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New catalytic technologies in Japan

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Abstract

Recent trends in R&D of catalytic technology in Japan (cleaner and more efficient production, environmental catalysts, and recycling processes) are overviewed and examples of recent achievements are listed. Examples are then described as zeolite-catalyzed organic reactions recently commercialized and expected to be commercialized: hydration of cyclohexene, synthesis of pyridine derivatives and gas-phase Beckmann rearrangement of cyclohexanone oxime. Finally, as an example of environmental catalysts, the NO_x storage–reduction type three-way automobile catalyst, is introduced.

Keywords: Catalytic technologies; Hydration of cyclohexene; Zeolite-catalyzed organic reactions; $DeNO_x$ catalyst

1. General trends in R&D

The title of this paper was suggested by the late Prof. Zamaraev when he visited Tokyo in 1995 on the occasion of IFEC'95 [1]. Here, after a brief note on possible major technologies of the 21st century, we attempt to describe the general trends of catalytic R&D activities in Japan.

It is likely that the life and information technologies will continue to grow in the first decade of the next century. However, at the same time, the technologies which support the basis of human activities such as those for the supply of energy and resources as well as those for the preservation of the environment will be seriously needed in the 2030s, since in this period, a shortage of energy, food and resources will be obvious, and environmental destruction will probably reach the capacity of the earth, unless we try hard to develop the technologies to overcome the crisis. In this respect, chemical technology and particularly catalytic technology must play key roles for the efficient production or conversion of matter and chemical energies.

The trends of R&D in Japan may be summarized shortly as follows. It is generally notable that R&D are becoming more strategic and specific, depending on the global management policy of each enterprise. The role of government in long-term R&D is a key issue now, as the governmental support has been relatively small in Japan. A basic law and the corresponding action program were established and the budget started to increase for five years from 1996:

1. As in other countries, cleaner or more environmentally friendly production of materials and chemical energies is becoming more and more important. Examples are the changes to solid acid

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from liquid acid catalysts, to catalytic oxidation from stoichiometric chemical oxidation, etc.

2. Catalytic processes which make use of less expensive and more abundant raw materials in a smaller number of reaction steps are always highly desired. Recently, this has been stressed particularly in the syntheses of fine chemicals, although the search for new functional compounds is also of great concern in this field.
3. The production of environmentally friendly materials and chemical energies (clean fuels) as well as environmentally friendly disposal and recycling systems are the targets of current research. Although economically acceptable recycling is now very limited in quantity, the importance of recycling or waste treatment will grow rapidly. This is particularly so for polymer and plastics manufacturers. Improvements of quality are also needed for transportation fuels, in order to meet the new stringent regulations and this will necessitate significant alterations in the oil refinery processes. JCAP (Japan Clean Air Program) has been initiated in 1997 jointly by the government and the oil and automobile industries.
4. A positive attitude to the application of catalysts in a wide range of new applications has been a strong point of Japanese R&D.
5. Examples of recent achievements in Japan have been summarized in earlier reviews [2,3], and also in a recent paper [4]. Some examples from the latter are listed in Table 1, with a few additions. Representative examples will be described in more detail below.

2. Hydration of cyclohexene in slurry reactor

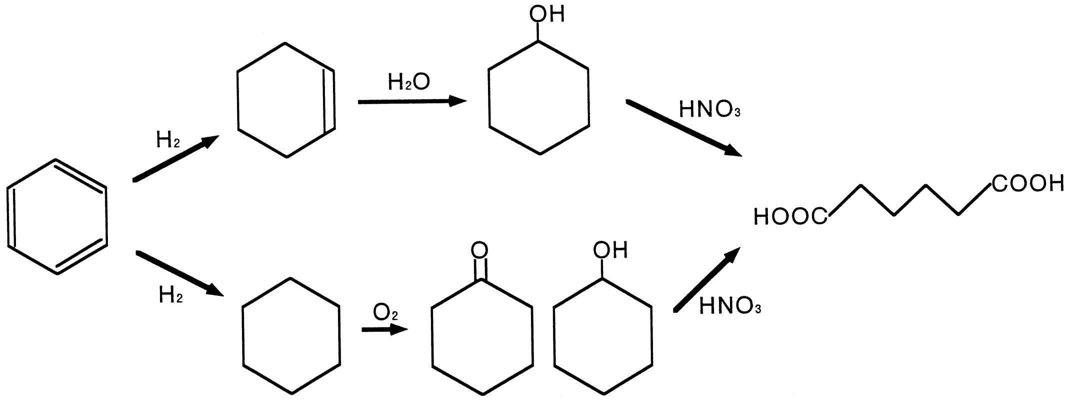
After recent developments of two processes using heteropolyacids [2], Asahi Chemicals have industrialized the production of cyclohexanol from benzene via partial hydrogenation and subsequent hydration. The two-steps are catalyzed by Ru and a zeolite, respectively. The new process is superior to the conventional two-step oxidation process in several respects: selectivity, safety, corrosion, and energy-consumption [5,6]. Scheme 1 provides a general idea of the merits of the new process.

