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Future possibilities of recently commercialized acid/base-catalyzed chemical processes

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Abstract

The recent acid/base-catalyzed chemical processes predominantly commercialized since the beginning of 1990s are reviewed in this paper.

They use successfully zeolites, heteropolyacids (HPAs), modified zirconia, ion-exchange resins (IERs), and superbase catalysts in homogeneous liquid-phase, heterogeneous liquid-phase and vapor-phase reactions.

Especially, the high position-selective performances of some solid acid/base-catalysts having controlled structure have contributed significantly to the improvement of the yields of target products. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acid/base-catalyzed reactions are one of the most important fields not only in the syntheses of commodity chemicals, but also in complicated procedures in the syntheses of specialty chemicals in the fields of pharmaceuticals, agrochemicals, and flavors/fragrances.

Typical reactions include following types:

- hydration/dehydration reactions;
- esterification/etheration/hydrolysis reactions;
- oligomerization/polymerization reactions;
- isomerization reactions;
- alkylation/acylation/substitution reactions.

In these reactions, following catalysts are still commercially used:

- inorganic/organic acid in liquid-phase homogeneous system
  - ○ sulfuric acid/oleum/HCl
  - ○ $AlCl_3/ZnCl_2/BF_3/HF/FSO_3H$
  - ○ heteropolyacid (HPA)
  - ○ *p*-toluenesulfonic acid/trichloroacetic acid
- inorganic acid in vapor-phase heterogeneous system
  - ○ silica–alumina and other mixed metal oxides
  - ○ solid phosphoric acid (phosphoric acid supported by diatomaceous earth)
  - ○ zeolites
- inorganic bases/in liquid-phase homogeneous system
  - ○ NaOH/KOH/alkali alcoholate

Most of these catalyst systems have been known to have following problems from the industrial point of view:

- high corrosiveness to require the expensive high class construction materials such as glass-lined

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steel, titanium-cladded steel, Hastelloy besides 304 and 316L stainless steels;
- difficulty of process-arrangement based on catalyst recycle;
- necessity of complete removal of trace of catalyst from the product mostly after deactivation by neutralization in order to avoid deterioration of the product;
- necessity of careful treatment of waste water-containing catalyst residue for avoiding pollution problems.

These problems are especially indispensable in liquid-phase homogeneous catalyst systems, and use of solid catalyst in both liquid-phase and vapor-phase reactions can eliminate these problems in the most cases.

From standpoint above, Catalyst Society of Japan had promoted and encouraged the development of new solid acid/base-catalysts applicable to industrial processes for 5 years from 1980 by organizing special committee, and various new catalysts had been proposed [1]. Some of the proposed new catalysts are becoming commercially applied.

Although, Tanabe and Hoeldrich have reviewed industrial application of solid acid/base-catalysts from the view point of university professors [2], the author would like to review the newly or recently commercialized chemical processes based on acid/base-catalyst, and how these new catalyst systems have replaced conventional catalysts, and what kind of influences are brought in the chemical industry from the standpoint of industrial chemical process engineer.

2. Acid-catalyzed liquid-phase homogeneous process

Although, many liquid-phase acid-catalyzed processes including esterification for manufacturing plasticizers (sulfuric acid), dehydrative esterification of acetonecyanohydrin to methyl methacrylate (MMA) (sulfuric acid), alkylation of benzene to ethylbenzene ($AlCl_3$), Prins reaction to derive metadioxane from *iso*-butene (sulfuric acid), Beckmann rearrangement (oleum), alpha-olefin oligomerization, preparation of petroleum resin and polybutene ($AlCl_3$, BF_3), oligomerization of tetrahydrofurane (THF) to poly(tetamethylene ether)glycol (PTMEG) (FSO_3H), isomerization of xylene to *p*-xylene (HF/BF_3), etc. use above-mentioned highly corrosive catalyst systems in the commercial processes, and this tendency has been much more noticeable in the syntheses of specialty fine chemicals.

The butyralization of polyvinylalcohol (PVOH) to polyvinylbutyral (PVB) as an intermediate layer of automotive front laminated safety glass is also out of exception by using HCl in aqueous medium.

