Thesis for the Degree of Master of Engineering

Synthesis of ortho-alkylated phenolic compound by position selective catalyst

by

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February 23, 2018

Synthesis of ortho-alkylated phenolic compound by position selective catalyst

(위치 선택성 촉매에 의한 ortho-알킬페놀류의 합성)

Advisor: Prof. Youngeup Jin

by
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위치 선택성 촉매에 의한 ortho-알킬페놀류의 합성

양관호

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요 약

본 연구는 페놀로부터 o-cresol 과 2,6-xyleneol 을 제조하는 ortho 위치의 선택성을 갖는 알킬레이션 촉매 및 공정을 개발하는 것으로 o-cresol 은 산화방지제나 반도체 봉지제인 EMC(에폭시 성형제품) 및 의,농약 중간체의 초기 원료로, 그리고 2,6-xylenol 은 폴리페닐렌 옥사이드의 모노머로 주로 사용되며 난연제나 차세대 산화방지제의 원료로도 사용된다. 이때 고순도의 제품이 요구되며 (o-cresol Min. 99.8%, 2,6-xylenol Min. 99.5%) 상기 사양의 고순도 제품은 천연 cresol 에서는 얻을 수 없기 때문에 합성법으로 얻고 있다. 반응물인 페놀이나 생성물인 알킬페놀은 고온에서 중합체를 쉽게 생성함으로 반응 중에 촉매가 급격히 비활성화 되어 장기간 연속 공정으로 운전하기 어려운 단점이 있다. 이와 같은 문제로 인하여 촉매 재생 공정을 포함해야 하며 초기 투자비용이 많고 운전이 까다로운 조건에서 제조 되고 있다. 따라서, 다양한 공정에 활용 가능하도록 촉매의 비활성화가 억제된 고활성, 장수명의 촉매를 개발하여 관련 산업의 국내 시장 상황 변화에 빠르게 대처할 수 있도록 독자 기술을 완성하고, 동시에 상업화 공정기술을 개발할 필요가 있다. MgO 를 주성분으로 한 염기성 촉매는 ortho 위치의 선택성이 뛰어난 반면 반응온도가 높고 (350~550℃), 산 특성이 강한 성분 촉매는 활성에 비해 위치 선택성이 떨어진다. 최근에는 Fe, V 등의 성분을 주축으로 한 다성분 산화물 촉매계가 연구, 보고되고 있다. 현재는 개량된 산화마그네슘계 촉매를 이용한 고정상 반응과, 철-바나듐계 촉매를 이용한 유동층 공정이 상업공정으로 운전되고 잇다. 본 논문에서는 연속 운전이 가능한 공업적인 활용성을 갖는 페놀의 ortho 알킬화 촉매/공정 연구를 실시 하였다. 그 결과 페놀의 ortho 위치선택성이 탁월한 촉매를 개발하고 기존 촉매보다 온화한 조건에서 고활성을 발현함을 확인하였으며 개발 촉매를 사용하여 재생과정 없이 3 개월 연속 운전이 가능함과 동시에 재생과정 포함 시 1 년 가능 할 것으로 예측된다. 생산된 제품은 고순도 (o-cresol 99.9%, 2,6-xylenol 99.7%)로 정제할 수 있음을 확인 하였다.

Chapter I. Introduction

I-1. The Background of Alkylation of Phenol

Ortho phenol derivatives are used as raw materials for medicines, pesticides, semiconducting encapsulants, EMC and PPO and are used as raw materials for flame retardants and antioxidants.

Particularly high-purity products are required (o-cresol 99.8% or more, 2,6-xylenol 99.5 or more). The products of the above specifications are obtained by a synthetic method because they cannot be obtained from natural cresols (extracted from petroleum and coal).

Phenol, a basic raw material for alkylphenols, is an excess supply in the domestic market, and it is necessary to develop new products including phenol derivatives.

The key to the development of alkylphenols manufacturing technology is to secure catalysts with high activity, high selectivity and long-term reaction stability, which is a difficult technique.

Since the reactant phenol or the product alkylphenol easily forms a polymer at a high temperature, the catalyst is rapidly deactivated during the reaction, and it is difficult to operate the catalyst continuously for a long period of time.

Due to such problems, the process including the catalyst regeneration process (high initial investment cost) or the fixed phase reaction process is manufactured under harsh conditions.

Therefore, it is necessary to develop proprietary and long-lived catalysts that inhibit deactivation of catalysts so that they can be utilized in various processes, to develop proprietary technologies to quickly respond to changes in the domestic market situation of the related industries.

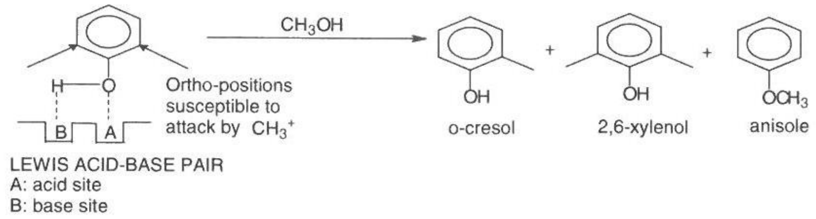
I-2. Status of Domestic and Foreign Related Technologies

Catalysts for o-alkylation such as metal oxides, doped metal cyclic compounds, mixed oxides, metal sulfates, phosphates, and zeolites have been studied. See Table 1.

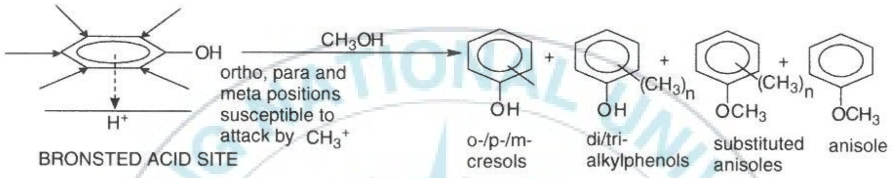
Table. 1. Alkylation catalyst systems and related patents of phenols

Catalyst system	Announcement	Reference
$Fe\text{-}V/SiO_2$ oxide system modified Fe-V oxide system	Asahi Chemical, others	JP 93,286,880, CA 117 : 69559
Mn 산화물계	Mitsubishi, others	JP 93,294,866, JP 94,25,041 JP 94,01,740 JP 94,01,739 USP 5,098,879, USP 4,546,093
Y-Zeolites	Texaco Chem, othes	USP 5,276,215, JP 93,97,737
Modified Zeolite system		CA 141 : 90833 CA 119 : 162821, CA 119 : 162824 CA 120 : 109912, CA 119 : 162815
Modified Al_2O_3 system		CA 119 : 252500, CA 119 : 119956 U.S.S.R 1,595,833
MgO & modified MgO	GE & others	USP 4,554,266, USP 3,974,229 USP 4,418,224, USP 4,554,267 CA 119 : 138869, USP 4,876,398
$AlPO_4\text{-}Al_2O_3$		CA 119 : 51728
$Fe_2O_3\text{-}SiO_2\text{-}CrO_3\text{-}GeO_2\text{-}K_2CO_3$	Mitsubishi	EP 419,045
$Fe_2O_3\text{-}MoO_3(WO_3)\text{-}Mg$ (Ba, Ca, La, Ce, Mn)	Huels	GP 3,522,345
V_2O_5/SiO_2, V_2O_5/Cr_2O_3		J. Mol. Cat, A : 96, 57-64(1995) Appl. Cat., 49, 165-174(1989)
Mg-Al hydrotalcites		Appl. Cat., 119, 241-252(1994)
TiO_2 modified TiO_2		Catalysis Commum., 7, 285-288(2006) Catalysis Commum., 5(2), 89-94(2004)
CuCoFe oxide system		Applied Catalysis A; 273, 35-45(2004)
Super acids & Heteropoly acid system		CA 142 ; 316519, CA 142 : 197642
$Fe_2O3/ZnAl_2O_4$		CA 142 : 394077

As shown in Table 1, catalysts composed of acidic or basic components are excellent in selectivity of ortho position as an alkylation catalyst for phenol, while catalysts having a high reaction temperature of about 350 to 550 ° C. and high acidity are more selective in position selectivity.



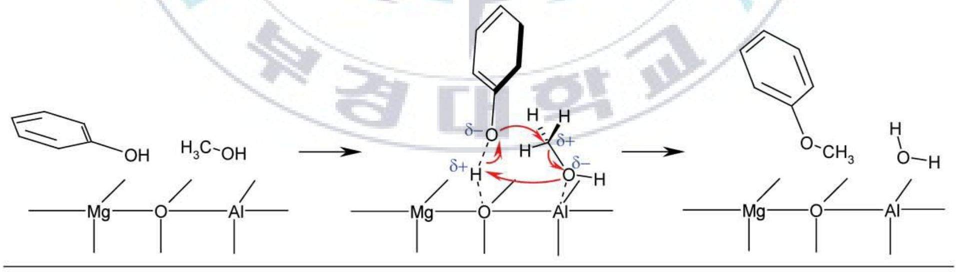
(a) Product selectivity on Lewis acid-base pair sites during perpendicular adsorption of phenol



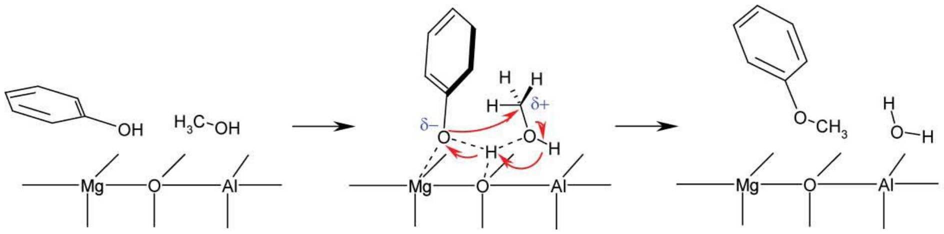
(b) Product selectivity on Bronsted acid sites during horizontal adsorption of phenol

Figure.1 Mechanism of alkylation of phenol with method [A.R.Gandhe, J,B,Ferandes/Catalysis Communication 5(2004)89-94]

Cooperation between strong basic site (responsible for phenolate formation), and Lewis acid site (responsible for methanol activation), on Mg/Al/O



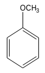
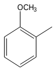
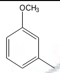
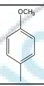
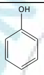
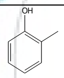
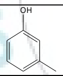
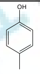
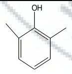
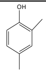
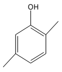
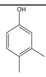
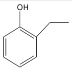
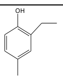
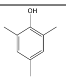
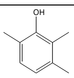
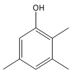
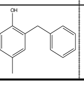
Cooperation between strong basic site (responsible for phenolate formation), and *in-situ* generated Brønsted acid site (responsible for methanol activation), on Mg/Al/O



Scheme 1. Mechanism of Phenol and Methanol reaction by Mg/Al/O [Dalton Trans, 2010, 39, 8527-8537 / The Royal Society of Chemistry 2010]

The catalyst have to high activity and selectivity, the distribution state of acid and base active sites of appropriate intensity is important as shown in Figure. 1. Recently, multi-component oxide catalyst systems based on Fe, V have been studied and reported.

Table 2. Methylation of phenol physical and chemical properties of product

Chemical name	Molecular formula		Molecular weight	density (g/mL)	Melting point (℃)	Boiling point (℃)	Vapor pressure	Vapor density	Solubility in water
methanol	—OH	CH_3OH	32.04	0.79 (25℃)	–94	64.7	127mmHg (25℃)	1.11	–
anisol		C_7H_8O	108.14	0.99	–37	154	10 mmHg (42℃)		1.6g/L (20℃)
2–methylanisol		$C_8H_{10}O$	122.16	0.98 (25℃)	0	170–172	Not available	–	–
3–methylanisol		$C_8H_{10}O$	122.16	0.96 (25℃)	0	175–176	Not available	–	–
4–methylanisol		$C_8H_{10}O$	122.16	0.96	0	174	Not available	–	–
phenol		C_6H_5OH	94.11	1.06–1.07	39–41	183	0.35 mmHg (25℃)	3.2	6.7
o–cresol		C_7H_8O	108.45	1.04–1.05	31	191	0.25 mmHg (25℃)	3.7	2.5
m–cresol		C_7H_8O	108.45	1.03	8~10	203	1 mmHg (52℃)	–	23 g/L (25℃)
p–cresol		C_7H_8O	108.45	1.034	32~34	202	0.2 hpa (20℃)	–	20 g/L (20℃)
2,6–xylenol		$C_8H_{10}O$	122.16		44~46	203	0.1 mbar (20℃)	–	10 g/L (20℃)
2,4–xylenol		$C_8H_{10}O$	122.16	0.97	21~23	211	0.1 mmHg (25℃)	–	0.5%(20℃)
2,5–xylenol		$C_8H_{10}O$	122.16	0.97	75	212	1.3 hpa (60℃)	–	1%(60℃)
3,4–xylenol		$C_8H_{10}O$	122.16	–	63~67	227	Not available	–	–
2–ethylphenol		$C_8H_{10}O$	122.16	1.03	–18	195–197	Not available	–	–
2–ethyl–5–methylphenol		$C_9H_{12}O$	136.19	–	–	–			
2,4,6–trimethylphenol		$C_9H_{12}O$	136.19	–	70~73	220	Not available	–	–
2,3,6–trimethylphenol		$C_9H_{12}O$	136.19	–	59–62	–	Not available	–	–
2,3,5–trimethylphenol		$C_9H_{12}O$	136.19	–	92–95	230–231	9.75 mmHg (60℃)	–	–
4–methyl–2–benzylphenol		$C_{14}H_{14}O$	198	–	–	–	–	–	–

Chapter II. Experimental

II-1. Development and demonstration of alkylation catalyst

II-1-1. Catalyst design and manufacturing method development

II-1-1-1. Catalyst design

Magnesium oxide (MgO) or modified MgO-based catalysts are used as catalysts for fixed-bed alkylation reactions, but they must be used at a high temperature of 400 °C or higher in the reaction conditions and have low catalytic activity.

