



CHAPTER II

LITERATURE REVIEWS

2.1 Aromatic Hydrocarbon

It is well known that aromatic hydrocarbons are important industrial chemicals which find a wide variety of uses in petrochemical industry. The key industrial products of aromatics are benzene, toluene, *o*-, *m*-, and *p*-isomers of xylene (BTX) which are useful feedstocks for producing various organic compounds and polymers. The demand for aromatics mainly benzene, toluene and xylenes remains strong (Table 2.1), and in this case, reforming and aromatization are widely used to meet the demand.

Table 2.1 Global demand of benzene toluene and xylenes

(www.meti.go.jp/english/information/downloadfiles/c0517PetroProe.pdf)

Global demand	Benzene	Toluene	Xylenes
Demand (million tons)			
2003	35.9	16.4	24.6
2009	45.9	21.3	34.7
Increase (million tons)			
2002-2009	10.1	4.9	10.1
Growth rate (%)	4.2	4.5	5.9

Although it is possible in principle to synthesize aromatics from simple aliphatic units, *e.g.*, benzene from acetylene or xylenes from diisobutene, so far these types of processes have not been used commercially. Aromatics are obtained almost exclusively from the fossil fuels, *e.g.*, coal, and oil. However, it is not economically feasible to isolate the limited quantities of aromatics present in unprocessed coal or oil. Suitable feedstocks for economical production of aromatics result from thermal or catalytic conversion processes in coke plants and refineries.

There are three primary sources for aromatics:

1. Catalytic reformat
2. Pyrolysis gasoline
3. Coal tar

In the process of refining oil, fractions rich in aromatics are obtained from refining (reforming) of gasoline and from cracking processes in olefin manufacture. These reformat gasoline and pyrolysis or cracked gasoline represents valuable sources of aromatics especially for BTX. The production of aromatics from these sources involves two types of processes: those which separate contained benzene, toluene and xylenes (BTX) and those which convert one form to another. One example of the latter, hydrodealkylation of toluene, is used to adjust the relative proportions of benzene and toluene as demand and economics dictate. In general, pyrolysis gasoline tends to be richer in total BTX than reformat.

2.2 Steam Cracking

Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into unsaturated hydrocarbons. It is the principal industrial method for producing the alkenes (or commonly olefins), including ethene (or ethylene) and propene (or propylene). In steam cracking, a gaseous or liquid hydrocarbon feed like Naphtha, LPG or Ethane is diluted with steam and then briefly heated in a furnace (obviously without the presence of oxygen). Typically, the reaction temperature is very high-around 850°C-but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is even reduced to milliseconds (resulting in gas velocities reaching speeds beyond the speed of sound) in order to

improve the yield of desired products. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger. The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time. Light hydrocarbon feeds (such as ethane, LPGs or light naphthas) give product streams rich in the lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in aromatic hydrocarbons and hydrocarbons suitable for inclusion in gasoline or fuel oil. The higher cracking temperature (also referred to as severity) favours the production of ethene and benzene, whereas lower severity produces relatively higher amounts of propene, C4-hydrocarbons and liquid products. The process also results in the slow deposition of coke, a form of carbon, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimize this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-cokings. Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

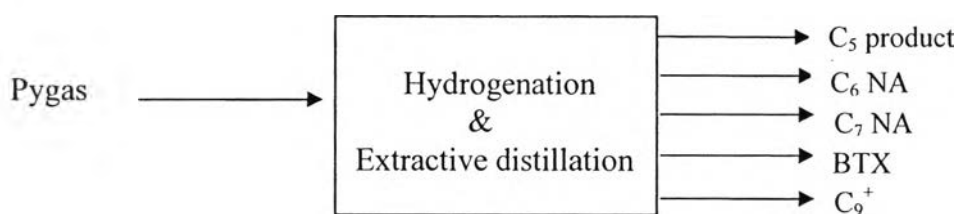
2.2.1 Steam Cracking By-product

Naphtha is often used to produce high-valued petrochemical ethylene and propylene by steam cracking. The main byproduct of this process is an intermediate boiling-point fraction known as pyrolysis gasoline or pygas which contains high BTX content. The amount and composition of pygas depend on the feedstock and operating condition of naphtha steamcracking. Typical weight composition of pygas is shown in Table 2.2.

