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Acid–base bifunctional catalysis: An industrial viewpoint

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Abstract

Acid–base bifunctional catalysis can be categorized into two types; a type in which acid and base interact simultaneously with the substrate, and a type in which acid and base interact successively with the substrate and the transformed substrate. The former simultaneous interaction of acid and base can be further categorized into two parts; a part in which both acid and base interact with the same substrate molecule in concerted manner (concerted mechanism), and a part in which acid and base interact independently with different molecules (go-together mechanism).

Acid catalyzed reactions are greatly affected by addition of base into the reaction system. Addition of base can be categorized into two types too; one in which base is doped on the catalyst to modify the acid–base properties of the catalyst (static doping), and one in which base is doped in the substrate to modify the catalytic action during the reaction (dynamic doping).

Several recent industrial processes are reviewed along these categorizations and it appears that acid–base bifunctional catalysis has a great impact on designing industrial technologies.

Keywords: Acid–base; Bifunctionality; Concerted mechanism; Industrial technology; Doping; Dynamic tuning; Static tuning

1. Introduction

Bifunctionality is a popular concept in understanding the roles of acid and base in catalytic systems, and it has been widely utilized in developing new industrial chemical processes.

Although bifunctionality is generally discussed as a practical contribution to the catalytic performance, it includes several meanings from the viewpoint of reaction mechanisms, and can be categorized into two types depending on whether the interaction of acid and base with the substrate takes place simultaneously or successively.

The case of simultaneous acid–base interaction can be further divided into two types. One type of the simultaneous interaction is, that the base and acid interact with the substrate in such a way that the base pushes the electron pair to one part of the substrate and the acid pulls the electron pair from the other part of the substrate. This type of interaction is called "concerted mechanism" of acid–base bifunctionality. The dehydration of 1-butanol on Na-doped alumina is an example of the reaction involving the concerted mechanism [1]. The interaction of the acidic site and the basic site with 1-butanol is shown in Scheme 1. In this case, the acidic site and the basic site interact simultaneously with one molecule at different positions. Both the acidic sites and basic sites share one catalytic function together.

The other type of the simultaneous interaction is that the acidic site interacts with one substrate molecule and the basic site with a different substrate molecule. Both interactions occur simultaneously but independently. The substrate activated by the acidic site reacts with the substrate activated by the basic site. Aldol condensations [2] and Tishchenko reactions are typical examples of a reaction involving this type of acid–base interaction. In the case of the Tishchenko reaction of benzaldehyde on CaO [3], one molecule of benzaldehyde interacts with a basic O^{2-} site of CaO to form the intermediate (A), while another molecule of benzaldehyde interacts with a Lewis acid site, Ca^{2+}, to form the intermediate (B), as is shown in Scheme 2. Subsequently, the intermediate (A) and the intermediate (B) react to form calcium benzoate and benzylate. Finally, the calcium benzylate and benzaldehyde react to form benzylbenzoate to complete the Tishchenko reaction. In this

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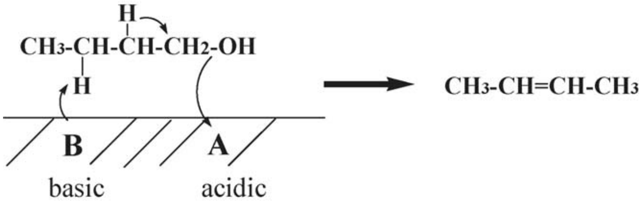


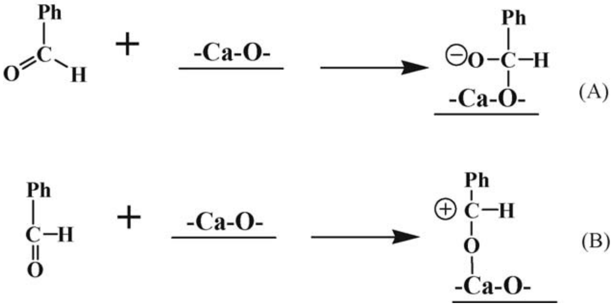
Scheme 1. Dehydration of *n*-butanol via “concerted mechanism”.

case, acidic sites and basic sites work separately, but they compose one catalytic function. Therefore, this type of acid–base bifunctionality is the other type of bifunctionality than the one involving a “concerted mechanism”. In the present paper, this type of bifunctionality is named “go-together mechanism”.

In the case of bifunctionality of successive interaction, the substrate interacts with a certain catalytic site to form an intermediate which interacts successively with the other type of catalytic site to form another intermediate or final product. A famous example of this bifunctionality can be found in the reforming of methylcyclopentane (MCP) catalyzed by a mixture containing SiO_2–Al_2O_3 and Pt/SiO_2 [4]. In this case, dehydrogenation and isomerization occur successively on different sites. The dehydrogenation of MCP occurs on the platinum and does not take place on the acidic sites of SiO_2–Al_2O_3. On the other hand, isomerization of cyclopentenes occurs on the acidic site as shown in Table 1. Each site has its own role in the independent reaction step. This example only shows the successive actions of two catalytic functions, and is not a case of acid–base bifunctionality. Later, some industrial technologies utilizing the acid–base bifunctionality of a catalyst will be introduced, in which the acid and the base take different roles successively.

In many cases, bifunctionality contributes to facilitate the progress of the reaction. Bifunctionality results in an enhancement of the reaction velocity, in improvement of the selectivity, in prolongation of the catalyst life etc. There are many commercial technologies along the concept of bifunctionality. The categorizations mentioned above are from the viewpoint of reaction mechanism.

We can categorize the acid–base bifunctionality from another viewpoint than that of the reaction mechanism. Doping of base, either on the acidic catalyst, or on the reaction mixture improves the performance of the catalyst in acid-catalyzed reactions in which acid–base bifunctionality is operating.



Scheme 2. Initial step of Knoevenagal condensation of benzaldehyde.

The concept of doping is widely used in many types of reactions such as acid- and base-catalyzed reactions, hydrogenations, oxidations etc., and are very useful concepts for industrial applications. Generally, doping induces different effects in different kinds of catalytic reactions. In the present paper, I will review doping effects which appear in acid-catalyzed reactions. Doping the acid-catalyzed reactions with base causes a typical acid–base bifunctionality.

A typical doping in acid-catalyzed reaction is the doping the acidic catalyst with base, which alters the acidic character of the catalyst. In many cases, the effect of doping with base is believed to weaken or tune the intrinsic acidic character of the catalyst which enables to improve its catalytic performance. The mechanistic concepts of doping has, however, not sufficiently been studied from a scientific viewpoint, probably because attention was focused on the improvement of the catalytic performance. In the present paper, I will categorize the doping into two types, and explain the roles of the doping component in each case.

The two categories of doping are so-called “static doping” and “dynamic doping”. The static doping is an addition of base to the acidic catalyst. In this case, the acidity of the catalyst is adequately tuned to smooth the desired reaction. In the case that too strong acidity is harmful to the catalytic performances, the static doping is very effective.

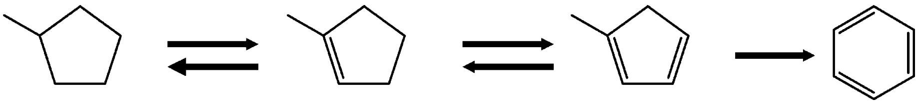
In Fig. 1, the typical behavior of the static doping is illustrated. The doping components interact directly with the main catalytic site to change its original acidic character. There are many industrial technologies working by this concept, and there are also many variations in the mechanisms by which the catalysis can be improved.