Fe-V catalysts can be operated at lower reaction temperatures, but they are used only as catalysts for the fluidized bed alkylation process due to the short catalyst life and control of the reaction heat.

However, the fluidized bed process, including the catalyst regeneration system, has a great burden to solve the economic and technical difficulties in industrialization of the developed catalyst process. Therefore, in this study, the primary goal was to develop a fixed bed reaction process.

Under these goals, we have developed an improved alkylation catalyst for fixed-bed reaction, which has been improved to a higher degree of industrial utility by using the most active Fe and V components as the parent components in the catalyst systems so far.

- Overcoming the problem of catalyst life in Fe-V catalysts
- Minimize the by-production of m, p-cresol, which is difficult to isolate and O-cresol and 2,6-xylenol
- Securing required characteristics for industrial catalysis of developed catalysts
- Catalytic properties of catalyst used for on-site regeneration of catalysts

In order to overcome the problem of catalyst life, the initial activity of the catalyst is maximized, and the reduction of reactivity due to deactivation is gently appeared.

In order to alleviate problems such as caulking and sintering which are the main causes of deactivation, a combination of catalyst components is required to ensure the self-activity. In addition, in order to suppress deactivation through response to external conditions, it is also considered to share the fragile components in response to the conditions.

By methylation reaction of phenol, as shown in Table 2, a wide variety of compounds are produced as primary and by-products.

Therefore, purification process becomes very complicated to obtain high purity o-cresol or 2,6-xylenol. Especially, m, p-cresol are practically difficult to branch because their boiling point is almost the same as 2,6-xylenol.

In other words, minimizing the load of the purification process is an important factor in securing the competitiveness of the development process.

This is achieved by minimizing the byproducts of difficult to separate materials by securing the selectivity of the catalyst.

In addition, in constituting the catalyst component, it is necessary to prevent the particle movement of the active component or the like due to the reaction heat to obtain the characteristics required for industrial catalysis, for example, the particle strength, and the catalyst properties are maintained.

✓ Catalyst systems: Fe-V, M1, M2, M3, M4

M1 = Ni, Co, Cu.…

M2 = Mn, Mo.…

M3 = Mg, Ca.…

M4 = ZnO, ZrO_2, TiO_2, SiO_2, SiC.…

II-1-1-2. Development of catalyst production method

Fe, and V components were prepared by co-precipitation method in order to maintain homogeneity between components and to mutual synergy effect.

In the catalyst composition, nitrate was used for the cation part such as Fe, Co, Zn, and ammonium salt was used for the anion parts V and Mo, and monoethanolamine was used as the solubilizing agent for increasing the solubility.

Monoethanolamine also acts as a co-precipitator of metal nitrates, which is a cationic moiety in the preparation of catalysts.

Ammonia water was used as co-precipitant to reduce the cleaning load when removing unnecessary cations in the cleaning process after coprecipitation.

The co-precipitation, the catalyst component in which the metal oxide has a high solubility in water were added by a method in which a co-precipitated slurry was washed and mixed.

II-1-1-3. Change of Catalyst Characteristics by Post Treatment Condition

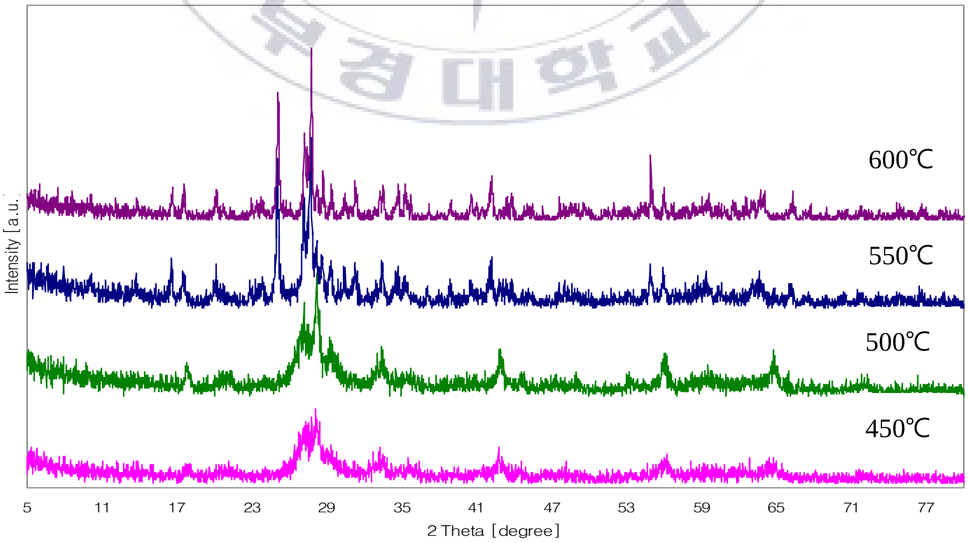


Figure 2 shows the XRD analysis results of the calcined temperature of the prepared Fe-V catalysts.

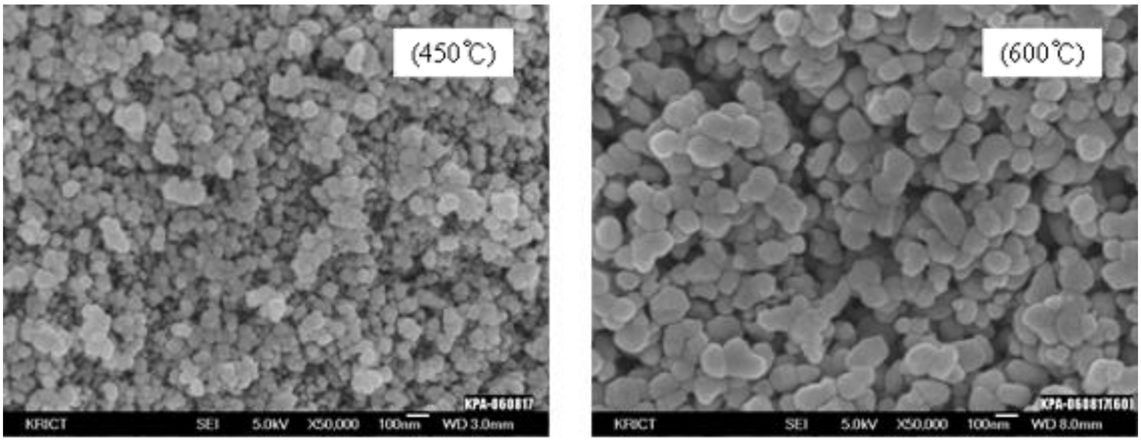


Figure 3 and Table 3 show the SEM and specific surface area of samples calcined at 450 °C and 600 °C.

Table 3. Specific surface area change of Fe-V based catalyst with calcination temperature

Cacinating Temp. (℃)	Specific surface area (m^2/g)
450	45 - 50
600	13.1

As can be seen from the experimental results, it can be seen that the Fe-V based catalyst is not superior in thermal stability to other mixed oxide catalysts.

At below 500 ℃, it exists as a metastable state of $FeVO_4$ structure. At above 550 ℃, it crystallizes into $FeVO_4$ particles, and the crystallinity and particle size are rapidly increased and the specific surface area is decreased.

This is an index for setting the operation limit of the Fe-V based catalyst in the alkylation reaction, and it is recognized that controlling the temperature of the catalyst layer not to exceed 500℃ during the operation is very important for maintaining the activity of the catalyst for a long time.

In addition, it suggests that it is important to the thermal properties in order to improve usability as an industrial catalyst.

II-1-1-4. Screening test and reactivity evaluation

In order to compare the selectivity of the catalyst and the catalyst performance, reaction temperature was 345°C, the pressure was atmospheric pressure, WHSV = 1.6 hr $^{-1}$, the composition of the reaction was PhOH: MeOH: H_2O = 1: 5: 1 m/m/m H_2 Gas flow under standard conditions. Figure 4 shows the typical G.C.-chromatogram of the product. The column was a DB-200 capillary column.

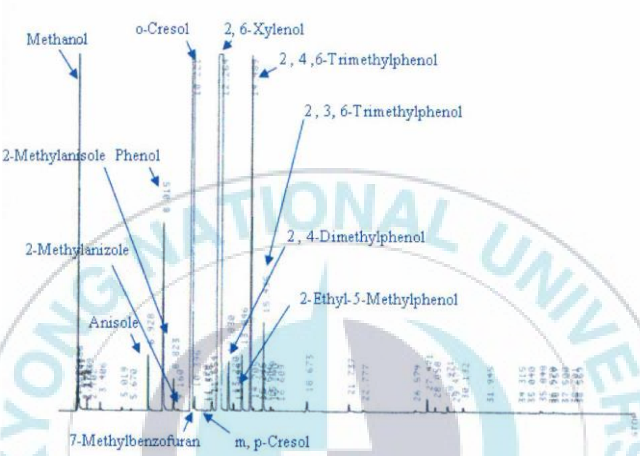


Figure 4. G, C-chromatogram of the product (column: DB-200)

II-1-1-4-a. Improvement effect of Ni, Co, and Cu components

5-1, 2, 3 and 4 show the experimental results of the catalysts prepared by adding Ni, Co, and Cu as M1 components to Fe and V, respectively.

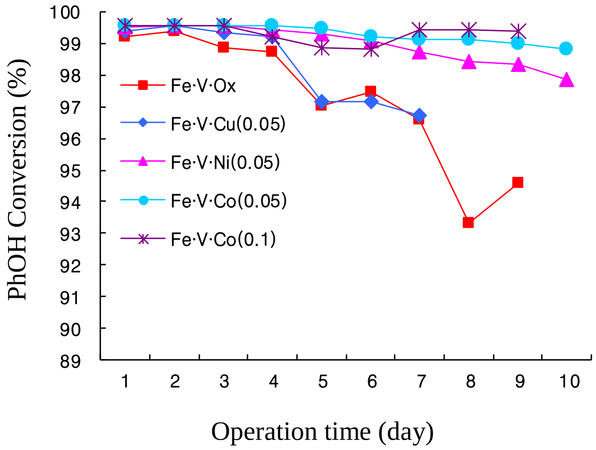


Figure 5-1. Change of conversion of phenol with improvement of Cu, Ni and Co components in Fe-V

Reaction condition

- Reaction temperature : 345℃
- Pressure : Normal pressure
- WHSV : 1.6hr^{-1}
- PhOH : MeOH : H2O = 1 : 5 : 1 m/m/m

Experimental results that are not specifically mentioned below. All of them are applied same reaction conditions.