Table 2.2 Typical weight composition of PYGAS (Medeiros *et al.*, 2007)

Composition	Amount (wt. %)
Paraffins + Naphthenics	12%
Olefins/Diolefins	6%,8%
Benzene/Toluene/Xylenes	28%,14%,7%
Styrene/ C ₉ ⁺ aromatics	3%,12%

Generally, pygas is composed of 70-80 wt.% aromatics and is subjected to solvent extraction to separate aromatics from the balanced non-aromatic hydrocarbons (Choi *et al.*, 2006). Such BTX-rich hydrocarbons need to be treated with further processing before BTX extraction, *e.g.*, hydrotreatment process, because the hydrocarbons contain large amounts of unsaturated or polyunsaturated species which can form gums (Table 2). The aromatic compounds obtained from pygas are separated as benzene, toluene, xylenes, and heavy C₉⁺ aromatics according to their boiling points (Figure 2.1).

**Figure 2.1** Pygas processing.

2.2.2 Pyrolysis Gasoline Upgrading

SK Corporation (2006) developed an advanced pyrolysis gasoline (pygas) upgrading (APUSM) technology based on a catalytic process for producing valuable benzene, toluene and xylenes (BTX) and liquefied petroleum gas (LPG) from pygas containing aromatics and non-aromatic hydrocarbons. Hydrodealkylation of heavy aromatics and hydrocracking of non-aromatic hydrocarbons occurred with facility in the conversion of pygas over a proprietary catalyst, metal promoted zeolite. This catalytic process produced benzene and toluene with high purity

corresponding to chemical grade while giving mixed xylenes with reduced ethylbenzene. The flow scheme of the APUSM process is presented in Figure 2.2 mono- and di-olefins contained in raw pygas need to be removed to prevent gumming of the gasoline. These compounds are selectively hydrogenated in a pygas hydrotreating (PGHT) unit. After passing through the PGHT unit, treated pygas (TPG) is combined with hydrogen and then is introduced into the APUSM catalytic reactor. Hydrogen is recycled through a recycle compressor (omitted in figure 2.2) and is mixed with high purity make-up hydrogen to maintain a desired molar ratio of hydrogen to hydrocarbon (ca. 3.0–6.0). Any down-flow fixed bed reactors in the refinery, e.g., idle fixed bed reforming reactor or hydrodealkylation vessel, can be utilized. Within the reactor, hydrocracking of non-aromatic hydrocarbons and hydrodealkylation of alkylaromatics in the presence of the catalyst. The reactor effluents are separated into gas and liquid products through a separator and stripper. The gas products separated in the top of the stripper consist mainly of fuel gas (C₂ and a very small amount of C₁ component) and LPG, which may be recovered as individual products such as ethane, propane and butane through conventional distillation units. The liquid products from the bottom of the stripper are further separated into benzene, toluene and xylenes by each distillation tower, respectively.

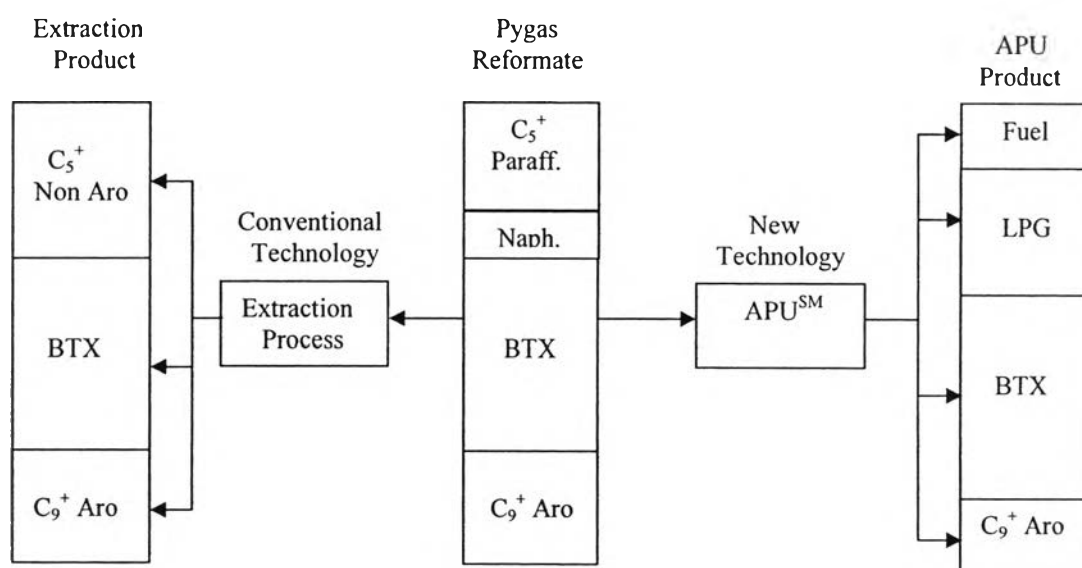


Figure 2.2 Concept of the APUSM technology. (Choi *et al.*, 2006)

