mechanism and the scientific nature of high yield and selectivity of cyclohexene were to be investigated. For the catalyst development, the researches were mainly focused on the supported catalysts and simple catalytic systems, but the yield and selectivity

was generally low, and there was no industrial value. As to the catalytic mechanism and the scientific nature of high yield and selectivity of cyclohexene, although much important progress had been made, there still existed different academic views that needed to be proved with the development of science and technology.

1.3 Domestic Research and Progress on Selective Hydrogenation Technologies of Benzene

In the year of 1991, the article entitled “partial hydrogenation of benzene into cyclohexene” was published in *Petrochemical Technology* by Wang. This article mentioned that the Asahi Kasei Company found a 60,000 t/a device on Mizushima for the production of cyclohexanone from cyclohexene through benzene selective hydrogenation in November 1988. And this device was put into operation in 1989. The cyclohexene has an active double bond and is widely used as organic chemical stocks. The cyclohexene, especially, could be directly oxidized into cyclohexanone and adipic acid, hydrolysis into cyclohexanol, which could not only shorten the production process of ϵ -caprolactam and adipic acid, but also has a relatively high economic profit. During the recent 20 years, researches about the new preparation process of cyclohexene have been conducted abroad, and the hydrogenation catalyst development is the key technology [53].

In 1992, the article entitled “Preparation of cyclohexanol from cyclohexene” was published in *China Synthetic Fiber Industry* by Shi. This article summarized the catalysts and process of benzene selective hydrogenation into cyclohexene via Asahi method, then the cyclohexene was further hydrolyzed into cyclohexanol. The industrial production of cyclohexanol from cyclohexene had induced the attention from China and abroad. Compared with the cyclohexane oxidation method, the cyclohexene method had advantages of less by-product (by-product cyclohexane could be further utilized), high carbon yield (close to 100%), energy saving, low material consumption, and pollution. So the intermediate cyclohexene is an important fine chemical stock and has a wider application perspective [54].

In 1992, the article entitled “The new preparation process of cyclohexanol and cyclohexanone” was published in *Modern Chemical Industrial* by Su, Ye, and Wu from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. This article introduced the process of benzene selective hydrogenation into cyclohexene, cyclohexene hydrolysis into cyclohexanol, cyclohexanol dehydrogenation into cyclohexanone, and benzene conversion into cyclohexene or phenylcyclohexane. Due to the advantages of the process, the conversion of benzene into cyclohexanol and cyclohexanone via cyclohexene has been paid more attention to, and it has been the strategic issue in the field of petrochemical industry. Cyclohexanol and cyclohexanone are all important chemical stocks, they could be used to produce nylon 6, caprolactam, adipic acid, civetone, rubber anti-aging agent (diphenol cyclohexane),

and fruit antiseptic (phenylphenol). It is a new route for benzene selective hydrogenation into cyclohexanol and cyclohexanone through the conversion of benzene into cyclohexene and phenylcyclohexane [2].

In the same year, the article entitled “The research on benzene selective hydrogenation into cyclohexene over surface modified catalyst” was published in *Chemical Reaction Engineering and Technology* by Ye, Pang, Huang, and Yi. This article stated that benzene would be completely hydrogenated into cyclohexane via the traditional gaseous catalytic method, and there’s no intermediate cyclohexene. In the view of thermodynamics, the hydrogenation of benzene into cyclohexane was easier to proceed than into cyclohexene. In addition, the cyclohexene was also easily hydrogenated into cyclohexane. But the selective hydrogenation product cyclohexene could be obtained on the modified catalysts. Cyclohexene was very active as it contained the double bond that could be applied in medicine, food, farming chemicals, fodder, polyester, and fine chemicals. Especially in the field of petrochemical industry, the chemicals produced from benzene could be simplified and efficient using cyclohexene as stock [55].

In 1993, the article entitled “New production technology of polyamide—partial hydrogenation of benzene into cyclohexene” was published in *Chinese Polymer Bulletin* by Ye, Pang, and Huang from South China University of Technology. This article introduced and commented on the new rout for polyamide production through benzene selective hydrogenation into cyclohexene. It illustrated the application perspective in industrial manufacture by comparing it with the existing process. It also reviewed the developing history, current status, and future tendency in the reaction process, catalyst preparation, reaction mechanism, separation, and application of cyclohexene. Compared with the cyclohexane oxidation route, the benzene selective hydrogenation method could save 1/3 hydrogen, the carbon yield could reach up to 100%. It was a natural resource and energy saving, procedure shorting and yield increasing, there was no environmental pollution step, and the reaction condition was relatively mild [1]. Successful development of selective catalytic hydrogenation of benzene to cyclohexene will give cyclohexene a wide application in the field of chemical industry and fine chemicals, etc.