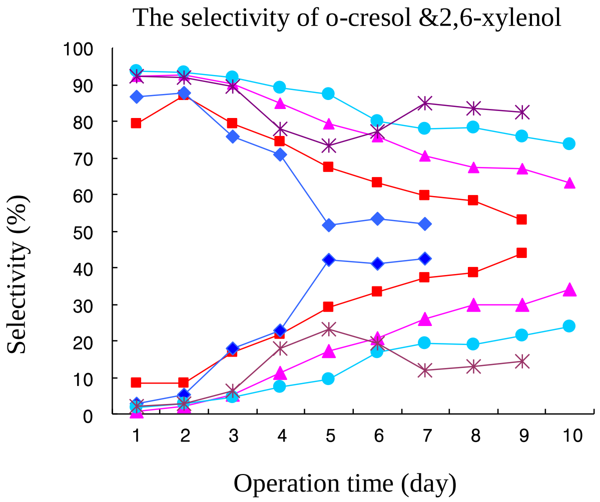


Figure 5-2. Change of selectivity of o-cresol and 2,6-xylenol with improvement of Cu, Ni and Co contents in Fe-V

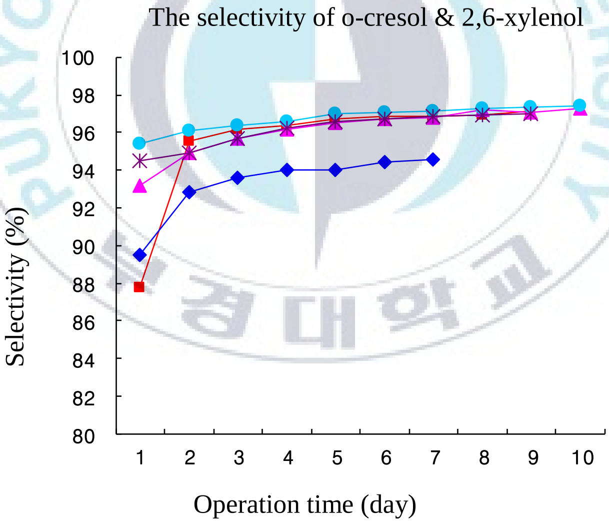


Figure 5-3. Selectivity of o-cresol and 2,6-xylenol due to improvement of Cu, Ni and Co in Fe-V

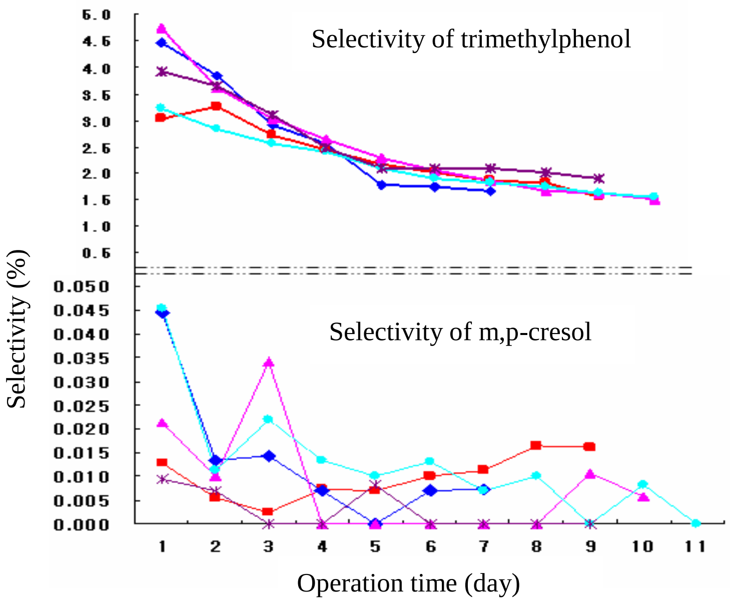


Figure 5-4. Change in selectivity of trimethylphenol and m, p-cresol according to the improvement of Cu, Ni and Co components in Fe-V

As an improvement agent, the effect of each component was investigated by using 0.05 to 0.1, that is, 5 to 10 mol% when Fe was 1.0, and the improvement effect of Ni, Co and Cu components as M1 component was shown in Figure. 5-1 and 5-2 as shown in the Figure, activity and selectivity were improved when modified with Co and Ni components, and the rate of activity decline with the elapsed time of operation showed a marked improvement in long term reaction stability. In particular, when 0.1mol of Co component was used with respect to 1mol of Fe, it showed high activity and stability.

Although, as shown in the results of 5-4, however it is insignificant, it is considered that it is necessary to appropriately suppress the m-, p-cresol due to a slightly higher rate.

The improvement by the above components was expected to suppress the desaturation of hydrogen in the hydrogen atmosphere slow down the rate at which coke is formed on the catalyst surface, thereby alleviating the deterioration of catalyst activity according to operating time.

The Cu component was effective to some extent at the initial stage of the reaction, but was not effective for long term operation, presumably due to the low thermal stability of the reduced Cu.

II-1-1-4-b. Mo, Mn components

6-1, 2, 3, and 4 show the results of investigating the performance improvement of catalysts by adding Mo, Mn components to Fe-V.

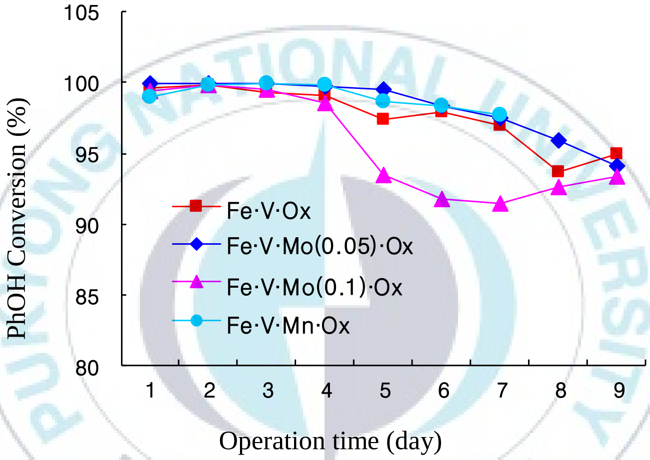


Figure 6-1. Change of conversion of phenol according to improvement of Mo, Mn components in Fe-V

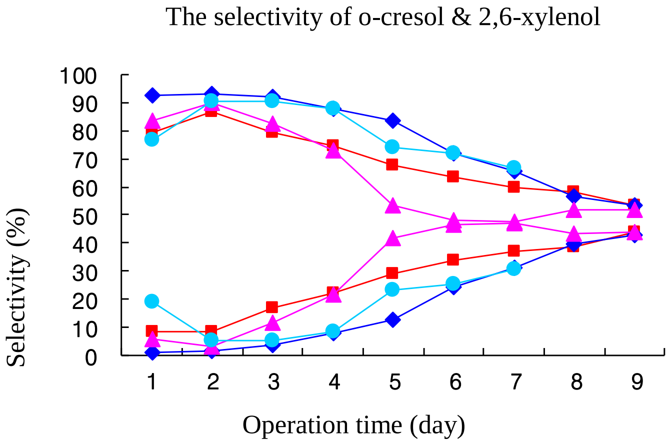


Figure 6-2. Change of selectivity of o-cresol and 2,6-xylenol with improvement of Mo and Mn in Fe-V

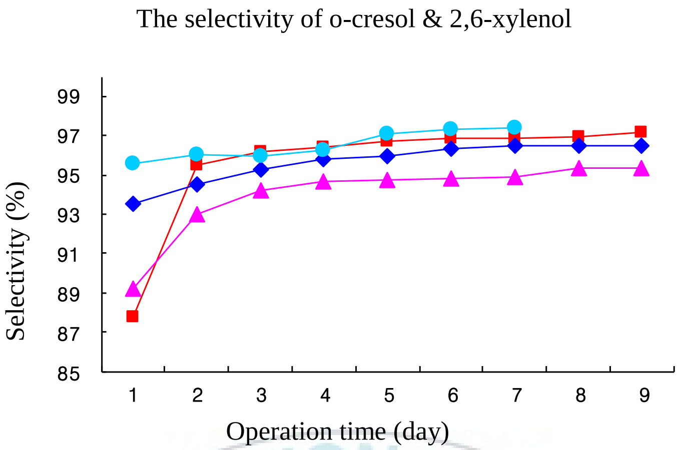


Figure 6-3. Selection of o-cresol and 2,6-xylenol depending on the improvement of Mo and Mn in Fe-V

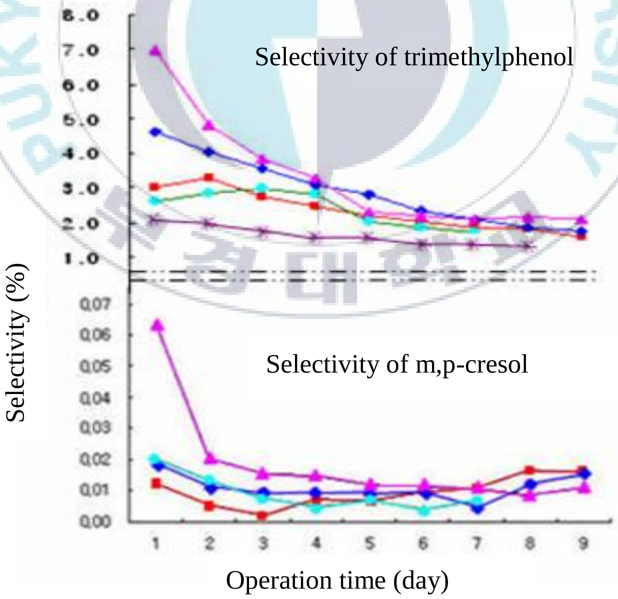


Figure 6-4. Change of selectivity of trimethylphenol and m, p-cresol according to improvement of Mo, Mn components in Fe-V

The addition of Mo and Mn did not show any significant improvement in Mo addition, but the selectivity of o-cresol and 2,6-xylenol decreased, which was negative.

However, the improvement of the Mn content did not contribute to the reaction activity and stability, but as shown in Figure. 6-3 and 4, the selectivity was slightly improved, and the effect of suppressing the by-product of trimethylphenol and m, p-cresol respectively.

Catalysts improved Mn component showed favorable results of inhibiting the by-product of trimethylphenol and m, p-cresol, but the relative amount of 2,4-xylenol was increased.

II-1-1-4-c. Improvement effect of Mg (Ca) component

Figure 7-1, 2, 3 and 4 show the results of investigation of the improvement effect of adding Mg components in Fe-V-Mn and Fe-V-Mn-Co systems.

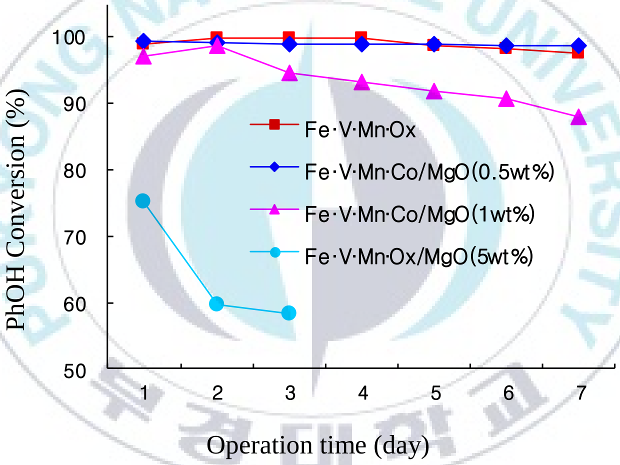


Figure 7-1. Change of Phenol Conversion by Modification of Mg Component in Fe-V-Mn-Co System

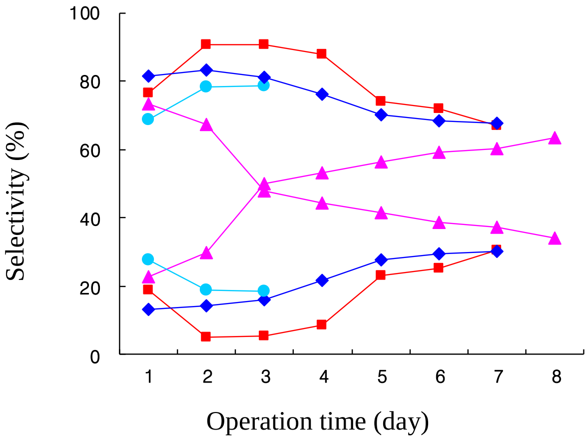


Figure 7-2. Change of selectivity of o-cresol and 2,6-xylenol with improvement of Mg component in Fe-V-Mn-Co system

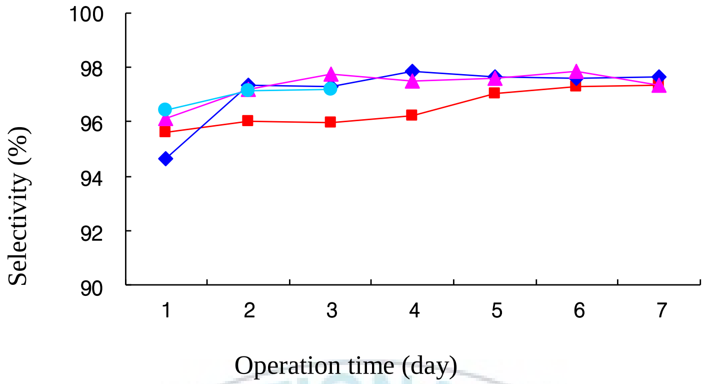


Figure 7-3. Selectivity of o-cresol and 2,6-xylenol due to improvement of Mg component in Fe-V-Mn-Co system

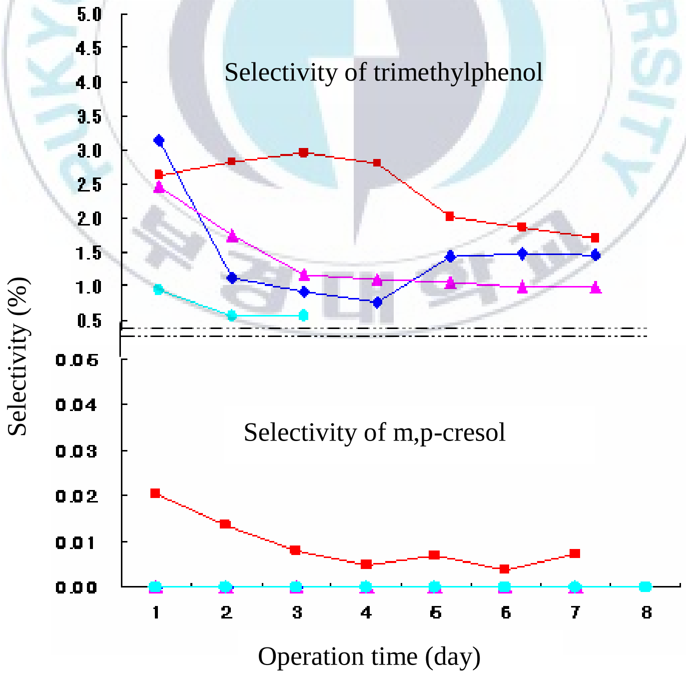


Figure 7-4. Change of selectivity of trimethylphenol and m, p-cresol according to improvement of Mg component in Fe-V-Mn-Co system

Experimental results showed that the addition of 0.5 wt% to the catalytic component reduced the activity and long - term stability of the catalyst.