By maintaining homogeneous liquid-phase, following processes using less corrosive HPA have been satisfactorily commercially applied in succession to hydration of propylene to *iso*-propanol:

- selective hydration of *iso*-butene contained in mixed butane/butene fraction to *t*-butanol as an intermediate for MMA production—PMo_{12}-type HPA replacing H_2SO_4, Asahi Chemical Industry [3];
- hydration of *n*-butenes to secondary butanol as an intermediate for methylethylketone (MEK) production by applying supercritical extraction—SiW_{12}-type HPA replacing H_2SO_4, Idemitsu Petrochemical [4];
- oligomerization of THF to PTMEG in THF/water binary medium—PW_{12}-type HPA replacing FSO_3H or FSO_3H/Ac_2O in THF, Asahi Chemical Industry [5].

These catalyst systems are applied in water-containing system, and the catalyst is recycled to the reaction by being separated from the product, even though the removal procedure of residual catalyst from PTMEG is indispensable.

In PTMEG manufacturing process, PTMEG formed in aqueous phase with dissolved HPA is transferred to THF-phase to enable control of average molecular weight of the product by adjusting water/HPA molar ratio of the reaction system.

$$PW_{12} = H_3PW_{12}O_{40} \cdot xH_2O,$$

$$SiW_{12} = H_4SiW_{12}O_{40} \cdot xH_2O$$

3. Solid acid-catalyzed heterogeneous process

There are already so many commercial processes by using solid acid-type catalysts represented, for example, by fluid catalytic cracking using silica–

alumina, ethylbenzene synthesis using zeolite, xylene-isomerization for *p*-xylene manufacturing over zeolite such as ZSM-5 and mordenite, ethylene-hydration to ethanol over solid phosphoric acid, etc. Alkylation, transalkylation, and isomerization processes of aromatic hydrocarbons belong to this category, and application of position-selective or regio-selective function of zeolite-type catalysts have contributed to process innovation by replacing silica–alumina and other mixed oxide-type catalysts having poor position-selective performance.

However, these solid acid-type catalysts have, in many cases, problems of less satisfactorily long catalyst life by the deposition of by-produced tar and carbonaceous materials over catalyst surface by also being catalyzed by acid sites to require the alternating operation of plural number of reactors between reaction and catalyst regeneration, or mounting of catalyst regeneration column combined with fluidized bed reactor for circulating catalyst between them.

In the liquid-phase acid-catalyzed reactions, especially in the reactions where water and/or lower alcohols participate, cationic ion-exchange resin (IER) has been applied successfully. But, sometimes it has the problems of low activity for the reactions requiring high acid strength, unsatisfactory activity caused by the difficulty of applying reaction temperature exceeding 100 °C, and swelling of catalyst in the organic reaction medium.

By utilizing solid catalysts in heterogeneous system, especially in liquid-phase system, the most of previously mentioned problems of the processes using homogeneous catalyst systems can be eliminated.

The author would like to show examples of recent successfully commercialized new solid acid catalyst base processes.

3.1. Hydration reaction

Cationic IER is well known in various hydration reactions, but there are following examples commercially applied in liquid-phase processes:

- selective hydration of *iso*-butene in mixed C_4-fraction to *t*-butanol as an intermediate for MMA—cationic IER in acetic acid/water medium, Mitsubishi Rayon [6] commercialized by Mitsui Chemical for Mitsubishi;
- acrolein-hydration to 3-hydroxypropionaldehyde as an intermediate for 1,3-propanediol—polyamine-polycarboxylic acid-type IER, Degussa [7], hydrated alumina-containing zeolite, Hoechst Celanese [8] (not yet commercialized);
- cyclohexene-hydration to cyclohexanol as an intermediate for adipic acid—high silica zeolite, Asahi Chemical Industry [9];
- direct amination of *iso*-butene to *t*-butylamine, pentasil zeolite under supercritical conditions, BASF [10].

Application of zeolite to liquid-phase reaction in the presence of water is innovative, because zeolite has been understood to have very low activity by the hydration of acid site. Therefore, hydrophobic high silica version is applied in cyclohexene–water binary system.