The key points of the second step, i.e., the hydration of cyclohexene, will be described here. An outline of the process is schematically illustrated in Fig. 1(A).

A ZSM-5 type catalyst, having a high Si/Al ratio and small particle size, is used in the liquid bi-phase system. According to the inventor, the high Si/Al provides hydrophobicity to the pore wall in the zeolite particle and concentrates cyclohexene in the pores, and the small pore suppresses the formation of bulky byproducts. Small particle size was needed not only

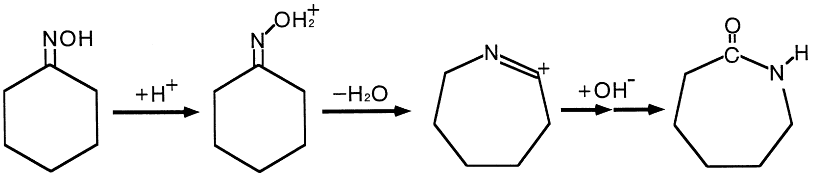
Table 1
New processes and catalysis

Process	Comments (catalyst, etc.)
Benzene to cyclohexanol	Partial hydrogenation (Ru cat.) and subsequent hydration (zeolite), 60 000 ton/year (1990)
ε-Caprolactam from cyclohexanol oxime	Gas-phase Beckmann rearrangement, silicalite, in the presence of alcohols (close to pilot)
Synthesis of pyridine derivatives	Pyridine, methyl pyridines from aldehydes (zeolites, 1990)
DeNO$_x$ of lean-burn automobile exhausts	Storage–reduction-type three-way catalysts (1994)
Deep desulfurization of gas oil	Improved Mo–Co HDS catalysts (ca. 1995)
Aromatization of LPG or light naphtha	Metallosilicate, Z-forming (demonstration plant, 1990–1991)
Syndiotactic polystyrene	Metallocene, 5000 ton/year (1996)
Cycloolefin copolymer	Metallocene, 4000 ton/year (1995)
MMA via methyl formate	New acetonecyanhydrin process, 41 000 ton/year (1996)
γ-Butyrolactone from MAH	Ru-catalyst, 10 000 ton/year (1997)
Acetic acid from ethylene	Pd+heteropolyacid, 100 000 ton/year (1997)
Aliphatic alcohols and amines	Utilization of vegetable oils
Phenol from toluene	Ni–Fe–Na oxide, gas-phase (pilot)
Pd-based automotive catalyst	Improved three-way catalysts
Catalysts for household appliances	Many commercialized examples including photocatalytic self-cleaning tiles
Recycling of waste plastics	Several demonstration and pilot plants



Scheme 1. Comparison of the new route for the production of adipic acid with the conventional process.

for easing the diffusion problems but also for making the outer surface of the catalyst particle hydrophilic. Due to this hydrophilicity of outer surface, the catalyst powders of which the inside is hydrophobic become stable in the aqueous phase. This speeds up the separation of the oil and aqueous slurry phase in a settler and facilitates the subsequent distillation of the oil phase to obtain cyclohexanol. If a liquid acid is used to catalyze hydration, cyclohexanol as well as cyclohexene are both distributed in the aqueous acid phase and the distillation of this phase causes dehydration of the cyclohexanol back to cyclohexene. Distribution of the components between the aqueous and organic phase, which was experimentally measured, is illustrated for the case of zeolite catalyst in Fig. 1(B).