However, the addition of Mg improves the selectivity of o-cresol and 2,6-xylenol. Especially, the by-product of trimethylphenol and m, p-cresol decreased.

II-1-1-4-d Dispersant and Binder effects

Experimental results for selecting dispersants and binders that can be used when controlling the catalytic activity per unit volume (or weight) in the production of industrial catalysts or when it is necessary to increase the particle strength of the shaped catalysts is shown in Figure 8-1-1 , 2, 3, and 4 are shown in Figure 8-1, 2, 3, and 4.

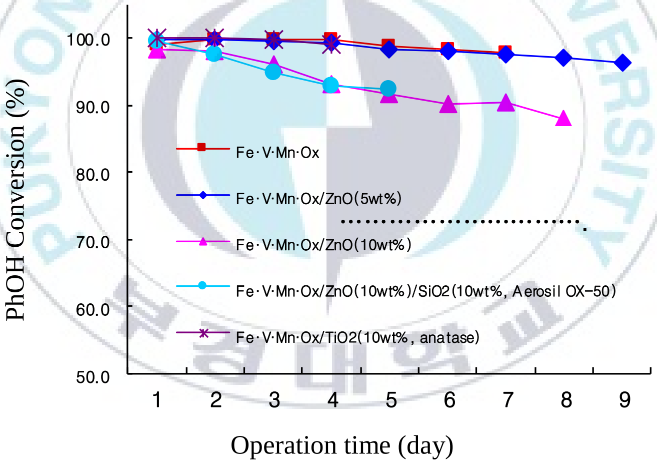


Figure 8-1. Change in conversion of phenol to Fe-V-Mn according to dispersant

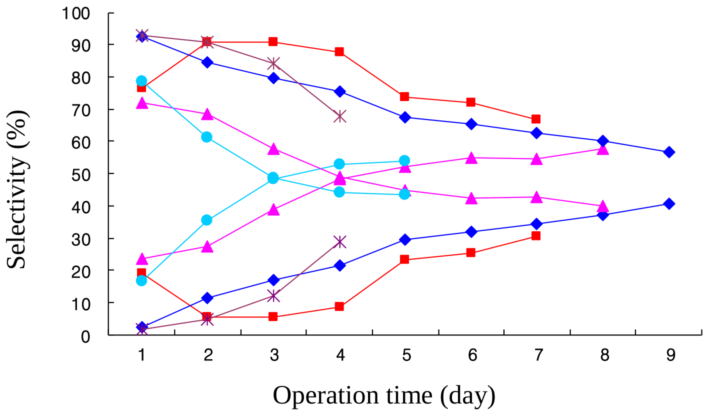


Figure 8-2. Change of selectivity of o-cresol and 2,6-xylenol depending on dispersant in Fe-V-Mn

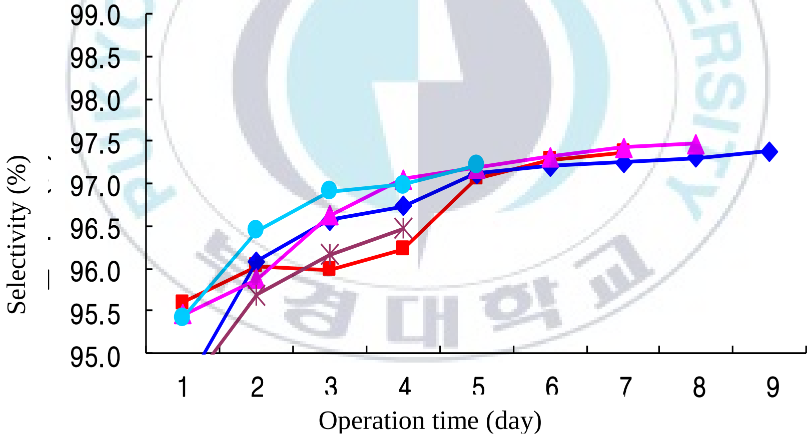


Figure 8-3. Selectivity of o-cresol and 2,6-xylenol depending on dispersant in Fe V-Mn

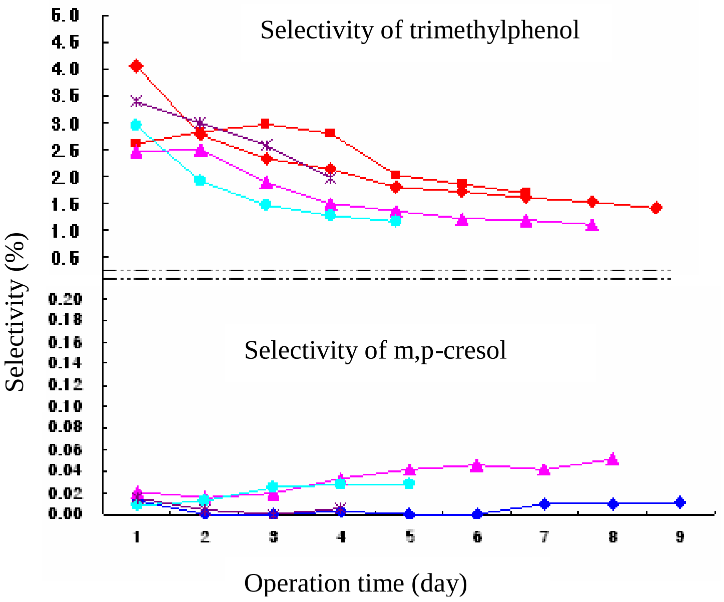


Figure 8-4. Change of selectivity of trimethylphenol and m, p-cresol according to dispersant in Fe-V-Mn

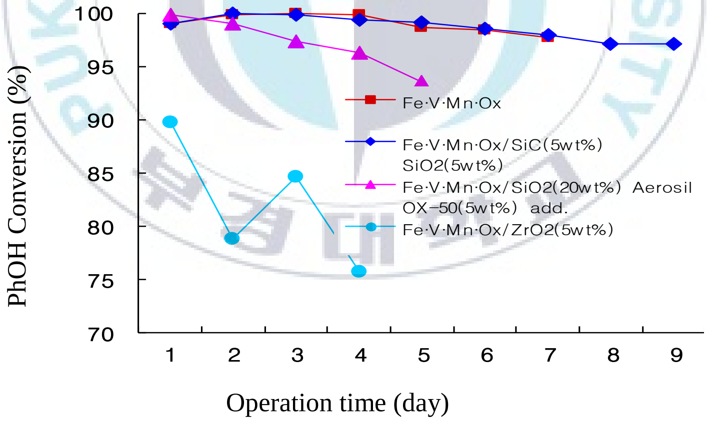


Figure 8-5. Change of Phenol Conversion Rate in Fe-V-Mn by Binder

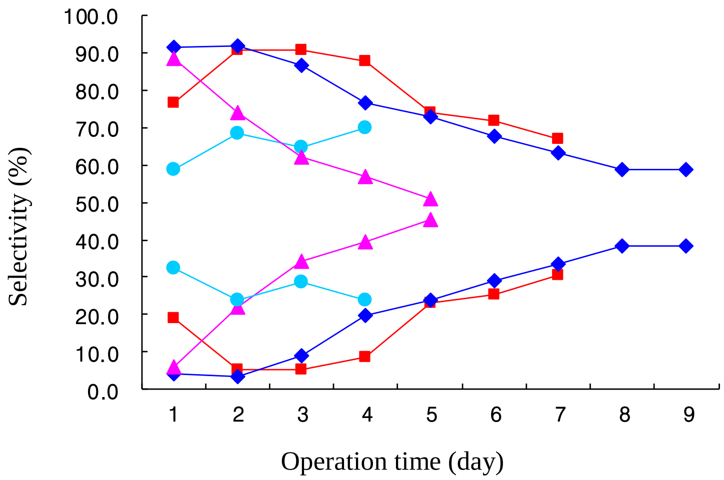


Figure 8-6. Change of selectivity of o-cresol and 2,6-xylenol depending on the binder in Fe-V-Mn

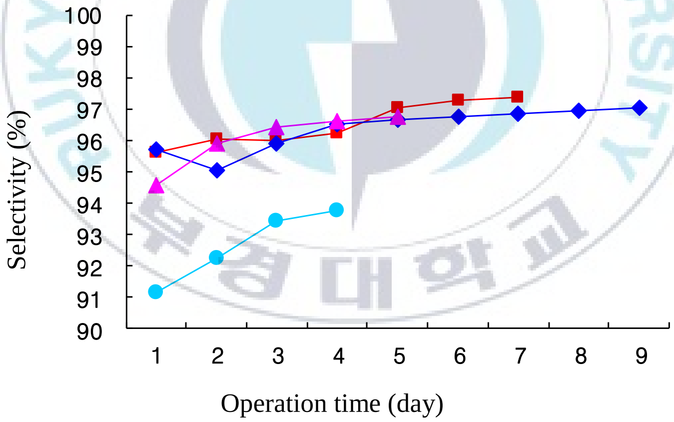


Figure 8-7. Selectivity of o-cresol and 2,6-xylenol depending on binder in Fe-V-Mn

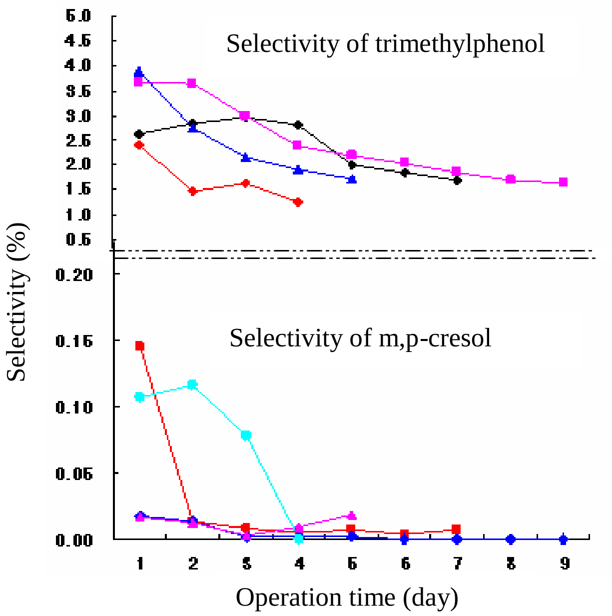


Figure 8-8. Change of selectivity of trimethylphenol and m, p-cresol according to binder in Fe-V-Mn

Experimental results show that the selectivity of o-cresol and 2,6-xylenol does not change even when ZnO or fumed silica (SiO_2) or TiO_2 (anatase) powder is used as a dispersant. However, addition of 10 wt% or more to the main component of the catalyst is not preferable because the activity becomes too low.

Particularly, when ZnO is used more than 10wt%, the amount of m, p-cresol is increased as shown in Figure. 8-4.

As the binder, SiO_2 was most suitable, but when the SiO_2 was used in an amount of 10 wt% or more, the reduction of the catalytic activity was remarkable, and the use amount was limited.

II-1-1-4-e Use of whisker to improve particle strength of compact

It is necessary to increase the particle strength in order to suppress the volume expansion of the shaped body particles due to the coke accumulated in the catalyst according to the elapsed time of the reaction. Whiskers are mixed and SiO_2 is used as the inorganic binder.