3.2. Dehydration reaction

In dehydration reactions too, new type of zeolite and mixed oxide-type catalysts have been commercially applied as they are typically shown as follows:

- methanol-amination with ammonia to dimethylamine in higher selectivity in vapor-phase (replacing silica–alumina)—alkali-modified mordenite, Nitto Chemical Industry [11], silicated zeolite, Mitsui Chemical [12];
- monoethanolamine-dehydration to ethyleneimine in vapor-phase (replacing liquid-phase reaction catalyzed by H_2SO_4)—$BaO/Cs_2O/P_2O_5/SiO_2$ (acid/base bifunctional), Nippon Shokubai [13];
- MTBE-decomposition to *iso*-butene/methanol (separation of *iso*-butene in mixed C_4-fraction via MTBE) in vapor-phase—$Al_2(SO_4)_3$-modified SiO_2, Sumitomo Chemical [14], boron pentasil zeolite (SNAM Progetti), etc. [2].

All of the above examples are vapor-phase processes, and better position-selectivity of zeolite compared with silica–alumina is utilized.

3.3. Esterification/etheration reaction

In the liquid-phase esterification, cationic IER has been widely used, while sulfuric acid-catalyzed processes are also still on stream. IER-type is also used for etheration, too.

Some examples of recently developed processes are shown as follows:

- methacrylic acid esterification in vapor-phase—silica–titania, Mitsubishi Chemical [15], not commercialized owing to the commercialization of cationic IER-catalyzed process of Mitsubishi Rayon [16] and H_2SO_4-catalyzed process of Nippon Shokubai/Sumitomo Chemical [17];
- vapor-phase ethylene-esterification to ethyl acetate—Cs-modified PW_{12}-type HPA, Showa Denko [18] and SiW_{12}-type HPA/SiO_2, BP Chemicals [19];
- MTBE synthesis by the reaction of *iso*-butene in mixed C_4-fraction with methanol as the first step of *iso*-butene separation via MTBE—cationic IER, Sumitomo Chemical [20].

The use of solid HPA in vapor-phase acid-catalyzed reaction for ethyl acetate production may be the first case of utilizing acid function of HPA in vapor-phase reaction, because usually redox function of it is utilized for vapor-phase oxidation reactions represented by methacrolein-oxidation to methacrylic acid in two-step air-oxidation method for manufacturing MMA from *iso*-butene or *t*-butanol.

3.4. Oligomerization reaction

Solid acid catalysts have been known to have activity for hydrocarbon-oligomerization, but $AlCl_3$-type and BF_3-type have been predominantly applied for the production of petroleum resin and poly(alpha-olefin) (PAO), while FSO_3H or its combination with acetic anhydride as a molecular weight regulator is used for oligomerization of THF to PTMEG.

Recently solid acid-catalyzed PTMEG manufacturing processes are becoming commercialized, and it is calling strong attention. They are shown as follows:

- liquid-phase THF-oligomerization to PTMEG—zirconia–silica in the presence of Ac_2O, Mitsubishi Chemical [21] WO_3-ZrO_2 or MoO_3-ZrO_2, TCC Chemical (Taiwan) (probably developed by Union Chemical Laboratories, Hsinchu) [22].

Similar solid acid-catalyzed method are believed to be developed by DuPont and BASF, although DuPont proposed a process to use Nafion-type perfluorosulfonic acid-type IER having superacid-type acid strength [23].

For alpha-olefin oligomerization, Lion in Japan applied solid catalyst prepared by the reaction of $AlCl_3$ with ketone in the presence of olefin [24], but it had not been commercialized. Besides it, Nafion-type and modified ZSM-12, etc. have been developed unsatisfactorily by the unsatisfactory yield of trimer + tetramer in oligomerization of octane–dodecene.

3.5. Condensation reaction

In the field of condensation reactions, following new applications are seen:

- liquid-phase aldehyde/ketone condensation to substituted pyridines—pentasil zeolite, Koei Chemical [25], Nepera [2];
- liquid-phase condensation of ethylene oxide with ammonia to monoethanolamine (replacing aqueous ammonia and cationic IER)—rare earth metal-modified saponite, Nippon Shokubai [26], Al–Si zeolite T, Berol/Nobel [2].

3.6. Isomerization reaction

For double bond-isomerization and skeletal-isomerization of olefins, various mixed oxide-type solid acid catalysts having different acid strength have been commercially applied, since many years ago, by selecting catalyst having most desirable acid strength, which is different for individual type of reaction. For skeletal-isomerization of paraffins for improving octane-value and isomerization of xylene applied for manufacturing *p*-xylene too, solid acid catalysts having high acid strength are successfully commercially applied.

