Effect of catalyst modification on hydrodealkylation of aromatic mixtures

Aromatik karışımların hidrodealkilasyonuna katalizör modifikasyonunun etkisi

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**Highlights**
- Catalytic hydrodealkylation of mesitylene in the presence of n-decane was studied.
- Effect of V, Cs, Ni, and Mo on the stability and activity of Cr-Al2O3 was investigated.
- The presence of n-decane accelerated the hydrodealkylation activity of mesitylene.
- V-Cs-Cr-Al2O3 showed most stable activity towards coking along with product selectivity and reactant conversion.

**Graphical Abstract**
The catalyst modified with V and Cs (V-Cs-Cr-Al2O3) has a comparable performance with the commercial catalyst Pyrotol (Houdry, USA) in terms of stability and reactant conversions.

**Aim**
It was aimed to investigate the effect of reaction temperature, WHSV, type and amount of chromium impregnation and promoters such as V, Cs, Ni and Mo to increase the activity and stability of Cr-Al2O3 catalyst to produce BTX by the hydrodealkylation of mesitylene.

**Design & Methodology**
Catalysts were prepared by the impregnation method, tested in a packed bed reactor, and reactants and products were analyzed by gas chromatography.

**Originality**
Cr-Al2O3 katalizörünün aktivitesi ve stabilitesi, V ve Cs ile modifiye edilerek iyileştirilmiştir./ The activity and stability of the Cr-Al2O3 catalyst was improved by modification of V and Cs.

**Findings**
Impregnation of Cr to Al2O3 was optimized, the activity and stability of the Cr-Al2O3 catalyst was improved by the addition of promoters (V, Cs, Ni and Mo).

**Conclusion**
The activity and stability of Cr-Al2O3 was improved by loading the V and Cs promoters to produce BTX from mesitylene.

**Declaration of Ethical Standards**
The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.
Effect of Catalyst Modification on Hydrodealkylation of Aromatic Mixtures

Research Article

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ABSTRACT

Hydrodealkylation of mesitylene in the presence of n-decane to benzene, toluene, and xylenes (BTX) over the promoted Cr2Al2O5 was studied. The effect of reaction temperature, WHSV, impregnation type, and amount of Cr and promoters such as V, Cs, Ni, and Mo on the stability and activity of Cr-Al2O3 was investigated. The addition of n-decane to mesitylene accelerated the hydrodealkylation activity of Cr-Al2O3 because of the formation of methyl- and ethyl-radicals. The catalyst modified with V and Cs (V-Cs-Cr-Al2O3) has a comparable performance with the commercial catalyst Pyrotol (Houdry, USA) in terms of stability, product selectivity, and reactant conversions.

Keywords: Cr-Al2O3, promoter, hydrodealkylation, hydrocracking, BTX.

Aromatik Karışımının Hidrodealkilasyonuna Katalizör Modifikasyonunun Etkisi

Özet

Promoter ile modifiye edilmiş Cr-Al2O3 yüzeyinde mezitilenin benzen, toluen ve ksilene hidrodealkilasyonu n-dekannın varlığındaki çalışılmıştır. Cr-Al2O3 katalizörünün aktivitesine ve stabilitesine, reaksiyon sıcaklığının, WHSV, krom impregnsasyonunun tür ve miktarı ve V, Cs, Ni ve Mo gibi promterlerin etkisi incelenmiştir. N-dekannın mezitilenin eklenmesi, metil ve etil radikallerinin ortasına bulunmasıyla, Cr-Al2O3 katalizörünün hidrodealkilasyon aktivitesini arttırdı. V ve Cs ile modifiye edilmiş katalizör (V-CS-Cr-Al2O3), stabilite, ürün seçiciliği ve girdi dönüşümü arasındaki ticari Pyrotol (Houdry, USA) katalizörü ile karşılaştırılabilir performans gösterdi.

Anahtar Kelimeler: Cr-Al2O3, promoter, hidrodealkilasyon, hidrokraking, BTX.

1. INTRODUCTION

Aromatics are important raw materials for the production of monomers for engineering plastics, polyesters, and phthalates, detergents, pharmaceuticals, etc. Among them, benzene, toluene, and xylenes (BTX) are the three basic aromatic starting reactions. Dickson et al. [1] reported the global demand for benzene (48 x 106 tons) and para-xylene (43 x 106 tons) with growth estimated at 3.5% and 7.5% per year, respectively. The BTX has mainly been produced from catalytic reforming of naphtha and naphtha pyrolysis [2,3]. The other production method of BTX is the hydrodealkylation of C9+ aromatics in the presence of a variety of catalysts such as metal oxides and zeolite catalysts [4–7]. Among studied catalysts, chrome-based catalysts are the most promising catalyst and mostly used in commercial processes [8,9].