2.2.3 C_9^+ Aromatics Upgrading

C_9^+ aromatic is also obtained from pygas that include n-propylbenzene, methylethylbenzene, trimethylbenzene, indane, tricyclodecane, etc. Particularly, a C_9^+ aromatics fraction in pygas possesses less industrial values, thus, it is usually being blended into gasoline pool to enhance its octane number or sold for solvent applications. However, in 2000 specifications for gasoline drastically limit its aromatics content from 50 to 35 vol. % resulting in increasing aromatics available for BTX production. Under circumstances, a demand for more BTX purification capacities is obvious, and therefore it is expected that direct BTX production by catalysis will have a substantial impact on the aromatics processes. It is, therefore, highly desirable to convert C_9^+ aromatics to the more useful BTX to prevent C_9^+ aromatics market saturation.

Many companies have developed technologies to add more value of C_9^+ aromatics by converting them to xylenes *e.g.*, UOP, ExxonMobil, Toray, and SK Corporation.

2.2.3.1 TAC9TM Technology

UOP has developed TAC9TM process, which involves several types of reactions of C_9 - C_{10} aromatics. Reactions include disproportionation, transalkylation, and de-alkylation used to selectively convert C_9 - C_{10} aromatics into mixed xylenes. The typical feedstock is a combination of C_9 and C_{10}^+ aromatics derived either from reformates or hydrotreated pyrolysis gasoline. The highly active TAC9 catalyst converts almost all ethyl, propyl, and butyl groups on aromatic rings to light ends by de-alkylation. The methyl groups react via disproportionation and transalkylation. By controlling the feed composition, a methyl balance for xylenes production is archived. The flow scheme of TAC9 process is shown in Figure 2.3.

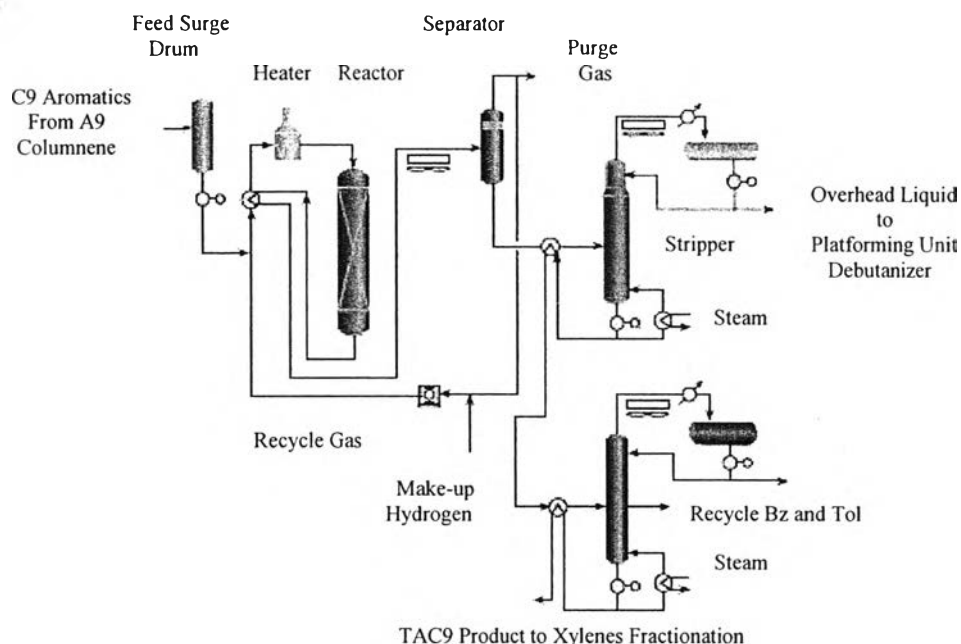


Figure 2.3 Flow scheme of TAC9 process. (www.uop.com/object/56%20TAC9.pdf)

