Status of Research on Petrochemicals*

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A start of petrochemical industries in Japan dates back in 1957, and the petrochemical industry has made a remarkable progress during the past ten years. Total ethylene producing capacity at present is 1,203,800 *t/y* and is expected to reach 1,900,000 million tons in 1969. During the past decade, extensive and intensive researches on petrochemical processes and products have been carried out. Outline of the researches in this field developed since 1963 will be described in this paper.

Production of Acetylene, Olefins and Dienes

Starting material used for the petrochemical industries in Japan is mainly petroleum naphtha. A prospective amount of naphtha consumption in 1966 is expected to exceed the line of eight million *kl*, and problems such as improvement for ethylene yield, importation of naphtha, installation of a simplified topping apparatus, appropriation of LPG, light oil or crude oil for starting materials, are being considered.

Tsutsumi studied the production of acetylene from light petroleum naphtha by partial oxidation process with oxygen under reduced pressure¹⁾. The joint-research by 23 leading Japanese companies including Chiyoda Chemical Engineering and Construction Co., Ltd. was made on the development for various modes of a flame cracking, aiming at the simultaneous production of acetylene and ethylene from petroleum naphthas²⁾. Kunugi et al.³⁾ reported a basic research on the method of obtaining acetylene and ethylene, or ethylene only, in a good yield by thermal decomposition of gaseous or liquid hydrocarbons by using hydrogen as a diluent. Tokuhisa et al.⁴⁾ reported that they observed the favorable formation of butadiene

at lower temperature region when thermally decomposing hydrocarbons with an adiabatic compressing apparatus. Reports were published regarding basic investigations on the production of acetylene, olefins, synthetic gases and town gas from natural gas⁵⁾, ethane⁶⁾, propane⁷⁾ and petroleum hydrocarbons⁸⁾.

Kunii derived theoretical equations evaluating hydrocarbon cracking furnaces and ensured his proposed equations by analyzing actual data with respect to their cracking and gasification modes⁹⁾.

Yasumori et al.¹⁰⁾ studied the selectivity of a Pd-catalyst in the course of catalytic hydrogenation of acetylene.

Takahashi et al.¹¹⁾ studied the dimerization reaction of ethylene by a NiO-SiO₂-Al₂O₃ catalyst and obtained butene-1 in 80% yield. For the production of butadiene, studies on the dehydrogenation¹²⁾ and isomerization¹³⁾ catalysts for *n*-butane and butenes have been carried out. Japanese Zeon Co.¹⁴⁾ developed a new extracting process, GPB Process, for butadiene, that enables to extract butadiene at low cost by extracting distillation with DMF solvent. Kiryu et al.¹⁵⁾ proposed a method of utilizing butane, butene and isobutylene effectively and collectively by chlorination of a B-B fraction which is free from butadiene.

As for the production of isoprene, several papers relating to the catalysts were published on the reaction of isobutylene with formaldehyde¹⁶⁾, production of methylpentenes by the dimerization of propylene followed by isomerization and thermal cracking for elimination of methane¹⁷⁾, and codimerization of ethylene with propylene¹⁸⁾. Hara et al.¹⁶⁾ succeeded in preparing isoprene at almost 100% selectivity by the reaction of isobutylene with an aqueous formaldehyde solution.

Regarding the synthesis of higher diolefins and diene-oligomers, selectivity of the cata-

* Received October 27, 1966.

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lysts was investigated widely and many patents were published in this respect¹⁹⁾.

Production of Aromatic Hydrocarbons

Amemiya et al.²⁰⁾ reported the separation of durenene by crystallization from various petroleum fractions. Tokuhisa and coworkers²¹⁾ reported that aromatic hydrocarbons of high purity were obtained by dehydrocyclization-hydrogenolysis of various hydrocarbons and petroleum fractions. Suzumura et al.²²⁾ studied the properties of chromia-alumina catalysts used for the preparation of aromatic hydrocarbons from petroleum hydrocarbons. Morii et al.²³⁾ studied the hydrogenolytic dealkylation of various alkyl aromatic hydrocarbons, and reported that they obtained, by using a copper-lined reactor, the selectivity for dealkylation in more than 90% without forming coke substances. Tokuhisa et al.²⁴⁾ made studies on the mechanisms of the thermal hydrogenolytic demethylation of toluene in the presence of hydrogen. Mitsubishi Petrochemical Co., Ltd.²⁵⁾ is operating a pilot plant for the production of benzene from thermally cracked residue of naphtha by thermal hydrogenolytic dealkylation process, and is ready for commercialization. Morikawa and others²⁶⁾ studied the reaction kinetics for dealkylation. Ozaki and coworkers²⁷⁾ studied the disproportionation of alkylbenzenes by silica-alumina catalysts, and Shiba et al.²⁸⁾ reported that an alumina-boria catalyst was better than the former in regard to the velocity and the selectivity.