The activity of the catalysts prepared using whiskers such as SiC (Advanced Composite Meterials, LLC), YS2A (Aluminum borate, Shikoku chemicals), Wollastonite (Calcium Silicate, NYCO) and Ludox AS-40 SiO_2 binder Test results.

Since the activity per weight of the catalyst unit is lowered depending on the amount of the whisker and SiO_2 used, the decrease in the activity gradually appears as the reaction time elapses.

However, the use of Wollastonite whisker was not preferable due to the rapid decrease of catalytic activity. This suggests that the Ca component is partially dissolved in the wollastonite, which has a great effect on the catalytic activity.

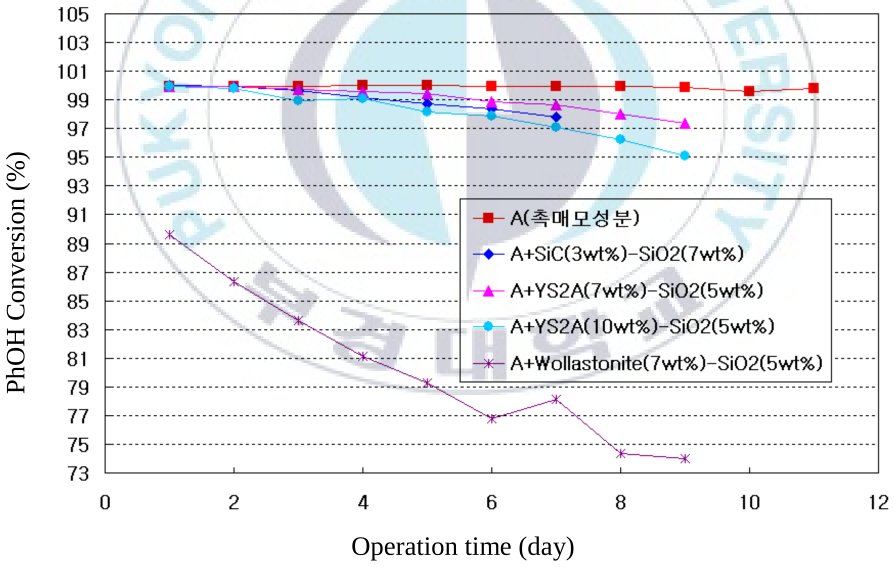


Figure 9-1. Change of catalytic activity by using whisker and SiO_2

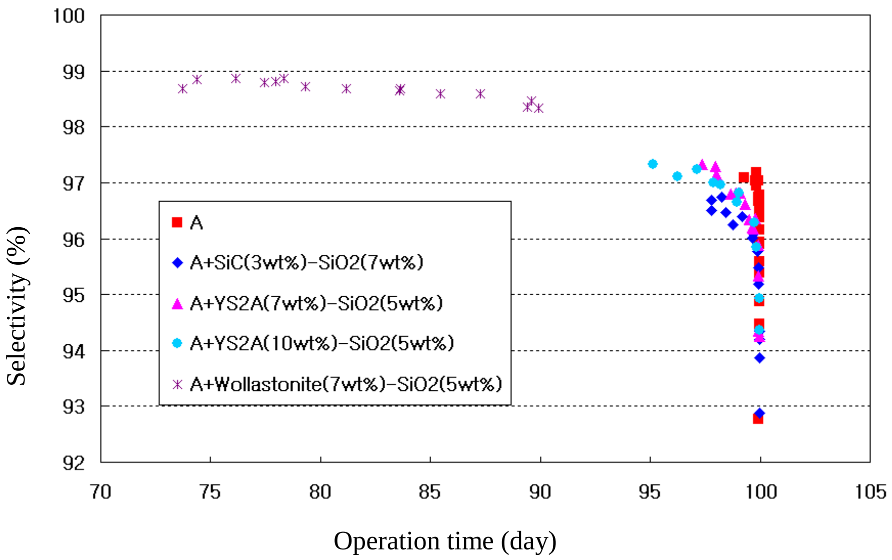


Figure 9-2. The selectivity of o-cresol, 2,6-xylenol according to the conversion ratio in the whisker and SiO_2 catalyst

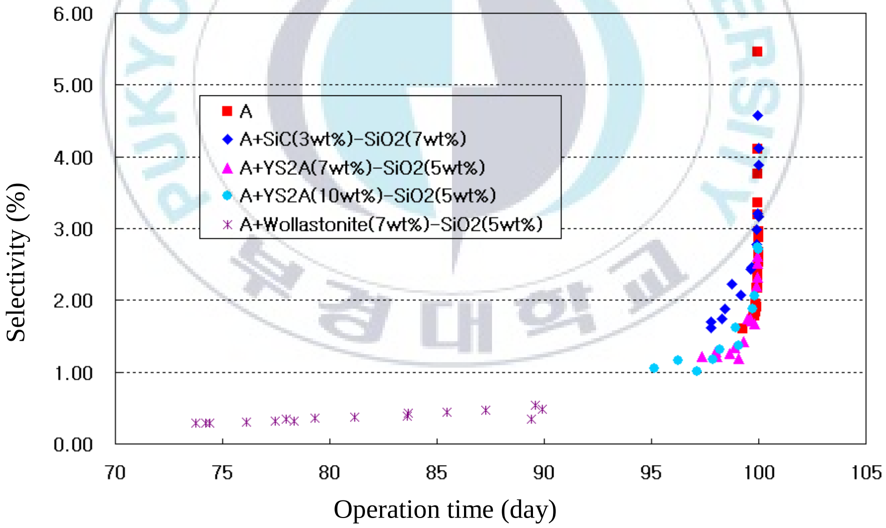


Figure 9-3. Changes in the by-product of trimethylphenol with conversion of whisker and SiO_2 catalysts

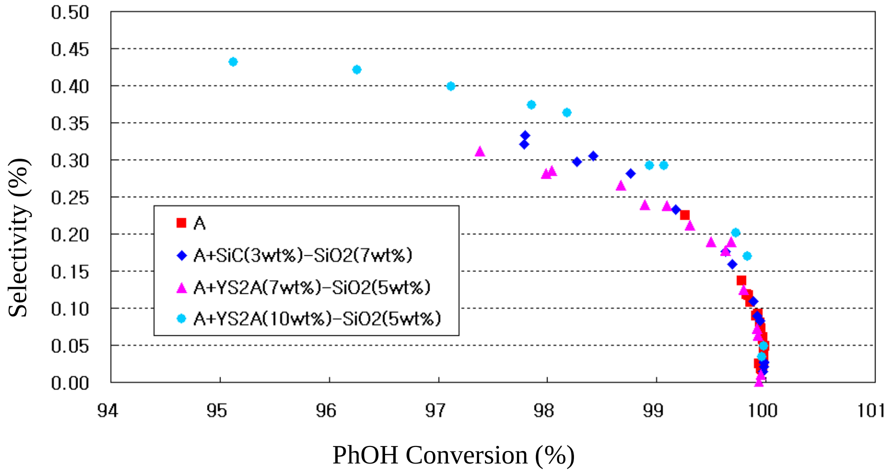


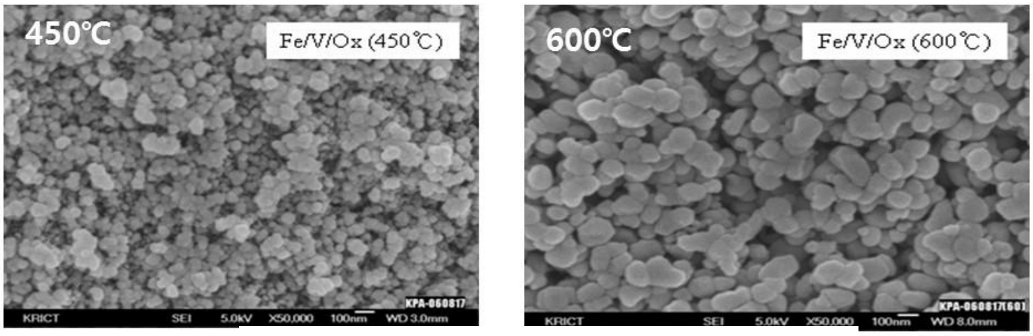
Figure 9-4. Changes in the by-product of 2,4-xylenol with conversion of whisker and SiO_2 catalysts

In the Figure. 9-4, the selectivity of O-cresol and 2,6-xylenol is slightly lowered by the use of whisker and SiO_2, and the selectivity is 0.5-1% lower than that of the parent catalyst, especially at a high exchange rate of 98% The larger the amount of SiO_2 used, the larger the amount of trimethylphenol by-product as shown in Figure.

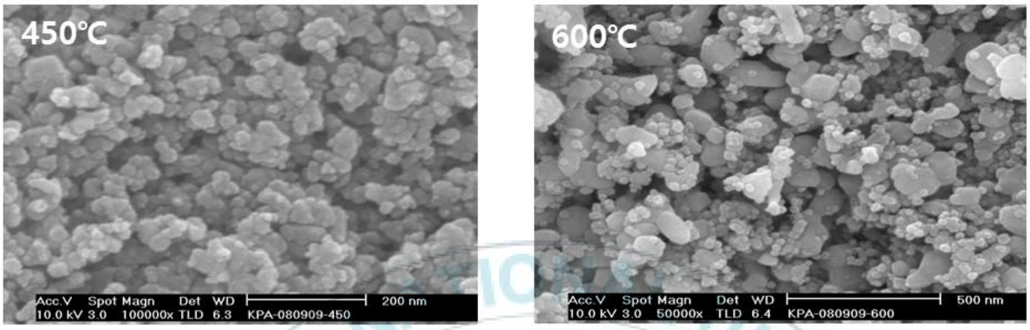
In addition, when the amount of YS2A was increased to 10 wt%, the amount of 2,4-xylenol was inevitably increased, as shown in Figure.

From the above experimental results, it can be seen that the whisker and SiO_2 are preferably used within 15 wt%, more preferably within 12 wt%, of the total amount of catalyst, and SiO_2 is about 5 wt%.

In the SEM image of Figure 9-5, crystal growth due to sintering is not completely suppressed by the use of whisker and SiO_2 binder in the catalyst calcined at 600 °C for 5 hours, but crystal growth It can be seen that it shows a considerably suppressed effect.



Whisker & SiO_2 are not used in the catalyst



YS2A(7wt%), SiO_2(5wt%) are used in the catalyst

Figure 9-5. Use of Whisker and SiO_2 and SEM according to calcinating temperature image

II-1-1-5 Improvement effect using MgO

Figure 10-1 shows that the activity decreases markedly with the amount of MgO added. However, as shown in Figure. 10-1 and Figure. 10-2, o-cresol is relatively higher in selectivity than o-cresol, which is not improved to MgO at 99.7% or higher conversion rate, and o-cresol and 2,6-xylenol is somewhat higher.

In particular, in Figure. 10-3 and Figures. 10-4 , the amount of trimethylphenol was not significantly different depending on the conversion of phenol, regardless of the addition of MgO. On the other hand, in the catalyst modified with MgO, the selectivity of 2,4-xleneol % to 96%, even if it is lower than 0.15%.