Hydrodealkylation of alkyl-aromatics over Cr2O3/Al2O3 is carried under high hydrogen atmosphere (60-70 105 Pa) at high temperatures (T> 600 °C) in order to removal of methyl groups on aromatic rings. However, high temperatures speed up the deactivation of the catalyst through coking formed by dehydrogenation, cyclization, aromatization and condensation reactions. A proper solution for the deactivation of the catalysts during hydrocarbon processing is the incorporation of various metals (Ni, Mo, V, Cs etc.) into the catalysts [7,10–14]. In addition to harsh operating conditions, the inherent acidity of alumina accelerates coking and sintering of the catalyst. To avoid deactivation and sintering, the treatment of the alumina with alkali salts (K or Ca) can decrease the acidity of alumina [15–17].

Based on the aforementioned studies, in this study, the effect of catalyst preparation conditions (impregnation time, Cr concentration) and various promoters (V, Cs, Mo and Ni) on the activity and stability of Cr-Al2O3 in the hydrodealkylation of mesitylene (1,3,5-trimethylbenzene) was investigated. In addition, n-
decane (10 % (mol)) into mesitylene was added in order to enhance hydrodealkylation of alkyl-aromatics via free radicals formed from its hydrocracking [18].

2. MATERIAL and METHOD

Commercial γ-Al₂O₃ used as a support for the preparation of catalysts was provided by Saint-Gobain Norpro and its surface area (BET), total pore volume, and average pore diameter are 208 m²/g, 0.58 cm³/g, and 69 Å, respectively. After calcination of γ-Al₂O₃ at 550 °C for 6 h, acidic sites were neutralized by aqueous solution of 1 wt. % KF to suppress cracking and transalkylation reactions. The neutralized samples were dried at 120 °C and then calcinated in the air at 600 °C for 2 h. The Cr-Al₂O₃-KF catalyst was prepared by impregnation of 15 wt. % of Cr₂O₃. Besides, Cr-Al₂O₃-KF catalysts were prepared with impregnation of the solution containing Cr₂O₃ both 5 wt. % and 10 wt. % (three times) and varied contact times for 2, 12, 24, 48 h with 15 wt. % of Cr₂O₃. In three times impregnation, after each impregnation of 5 wt. % and 10 wt. % of Cr, the samples were dried at 120 °C and calcinated at 600 °C for 2 h. The addition of promoters to Cr-Al₂O₃-KF was performed with aqueous solutions of 15 wt. % Cr₂O₃ containing 1 wt. % of Mo, Ni, V, and Cs using (NH₄)₂MoO₄, Ni(NO₃)₂.6H₂O, H₃VO₃, and CsNO₃ salts.

To determine the hydrodealkylation and hydrocracking activities of the catalysts, a model mixture of 1,3,5-trimethylenzene (mesitylene) and n-decane (90:10(mol)) was used as a feed. The catalytic activity tests were carried out in a conventional fixed-bed flow reactor. The reactor was made of 1 cm O.D. stainless steel tube and 30 cm in length. The catalysts (5 cm³) were filled into the reactor and then added with ceramic particles to evaporate the raw material by heating the feedstock at the reactor inlet. Before activity tests, the catalysts were activated at 600 °C for 5 h with 50 cm³/min of pure H₂ and then tested with mesitylene+n-decane(90:10) mixture in the range of 600-625 °C with 28.4 cm³/min of H₂ (H₂/raw material mol/mol=5). Stabilization tests of catalysts were performed for 6 h with 11.4 cm³/min of H₂ (H₂/raw material mol/mol = 2:1). The ratio of hydrogen to liquid reactants was chosen lower for acceleration of heating. After cooling, the reaction products were separated into gas and liquid products. Liquid products were analysed by OV-101 packed column on ‘Varian 3400’ gas chromatography. In addition, catalytic performances of catalysts prepared were compared to a commercial Pyrotyl H-9430 catalyst (Houdry, USA) under same operating conditions.

The conversion, selectivity and stability of a given product for the hydrodealkylation reaction were defined as follows:

\[ X = \frac{1 - C_{\text{Mo}}}{C_{\text{Mo}}} \]  
\[ S = \frac{Ci}{(C_{\text{Mo}}-C_M)} \]  
\[ \text{Stability} = \frac{X}{X_0} \]

where, Cₘ₀ and Cₘ represent the concentrations of mesitylene at the inlet and outlet of the reactor, respectively, Ci indicates concentration of products such as benzene, toluene and xylene(s) at the outlet of the reactor. X and S show conversion of reactants and selectivity of products, respectively. X₀ indicates an initial conversion.