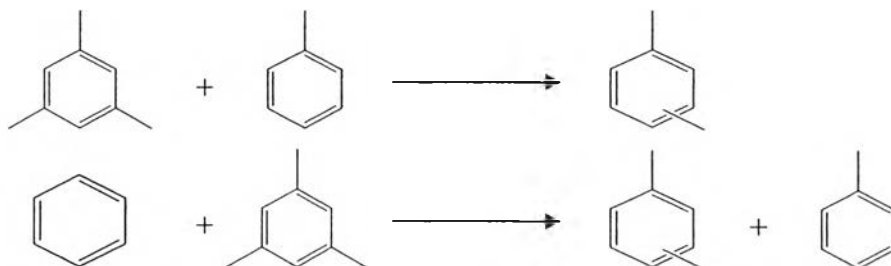
2.2.3.2 *TransPlusSM* Technology

TransPlusSM is ExxonMobil's new heavy aromatics transalkylation technology. This technology offers refiners a low cost solution for upgrading heavy aromatic streams. *TransPlus* can effectively process feeds ranging from 100% C_9^+ aromatics to mixtures of C_9^+ aromatics with either toluene or benzene depending on the product slate desired. The process utilizes an ExxonMobil proprietary zeolite based catalyst that has excellent yield performance while exhibiting a high tolerance towards heavy aromatic species which can potentially shorten catalyst life. The *TransPlus* operating condition is shown in Table 2.3.

Table 2.3 TransPlus operating conditions (Stachelczyk *et al.*, 2000)

Temperature (°F)	775-925
Pressure (psig)	200-400
Hydrogen/liquid feed (molar)	1.0-3.0
Weight hourly space velocity (h ⁻¹)	2.0-3.5
Toluene+ C ₉ +C ₁₀ conversion (wt %)	35-50

Mechanistically, the TransPlusSM process works by first dealkylating ethyl and higher alkyl groups leaving primarily methyl aromatics behind. The remaining feed components are then converted via disproportionation and transalkylation to produce a near-equilibrium product. Examples of major reactions are shown in Figure 2.4.

Transalkylation**Disproportionation****Dealkylation****Figure 2.4** TransPlus reactions. (Stachelczyk *et al.*, 2000)

The reactions that commonly see in developed technologies are transalkylation, disproportionation, and dealkylation. Conventional transalkylation and disproportionation reactions cannot be taken place without toluene as a raw material. In order to upgrade C_9^+ aromatics, hydrogenolysis is the candidate method to convert C_9^+ aromatics to xylenes without the addition of toluene.

2.3 Hydrogenolysis Reaction

Hydrogenolysis is the catalytic chemical reaction whereby the molecule of H_2 is added over C-C bond or C-hetero atom bond, effectively causing a lysis of a bond (Figure 2.5). The heteroatom may vary, but it usually is oxygen, nitrogen, or sulfur.

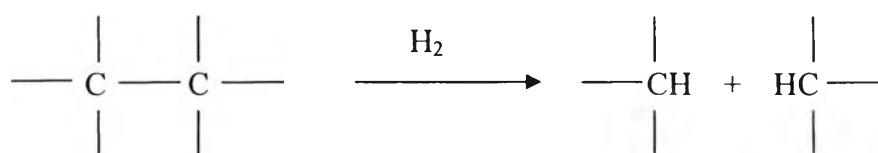


Figure 2.5 Hydrogenolysis reaction. (<http://goldbook.iupac.org/C00897.html>)

A classical example of hydrogenolysis is debenzylation while a commercial large-scale example of hydrogenolysis is the RaneyNickel catalyzed “desulfurization” of substituted thiophene rings, which is a general method for the synthesis of certain hydrocarbons. Unfortunately, relatively few studies have been performed on C-C bond scission of alkyl chain of alkylaromatic compounds, in contrast to the number of studies on the hydrogenolysis of alkenes. The hydrogenolysis of alkanes over supported metal catalysts maintains its interest both for the theoretical aspects and also because of its industrial applications. Simple alkane such as ethane, propane, n- and iso-butane can be used as archetype molecules for studying hydrogenolysis reactions.

The hydrogenolytic splitting of the side chain in alkyl aromatic compounds is catalyzed by a number of metals and oxides. In industry, chromium oxide on alumina seems to be used most frequently as a catalyst for this type of reaction. However, the literature reveals that catalysts containing molybdenum oxide are also sufficiently

active for this purpose. Around 1960, several authors studied the hydrodealkylation of toluene, xylenes, and methylnaphthalene on molybdenum oxide/alumina or cobalt oxide-molybdenum oxide/alumina catalysts.