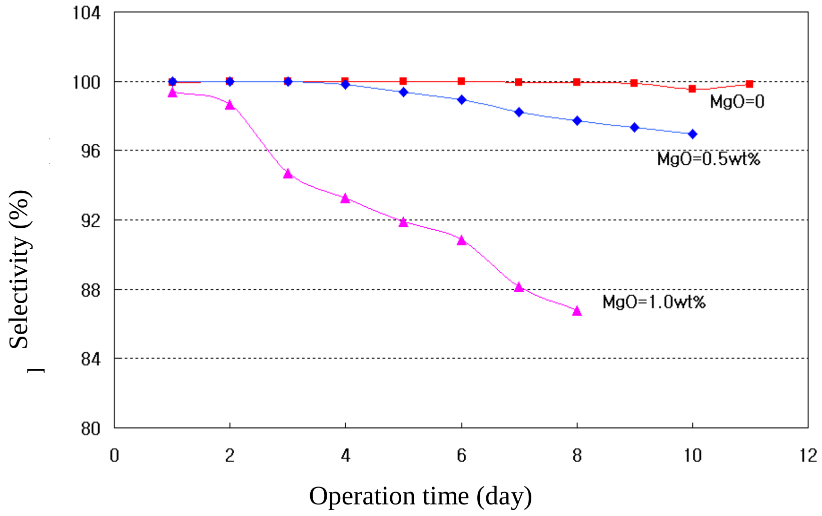


Figure. 10-1 Change of Conversion Rate by Addition of MgO in FeVMnCo / SiO_2 Catalyst

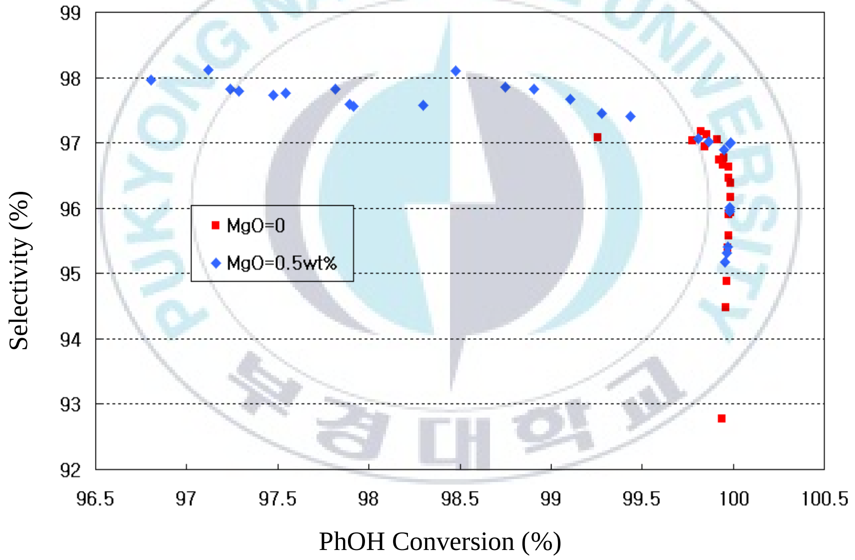


Figure. 10-2 Selection of o-cresol and 2,6-xylenol depending on conversion of phenol in MgO-modified catalyst

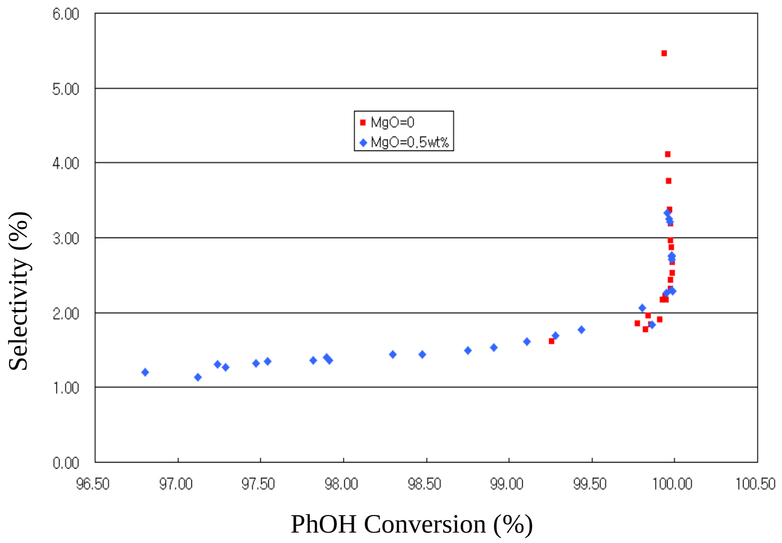


Figure. 10-3. Change in trimethylphenol production by phenol conversion in MgO-modified catalyst

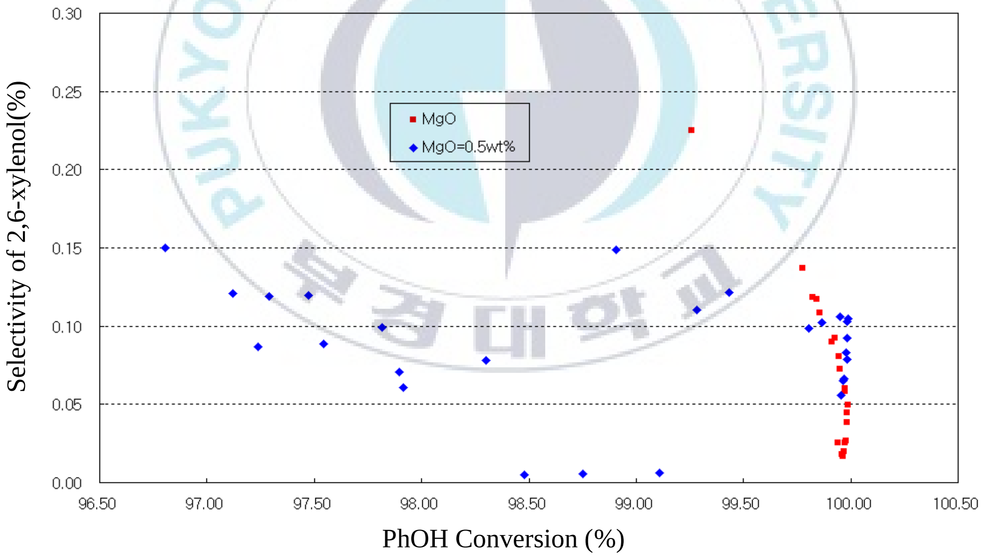


Figure. 10-4. Changes in the amount of 2,4-xylenol produced by phenol conversion in MgO-modified catalysts

From the above results, it was confirmed that the catalyst composed of FeVCoMn (Mg) Ox-Whisker (7wt%) SiO_2 (5wt%) was developed for the fixed alkylation reaction of phenol.

II-1-2. Long-term reaction stability investigation

II-1-2-1. Reaction stability of catalyst depending on reaction atmosphere

Figure 11 shows the results of a long-term reaction stability of the catalyst depending on the reaction atmosphere with the gas supplied with the reactant during the alkylation reaction. The comparative experiments were performed on FeVMnOx based catalysts, and the results of FeVMnCoOx based catalysts with Co added to the catalysts were also shown for reference.

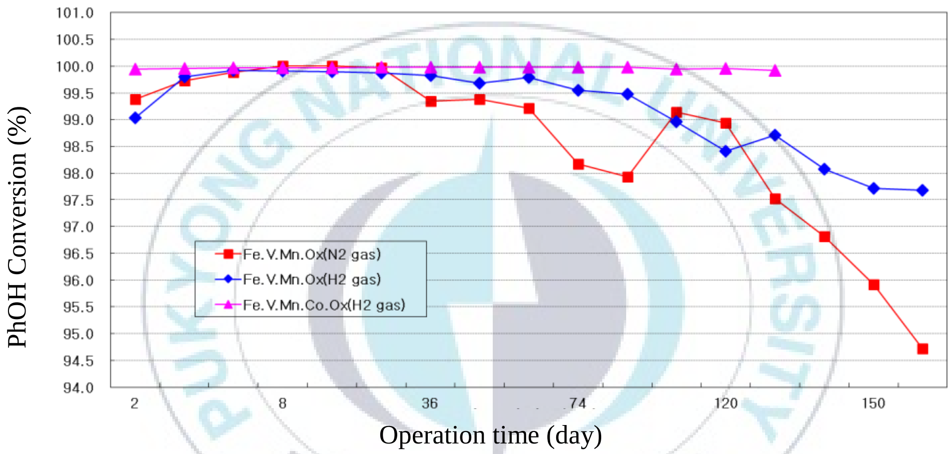


Figure 11. Reaction atmosphere effect on long term reaction stability of catalyst

As shown in the figure, when the reaction was carried out in a reducing reaction atmosphere using hydrogen, the deactivation of the catalyst progressed more slowly in the nitrogen atmosphere. In particular, the catalyst containing the reducing component was more inactivated respectively.

It is considered that the activation of hydrogen on the catalyst surface alleviated the formation of coke derived from the reactant phenol or alkylphenol product.

II-1-2-2. Long-term reaction stability and activity recovery after regeneration

II-1-2-2-a. Long-term reaction stability investigation

The long - term stability of the developed catalysts was investigated in a reducing reaction atmosphere.

Figure 12-1, 2, 3, and 4 show the results. Figure 10-1 shows different phenol conversion ratios over the elapsed time of operation, Figure 10-2 shows the selectivity of o-cresol and 2,6-xylenol, Showed the selectivity of o-cresol and 2,6-xylenol, and Figure. 10-4 showed changes in the by-product of trimethylphenol and m, p-cresol.

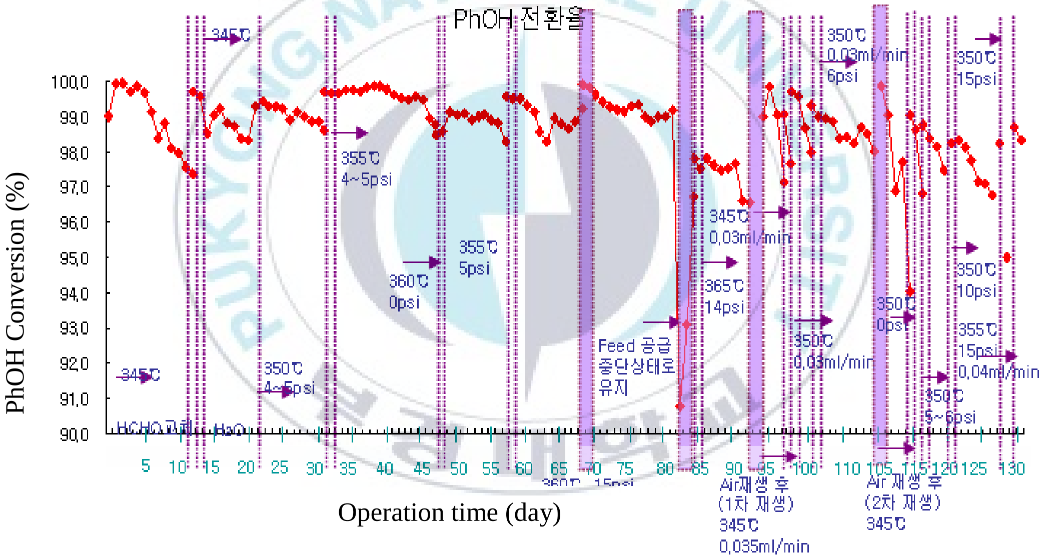


Figure 12-1. Change in conversion rate at different elapsed time of development catalyst

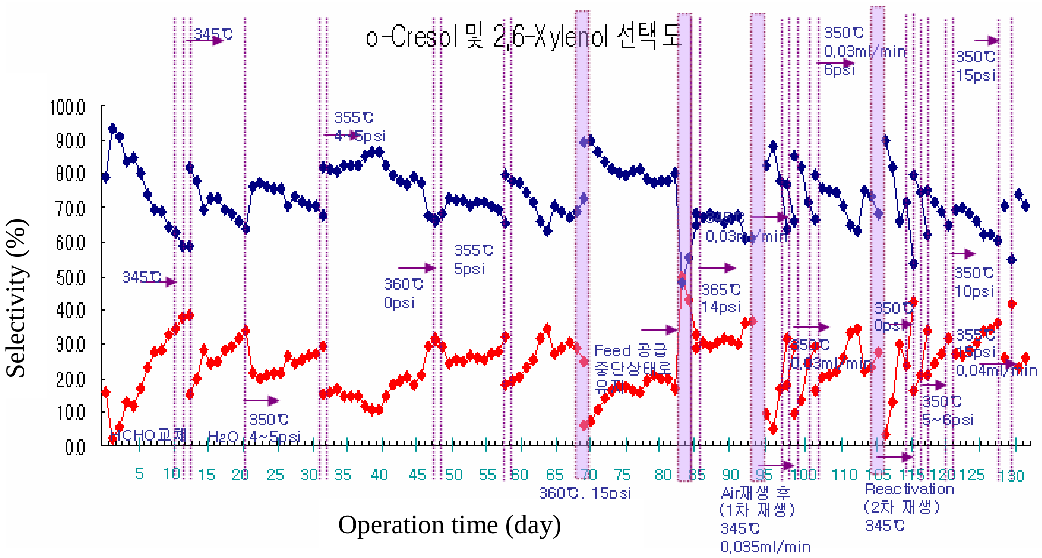


Figure 12-2. Change of selectivity of o-cresol and 2,6-xylenol with the elapsed time of development catalyst