The dynamic doping is an addition of base to the reaction medium. In contrast to the static doping, the dynamic doping does not change much the acidic character of the catalyst, but affects the surrounding circumstance of the main catalytic site to suppress side-reactions. Dynamic doping includes factors like co-solvent, additional substrate, additives to liquid phase reactions, and specific carrier gas in vapor phase reactions. Typical behavior of the dynamic doping is illustrated in Fig. 2.

There are many industrial technologies along the concept of the dynamic doping if we look for them in the reactions other than acid-catalyzed ones such as hydrogenation. An example is the partial hydrogenation of benzene to cyclohexene which is a very famous commercial technology established by Asahi Chemical Co. Ltd. in 1990 [5]. The patents describe the main catalyst to be a nano-sized Ru-base alloy. The selectivity to cyclohexene increases drastically on addition of a certain Zn salt into the aqueous phase [6]. The addition of the Zn salt does not change the character and morphology of the Ru-based alloy, but changes the selectivity drastically. It is suggested that the addition of the Zn salt suppress the consecutive hydrogenation of cyclohexene to cyclohexane by facilitating the desorption of cyclohexene from the catalyst surface. In this way, the dynamic doping can change the catalytic performance even it does not change the character of the main active site of the catalyst.

Generally most of the commercial technologies have been discussed little, because they include very important know-how

Table 1
Conversion of MCP catalyzed by acid, metal and their mixtures

Catalyst	Liquid product analysis (mol%)			
				
SiO_2–Al_2O_3	98	0	0	0.1
Pt/Al_2O_3	62	20	18	0.8
SiO_2–Al_2O_3 + Pt/Al_2O_3	65	14	10	10.0

Reaction conditions: 773 K, 82 KPa H_2 partial pressure, 21 KPa MCP, 2.5 s residence time.

as intelligent properties. In the present paper, many examples of industrial processes are reviewed along the above mentioned categorization of the acid–base bifunctionality. Many of the references are from patents and not from academic journals. Although the patents are abundant in realistic applications, they are lacking sufficient information from the scientific viewpoint. In such cases, it is tried to refer to the most plausible explanation. The usefulness of the categorization of the acid–base bifunctionality in designing the industrial technology is demonstrated.

2. Bifunctional catalytic system

2.1. Catalytic system working on "concerted mechanism"

2.1.1. Vapor phase hydrogenation of caboxylic acids to corresponding aldehydes

This process was proposed by Mitsubishi Chemical Co. in 1988 [7]. Modified ZrO_2 is used as a catalyst for the production of various aromatic aldehydes. Later, a modified Cr_2O_3 catalyst was developed for the production of aliphatic aldehydes [8].

Typical catalytic performances of the catalysts are summarized in Table 2. Various kinds of aromatic carboxylic acids are converted to the corresponding aldehydes almost quantitatively over the chromium-modified ZrO_2. In the case of hydrogenation of aliphatic carboxylic acids over unmodified (very pure and high crystalinity) Cr_2O_3, not only selective hydrogenation but also suppression of double bond migration of olefins is realized. Spectroscopic analysis and TPD results suggest that these catalysts have both very weak acidic and very weak basic characteristics and the surface carboxylate species are formed by adsorption of benzoic acid via interaction of the acid group with ZrO_2. It was confirmed that the adsorbed carboxylate species convert to benzaldehyde under reaction condition. The kinetic study suggested that the rate-determinating step is activation of a hydrogen molecule via dissociative adsorption [9]. Based on these experimental results, the reaction mechanism is proposed as shown in Scheme 3. In this mechanism, both benzoic acid and hydrogen molecule adsorb on catalyst surface heteroritically and interact to form benzaldehyde on "concerted mechanism".

Even by using pure ZrO_2 calcined at an adequate temperature, the hydrogenation takes place selectively, but the activity is very poor. By modification of ZrO_2 with chromium, the specific surface area is drastically increased. It becomes clear that the activity is nearly proportional to the specific surface area. It is suggested that both acidic sites and basic sites on ZrO_2 itself are the main active components of the catalyst, and that the addition of chromium contributes to keeping the surface area large by suppressing the sintering of ZrO_2. Furthermore the addition of the Cr^{3+} is considered to contribute to the activation of hydrogen, too [10].

2.1.2. Vapor phase dehydration of ethanolamine by modified Cs–P–SiO_2

This process was established by Nippon Shokubai Co. to produce ethyleneimine by intramolecular dehydration of ethanolamine [11]. As shown in Scheme 4, the desired reaction is competing with several side reactions. One side reaction is the base-catalyzed deamination to produce acrolein, and the other one is the acid-catalyzed dehydration to produce morpholine, pyrazine etc. Therefore, it was necessary to obtain a high catalytic performance for the target reaction and simultaneously

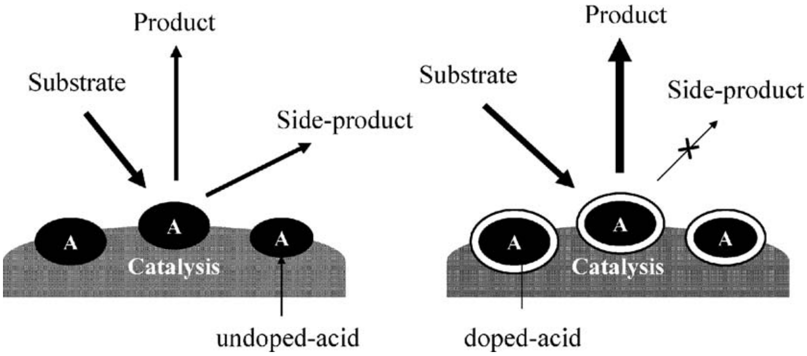


Fig. 1. Typical behavior of acid catalyst by static doping.

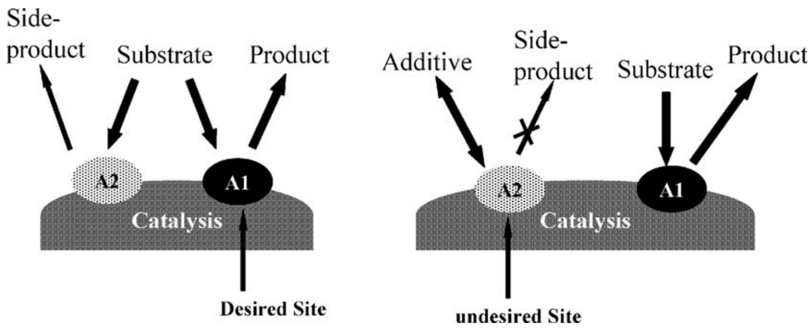


Fig. 2. Typical behavior of acid catalyst by dynamic doping.

restrain the side reactions. Considering that rather strong acid–base characters are required for two side reactions, it was expected that very weak acid or base would be effective as a catalyst for the selective intramolecular dehydration.

Table 3 summarizes the results of catalyst screening. The numbers which are included in the notation of the catalyst represent the molar ratio of the mixed oxides. For example, Si_{10}–Mg_1 represents a mixed oxide composed of SiO_2 and MgO in the molar ratio 10:1. Each catalyst was measured for the acid–base strength by acid–base indicators [12]. It is clear from Table 3 that coexistence of very weak acidity and very weak basicity is preferable for the catalyst to realize high activity and selectivity. Among the catalysts examined, the SiO_2 to which Cs and P were added together showed a high catalytic performance. It was proposed that the very weak acidic character induced by P and the very weak basic character induced by Cs work simultaneously as is shown in Scheme 5 [13]. Therefore, the main reaction proceeds via an acid–base bifunctional concerted mechanism. At the same time, the very weak acidity leads to the suppression of two main side reactions normally catalyzed by strong base and acid.