In the production process of 2,6-naphthalene dicarboxylic acid (NDA) or 2,6-dimethyl naphthalate (NDC) as an intermediate for poly(ethylene 2,6-naphthalate) (PEN), zeolite-type catalysts are believed to be applied by Amoco Chemical (now BP Chemicals) under license of the process developed by Teijin, as they are shown as follows:

- (*o*-xylene/butadiene to 5-*o*-tolylpentene-2) to 1,5-dimethyl-tetralin (1,5-DMT) in liquid-phase—thermally-stabilized Y-zeolite [27];

- 1,5-DMT to 1,5-dimethylnaphthalene (1,5-DMN)—vapor-phase or liquid-phase dehydrogenation using conventional dehydrogenation catalyst;
- 1,5-DMN to 2,6-DMN (liquid-phase isomerization)—H-mordenite/alumina [28] or ultra-stabilized Y-zeolite [29].

For skeletal-isomerization of paraffins for improving octane-value, sulfated zirconia is believed to be developed in pilot plant stage by the cooperation of Cosmo Oil with Mitsubishi Heavy Industries [30].

In completely different field, Beckmann rearrangement of cyclohexanone–oxime to caprolactam (CPL) is catalyzed by oleum, and it brings indispensably by-production of large amount of low value ammonium sulfate by requiring ammonia necessary for neutralizing oleum after the reaction. In order to solve the problem, solid-catalyzed method had been developed in pilot plant stage by Bayer and Mitsubishi Chemical, independendtly [31]. For this purpose boric acid or titania–boria treated with alkali for reducing strong acid site had been applied predominantly in vapor-phase reaction.

Recently, Sumitomo Chemical has released a project to commercially apply vapor-phase rearrangement process having following characteristics:

- cyclohexanone–oxime to CPL in vapor-phase (probably in fluidized bed method by using methanol as a carrier gas and by circulating catalyst between reactor and regeneration reactor for treating deactivated catalyst with high temperature air)—indium-loaded pentasil zeolite, Sumitomo Chemical [32].

3.7. Other reactions

In alkylation reactions of aliphatic and aromatic hydrocarbons already zeolite-type catalysts having appropriate micropore size and controlled acid strength/acidity have been commercially applied by replacing $AlCl_3$-type, BF_3-type, etc. High silica zeolite, Y-zeolite, mordenite, etc. are also being applied.

In *p*-position-selective chlorination and selective isomeriztion of chlorinated aromatic hydrocarbons, too, zeolite-type catalysts are becoming applied in the syntheses of agrochemical intermediates. They are KL-zeolite, L-zeolite, Y-zeolite, etc. [33].

4. Base-catalyzed process

Compared with acid-catalyzed liquid-phase and vapor-phase processes, the number of base-catalyzed processes is rather limited, and most of them are liquid-phase homogeneous systems using dissolved NaOH/KOH or alkali alcoholate. The process based on anionic IER is regarded to be quite rare.

In methanolysis reaction of poly(vinyl acetate) to PVOH methanol-solution of NaOH is usually used, and $Ca(OH)_2$ is proposed for methanolysis of PTMEG-diacetate to PTMEG by producing methyl acetate as a by-product [34].

In heterogeneous systems, preparation of 2,6-dimethylphenol by dialkylation of phenol with two molecules of methanol over MgO-type catalyst such as $MgCO_3/MnO_2$ proposed by General Electric [35] may be a representative of rare case, and the high position-selectivity is considered to be utilized.

In the processes catalyzed by anionic IER following processes are proposed:

- acrylate/HCHO-condensation to alpha-hydroxymethylacrylate in liquid-phase—anionic IER, Nippon Shokubai [36];
- methanol-carbonylation with CO to methyl formate in liquid-phase for replacing alkali alkoxide—strong anionic IER, Mitsubishi Gas Chemical [37].

As a special case, Mitsubishi Chemical has commercialized a process for hydrogenating aromatic carboxylic acids in vapor-phase to corresponding aromatic aldehyde over Cr-modified zirconia, which is regarded to be acid/base bifunctional catalyst [38].