The other important innovation in this process exists in the regeneration of the catalyst. Wet oxidation with H_2O_2 successfully removes the organic deposits and the treatment in the controlled pH range returns the aluminum ion back to the zeolite framework as indicated by the recovery of acid quantitatively after the treatment. 60 000 ton/year of cyclohexanol have been produced by this process since 1990.

3. Gas-phase Beckmann rearrangement of cyclohexanone oxime and synthesis of pyridine derivatives

There have been many attempts to replace the conventional process which utilizes fuming sulfuric acid by a gas-phase solid acid process. This long-term wish is about to be fulfilled by using a silicalite-type catalyst, which is almost non-acidic, in the presence of methanol in the feed.

A research group of Sumitomo Chemicals have found that the rate and selectivity increased with a decrease in the acid amount or an increase in the Si/Al ratio [7]. A constant selectivity of about 80% was obtained for a Si/Al ratio greater than 1000. The reaction appeared to proceed on the outer surface of the zeolite particle as the rate increased with increasing outer surface area.

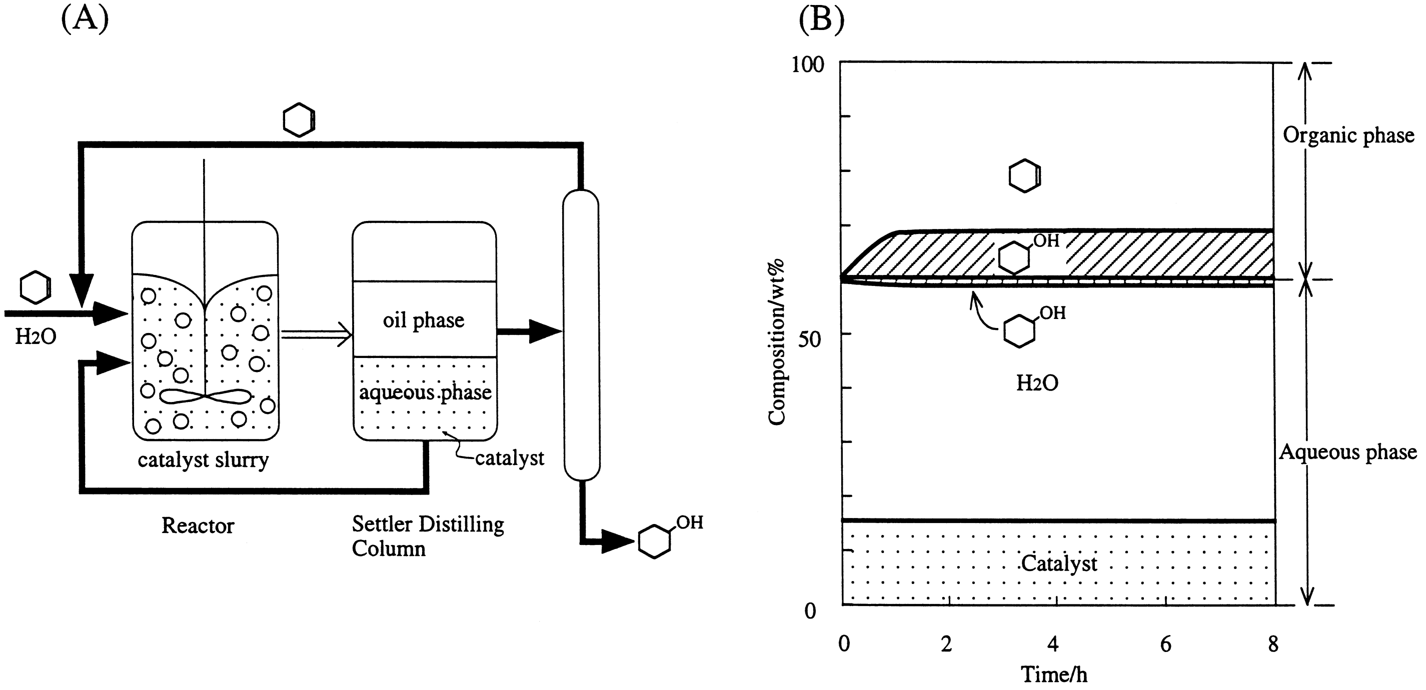


Fig. 1. (A) Outline of the process for hydration of cyclohexene. (B) Distribution of components in organic and aqueous phase in the reactor. Cyclohexene/H_2O/zeolite=2.4/2.7/1.