In 1996, the article entitled “The Ru catalyst developing progress for benzene hydrogenation into cyclohexene” was published in *Speciality Petrochemicals* by Tang. This article pointed out that the production of adipic acid from the oxidation of cyclohexene, which was prepared through hydrogenation of benzene, was the universally applied traditional process in the world. The cyclohexane oxidation route existed the problems of serious side reactions, low conversion, complicated process, and poor security. The selective hydrogenation of benzene into cyclohexene, followed by hydrolyzing into cyclohexanol and oxidizing into adipic acid, was an alternative route for adipic acid production. But the key problem was the development of catalysts for selective hydrogenation of benzene. While this study in our country only on the start-up stage, to quicken the research work and industrial step had significant on our adipic acid and polyamide industry [56].

In 1997, the article entitled “The research progress on benzene selective hydrogenation into cyclohexene” was published in *Speciality Petrochemicals* by Jia, Zhang,

Xu, and Lin that from Dalian Institute of Chemical Physics, Chinese Academy of Sciences. This article reviewed the research progress on selective hydrogenation of benzene into cyclohexene in liquid phase over Ru catalysts and introduced the characterization of Ru catalysts prepared by the chem-mixed method and its effect on benzene selective hydrogenation into cyclohexene in liquid phase. As early as 1901, it was well-known that cyclohexene could be prepared through benzene hydrogenation, but cyclohexene was easily hydrogenated into cyclohexane. So it was a dream for preparing cyclohexene through benzene hydrogenation at that time. The selective hydrogenation of benzene into cyclohexene had stimulated researchers' interests for it was an economic industrial route. The selective hydrogenation of benzene into cyclohexene had been industrialized in Japan, the corrosion problems of additives had been resolved, and the key point was to enhance the yield of cyclohexene. This reaction had a good application perspective in our country [4].

In sum, it is easy to figure out, at the beginning of 1990s, the scientists and scholars from petrochemical industry, petrochemical fiber companies, Chinese Academy of Sciences, and universities focused their attention on benzene selective hydrogenation technologies. And they introduced the developing history and current status for our readers. By comparing the benzene selective hydrogenation with traditional benzene completely hydrogenation technologies, it was of great significance for the development of selective hydrogenation technologies.

It was reported that the studies on catalyst preparation and related fundamental theory for benzene selective hydrogenation into cyclohexene have been conducted by "Taiwan National Central University", Fudan University, Dalian Institute of Chemical Physics (Chinese Academy of Sciences), East China University of Science and Technology, Sichuan University, Hebei University of Technology, Institute of Chemistry (Chinese Academy of Sciences), and so on.

During 1997 and 2001, the La and Zn binary oxides supported Ru catalyst was researched in aqueous sodium hydroxide by Taiwan scholars. The results showed that the binary oxides $\text{La}_2\text{O}_3\text{--ZnO}$ were better than La_2O_3 or ZnO for the enhancement of yield and selectivity of cyclohexene. Because the ZnO component could promote the hydrophily of Ru catalyst, leading to the slow adsorption of benzene on the catalyst and the fast desorption of cyclohexene from the catalyst. The further hydrogenation rate was decreased and the selectivity of cyclohexene was increased. This slow adsorption mechanism explained all the binary support could reduce the hydrogenation rate of benzene on Ru catalyst and promote the selectivity of cyclohexene. The scholars also proposed that the benzene, hydrogen, and cyclohexene adsorb on the same active sites competitively. With the increase in hydrogen pressure, the hydrogenation rate of benzene was accelerated. When the coverage of hydrogen was equal to benzene, the hydrogenation rate of benzene reaches the maximum [57–61].

In 1999, the amorphous alloy catalyst Ru–B reported by Fudan University was used for benzene selective hydrogenation into cyclohexene. The amorphous alloy could provide more active sites due to the short-range order, long-range disorder, isotropy, and highly unsaturated coordinate on the surface. In the amorphous alloy structure of Ru–B, Ru was metallic state and B was elemental and salt states, the electron transferred from B to Ru. With the increasing percentage of B, the yield and

selectivity of cyclohexene was all promoted [62, 63]. In 2004, it was proved by XPS that the Zn^{2+} could be reduced into Zn due to hydrogen spillover. The percentage of Zn was 1.1 wt.% in the reduced catalyst, the Zn formed alloy with Ru, covering the highest active sites reversely. The electron transferred partially from Ru, changing the electronic structure of Ru and affecting the activity and selectivity of the catalyst [64–66]. From 2008 to 2009, the Ru-Ba/SBA-15 and Ru-Ce/SBA-15 catalysts were developed by Fudan University using a double solvent method. The CdSO_4 and ZnSO_4 were used to modify the catalytic performance of Ru-La/SBA-15 [67–69]. From 2012 to 2014, Fudan University designed a Ru/B– ZrO_2 catalyst and proved the additive active sites was the Lewis acid sites on the support. The proposal of additive active sites could provide the new method for the development of selective hydrogenation catalyst [70, 71].

From 2006 to 2009, Dalian Institute of Chemical Physics (Chinese Academy of Sciences) reported a SiO_2 stabilized colloid Ru catalyst by micro-emulsion method. This catalyst has high activation and selectivity due to the higher distribution of Ru (4 nm), and the more exposure active sites than SiO_2 supported Ru catalyst. This research also reported another Ru-cordierite catalyst used for fixed bed process, after the modification with $\text{ZrO}_2\text{--Al}_2\text{O}_3$ or Al_2O_3 coating, the relative high yield of cyclohexene could be obtained under low space velocity. The core–shell distribution of active components, large aperture, and the formation of Taylor flow were the determining factors for the high activation and selectivity [72–76].