Addition of the components such as alkali and acid to a catalyst is generally called ‘‘doping’’. Although ‘‘doping’’ is an important method to prepare an efficient catalyst, the method of proper ‘‘doping’’ has not sufficiently been established, because ‘‘doping’’ has been paid little attention from the scientific viewpoint. To clarify the role of the components used in ‘‘doping’’ from the mechanistic viewpoint contributes much to the science of catalyst preparation.

2.1.3. Amination of ethyleneoxide to produce diethanolamine

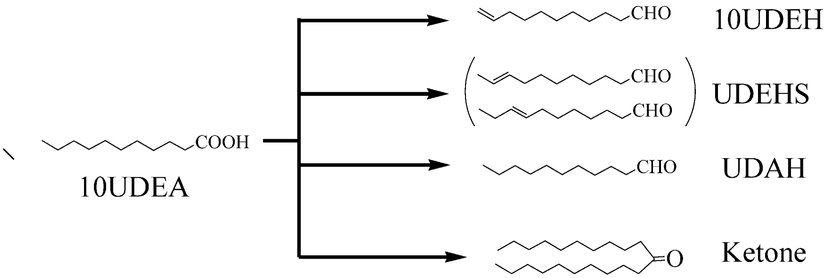
Recently, Nippon Shokubai Co. established another new catalytic system along the concept working on ‘‘concerted mechanism’’ [14].

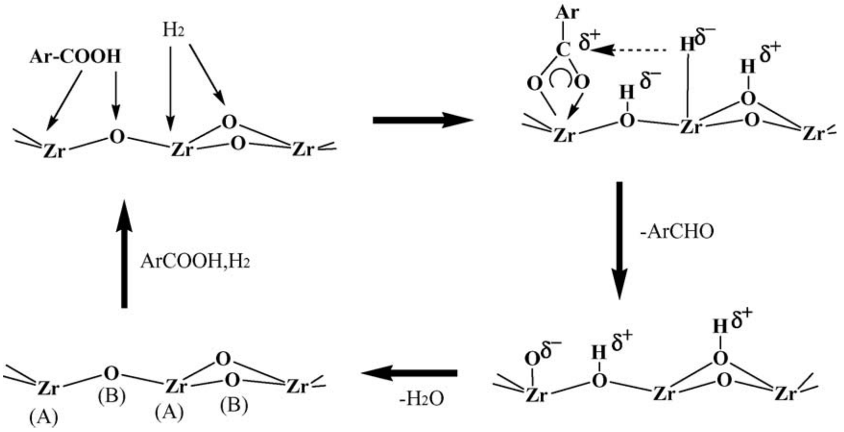
Ethanolamines (EA) are produced from ethylene oxide (EO) and ammonia even in the absence of catalyst. Some catalysts such as ZSM-5 can promote the reaction, but their activities are

Table 2
Hydrogenation of various carboxylic acids over the oxide-catalysts

Catalyst	Carboxylic acid/esters	Conversion (%)	Selectivity (%)
Cr–ZrO_2	Benzoic acid	98	98
	m-Phenoxybenzoic acid	97	97
	Cyclohexanecarboxylic acid	95	95
	Methyl nicotinate	86	86

		Temperature (K)	Conversion (%)	Selectivity (%)		Isomerization ratio 10UDEH/UDEHS
				UDEH	Ketone	
ZrO_2	10-Undecelenic acid	603	97	10	79	–
Cr–ZrO_2		603	87	83	16	0.38
Cr_2O_3		643	74	98	1	0.96
Doped-Cr_2O_3		643	32	43	55	0.87
γ-Al_2O_3		603	8	3	96	–



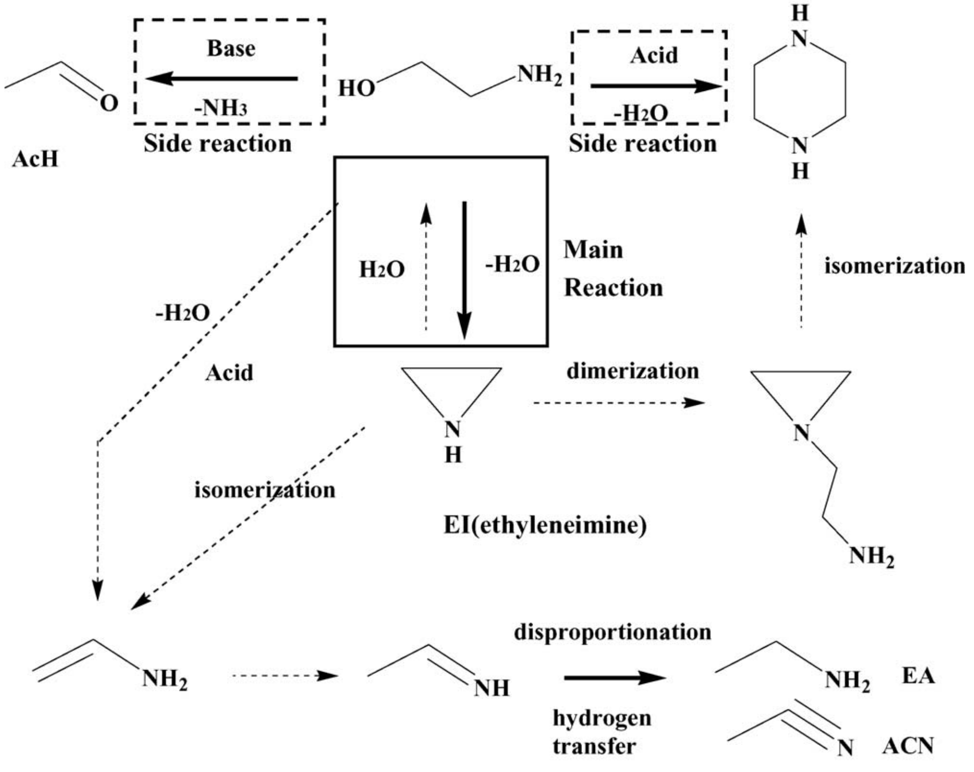


Scheme 3. Reaction mechanism of partial hydrogenation of carboxylic acid on modified ZrO_2.

low. Therefore, the non-catalytic reaction prevails over the catalytic reaction, and the product distribution is controlled by thermodynamic equilibrium. As a result, selective formation of mono-ethanolamine (MEA) or diethanolamine (DEA) was difficult.

The ZSM-5 into which La is introduced realizes not only high activity but also high selectivity for the formation of DEA as is shown in Table 4. By comparison of the rate constants, selective formation of DEA and drastic suppression of TEA formation are the characteristic for La–ZSM-5 catalyst.

Although there are not sufficient studies on the characterization of the catalyst, especially about the position of the La^{3+} ions and the acid–base properties, the catalytic performance suggests many specific characters. By introducing large La^{3+} ions into ZSM-5, its catalytic activity drastically increased; the reaction temperature required to keep more than 90% conversion was lowered by 40 K. Considering the large ionic radius of La^{3+}, lattice substitution of La into MFI structure is very difficult [15]. It is reasonable to consider that a large amount of the introduced La^{3+} ions are located in the zeolite cavities. This explains the high selectivity for DEA because the narrow space of zeolite cavity inhibits the formation of bulky TEA. On the other hand, the enhancement of the activity cannot be explained by the steric hindrance. If only steric hindrance occurred on introduction of La^{3+}, the reaction velocity would have been decreased, because both the diffusion of the substrates and the space required for the formation of the intermediates in transition state should be limited. Never-



Scheme 4. Several coexisting reactions with EI (ethyleneimine) formation.