Table 2
Synthesis of ε-caprolactam from cyclohexanone oxime in the gas-phase catalyzed by ZSM-5 type zeolites

Catalyst	Time on stream (h)	Conversion (%)	Selectivity (%)
Si/Al=147 000	1.25	99.4	89.2
	6.25	98.7	91.2
	3.25 (without methanol)	100	79.6
	6.25 (without methanol)	97.8	81.3
Si/Al=7000	2.25	99.4	87.4
	6.25	98.0	87.8
Si/Al=50	2.25	80.9	78.2
	6.25	44.8	75.0
Si/Zr=2400	1.25	99.8	83.3
	3.25	99.8	95.4
Si/Ti=90	1.25	98.2	83.3
	6.25	91.7	84.8

Oxime/methanol/benzene=1/2.3/11.5 in weight. 623 K, WHSV=2.6/h.

The group later made another important finding: that the selectivity and catalyst life increased dramatically when methanol was mixed with the feed, giving a conversion>99% and a selectivity of 92% [8,9]. There is an optimum concentration of alcohol: too high a concentration of methanol suppresses the rate although the selectivity maintains a high level. The recovery of methanol at the outlet was above 98%. As for the kind of additives, methanol and ethanol exhibited similar effects; however, higher alcohols, phenol, acetaldehyde and acetic acid caused greater deactivation and lower selectivity. The performance of this system is good enough to be considered for industrialization. Examples are given in Table 2. Typical reaction conditions are; Si/Al of zeolite=147 000, 350°C, 1 atm, oxime/alcohol=40, W/F=40 g cat/mol/h.

Koei and Sumitomo group developed a new process for the synthesis of pyridine derivatives using modified ZSM-5 type catalysts. Typical data are shown in Table 3. They obtained a yield of pyridine about 30% higher than with SiO_2–Al_2O_3 and 10–15% higher than with modified SiO_2–Al_2O_3. A catalyst deactivated by coke formation was successfully regenerated by thermal treatment at 723–823 K in air containing methanol. As for the 2- and 3-methylpicolines, their yields were significantly improved by using similar metal-loaded ZSM-5 type catalysts.

Table 3
Synthesis of pyridine and its derivatives from acetaldehyde and formaldehyde

Catalyst	Yield (%)				
	Pyridine	Picoline			Total
		α	β	γ	
SiO_2–Al_2O_3	33	4	11	4	52
H–ZSM-5	42	3	11	5	61
Tl–ZSM-5	63	6	9	3	81
Pb–ZSM-5	60	7	8	4	79
Co–ZSM-5	57	6	7	8	78

$CH_3CHO/HCHO/NH_3$=2/1/4 (molar ratio), SV=1000/h, 723 K.

4. NO_x storage–reduction (NSR) catalyst for automotive lean-burn engines

Abatement of dilute NO_x in the exhaust gas from lean-burn and diesel engines is of great concern in advanced countries, since in spite of the application of the two established catalytic $DeNO_x$ technologies, NH_3-SCR (selective catalytic reduction) and TWC (three-way catalyst), the NO_x concentration in the atmosphere is still high. Reduction of NO_x with hydrocarbons (HC–SCR) is a promising catalytic technology and much effort has been devoted to this subject. However, there remain several serious problems to be solved.

The Toyota group has recently succeeded in developing an alternative catalytic system for the reduction of NO from automotive lean-burn engines (including direct injection-type) [10,11]. These engines exhibit higher fuel efficiencies.

Three-way catalysts containing a basic oxide such as BaO in addition to precious metals (mainly Pt) and CeO_2 are used. Under oxidizing (lean) conditions, NO is oxidized by O_2 on the precious metal to give NO_2, which is then stored as nitrate on the catalyst surface by reacting with the basic oxide. The nitrate is reduced to N_2 under reducing (or stoichiometric) conditions. The catalyst functions quite well by alternating opera-