3. RESULTS AND DISCUSSION

3.1. XRD

The XRD patterns of γ-Al₂O₃ and Cr-Al₂O₃-KF catalysts were reported previously [19]. Namely, the main diffraction lines of γ-Al₂O₃ were observed at about 32, 37, 47 and 66°, indicating the phase of γ-Al₂O₃. Modification of γ-Al₂O₃ with KF insignificantly affected the pattern of γ-Al₂O₃. The impregnation of Cr led to an appearance of peaks at about 24, 36, 50, 56 and 61° due to formation of Cr₂O₃. The Pyrotyl catalyst showed similar XRD pattern to Cr-Al₂O₃ because its content is similar to Cr₂O₃. The increase of Cr loading into γ-Al₂O₃-KF led to an increase in the intensity of Cr₂O₃ due to changing of crystal size. The peaks of Ni, Mo, V and Cs in the XRD pattern of promoted catalysts were not observed due to their low concentrations.

3.2. Activity Results of Catalysts

The effect of n-decane on mesitylene hydrodealkylation over Cr-Al₂O₃ catalysts

The hydrodealkylation of mesitylene in the presence of n-decane over Cr-Al₂O₃-KF was studied and the results obtained were illustrated in Fig. 1. Mesitylene conversion with adding of n-decane increased. While benzene and toluene selectivities increased particularly by adding of n-decane, xylene selectivities decreased as a result of consecutive reactions. Similar findings were reported by Alibeyli et al. [18] that non-aromatic hydrocarbons such as cyclohexane, hexane accelerated the hydrodealkylation reactions via the contribution of methyl and ethyl radicals formed with thermal or catalytic cracking of non-aromatics. It is reported that the hydrodealkylation mechanism of alkyl-benzene involves free radicals for thermal and carbonium ion mechanism in catalytic reactions [20,21], indicating that both mechanisms in the presence of n-decane over Cr-Al₂O₃ occur.

The effect of impregnation conditions on the stability of Cr-Al₂O₃

The effect of impregnation time and impregnation stages on the catalytic performance of Cr-Al₂O₃ was studied and the results obtained were shown in Fig. 2. After 6 h-operation time, the mesitylene conversion on the Cr-
Al₂O₃ prepared with 48 h-impregnation varied from 10% to 8.5%, indicating its high stability. In contrast, Cr (2 h)-Al₂O₃-KF catalyst initially showed the highest activity, but it decreased more rapidly with time on stream, from 14.5% to 8%. The improved stability of the catalyst prepared with 48 h-impregnation times of Cr might be related to homogenous distribution of Cr. For this, Cr-Al₂O₃ catalysts containing 15 wt. % Cr and 30 wt. % Cr were prepared with three stages of Cr and results obtained were shown in Fig. 2. Irrespective of Cr amounts, a gradual impregnation of Cr decreased the stability of catalysts. It can be suggested that for the impregnation of Cr at a single stage the chrome ions interact with alumina and then the calcination leads to stabilization of Cr as a Cr₂O₃ by the alumina support. However, for three-stage impregnation, although first stage impregnation is similar to single-stage impregnation, at second and third stages, Cr ions interact not only alumina support but also Cr₂O₃ and these interactions might affect homogenously distribution and oxidation states (Cr₂O₃, CrO, etc.) of Cr.

For different impregnation times, selectivity results of BTX and stability of catalysts are listed in Table 1. For incorporating time of Cr to Al₂O₃-KF, the stability of catalysts for 12 h and 48 h is better than those of 2 h based on toluene (Sₜ/ₚ) and benzene (Sₜ/ᵦₚ) formation. These findings might be due to more homogenously dispersion of Cr on Al₂O₃-KF. The impregnation time longer than 12 h has no further positive effect on the the selectivities of BTX. Furthermore, activity and long-term stability results of catalysts containing 15 wt. % Cr and 30 wt. % Cr prepared in three steps with solutions of 5 wt. % and 10 wt. % Cr to improve the dispersion of Cr on Al₂O₃-KF showed that gradual impregnation of chromic insignificantly altered the activity and stability of the catalysts. The increase of Cr amount from 15 wt. % to 30 wt. % caused a decrease in the mesitylene conversion by a decrease in the active surface area. This was also reported by Delahay and Duprez [22] that well-dispersed catalysts lead to the electron affinity of the metal, which accelerates to activity and selectivity of the catalyst. However, in this study, homogenously dispersion of Cr on the surface of Al₂O₃ insignificantly improved either catalytic activity or catalyst stability.
Effect of various promoters to Cr-Al<sub>2</sub>O<sub>3</sub> catalyst