Shephard *et al.* (1963) studied the reaction of *o*-ethyltoluene on 0.5% platinum- γ -alumina catalysts in the presence of excess hydrogen using a microreactor pulse technique. The product distribution shows that indane and indene which are the products from dehydrocyclization reaction were the major products and that the yield of the former was somewhat higher. Hydrocracking of C₉ reactants to C₆-C₈ alkylbenzenes was a relatively minor reaction and did not account for more than 25% of the transformed hydrocarbon. The preferential formation of toluene from *o*-ethyltoluene suggests that ethyl is more easily removed than a methyl group. They also found that dehydrocyclization and hydrogenolysis occur simultaneously.

Covini *et al.* (1965) investigated the effect of intrinsic acidities of alumina in molybdena-alumina catalysts upon the hydrogenolysis and isomerization of alkylbenzenes (*o*-, *m*-, and *p*-xylene, ethylbenzene, *n*-propyl- and isopropylbenzene, *n*-, *sec*-, and isobutylbenzene). It was found that in the presence of molybdena-alumina catalysts the extent of isomerization increases with the increase in intrinsic acidity of the aluminas. It was also found that molybdena-alumina catalyst is much more effective for isomerization than alumina. The hydrodealkylation of alkylbenzenes to benzene and to the corresponding alkanes depends on the nature of the alkyl groups and on the acidity of the molybdena-aluminas but the selectivity of the hydrogenolysis of α - β and β - γ bonds is not influenced by the acidity of the molybdena-alumina catalysts. They also found that the catalyst activity towards hydrogenolysis decreases sharply at the beginning of the experiment and more slowly later but the isomerization properties of the catalyst seem to be only little affected with time.

Tamio *et al.* (1982) invented an improvement in a process for producing industrially more valuable aromatic hydrocarbons such as benzene, toluene, and xylene by selectively dealkylating alkyl-substituted aromatic hydrocarbon especially ethyl group-containing benzene such as ethyltoluene, diethylbenzene, and

ethylxylene. ZSM-5 zeolite was used as a base of the hydrodealkylation catalyst. They found that ZSM-5 catalyst containing noble metals of Group VIII of the periodic table have superior selectivity of hydro-deethylation reaction, and give useful benzene and xylenes at high recovery ratios. The zeolite was not modified with a noble metal show that the alkyl group containing at least 2 carbon atoms can be hydrogenated and dealkylated, but at the same time, demethylation reaction tends to take place. However, a zeolite modified with a noble metal (Pt, Pd, and Rh), dealkylation reaction involving the elimination of the methyl group bonded to the aromatic ring is greatly inhibited and side-reactions scarcely take place while dealkylation reaction of the alkyl substituent having at least 2 carbon atoms proceeds selectively, and that activity of the catalyst does not appreciably decrease even when the catalyst is used continuously over a long period of time, and the active lifetime of the catalyst can be maintained long.

Duprez *et al.* (1985) studied steam and hydrogen conversions of a series of mono- and dialkylbenzenes at 713 K on variously supported platinum and nickel catalysts. Three main types of reaction were observed: dealkylation (C-C bond splitting in the side chains), dehydrogenation (into alkenylbenzene), and degradation (ring opening). It is found that in the presence of steam, the monalkylbenzene mainly dealkylated into benzene on Pt and Ni. Nevertheless, Pt is characterized by a very high relative activity in dehydrogenation and by the absence of ring opening. The inverse behavior is observed on Ni. In the presence of hydrogen, the product spectra are deeply modified. Ring opening is considerably inhibited, whereas the primary C-C bond ruptures shift toward the middle and the end of the chain.

Csicsery (1987) studied the reactions of 1-methyl-2-ethylbenzene on platinum by varying supports. Experiments were run at atmospheric pressure, 400°C, with a liquid hourly space velocity (LHSV) of 8 and with a hydrogen-to-feed molar ratio of 3. Silica, alumina, and silica-alumina were used as supports. He divided the reactions over supported platinum catalyst into the reactions that are catalyzed by the platinum (dehydrocyclization, ring opening, hydrogenolysis, and dehydrogenation) and catalyzed by acid (isomerization and transalkylation). He found that dehydrocyclization, ring opening, and hydrogenolysis over Pt-aluminas and Pt-silica increase with increasing Pt surface area and residence time. Both isomerization and

transalkylation increase with increasing support acidity. These two reactions are about 100-300 times faster over platinum on a strongly acidic silica-alumina support than over platinum on silica. He also found that under usual reaction conditions, catalyst deactivation is moderate.