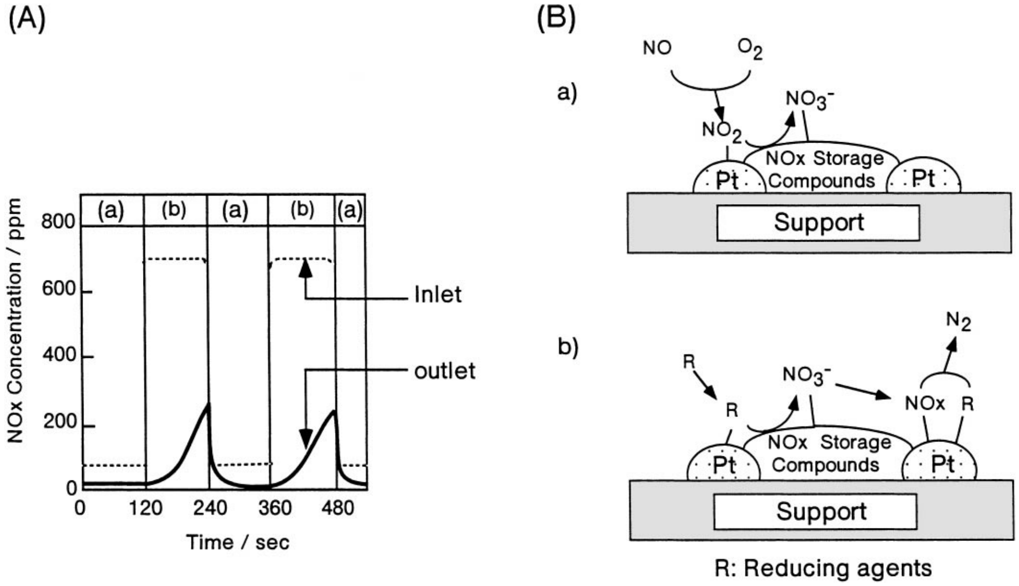


Fig. 2. (A) The performance of NSR catalyst for DeNO$_x$. Broken line: NO concentration in inlet gas, and solid bold line: NO in outlet gas. The inlet gas was alternated every 120 s between reducing (a) and oxidizing (b) conditions. Catalyst: Pt/BaO/alumina. Gas composition for reducing conditions (a) NO=70 ppm, O_2=0.6%, C_3H_6=2,000 ppm, CO=0.5%, H_2O=10%, CO_2=14.5%, and N_2=balance, and for oxidizing conditions (b) NO=700 ppm, O_2=4%, C_3H_6=800 ppm, CO=0.1%, CO_2=12.7%, and N_2=balance. (B) Possible working mechanism of NSR catalyst; (a) NO$_x$ storage and (b) NO$_x$ reduction step.

tion between lean and stoichiometric conditions, as seen in Fig. 2.

A high dispersion of the basic oxide and its close contact with the precious metal are very important, since these suppress the irreversible formation of sulfate (oxidation of sulfur in the fuel) and increase the durability. When the particle size is very small, the sulfate formed is relatively unstable and decomposes under reducing conditions. This reaction is probably also catalyzed by precious metal. The performance at the initial stage is determined by the rate of storage. The subsequent reduction of the nitrate is not the limiting factor, as evidenced by the invariance of the performance with a change in the kind of reductant in the model exhaust gas.

A fresh catalyst shows about 90% NO$_x$ reduction on a vehicle test installed with a 1.8 l lean-burn engine (Japanese 10-15 mode test with Japanese regular gasoline (sulfur: 30 ppm)). After a durability test, corresponding to 100 000 km, more than 60% of the NO$_x$ is reduced. Future improvements needed are a tolerance for high sulfur fuel and applicability to diesel engines.

5. Concluding remarks

Although new catalysts are greatly needed in various areas, it is not easy to realize those catalysts due to the severe requirements for the catalytic performance. The situation is typically so in the case of environmental catalysts of the end-of-pipe type. The catalysts need to react selectively with the extremely low concentrations of molecules with large concentration of inhibiting compounds. Deep desulfurization of fuel is another example where high selectivity is required under rather dirty conditions. Thus, it may be obvious that new catalytic technologies based on new concepts and materials are necessary to meet these requirements. In Japan, we are now running a three-year research project called "catalytic chemistry of unique reaction fields", hoping to promote R&D in this direction [12]. The main themes of this project are: (i) the design of active sites at molecular/atomic levels, (ii) principles for the design of multi-functional catalysts, (iii) new catalyst materials providing unique reaction fields, (iv) reaction engineering taking into account of molecular dynamics, and (v) novel environmental catalysts.

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