Table 3
Catalytic performance of various oxides for EI (ethyleneimne) formation

Catalyst	Ho Acid	H- Base	Temp K	SV hour	MEA Conv.(%)	Select(%) EI	Select(%) AcH	Select(%) Pyrazine
Mg	<18.4		673	1000	25.8	-	85.2	-
Si	+3.3<		643	2500	11.6	57.4	17.3	23.3
Si_{10}-Mg_{1}	+4.8<<+9.3 WA+WB		643	1000	25.7	80.1	12.1	7.8
Si_{10}-Mg_{1}	+4.8<<+9.3		673	1000	45.5	74.6	9.4	16.0
Si_{10}-Cs_{1}	+4.8<<+9.3		673	1000	72.7	48.2	43.7	2.4
Si_{10}-Na_{1}-$P_{0.3}$	VWA+WB +6.3<<+9.3		643	2500	21.4	67.8	8.6	20.9
Si_{10}-K_{1}-$P_{0.5}$	+4.8<<+9.3		643	2500	51.1	70.1	8.2	18.8
Si_{10}-Rb_{1}-$P_{0.8}$	+6.8<<+8.3 VWA+VWB		643	2500	70.7	76.4	7.6	11.8
Si_{10}-Cs_{1}-$P_{0.8}$	+6.8<<+8.3		643	2500	70.1	78.7	10.6	5.8

MEA Conc.; 5 vol% in N_2

WA;Weak Acid VWA;Very Weak Acid
WB;Weak Base VWB;Very Weak Base

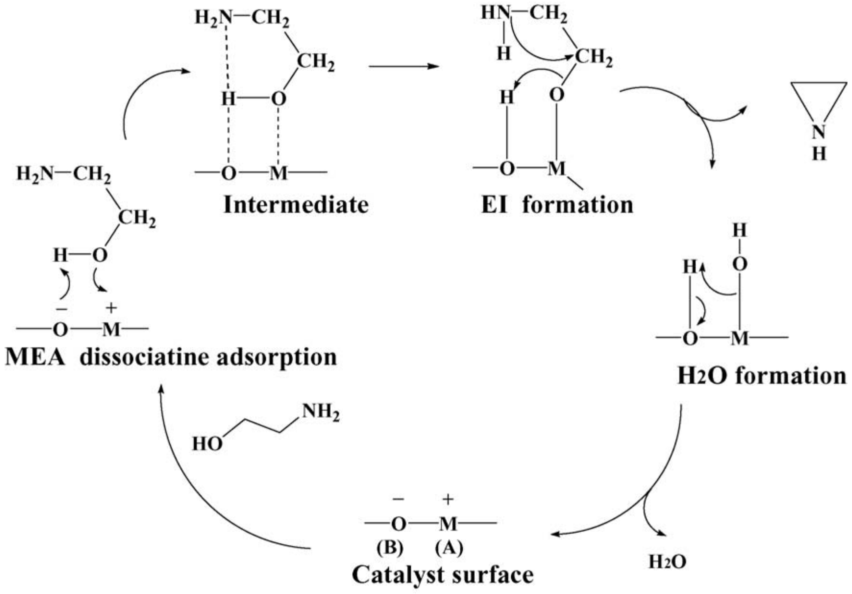
theless, the reaction velocity increased. It is reasonable to consider that the acid–base character is changed adequately by introduction of La^{3+}.

As mentioned above, *N*-alkylation reactions on acid sites proceeds via a concerted mechanism. One can explain that the La^{3+} ion, the acid site of zeolite, and the substrates interact together to formulate an adequate intermediate for the reaction to proceed by concerted mechanism. However, further study is necessary to clarify the real role of the La^{3+} ion.

To the best of my knowledge, this is the first example in which both bifunctionality and shape selectivity are realized at the same time.

2.1.4. Polyoxyalkylenediol formation from alkanediol catalyzed by doped sulfuric acid

Another example is the dehydration of alkanediol to form a condensed polyol, catalyzed by a base-doped sulfuric acid, which is patented to Mitsubishi Chemical Co. [16]. Pure



A; Acid site(Si or P)
B; Base site(O)

Scheme 5. Proposed mechanism of EI (ethyleneimine) formation.

Table 4
Selective DEA formation on La–ZSM-5

Catalyst	WHSV /hr	Temp K	EO Conv. (%)	α	β	γ
SiO_2-Al_2O_3	6.3	380	92.2	9.2	14.0	0.7
SiO_2-Al_2O_3-Na_2O	6.2	381	96.0	6.8	8.8	0.8
SiO_2-Y_2O_3	11.5	389	97.6	7.0	8.2	0.9
H-ZSM-5(Si/Al=28)	10.4	384	91.2	7.7	6.5	1.2
La-ZSM-5	10	343	100.0			
La/Al=0.017				7.8	0.6	12.8
La/Al=0.1				8.5	0.2	39.9
La/Al=0.12				8.7	0.2	50.1

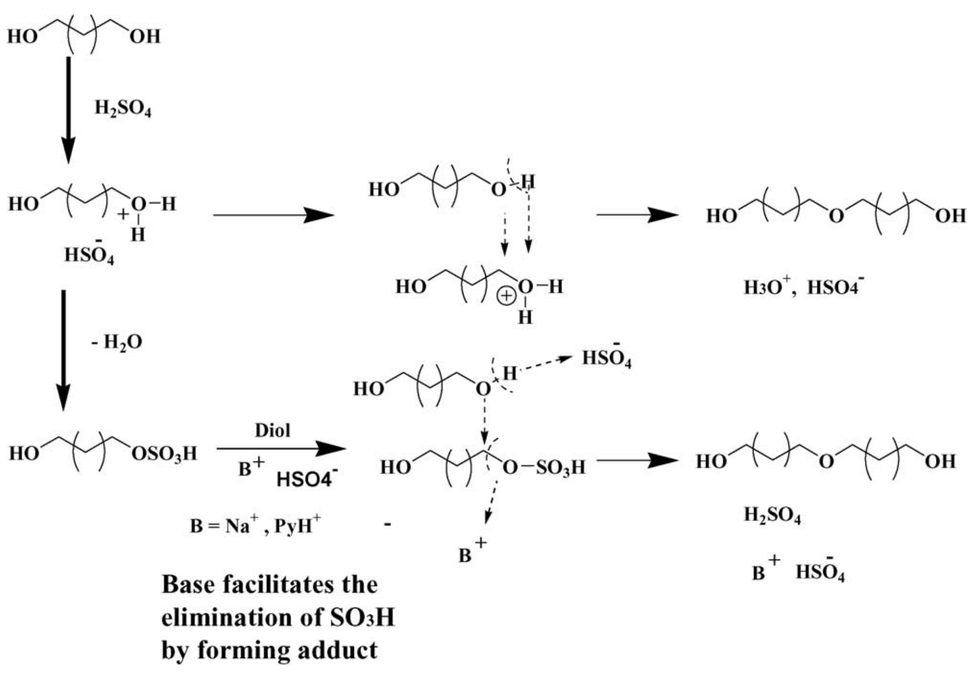
$R_1 = k_1[C_{NH3}][C_{EO}]$ $\alpha = k_2/k_1$
$R_2 = k_2[C_{MEA}][C_{EO}]$ $\beta = k_3/k_1$
$R_3 = k_3[C_{DEA}][C_{EO}]$ $\gamma = k_2/k_3$

sulfuric acid catalyzes the dehydration reaction, but upon elimination of HSO_4^- a terminal olefin and polymeric blackish residue are formed as by-products. Without addition of base into sulfuric acid, the side reactions are dominant, and the yield of the target product of polyol is very low. However, introduction of bases such as NaOH and pyridine (Py) facilitates the elimination of HSO_4^- and the successive nucleophilic attack of alkanediol to produce the final product. The reaction mechanism is considered as illustrated in Scheme 6. According to this reaction mechanism, alkali ion works as a Lewis acid, and HSO_4^- works as a base by concerted mechanism. It is very unique that a tiny amount of alkali against H_2SO_4 is not neutralized but work catalytically even in the liquid phase.