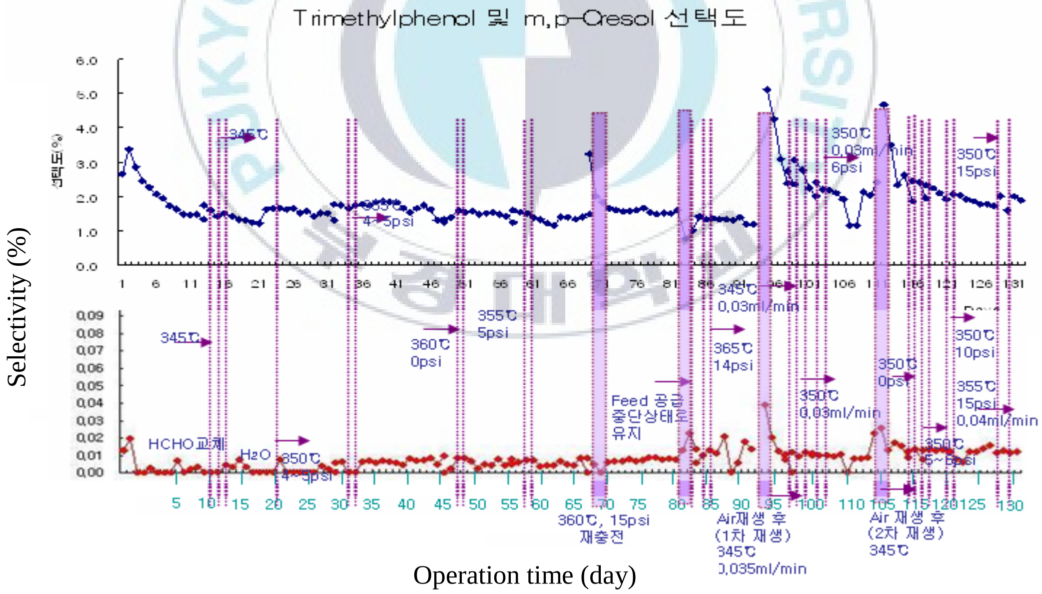


Figure 12-3. Selectivity of o-cresol and 2,6-xylenol depending on elapsed time of development catalyst

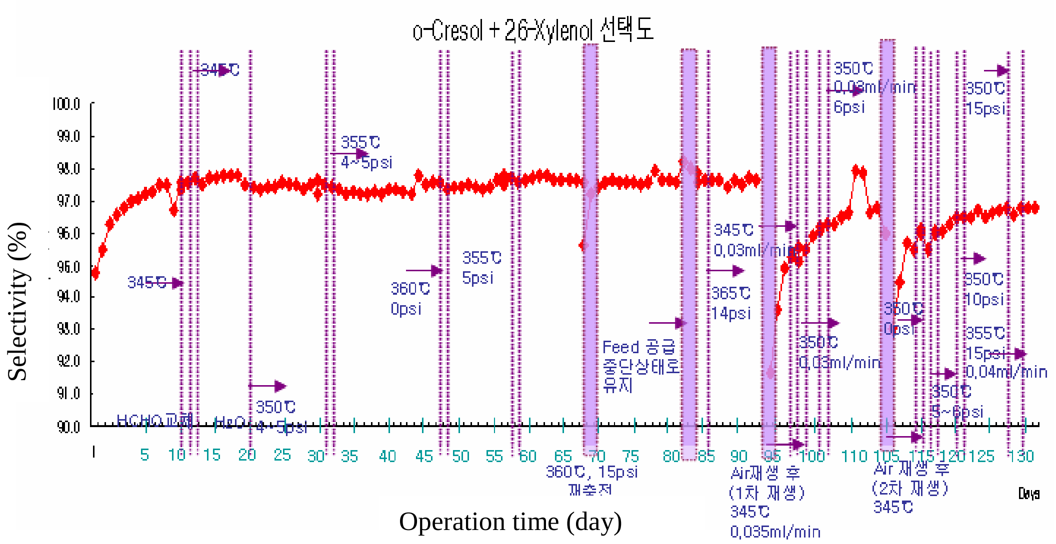


Figure 12-4. Change of selectivity of trimethylphenol and m, p-cresol according to elapsed time of development catalyst

The reaction conditions were controlled to maintain the conversion of phenol over 97%. The reaction temperature was changed from 345 to 360 °C and the reaction pressure was changed from normal pressure to 15 psi.

It is confirmed that the reaction result is capable of continuous operation for 90 days or long within the range of the described change in the operating conditions.

The selectivity of o-cresol was in the range of 10 to 40% and the selectivity of 2,6-xylenol was in the range of 55 to 90% when the conversion of phenol was 97% or more. As shown in Figure. 12-3, was maintained over 97% except for the initial stage of the reaction.

At this time, the by-product selectivity of the trimethyl phenols was within 2% except for the initial stage of the reaction, and m and p-cresol exhibited excellent activity and selectivity with a by-product selectivity of 0.015% or less.

However, the determination of the continuous operation time in the progress of the alkylation reaction of phenol under the above-mentioned reaction conditions in the form of the fixed-phase reaction requires that the produced coke simultaneously causes the expansion of the catalyst particles rather than the decrease in activity by deactivation of the catalyst, It is confirmed that the present invention has a decisive effect on the clogging phenomenon. Thereafter, the reactor was charged with the catalyst, and the decarboxylation was carried out at 400°C under an air flow. Thereafter, the same alkylation reaction was carried out continuously, and a second decarboxylation process was performed again under air flow. The changes of activity of air regeneration were compared and investigated.

II-1-2-2-b. Changes in activity and selectivity due to air regeneration

Figure 13 and 14 show the results of the activity and selectivity changes at the same reaction temperature of the catalyst regenerated under air flow after the continuous reaction as described above according to the elapsed time of operation.

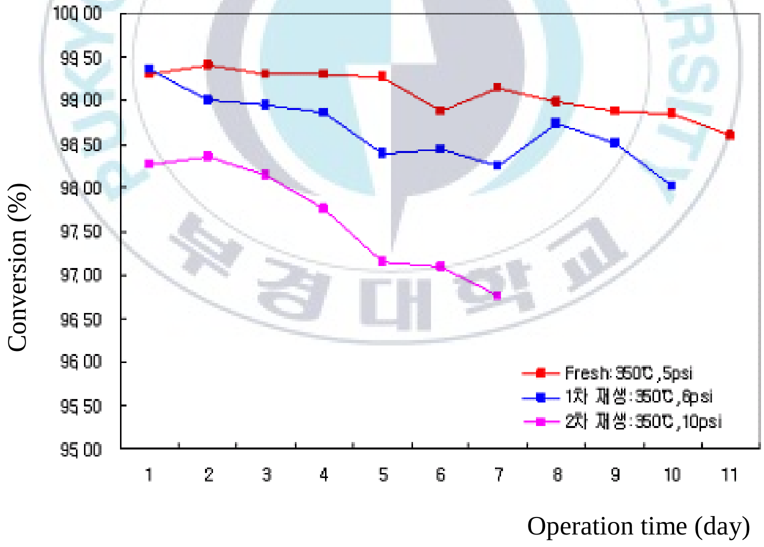


Figure 12. Change of phenol conversion rate with the elapsed time of regenerated catalyst

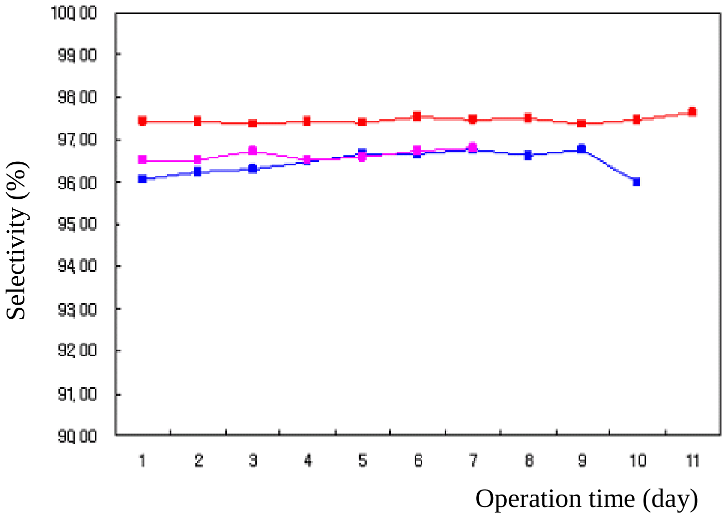


Figure 14. Selectivity variation of o-cresol + 2,6-xylenol with the elapsed time of regenerated catalyst

The catalytic activity was slightly reduced as the regeneration was repeated. However, as shown in Figure. 11, it is shown that sufficient activity is maintained even after two or more regeneration and continuous operation is possible.

The selectivity of o-cresol and 2,6-xylenol was also decreased by 1 to 1.5% after one regeneration but was not changed by subsequent regeneration and maintained a selectivity of over 96% overall.

II-1-2-2-c. Changes in Catalytic Properties due to Long-term Operation and Regeneration

Figure 15 shows the XRD patterns for fresh, used and used catalysts used in the long-term stability evaluation of 3,120 hours for regenerated catalysts decarboxylated in air atmosphere.

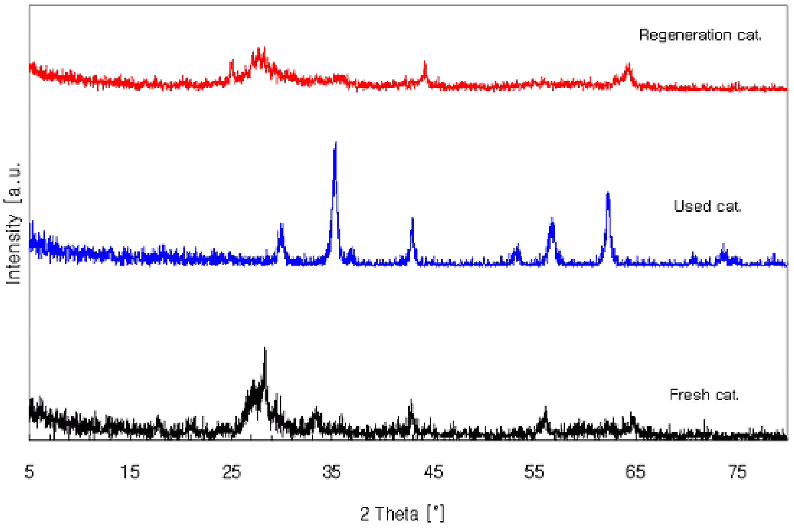


Figure 15. XRD patterns of catalysts (fresh, used, regenerated) used in long-term stability evaluation

XRD shows that the activation state of the Fe-V catalyst in the alkylation reaction of phenol has Fe_2VO_4 structure.

That is, in a metastable $FeVO_4$ structure of a fresh catalyst having iron and vanadium in an oxidation state of Fe^{3+} and V^{5+}, the oxidation and reduction of $FeVO_4$ structure, which has a Fe_2VO_4 structure in which iron and vanadium are reduced during the reaction, It can be seen that the reduction cycle proceeds smoothly.

Also, the XRD shows that the developed catalyst does not have a large crystal growth even after 3,120 hours of long-term operation.

Figure 16 shows the SEM according to state of the catalyst. In the SEM, the used catalyst shows a series of processes in which the catalyst particles are agglomerated by carbonization or coke and they are removed by air regeneration can see.

As a result of the BET on the catalysts shown in Table 6, the regenerated catalyst had a slight decrease in specific surface area but was not severe, and the specific surface area of the used catalyst was larger than the fresh catalyst.

This is thought to be due to the fact that the state of the coke is partially present in the activated carbon state having a large specific surface area in the used catalyst in which the coke is formed.