In recent years, interest in solid superbase catalysts are being strengthened outstandingly. The reasons for that can be summarized as follows:

- very high selectivity some times enabling deleting of special purification of the target product;
- significantly suppressed formation of by-produced tar and/or carbonaceous materials causing catalyst deactivation over the catalyst surface;
- applicability to side chain alkylation of alkylaromatics without promoting ring-alkylation.

These characteristics are utilized effectively in following recently commercialized base-catalyzed processes:

- double bond-isomerization of 2,3-dimethylbutene-1 to 2,3-dimetylbutene-2 in the synthesis of pyrethroid intermediate—Na/NaOH/alumina, Sumitomo Chemical [39];
- isomerization of 5-vinylbicyclo[2,2,6]hept-2-ene to 5-ethylidenebicyclo[2,2,1]hept-2-ene as a EPDM-third monomer working as curing site—Na/NaOH/alumina, Sumitomo Chemical [39];
- side chain alkenylation of *o*-xylene with butadiene to 5-*o*-tolylpentene-2 as the first step for deriving NDA via 1,5-DMT, 1,5-DMN and 2,6-DMN, Na/K_2CO_3, Teijin [40], and K/alumina or K/K_2CO_3 Amoco Chemical [41].

5. Conclusions

By summarizing above-mentioned examples, the characteristics of recently developed important new catalyst systems and their remaining R&D subjects are summarized.

5.1. Zeolite-type catalyst

- Already widely used application in vapor-phase and liquid-phase reactions by emphasizing high position-, regio-, or shape-selectivity mainly in hydrocarbon conversion reactions.
- Successful application to shape-selective reactions for vapor-phase amination of methanol and liquid-phase position-selective chlorination of substituted aromatics.
- Successful application to liquid-phase hydration, where water is participated, in cyclohexene-hydration, by applying high silica zeolite.
- Successful application to liquid-phase condensation reactions and position-selective substitution reactions of substituted aromatics.
- New application to vapor-phase Beckmann rearrangement by high silica zeolite.
- Wide possibility of changing activity and selectivity by selecting micropore size and acid strength/acidity by cation-exchange.
- Remaining subjects in essential suppression of rapid deactivation caused by deposition of tar and/or carbonaceous by-products over acidic catalyst surface by modification of acid-site or addition of modifier in feed.

5.2. HPA-type catalyst

- Effective application to liquid-phase hydration and THF-oligomerization in dissolved homogeneous-form in aqueous medium.
- New application to non-oxidative vapor-phase reaction such as ethyl acetate synthesis.
- Remaining subjects in development of liquid-phase heterogeneous system for the reactions, where water and/or alcohol is participated as one of the reactants or products by taking into consideration of application of Cs-modified HPA confirmed in laboratory scale [42].

5.3. Zirconia-type catalyst

- New application of zirconia–silica, and WO_3-ZrO_2 or MoO_3-ZrO_2 to THF-oligomerization to PTMEG.
- Application to vapor-phase selective hydrogenation of carboxylic acid to corresponding aldehyde by Cr-modified zirconia.
- Possibility of sulfate-loading zirconia with high acid strength (close to superacid), when elimination of remaining sulfate group can be significantly suppressed during long-term operation.

5.4. Superbase-type catalyst

- Effective application to side chain alkylation for alkyl-aromatics, and high selectivity for double bond-isomerization of olefinic compounds without causing tar-formation.
- Possibility of application in place of solid acid catalysts having problem of catalyst deactivation by tar-formation over the catalyst surface.

5.5. IER-type catalyst

- Already widely used in liquid-phase reactions, where water and/or alcohol is participated as the reactant or product.
- Remaining development subjects in elevation of applicable temperature range to a level of 160–170 °C for improving reaction rate, and improvement of acid strength by introducing electron-attracting group in the matrix for widening applicable type of reactions, and suppression of swelling in organic reaction medium (suggested application of

perfluorosulfonic acid-type resins represented by Nafion-type).

The author would like to encourage the challenge of young researchers not only in universities, but also in industry to bring break-through for overcoming above-mentioned various barriers.

Because of the current activities of the author, he has overviewed recent developments appeared after 1990, which have been regarded to be important from the standpoint of industrial chemical process engineer based on his own experiences and knowledge.

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