2.2. *Catalytic system working on "go-together mechanism"*

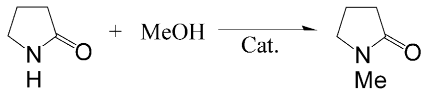
Though many base-catalyzed condensation reactions such as aldol condensation [2], Claisen condensation [17], Tishchenko reaction [3], Knoevenagel condensation [18] etc. are in this category, recent new industrial technologies are few.

Generally these reactions are catalyzed by strong bases, and this may be the reason why we can only find a small number of industrial applications. Considering an industrial technology, a



Scheme 6. Dehydration of alkanediol catalyzed by alkali-doped H_2SO_4.

Table 5
N-methylation of 2P to NMP



2-pyrrolidone (2-P)
N-methyl-2-pyrrolidone (NMP)

Catalyst	2P conversion (%)	NMP yield (%)	NMP selectivity (%)
Al_2O_3	69	63	91
Treated with H_3BO_3	69	47	68
Treated with Na_2CO_3	52	50	96
Cs_2O/SiO_2*	62	61	98

Catalyst, 1.0 g; 2P, 1.49 mmol/h; MeOH, 2.23 mmol/h; N_2, 4.46 mmol/h 300 °C (*400 °C) at atmospheric pressure.

facile elimination of the product from the catalyst and thereby avoiding adsorptive poisoning is very important to keep the stability of the catalyst. Strongly basic catalyst retains the product firmly on the surface, and are not suitable for practical application.

The recent strong desire to synthesize plant-based chemicals with zero-emission may increase the value of these condensation reactions, because almost all of the chemical fragments in the plant have oxygen-containing functional groups such as hydroxyl group, formyl group, oxy group, oxycarbonyl group, and carboxylic group. In order to convert these oxygen containing compounds to the current raw materials produced from petroleum, these condensation type reactions are key reactions. Production of C4 chemicals from ethanol is such an example. It is known that the formation of *n*-butanol and butadiene from ethanol is catalyzed by Mn-doped clay and alkali-doped SiO_2 via an aldol condensation [19]. This reaction is initiated by base-catalyzed dehydrogenation of ethanol to form acetaldehyde which subsequently undergoes aldol condensation to produce C4 chemicals. The aldol condensation involves ‘‘go-together mechanism’’. Recently Sangi Co. announced a new catalyst, based on a metal substituted hydroxyapatite, for this reaction [20]. In order to gain a high yield, the catalyst seems to be designed to have very weak acid–base character, which is preferable to proceed the reaction smoothly by ‘‘go-together mechanism’’.

By using the catalyst with very weak acid–base character, easy removal of the product from the catalyst and improvement of the stability of catalytic performance are expected. The following example demonstrates the effectiveness of this concept.

2.2.1. Vapor phase methylation of 2-pyrolidine by apparently neutral oxide

This process was proposed by Mitsubishi Chemical Co. [21].

Generally, an alkali treatment of an oxide catalyst gives strong basicity to the catalyst, and an acid treatment gives a strong acidity. It is well known that superacid such as SO_4^{2-}–ZrO_2 and superbase such as Na–Al_2O_3 are prepared along this concept [22]. On the contrary, acid treatment or base treatment affords very different acid–base characters in some cases. Treatment with a certain type of acid and base results in the formation of very weak base or almost neutral character. Cs loaded on silica showed a high selectivity for the methylation of 2-pyrolidone (2P) to *N*-methylpyrolidone (NMP) as shown in Table 5. Alumina carefully treated with Na_2CO_3 also showed a high selectivity. Table 6 shows the acid–base properties measured by acid–base indicators. It is suggested that high activity and high selectivity need a catalyst containing a combination of very weak acidity and very weak basicity. As shown in Scheme 7, *N*-alkylation over Al_2O_3 takes place via protonation of the alcohol on the acidic hydroxyl group of Al_2O_3, followed by charge transfer between the protonated species and amine. Therefore, this reaction is categorized into the reaction working on a go-together mechanism. Although the acid–base character of the catalysts is almost neutral, the catalyst shows an excellent catalytic performance. It is suggested that the very weak base promotes the activation of 2P to facilitate the charge transfer.

Because of the very weak acid–base character of the catalyst, it is difficult to get a conclusion that this reaction works on ‘‘concerted mechanism’’. Further kinetic study combined with spectroscopic surface analysis is necessary.

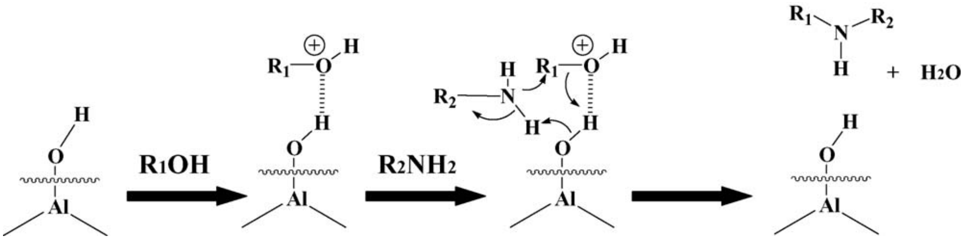
2.3. Catalytic system working on successive reaction

It is difficult to distinguish a certain reaction in this category from a reaction described in Section 2.1 or 2.2 based on the exact definition, because the difference in the residence time between the simultaneous reaction and the successive reaction is not clear. Therefore, in the present paper, the successive reaction is defined as the reaction in which the acid-catalyzed step and the base-

Table 6
Acid character of various catalysts measured by acid–base indicators

Catalyst	NMP selectivity (%)	Ho					
		+3.3	+4.8	+6.8	+7.2	+9.3	+15.0
Al_2O_3	91	×	×	○	○	×	×
Treated with H_3BO_3	68	×	○	○	×	×	×
Treated with Na_2CO_3	96	×	×	×	○	×	×
Cs_2O/SiO_2	98	×	×	×	○	×	×

+3.3, methyl yellow; +4.8, methyl red; +6.8, neutral red; +7.2, bromothymol blue; 9.3, phenolphthalein; +15.0, 2,4-dinitroaniline.



Scheme 7. Proposed mechanism of *N*-alkylation of alcohol with primary amine.

catalyzed step can be clearly separated in the reaction mechanism or in the process technology.

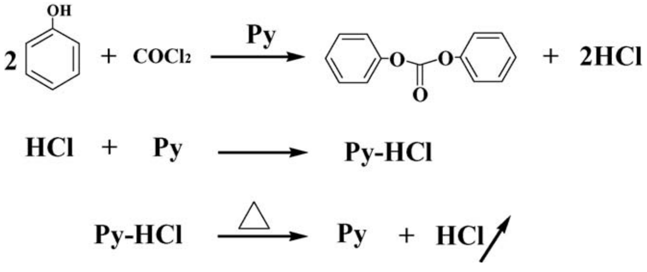
Methyl isobutyl ketone (MIBK) production from acetone is a historical example of a commercial technology in this category. In this case, the aldol condensation at initial step, the successive dehydration and the final hydrogenation reaction can be distinguished each other from the mechanistic viewpoint.