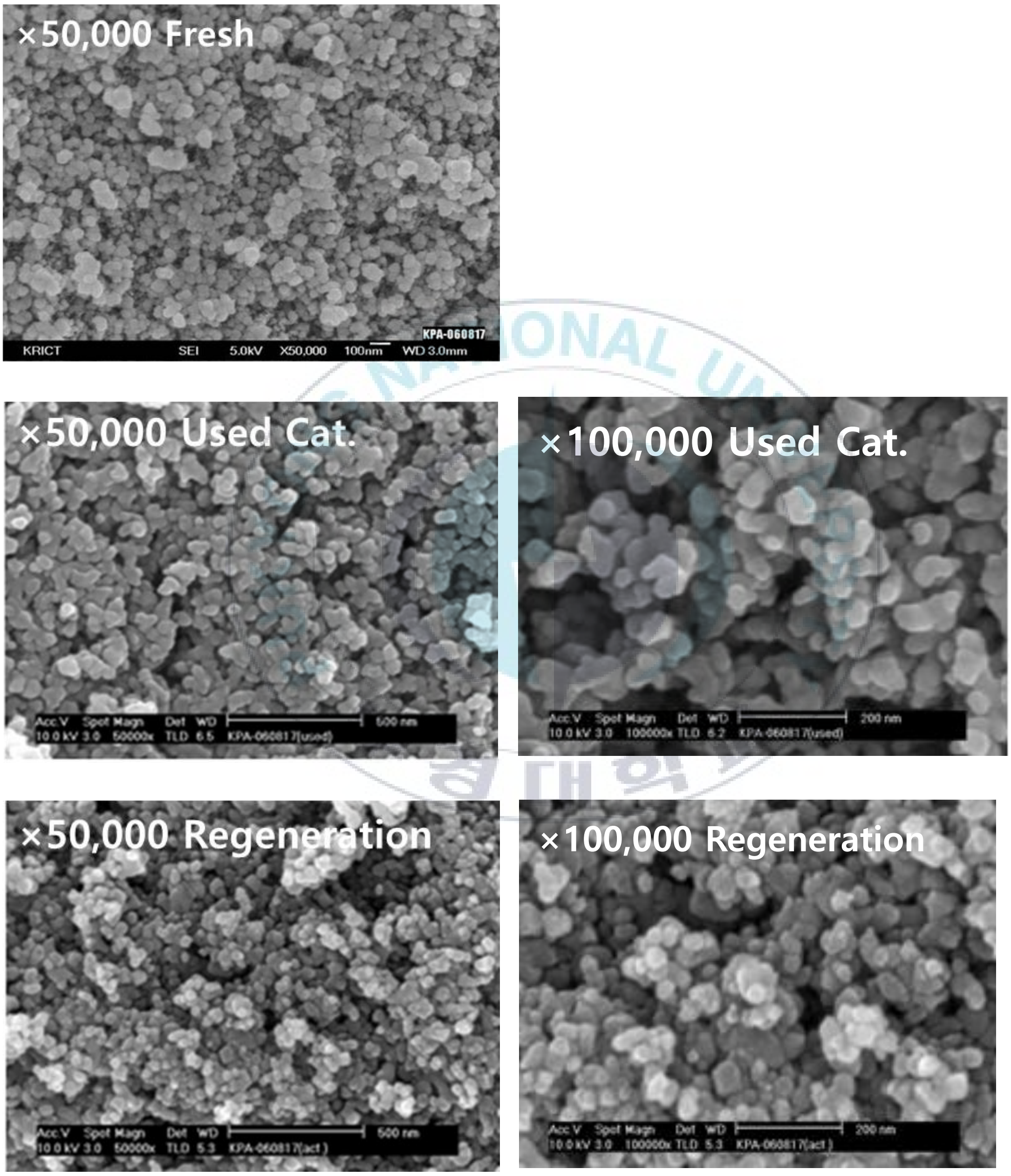


Figure 16. SEM images of catalysts used for long-term stability evaluation (fresh, used, regenerated)

Table 3. Specific surface area of the catalyst used in the long-term stability evaluation

Catalyst	Specific surface area (m^2/g)
Fresh	49.0
Used	62.2
Reactivation	40.3

II-2. Basic design of distillation process

II-2-1. Distillation Process Outline

The whole process of the distillation process to obtain O-cresol and 2,6-xylenol is shown in Table 4.

Table 4. Distillation process to obtain high purity o-cresol and 2,6-xylenol from the alkylation product

Materials	Ratio (wt%)	wt%
MeOH	39.71	0.00
H_2O	17.35	
anisol	0.04	0.09
Phenol	1.93	4.49
2-methylanisol	0.03	0.07
o-cresol	11.87	27.64
m,p-cresol	0.05	0.12
2,6-xylenol	27.71	64.53
2-ethylphenol	0.01	0.02
2,4-xylenol	0.26	0.61
2-ethyl-5-methylphenol	0.05	0.12
2,4,6-trimethylphenol	0.63	1.47
2,3,6-trimethylphenol	0.16	0.37
heavier	0.20	0.47
Sum	100.00	100.00

The distillation is carried out by passing the crude material produced in the reaction through four distillation columns continuously, separating the methanol and water in the first column, separating the phenol from the second column, separate o-cresol, separate 2,6-xylenol from the fourth column and separate the remaining high boiling point material into the bottom of the column and treat with waste oil.

All of these processes are carried out continuously, and methanol, water and phenol are recovered and reused.

The typical composition of the pre-distillation alkylation catalyst reaction product is as shown in Table 4. Except for methanol and water, o-cresol and 2,6-xylenol exist in a weight ratio of about 3: 7.

II-2-1-1. Laboratory scale distillation purification experiment

In the laboratory distillation experiment, the methanol and water were first removed from the alkylation product, and the remaining products were separated from the o-cresol and 2,6-xylenol using distillation columns of theoretical plates of 20 stages and 40 stages.

II-2-1-1-a. Distillation purification in a 20 stages column

The composition of crude oil before distillation is shown in Table 4, and methanol and water were separated and removed at 130 at normal pressure. After that, 2,533 g of a sample in which methanol and water were removed was tried at 20 atmospheric pressure using a 20-stage column.

The experimental results are shown in Table 18, and the three components of phenol, o-cresol and 2,6-xylenol were obtained by distillation without separating from the beginning to the end.

Table 4. Distillation purification results using a 20-stage column

Name	Wt(g)	GC			
		PhOH	o-Cresol	2,6-Xylenol	etc.
Crude	2,522.0	5.47	32.16	60.68	1.69
Receiver-1	88.7	21.07	46.10	32.19	0.64
Receiver-2	184.4	15.70	47.82	36.19	0.29
Receiver-3	515.3	6.04	40.06	53.73	0.17
Receiver-4	862.1	2.44	29.16	66.77	1.63
Receiver-5	212.6	0.88	22.99	73.94	2.19
Sum	1863.1	5.46	34.12	59.31	1.11

In receiver 2, the o-cresol ratio was the highest (47.8%) and the receiver 5 had the highest 2,6-xylenol content (73.9%).

It was considered impossible to separate o-cresol and 2,6-xylenol at a high purity in the 20-stage column, and further separation into a 40-column was attempted.

II-2-1-2-b. Distillation purification in a 40 column

Distillation purification in a 40 column 1863.1 g of a sample in which water and methanol were removed was distilled at a normal pressure using a 40-column column. Unlike the 20 column column experiment, the column was refluxed in the distillation column to keep the temperature equilibrium and received a small amount.

The experimental results are shown in Table 5.

Table 5. Distillation purification experiment results in a 40-stage column

Name	Weight	GC _ .			
		PhOH	o-Cresol	26-Xylenol	etc.
Crude	1,863.1	5.47	32.16	60.68	1.69
Receiver-1	3.6	79.15	16.48	0.24	4.13
Receiver-2	33.2	86.21	12.09	0.09	1.61
Receiver-3	34.4	73.43	25.39	0.62	0.56
Receiver-4	41.0	47.42	52.01	0.28	0.29
Receiver-5	30.9	32.42	64.92	2.50	0.16
Receiver-6	62.9	10.52	83.44	5.96	0.08
Receiver-7	62.2	7.01	80.14	12.79	0.06
Receiver-8	62.1	7.36	78.47	14.17	0.00
Receiver-9	51.0	7.94	88.09	3.97	0.00
Receiver-10	94.8	3.64	87.10	9.26	0.00
Receiver-11	96.7	1.94	79.12	18.93	0.01
Receiver-12	115.5	0.83	57.59	41.58	0.00
Receiver-13	106.0	0.42	47.4	52.18	0.00
Receiver-14	71.3	0.26	46.04	53.70	0.00
Receiver-15	92.6	0.09	34.94	64.97	0.00
Receiver-16	102.3		18.02	81.98	0.00
Receiver-17	97.6		12.01	87.99	0.00
Receiver-18	83.2		7.37	92.63	0.00
Receiver-19	91.6		3.49	96.51	0.00
Receiver-20	99.5		1.09	98.91	0.00
Receiver-21	**64.5**		**0.48**	**99.52**	**0.00**
Receiver-22	**49.3**		**0.19**	**99.81**	**0.00**
Receiver-23	**50.1**		**0.06**	**99.94**	**0.00**
Receiver-24	**33.1**		**0.05**	**99.95**	**0.00**
Residue	**163.0**			**85.23**	**14.77**
Total	1792.4				

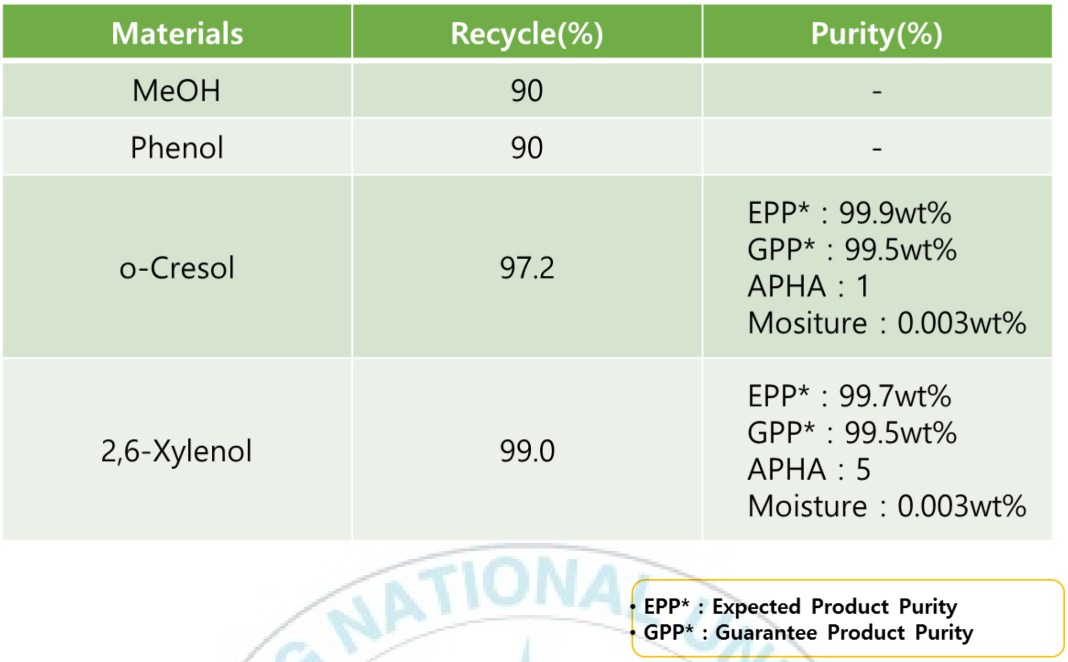
Distillation experiments showed that o-cresol was separated from receiver 9 by 88.09%. In 20th stage, the improvement was considerably improved from 47.8% but the target purity was not reached yet. In the case of 2,6-xylenol, high purity products up to 99.95% were obtained. In order to obtain o-cresol in high purity, the receivers 6 to 11 of Table 7 having a high content of o-cresol were separately separated and a third distillation experiment was conducted using the same 40-stage column.

The experimental results are shown in Table 7, and o-cresol can be obtained up to 99.0% of purity.

Table 6. Third distillation test results of samples with high O-cresol content

Name	Weight	GC			
		PhOH	o-Cresol	26-Xylenol	etc.
Crude	**429.7**	**5.37**	**80.49**	**13.41**	**0.73**
Receiver-1	22.3	73.12	26.73	0.03	0.12
Receiver-2	7.3	48.10	51.48	0.03	0.39
Receiver-3	9.3	19.79	79.76	0.04	0.41
Receiver-4	11.8	7.39	92.44	0.05	0.12
Receiver-5	11.8	3.08	96.79	0.06	0.07
Receiver-6	9.7	2.18	97.53	0.06	0.23
Receiver-7	6.2	2.07	97.61	0.05	0.27
Receiver-8	6.1	3.11	96.54	0.03	0.32
Receiver-9	8.0	1.71	97.52	0.03	0.74
Receiver-10	29.8	0.44	99.43	0.10	0.03
Receiver-11	**28.1**	**0.12**	**99.63**	**0.25**	**0.00**
Receiver-12	29.3	0.05	99.16	0.56	0.23
Receiver-13	27.9	0.03	99.44	0.29	0.24
Receiver-14	24.1	0.02	99.34	0.63	0.01
Receiver-15	22.2	0.01	99.41	0.35	0.23
Total	253.85				

Table 7. Distillation production process results



Materials	Recycle(%)	Purity(%)
MeOH	90	-
Phenol	90	-
o-Cresol	97.2	EPP* : 99.9wt% GPP* : 99.5wt% APHA : 1 Mositure : 0.003wt%
2,6-Xylenol	99.0	EPP* : 99.7wt% GPP* : 99.5wt% APHA : 5 Moisture : 0.003wt%

- **EPP* : Expected Product Purity**
- **GPP* : Guarantee Product Purity**

Chapter III. Conclusion

Ortho alkylated phenolic compound has developed to new catalysts with excellent catalytic properties and confirmed that they can be industrialized into stationary and meteorological processes using developed catalysts. (FeVCoMn(Mg)Ox-Whisker(7wt%)SiO_2(5wt%)

The developed catalyst showed higher activity than the existing catalyst process under very mild reaction conditions.

It was confirmed that products produced using this developed catalyst can be purified with high purity of 99.9% and 2,6-xylenol 99.7%.

For the future work, it need to consider the scale up factor and check the exact life time of catalyst. The effect of molding method should be verified depends on catalyst shape in Pilot scale with examination of economic efficiency of development process.

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