Hoang-Van *et al.* (1987) studied hydrogenolysis of ethylbenzene at 280-400°C over a supported nickel catalyst derived from nickel hydroaluminate. The results show that the rate of the first demethylation of ethylbenzene (into toluene) is significantly larger than that of those second demethylation (into benzene) and of the reapture of the aromatic nucleus (into methane). Toluene is always the main reaction product but the selectivity into toluene decrease when the temperature increases, whereas the selectivity into benzene increases. They also found that when the contact time is increased at a given temperature, the selectivity into benzene should increase and that into toluene decrease because of the time allowed for the sequential hydrodemethylation. Finally, they concluded that the sequential hydrodealkylation of alkylbenzene over nickel are preferentially adsorbed perpendicularly to the metal surface by fixation of the terminal carbon of the alkyl chain.

Kumata *et al.* (1995) investigated the catalyst for hydrogenolytic dealkylation of alkyl aromatic hydrocarbons having 8 to 10 carbon atoms in order to produce benzene, toluene, and xylene. An alkyl-substituted aromatic hydrocarbon, particularly an aromatic hydrocarbon substituted with an alkyl group having 2 or more carbon atoms. This invention found that a catalyst prepared by supporting rhodium on a crystalline metallo-silicate carrier exhibits catalytic activity in lower temperature and has high reaction selectivity and prolonged duration. They also found that replacement of part of alumina and/or silica of crystalline aluminosilicate with iron or lanthanum metal provides a catalyst having particularly high selectivity to demethylation while markedly inhibiting decomposition or disproportionation. While crystalline aluminolanthanosilicate or crystalline aluminoferrosilicate is used, the reaction selectivity is further improved to increase the production ratio of more useful xylene.

Wu *et al.* (1998) invented a catalyst composition which can be used to convert a C_9^+ aromatic compound to a C_6 to C_8 aromatic hydrocarbon via hydrodealkylation process. The catalyst composition is a molybdenum- and zinc-

promoted alumina (Mo/Zn promoted alumina). The process for producing the composition which comprises: (1) contacting an alumina with a molybdenum compound and zinc compound in a liquid medium under a condition sufficient to incorporate the molybdenum compound and zinc compound into the alumina to form a modified alumina wherein the volume of the liquid medium is larger than the bulk volume of alumina; (2) removing the excess liquid medium; (3) drying the modified alumina; and (4) calcining the modified alumina to a Mo/Zn-promoted alumina under a condition sufficient to effect the conversion of the molybdenum compound and zinc compound to corresponding oxides. The liquid feed in this run was heavy C_9^+ aromatic compounds obtained in a gasoline aromatization process. The results shown that the invention catalyst had significantly higher yield of BTX and xylenes than control catalysts B (promoted with Mo and Zn, but made by conventional impregnation method) and control catalyst C (promoted with Mo and Zn, made by conventional impregnation method followed by steam treatment). The result also show that the invention had better selectivity to BTX than the control catalysts

Toppi *et al.* (2002) studied the influence of the metallic and acidic phases on *n*-Propylbenzene hydrodealkylation under reforming operating conditions (773K, 5 bars, and $H_2/HC = 5$). Silica-supported platinum (Pt/SiO₂ and PtSn/SiO₂) and aluminum (Al₂O₃ and 1 wt% Cl-Al₂O₃) were chosen to evaluate the influence of metallic and acidic phase, respectively. It was found that hydrodealkylation reaction occur to a significant extent over both functions through either hydrogenolysis reactions over the metallic catalyst or cracking reactions over the acidic catalyst. Over both Pt/SiO₂ and PtSn/SiO₂, two types of reaction sequences are proposed: (i) through adsorption on a single site for the formation of benzene, and (ii) through adsorption on two adjacent sites for the formation of toluene and ethylbenzene. On this type of site, benzene exhibits the lower selectivity on monometallic Pt/SiO₂ catalyst, whereas its selectivity is significantly increased on the promoted catalyst (PtSn/SiO₂). Over Al₂O₃ and 1 wt% Cl-Al₂O₃ (i) benzene is formed on strong Brønsted acid sites via a carbocation pathway, and (ii) toluene and ethylbenzene are formed via a radical pathway on strong and weak Lewis acid sites, respectively. On this type of site, the hydrodealkylation products are formed and benzene is the major product over the chlorinated alumina catalyst.