During 2007 and 2010, East China University of Science and Technology researched the benzene selective hydrogenation into cyclohexene over Ru–Zn/ ZrO_2 through theory calculation and experiment. The precursor of Ru catalyst was reduced in ZnSO_4 solution, the reduced Zn formed alloy with Ru. Whether in the stage of reduction or hydrogenation, atomic Zn universally existed in the bulk phase or on the surface of Ru-based catalyst, leading to the decreasing the chemical adsorption energy of benzene and cyclohexene. Especially for the chemical adsorption of cyclohexene, the passivated surface of catalyst inhibited the further hydrogenation of cyclohexene. The experimental results and theory proved the existence of the optimal extent of Zn. The Zn atoms affected the catalytic activation and cyclohexene selectivity through adsorption and surface reactions [77–81].

In 2008, Sichuan University reported an amorphous alloy catalyst RuCoB/ $\gamma\text{--Al}_2\text{O}_3$ through reduction-impregnation method, Co oxides and B element could promote the distribution of Ru. The additives of amine and alcohol could stabilize the monimolinnion around catalyst and decrease the adsorption of cyclohexene on active sites. The yield of cyclohexene could be obviously increased in the presence of ZnSO_4 and ethylenediamine [82, 83].

In 2009, Hebei University of technology reported a Ru–Zn/ SiO_2 catalyst prepared by the water/oil microemulsion method. The size of Ru particles was controlled by adding hydrazine hydrate, and the Ru species were highly distributed to form micro-crystalline, which would be a benefit for enhancing the selectivity of cyclohexene [84].

From 2011 to 2015, the Institute of Chemistry (Chinese Academy of Sciences) reported a Ru–Cu/ ZnO catalyst prepared by deposition–precipitation and

impregnation- co-precipitation method, the selectivity of cyclohexene could be obviously promoted in aqueous NaOH solution. In the structure of $\text{Ru/ZnO-ZrO}_x(\text{OH})_y$ catalyst, the hydroxyl group, Zn, and Zr atoms existed synergistic effect, so the yield of cyclohexene could be high without any additives [85, 86]. It also reported another Ru-Cd/BEN catalyst [87, 88]. The Ru/HAP and Ru-Zn/HAP catalysts were also prepared by the ion exchanging method with the nontoxic, rich in nature support of HAP and the NaOH was selected as a modification agent, the yield of cyclohexene could be relatively high [89]. The selectivity of cyclohexene over Ru/TiO₂ catalyst in aqueous NaOH solution could be obviously enhanced through the addition of little ZnO. Because the ZnO would form $\text{Na}_2\text{Zn}(\text{OH})_4$ in aqueous NaOH solution, which could efficiently inhibit the further hydrogenation of cyclohexene [90].

The selective hydrogenation of benzene into cyclohexene and its downstream products have an impressive market perspective. In 1995, Henan province spent 3 billion RMB for introducing the process of benzene selective hydrogenation into nylon 66 salt (60,000 t/a) and put it into production in 1998. This was the first apparatus in China, and the second in the world. But the catalyst preparation technology was monopolized, restricting the autonomously and sustainably development of Chinese companies. To solve the technology problem, Zhengzhou University has carried out the research on the catalyst preparation method since 1998.

During 1998 and 2007, Zhengzhou University developed the first generation amorphous alloy catalyst Ru-M-B/ZrO₂ ($M = \text{Fe}$ and La) with the main indexes of 40% benzene conversion, 80% selectivity of cyclohexene, and above 32% yield of cyclohexene.

With the support of Educational Natural Science Foundation of Henan Province (The development of catalyst with high activity and selectivity for benzene selective hydrogenation, No. 2000100014) and Key Scientific and Technological Project of Henan Province (The development of catalyst for benzene selective hydrogenation into cyclohexene, No. 001090107), the later project passed provincial identification in 2001. And the catalyst and its preparation method for benzene selective hydrogenation into cyclohexene was applied for national invention patent in the same year [91]. In 2004, the catalyst and its preparation, modulation, and regeneration methods for benzene selective hydrogenation into cyclohexene were applied for the national invention patent [92].

Under the support of technical innovation found for small and medium enterprises in science and technology (The catalyst and process for benzene selective hydrogenation into cyclohexene, No. 02C26214100384), three pilot results “The catalyst and process for benzene selective hydrogenation into cyclohexene”, “The catalyst preparation and application technologies for benzene partial hydrogenation into cyclohexene”, and “The apparatus and process for benzene partial hydrogenation into cyclohexene” passed the identification of Henan department of Science and Technology. The catalyst and its preparation method, and the hydrogenation process were applied for the national invention patent [93].

The comment on “catalyst and catalytic process for benzene selective hydrogenation into cyclohexene” was that “The research on catalyst and process for benzene partial hydrogenation into cyclohexene was completed by Zhengzhou University in