2.3.1. Diphenyl carbonate (DPC) formation from phenol and phosgene in the presence of pyridine

This process was established commercially in 2000 by Mitsubishi Chemical Co. [23]. As shown in Scheme 8, pyridine enhances the reaction velocity of DPC formation from phenol and phosgene by functioning as a base to form Py/HCl salt quantitatively. Py/HCl salt is successively decomposed by elevating the reaction temperature and the regenerated pyridine is recycled. As a result, pyridine behaves like a catalyst even though it is a reagent in a stoichiometric reaction. Very small amount of pyridine is necessary to operate this commercial process. Although pyridine stands at the position out of the traditional definition of catalyst, it is clear that both acid and base are functioning successively and independently. As an industrial technology, it is worthwhile to note. It looks like the role of copper ion in the classical Wacker oxidation in which copper ion assists Pd catalyst by making stoichiometric redox cycle between Cu(I) and Cu(II) [24].

2.3.2. Liquid phase Beckmann rearrangement of cyclic oximes

In the conventional Beckmann rearrangement process for caprolactam (CL), sulfuric acid is used as a stoichiometric reagent. Because high purity of the product is required, a mild reaction condition in the liquid phase is more preferable than a vapor phase reaction at high temperature. Mitsubishi Chemical Co. has filed many patents along this concept [25]. The catalytic system is composed of cyclic oxime (CYO), dimethylformamide (DMF), and *p*-toluene sulfonic acid anhydride (PTSA). This combination produces CL with a turnover number (TON) of 25 and cyclododecyllactam with a TON more than 100.



Scheme 8. Reaction scheme of diphenyl carbonate formation under the presence of pyridine.

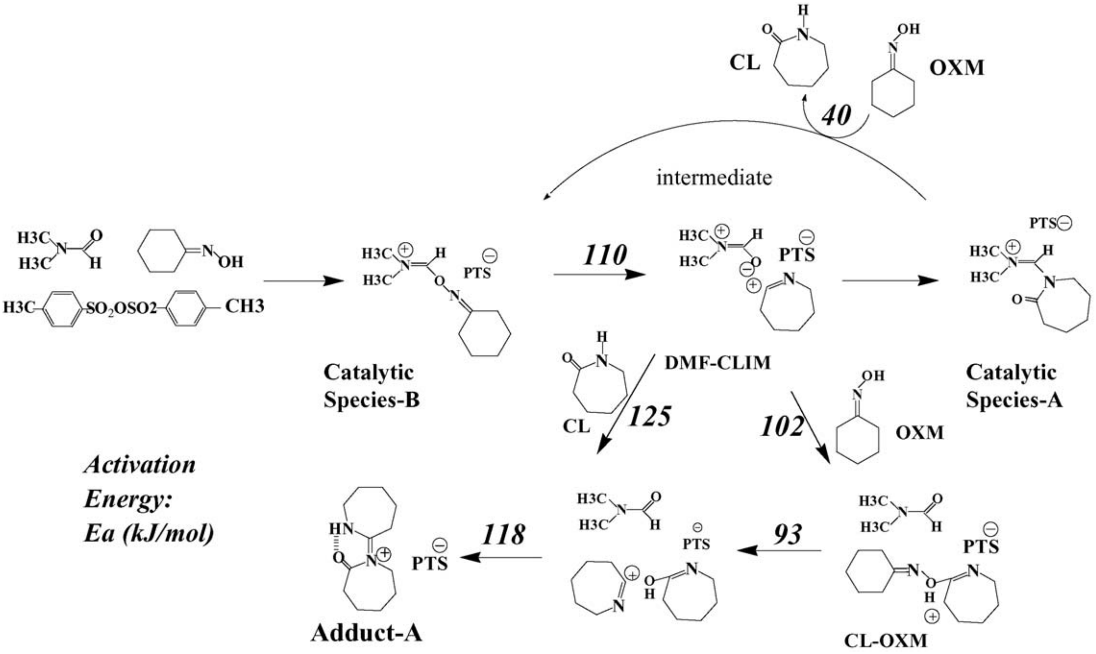
By combination of kinetic study using micro flow reactor with in situ NMR analysis of the intermediates and the products, a reaction mechanism was postulated including the activation energies for the main steps as is shown in Scheme 9. It is proposed that the iminium cation induced from DMF and CHO is the initial intermediate (species B). The initial cationic species is formed by the interaction between DMF (acid) and CYO (base) in the presence of PTSA. The cationic species is successively transformed into its isomer (species B). Species A reacts with CYO to produce CL catalytically. In this system, the stoichiometric amount of the acid (DMF) and the base (CYO) combines to formulate an acidic species via dehydration reaction under the presence of PTSA and the acidic species successively react with CYO (base) to produce CL catalytically.

It is easy to separate the former step for the formation of the active species from the latter step of the catalytic Beckmann rearrangement not only from the mechanistic viewpoint but also from the viewpoint of process technology. Therefore, the Beckmann rearrangement of the above system is categorized into the acid–base bifunctional catalytic system working on successive reaction mechanism.

2.3.3. Vapor phase ketonization of carboxylic acid

This is a series of very elegant catalytic reactions to produce various kinds of ketones as shown in Scheme 10. BASF, Daicel Chem. Ind., Takeda, Chisso Co. etc. have filed many patents [26]. According to the patents, the substrates are carboxylic acids and the effective catalysts are alkali-doped ZrO_2 and alkali-doped TiO_2. The reactions take place at a high temperature, over 623 K. The corresponding ketones are obtained in high yield.

The reaction mechanism proposed for the formation of cyclopentanone from adipic acid is shown in Scheme 11. Initially, a Claisen-type condensation takes place to form ketocarboxylic acid, and the ketocarboxylic acid is successively converted to cyclopentanone with elimination of CO_2. It is considered that base catalyzes the former reaction and acid catalyzes the latter reaction [8]. Although we can find little literature about this reaction except patents, it is clear that bifunctionality of successive interaction is operating in the formation of cyclopentanone from adipic acid.



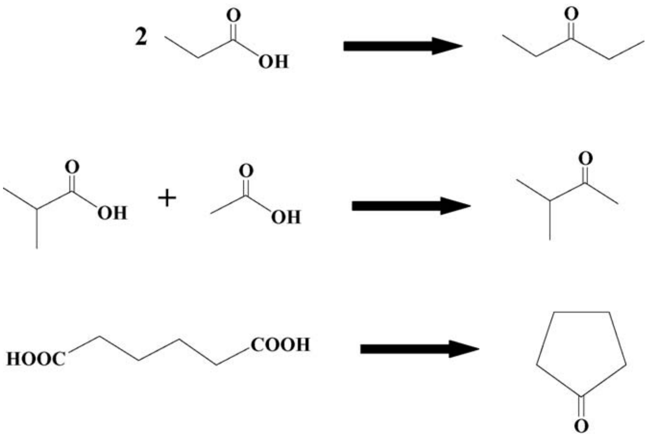
Scheme 9. Reaction mechanism of Beckmann rearrangement in liquid phase.

3. Acid-catalyzed reaction modified with base

The accumulated knowledge about ‘‘doping effect’’, ‘‘effect of additives’’ and ‘‘co-catalyst’’ is included in the establishment of the industrial catalytic processes. The terms ‘‘doping effect’’, ‘‘effect of additives’’ and ‘‘co-catalyst’’ are convenient to express the enhancement of catalytic performances, and have been used without further explanations. Some of the terms, however, can be categorized into the acid–base bifunctionality as discussed in the previous sections. In the present section, two types of doping with base are discussed.