With respect to the separation by crystallization of *p*-xylene from mixed xylenes, Amemiya et al.²⁹⁾ reported a basic study. Tokuhisa et al.²⁹⁾ reported that the industrial scale of separation for *p*-xylene is feasible by transalkylation.

Tokuhisa et al.³⁰⁾ suggested a commercial possibility of producing ethylbenzene by a destructive alkylation of benzene with *n*-hexane. They also reported that easily separable ethylbenzene, propylbenzene and trimethylbenzene were obtained simultaneously in good yield by the transalkylation of a C_6 -mixed aromatic fraction from reformed heavy naphtha with benzene in the

presence of an aluminum chloride catalyst at 80°C under atmospheric pressure³⁰⁾. Similarly, toluene, ethylbenzene, mixed xylenes, propylbenzene and naphthalene can be manufactured from a C_{10} - C_{12} aromatic fraction at low cost. Furthermore, they³¹⁾ reported that styrene was obtained at 90% selectivity by a high-temperature gas-phase reaction of ethylbenzene with chlorine. In regard to the alkylation, studies were made on the sulfuric acid catalyst³²⁾, binary catalysts of organo-aluminum compound with vanadium halide or oxyhalide³³⁾, combined catalysts of BF_3 -series³⁴⁾, and aluminum sulfate-silica gel catalysts³⁵⁾ and so forth.

Asahara et al.³⁶⁾ studied the synthesis of straight-chain alkylbenzenes by the telomerization of toluene with ethylene.

Oxidation of Petroleum Hydrocarbons

A joint-investigation of Government Chemical Industrial Research Institute (Tokyo) with Tekkosha Co., Ltd. is now in process regarding a method of preparing acetic acid by liquid phase oxidation of naphthenic petroleum naphtha³⁷⁾. In this process, 3-30 parts formic acid, 50-70 parts acetic acid, 5-15 parts propionic acid, 2-6 parts lactic acid, 2-5 parts succinic acid, and 10-30 parts acetone and other mixed solvent were obtained from 100 parts of naphtha in the presence of manganese naphthenate at 140-180°C and under 30-50 atm. pressure.

Production of ethylene oxide by oxidizing ethylene in the presence of silver catalyst is widely commercialized, but a number of other researches are still carried out with respect to a reaction mechanism, rationalization of the process, increase of yield by the improvement for the catalyst and reaction conditions³⁸⁾. Both liquid-phase oxidation³⁹⁾ and gas-phase oxidation⁴⁰⁾ have been investigated on the point of producing acetaldehyde from ethylene.

Regarding the production of propylene oxide by direct oxidation of propylene, selection of a catalyst, diluent, additive, reaction mechanisms and conditions are widely investigated for both gas- and liquid-phase oxidations but no remarkable result was hitherto obtained⁴¹⁾. Production of acrolein or meta-

crolein from propylene or isobutylene has been widely investigated in the fields of the exploration of catalysts, reaction conditions, concentrating method for acrolein, etc. Asahi Chemical Industries Co., Ltd. succeeded in developing a new manufacturing process of highly concentrated acrolein by use of a copper-selenite catalyst⁴². Ishikawa et al.⁴³ found that Fe-As catalyst exhibits a good activity and they are conducting an extensive research on the preparation of catalyst and reaction mechanisms. Nagai et al.⁴⁴ synthesized metacrolein in 85–90% yield by the reaction of propionaldehyde with formaldehyde in the presence of an acidic catalyst.

A number of researches have been carried out regarding improvement of the catalyst and a method of prohibiting unfavorable polymerization in the process of preparing acrylic acid or metacrylic acid from acrolein or metacrolein, respectively⁴⁵. Japan Catalytic Chemical Industry Co., Ltd.⁴⁶ found that a Mo-Co-Te-Sn catalyst was effective in case of producing acrylic acid in good yield by a direct one-step oxidation of propylene. It is reported that they are working for the commercialization test.

Shiba et al.⁴⁷ studied the reaction of producing acetone by Wacker process from the view-point of kinetics. Kato et al.⁴⁸ found that a cobalt salt-phosphoric acid catalyst was especially suitable for the preparation of acetone by liquid phase oxidation of isopropyl alcohol.

Regarding the oxidation of aromatic hydrocarbons, many researches have been made on the exploration of the catalyst and reaction mechanisms. Several papers⁴⁹ were published with respect to the direct oxidation of benzene to phenol, leaving many points to be investigated in the future. Many papers were published in regard to the synthesis of maleic anhydride⁵⁰ from benzene, of benzoic acid and phthalic acids⁵¹ by oxidation for side-chain of aromatics.