3.1. Static doping

Doping is a popular method to improve the performance of a catalyst. The surface of a heterogeneous catalyst has various acid–base characters. Some of them may disturb the desired reaction by promoting the side reactions. These harmful characters should be decreased by doping, resulting in an improvement of the performance of the catalyst. The doping results in the formation of desired acidic and/or basic sites, as well as the elimination and/or decrease of the undesired sites, as is shown in Fig. 1. In this case, the character of the catalyst changes permanently by doping. Therefore, this type of doping may be called ‘‘static doping’’.



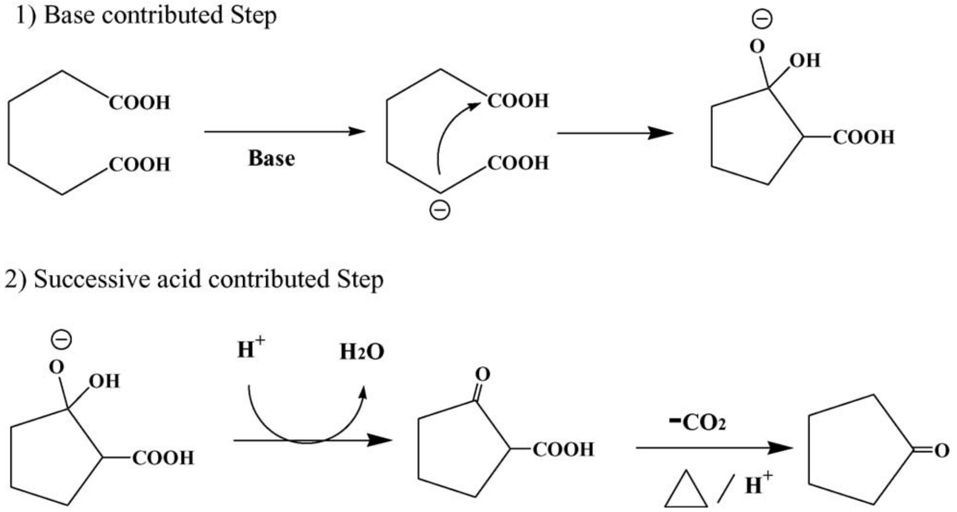
Scheme 10. Several examples of ketonization of carboxylic acid in vapor phase reaction.

Among the examples described in the previous section, those described in Sections 2.1.2, 2.1.3, 2.1.4, 2.2.1 and 2.3.3 belong to this type of doping. Doping effects are discussed from the viewpoint of the reaction mechanism.

While it is normal that the acidic character of the catalyst is changed by doping with base, static doping brings about an additional effect. An example of this effect on the catalytic performance of an oxidation reaction is described below.

3.1.1. Vapor phase oxidation of toluene derivatives by alkali-doped V catalyst

As mentioned above, doping with alkali is a useful method for designing a catalyst for acid- and base-catalyzed reactions. This methodology is also applicable for designing a catalyst for oxidation reactions. Nippon Shokubai Co. established the catalytic technology for the vapor phase oxidation of *p*-methoxytoluene to the corresponding aldehyde by use of doped V_2O_5 catalysts [27]. In Fig. 3, the selectivities at 50% conversion are plotted against the activities for V_2O_5 catalysts doped with different elements. The activity is represented by $T_{50\%}$ which means by the temperature to give 50% conversion. By addition of Cs and Rb, high activities were obtained but the selectivity decreased. By addition of Tl and K, moderate activities and selectivities were realized. It is considered that abstraction of methyl hydrogen is the key step for the oxidation. A strong acidity is required to abstract the methyl hydrogen.



Scheme 11. Proposed mechanism of ketonization of adipic acid to cyclopentanone via acid–base successive reactions.

However this would also promote further oxidation or combustion to CO_2. Therefore, tuning of acidity is required to obtain the catalyst showing moderate activity and high selectivity. The principal concept in catalyst design for this oxidation is almost the same as that for acid- and base-catalyzed reactions. It is very useful for the industrial application to design the oxidation catalyst from the viewpoint of acid–base character. Design of the catalyst for ammoxidation of propane (Mo–V–Nb–Te–O) first proposed by Mitsubishi Chemical Co. was done along this concept [28]. The catalyst was designed to include oxidation components and doping components to tune the acidity, and is not a product of random screening.

3.2. Dynamic doping

As described in the preceding section, the static doping is the most popular method to improve the catalytic performance. The change in the characters of catalyst is permanent. On the other hand, there is a method of doping in which unmodified catalyst works well by the contribution of a certain reactive molecule coexisting with the main substrate. The concept is explained in Fig. 2. The effect of this type of doping is temporary, and we can call the method ‘‘dynamic doping’’.

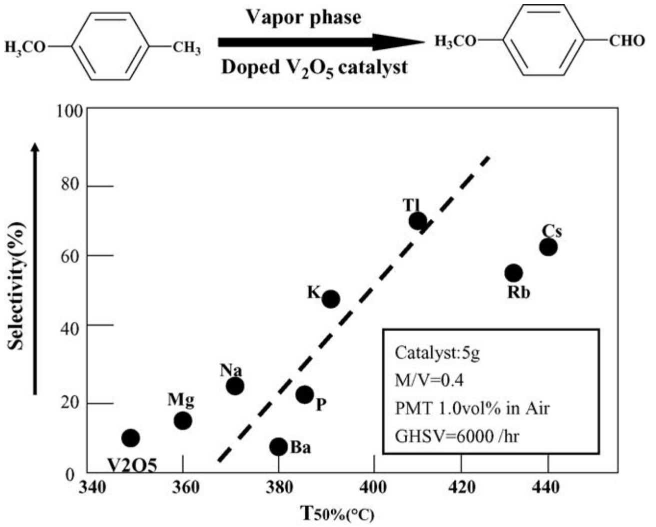


Fig. 3. Partial oxidation of *p*-methoxytoluene catalyzed by doped V_2O_5 catalyst.

3.2.1. *Vapor phase Beckmann rearrangement for caprolactam in the presence of methanol*

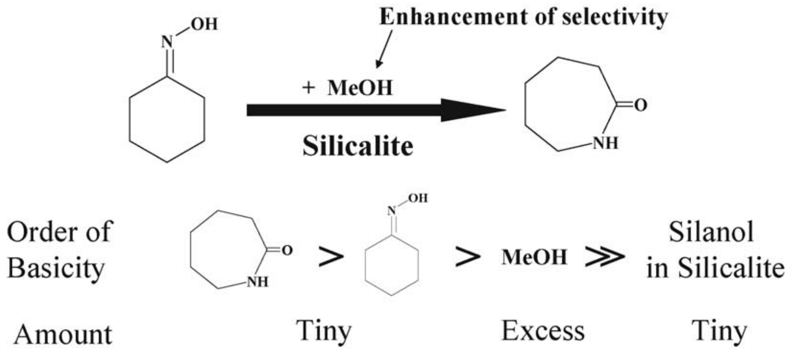
Sumitomo Chemical Ind. Co. has commercialized its long-dream technology of the vapor phase Beckmann rearrangement for caprolactam since 2002 [29]. Al-free MFI type zeolite is used as a catalyst in the process. It is proposed that the active site is a silanol nest having very weak acidity [30]. It is also reported that the addition of methanol is very important to improve the selectivity to the level having economical advantage. In Table 7 the catalytic performances of various processes patented to different companies are compared [31]. In all the processes, various coexisting compounds are used.