Ohta et al.⁵² investigated a new catalyst which enables to produce terephthalic acid by liquid-phase oxidation of *p*-xylene and detailed on Co-Br catalysts. Takegami et al.⁵³ studied the effects of catalyst containing bromine by the liquid phase air oxida-

tion of *p*-xylene or *p*-toluic acid in the presence or absence of acidic solvents. Fukui et al.⁵⁴ studied the liquid phase oxidation by onium salt type catalysts. Yamashita et al.⁵⁵ investigated accelerating effects by ketones on the oxidation, and Takaya et al.⁵⁶ reported that terephthalic acid can be easily obtained by a single stage oxidation of *p*-xylene with ozonized oxygen or air at 90°C in the presence of similar catalyst to SD process. Shigeyasu et al.⁵⁷ succeeded in separating and subsequently elucidating the structure of the impurities contained in the terephthalic acid produced by the liquid phase air oxidation of *p*-xylene. Many researches are now being carried out in regard to the synthetic method of terephthalic acid by using a similar method to Henkel process^{58,59}.

Furthermore, there are many papers published in regard to the production of polybasic acid by catalytic air-oxidation of polyalkyl benzenes. Ohta et al.⁶⁰ found that a V-P-O catalyst was good for the production of pyromellitic dianhydride by gas phase oxidation of durene or tetraalkyl benzenes.

Moreover, alkaline liquid-phase oxidation of alkyl naphthalenes^{61,62} and gas phase oxidation of naphthalene^{51,63} were reported.

Asaka et al.⁶⁴ succeeded in obtaining glutaric acid in 80–95% yield by oxidation of cyclopentane with NO₂ in a liquid phase. In regard to the synthesis of cyclohexanone and cyclohexanol by liquid phase oxidation of cyclohexane, papers are published with respect to the controlling of formation ratio between nol and none, and to the improvement for conversion and yields⁶⁵. Regarding a catalyst which enables to convert cyclohexanol to cyclohexanone by gas-phase dehydrogenation other papers are also reported⁶⁶. Ohta et al.⁶⁷ reported that adipic acid can be obtained selectively under suitable conditions by one-step oxidation of cyclohexane without using solvent.

Ammoxidation

Morikawa et al.⁶⁸ studied the fluid catalytic synthesis of acetonitrile from acetylene reacting with ammonia. Ozaki et al.⁶⁹ studied the catalysts for the synthesis of acetonitrile

from ethylene or propylene with ammonia, and hydrogen cyanide from acetonitrile with ammonia. In regard to the synthesis of acrylonitrile by ammoxidation, improvement for selective oxidizing ability of the catalyst or a method of recovering nitriles from the product are reported in various patents. Kitahara et al.⁷⁰⁾ investigated the one-step and two-step synthesis of metacrylonitrile from isobutylene and metacrolein by ammoxidation with respect to the catalysts and reaction conditions.

Ishii et al.⁷¹⁾ reported that isobutylnitrile was obtained quantitatively by treating isobutylaldehyde with ammonia in the presence of alkaline Al_2O_3 type catalysts.

Ammoxidation of aromatic hydrocarbons such as toluene and xylene was investigated with respect to the catalysts, reaction mechanisms and reaction conditions, and a new process for production of phthalonitriles or terephthalic acid in good yield from xylenes is now considered⁷²⁾. Saito et al.⁷³⁾ explained that the reaction mechanism of ammoxidation on the V_2O_5 catalysts should follow as that stable nitriles can be formed by the reaction of ammonia with aldehydes or acids. Tarama et al.⁷⁴⁾ studied a reaction of forming benzonitriles by gas-phase oxidation of alkylbenzenes with $SO_2 + NH_3$ on the active alumina catalysts, and proposed a hypothesis of hydrogen-elimination reaction by $\cdot Sx$ radicals.

Oxychlorination

Kureha Chemical Industry Co., Ltd.⁷⁵⁾ developed an adroit process to manufacture vinyl chloride by treating a diluted mixed gas of acetylene and ethylene obtained by flame cracking of light naphtha with hydrochloric acid, and unchanged ethylene is then treated with chlorine, giving ethylene chloride, and finally turned to vinyl chloride by thermal decomposition. Regarding the oxychlorination method, studies are carried out on the improvement of the catalysts and the reaction mechanisms⁷⁶⁾. Toyo Koatsu Industries, Inc. developed a two-step process, a combined direct chlorination method with an oxychlorination method. Imai and Ohta⁷⁷⁾ succeeded in obtaining perchloroethylene in

good yield from tetrachloroethane with oxygen.