There are few reports which discuss the roles of the coexisting compounds like methanol. Considering the order of basicities of cyclohexanoneoxim (CYO), caprolactam (CL), and methanol against the acidity of the silanol nest of the Al-free MFI type zeolite catalyst, it is reasonable that a competitive adsorption takes place for these compounds. The concentration of methanol is high enough to cover the undesired acidic sites and keeps the catalytically active silanol nests untouched. In this way side reactions are suppressed. Therefore, CYO behaves as a base to the acidic silanol nest, methanol behaves as a base to the acidic sites for side reactions. The competitive reactions between these bases with the acid take place. The relationship among these bases and acid is summarized in Scheme 12.

It is well known that methanol converts easily to olefinic hydrocarbons on Al containing zeolite catalysts, which is the so called MTO reaction [32]. By eliminating Al from the catalyst, the MTO reaction becomes negligible under the reaction conditions at about 620 K. Therefore, in this system, coexisting

Table 7
Effect of alcohols on vapor phase Beckmann rearrangement

Patent assignee	Catalyst	Coexisting vapor	WHSV (h^{-1})	Conversion (%)	Selectivity (%)
UOP	SAPO-11	CH_3CN	0.54	98	95
Sumitomo	High silica MFI	Benzene	3.0	74	72
	High silica MFI	Methanol	3.3	99	87
Mobil	ZSM-5	Benzene	0.05	99	89
Degussa	B-MFI	Methanol	0.25	99	93
Ube	Zeolite-L	*n*-Hexanol	0.83	99	97
Sumitomo	ALPO-5	Ethanol	0.45	27	88
Enichem	SiO_2-Al_2O_3	Methanol	2.0	99	78



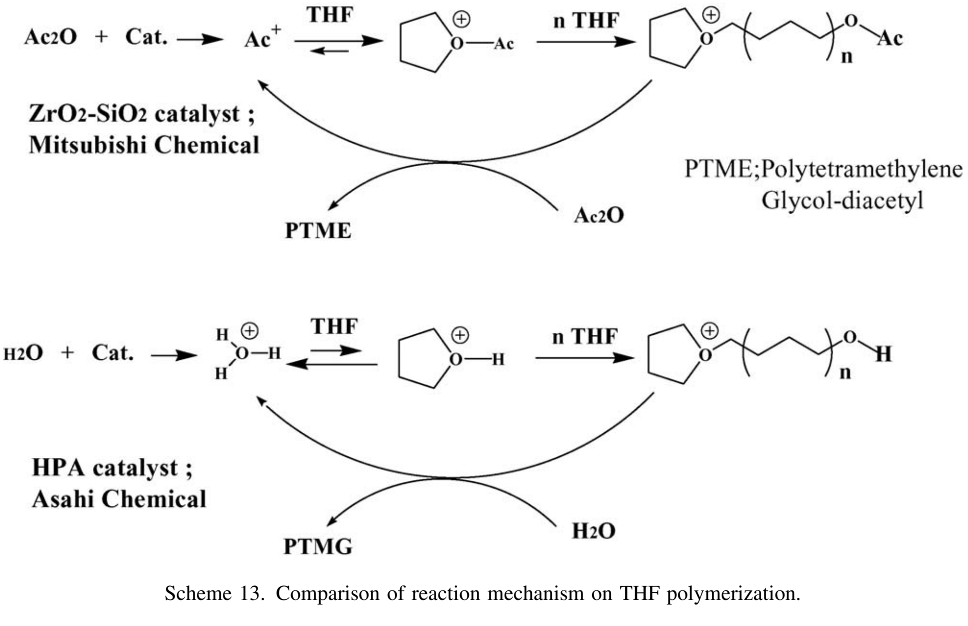
Scheme 12. Relationship among substrates and product with active site in vapor phase Beckmann rearrangement.

methanol plays a role to suppress the side reactions without suppressing the main reaction. In this way, coexisting base can contribute to the enhancement of the performance of the catalyst.

3.2.2. Polymerization of THF in the presence of water or acetic anhydride

Polytetramethyene glycol (PTMG or poly-THF) is now a member of bulk chemicals. Several commercial catalytic processes have been established in Japan during the past two decades.

Asahi Chemical Co. has established a process using heteropolyacid (HPA) as catalyst [33]. In the process, both a highly concentrated HPA and a tiny amount of water equivalent to the strongly coordinated water are required to promote the reaction efficiently. It is believed that, at first, the strong Broensted acid (HPA) induces the generation of a hydroxonium cation, and that a successive nucleophilic attack of the hydroxonium cation to the basic THF takes place. A high concentration of HPA is required to keep the concentration of the



Scheme 13. Comparison of reaction mechanism on THF polymerization.

hydroxonium ion in equilibrium high. This is a quite simple acid-catalyzed reaction to produce directly PTMG form THF (base).

Mitsubishi Chemical Co. has established a process using a Lewis acidic ZrO_2–SiO_2 catalyst [34]. In this process, acetic anhydride is used as an initiator (base to catalyst) as well as a terminator (base to the intermediate). It is believed that the acetyl oxonium cation induced by the Lewis acid site on the catalyst is generated in the initiation step. The successive propagation takes place by the nucleophilic attack of the acetyl oxonium cation to THF, and, finally, the termination takes place by the addition of AcO^- to the propagating intermediate to produce diacetoxy ester (PTME). In this case, the generated acetyl oxonium cation is stable enough to move to the successive propagation. As a result a high productivity is obtained. The obtained PTME is converted to PTMG by alcoholysis. Although this reaction is composed of two steps, its high productivity is worthwhile to compensate for the two-step procedure.

The difference between the two above mentioned catalytic systems is compared in Scheme 13. Both systems are not categorized into a acid–base bifunctional system in a normal sense, but categorized into a simple acid-catalyzed reaction system. Water and acetic anhydride play a role in the generation of the key intermediates which participate as a base in the acid-catalyzed process, while the apparent basic substrate to the acids is always THF.

Although the competitive interaction of two kinds of bases (water and acetic anhydride) to the acidic catalyst control the reaction performance, they do not affect the intrinsic character of the main catalysts. Therefore, the doping of water and acetic anhydride should be categorized into dynamic doping.

4. Summary

The concept of acid–base bifunctionality is very useful in designing various kinds of catalysts. The bifunctionality is categorized into two types; simultaneous interaction and successive interaction. The former type is further categorized into two mechanisms being the concerted and go-together mechanism. Many commercial technologies established recently are reviewed along these categorizations.

Considering the large number of the established technologies, it seems that the bifunctional catalytic system in which the concerted mechanism is operating is quite suitable for industrial application. This may be because the combination of weak acid and weak base is effective for the target reaction when they work in concerted manner. On the other hand, the systems working on the go-together mechanism and those working on the successive interaction are scarce. In these cases, strong acid or strong base is normally more effective than weak acid or base for activation of the substrates but strong interaction of acid or base with the final product makes it difficult to desorb the final product from the catalyst surface, which is not favorable for industrial application.

Acidic catalysts whose acidities are tuned by doping with base are also categorized into two types, static doping and dynamic doping. Most of the acid–base bifunctional catalysts belong to the catalysts prepared by the static doping by which the intrinsic acidities of the catalysts are changed. On the other hand, the catalytic performances are improved by the dynamic doping with base which is added to the reaction mixture without changing the intrinsic acidity of the catalyst.

To understand the real features of the industrial technologies from the viewpoint of the reaction mechanisms, in relation to the doping effects, is a very useful tool in designing the catalysts for future industrial processes.

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