Oxyacetylation

Miyazawa⁷⁸⁾ reported that a $3ZnO-Cr_2O_3$ -active carbon catalyst was found to be effective for producing vinyl acetate from acetylene in the gas phase. Regarding the direct synthesis of vinyl acetate from ethylene in the liquid phase, studies on reaction mechanisms, conditions and catalysts have been carried out⁷⁹⁾. Tsutsumi et al.⁸⁰⁾ succeeded in the direct synthesis of vinyl acetate by treating ethylene with acetic acid at $80^\circ C$ and 30 atm. pressure in the presence of oxygen by using metal palladium instead of palladium chloride as a catalyst. They also succeeded in obtaining ethylene diacetate from EDC in an acetic acid anhydride and then obtained vinyl acetate in 81% yield by thermal decomposition of ethylene diacetate.

Telomerization

Asahara and others studied the telomerization reaction of ethylene with carbontetrachloride⁸¹⁾ or alcohol and others⁸²⁾ as chain transfer agents. Hara et al.⁸²⁾ obtained tert-amyl alcohol in about 95% selectivity by the telomerization of iso-propyl alcohol and ethylene at $130-140^\circ C$.

Synthesis with Carbon Monoxide

Regarding the methanol-synthesis from hydrogen and carbon monoxide or carbon dioxide, the relation between activity of the catalyst and its structure has been investigated on the catalysts as $ZnO-Cr_2O_3$ or $Cu-Zn$ system⁸³⁾. Uchida et al.⁸⁴⁾ studied the effects of titanium oxide and chromium oxide on the molybdenum oxide catalyst in the production of formaldehyde from methanol. Ohtsuka et al.⁸⁵⁾ compared the activities of various types of catalysts in the formaldehyde-synthesis by catalytic oxidation of methane and found the oxides of nitrogen excellent. Nakai et al.⁸⁶⁾ and Takegami et al.⁸⁷⁾ reported the effects of various additives in the Fischer-Tropsch reaction.

Concerning Oxo-reactions, many studies were made on the catalysts, reaction modes, product composition, separation and recover-

ing methods⁸⁸). Uchida et al.⁸⁹ found that addition of magnesium methylate or pyridine enabled to increase remarkably the dimer amount of butylaldehyde in the hydroformylation reaction of propylene by using cobalt carbonyl, and that preceding addition of iron carbonyl facilitated the reduction of formed aldehyde to the alcohol.

Regarding one-step synthesis of acetic acid from methanol and carbon monoxide, a precise investigation was carried out at Government Chemical Industrial Research Institute, Tokyo, which showed that the presence of cobalt-complex facilitated the reaction⁸⁹.

Takezaki et al.⁹⁰ studied the reaction among propylene, carbon monoxide and water, and found that the 97% reactant was converted to iso-lactic acid in the presence of HF-H₂O (water content 20%) catalyst under high pressure. They also found that *p*-tolualdehyde was obtained in 90% yield by the reaction of toluene and carbon monoxide by using BF₃-HF in the homogeneous liquid phase operation. Uchida et al.⁹¹ studied the hydroesterification of propylene with carbon monoxide and methanol and succeeded in increasing the reaction rate of hydroesterification to such a high level as to be comparable with that of hydroformylation.

Tsuji et al.⁹² studied the stoichiometric reaction of carbon monoxide against the π -complex between unsaturated hydrocarbons and transition metals, and found that a straight-chain acid could be formed by carbon monoxide selectively attacking to an end group in the case of α -olefins.

Others

Amagasa et al.⁹³ found a method of producing cyclohexenes and cyclohexadienes at low cost by partially reducing benzene, toluene and xylenes with metal sodium in liquid ammonia.

Imai et al.⁹⁴ had been exploring a suitable catalyst for the direct synthesis of ethanol from ethylene and water, and found that an ordinary catalyst, silicotungstic acid on silica gel, added with inorganic acid salts showed an excellent activity. Uchida et al.⁹⁵ elu-

cated structural factors contributing to the activity for ethylene hydration of supported silicotungstic acid catalysts. Eto⁹⁶ reported the mechanism on a directly synthetic reaction of butanol from ethanol in the gas-phase.

Toyo Rayon Co., Ltd.⁹⁷ investigated a reaction of synthesizing cyclohexanoneoxim by photochemical reaction of cyclohexane with nitrocy chloride from the view-point of chemical engineering and succeeded in developing a unique process. Kimura et al.⁹⁸ attempted to synthesize ϵ -caprolactam directly from cyclohexanone and primary nitro-paraffin, the latter being used as a source of hydroxylamine.

Furthermore, many other researches are now being conducted concerning the synthesis and properties of high molecular substances such as plastics, elastomers and others, but these are excluded in this paper.

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