A probable solution for the deactivation of catalysts during heavy aromatics processing is to incorporate various metals to the catalyst to hydrogenate polyaromatic coke precursors. Therefore, the hydrodealkylation results of mesitylene over Cr-Al<sub>2</sub>O<sub>3</sub> supported with 1 wt. % of Cs, V, Mo and Ni are shown in Fig. 3. Mesitylene and n-decane conversions increased above 550 °C. The addition of Ni into Cr-Al<sub>2</sub>O<sub>3</sub> increased significantly alkyl-benzene conversion compared with other catalysts. However, it is an undesirable metal for hydrodealkylation of mesitylene due to strong hydrocracking activity for benzene[23]. Moreover, almost all of the catalysts showed almost 98-100 % hydrocracking activity of n-decane as seen in Fig. 3. Although the hydrocracking of n-decane on the Cr-Al<sub>2</sub>O<sub>3</sub> and Mo-Cr-Al<sub>2</sub>O<sub>3</sub> was accelerated between 500 and 550 °C, it increased on the other catalysts above 550 °C. It might be depended on the catalyst type, which was reported by Roussel et al. [24] that the transformation of n-decane occurred through two types of reactions: a bifunctional transformation and a "direct cracking" reaction. The bifunctional mechanism occurs not only on silica-alumina support with low acidity which is lowered by ammonia adsorption, but also at a high reaction temperature [25,26]. Based on these findings, it can be pointed out that n-decane converts to gas products with a bifunctional mechanism on catalysts contain Cr and Al<sub>2</sub>O<sub>3</sub>-KF. Moreover, Fig. 4 shows a comparison of mesitylene conversions onto promoted Cr-Al<sub>2</sub>O<sub>3</sub>. While the promoted catalysts showed remarkable low catalytic activity at 550 °C or above, their activities relatively increased above 600 °C. Tatsui et al. [27] reported that V and Mo alumina catalysts show considerable stable activity in dealkylation of heavy aromatic oils. Therefore, the variations in the stability of promoted Cr-Al<sub>2</sub>O<sub>3</sub> catalysts were investigated.

Table 1. Selectivity variations of BTX with time on the stream for hydrodealkylation of mesitylene in the presence of n-decane over Cr-Al<sub>2</sub>O<sub>3</sub>-KF catalysts.

| Samples | t (h) | S<sub>Benzene</sub>% | S<sub>B</sub>/S<sub>Bo</sub> | S<sub>T</sub>/S<sub>To</sub> | S<sub>X</sub>/S<sub>Xo</sub> | S<sub>XYlenes</sub>% | S<sub>T</sub>/S<sub>To</sub> | S<sub>X</sub>/S<sub>Xo</sub> |
|---------|------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Cr-Al<sub>2</sub>O<sub>3</sub>-KF | 2 | 13.6-7.5 | 0.55 | 17.2-13.2 | 0.76 | 69.2-79.0 | 1.1 |
| Cr-Al<sub>2</sub>O<sub>3</sub>-KF | 12 | 11.4-8.7 | 0.76 | 17.4-14.3 | 0.82 | 71.7-77.0 | 1.0 |
| Cr-Al<sub>2</sub>O<sub>3</sub>-KF | 24 | 12.4-8.3 | 0.67 | 19.0-14.0 | 0.74 | 68.3-78.0 | 1.1 |
| Cr-Al<sub>2</sub>O<sub>3</sub>-KF | 48 | 11.3-7.4 | 0.65 | 16.0-12.5 | 0.78 | 72.7-80.0 | 1.1 |
| Cr-Al<sub>2</sub>O<sub>3</sub>-KF | 15 wt % Cr<sup>a</sup> | 12 | 11.2-6.1 | 0.54 | 19.2-11.8 | 0.61 | 69.5-82.0 | 1.2 |
| Cr-Al<sub>2</sub>O<sub>3</sub>-KF | 30 wt % Cr<sup>a</sup> | 12 | 13.6-7.5 | 0.55 | 17.2-13.2 | 0.77 | 69.0-79.0 | 1.1 |

<sup>a</sup>15 wt % Cr and 30 wt % Cr were impregnated to Al<sub>2</sub>O<sub>3</sub>-KF with three steps. <sup>b</sup>S<sub>B</sub>/S<sub>Bo</sub>, S<sub>T</sub>/S<sub>To</sub>, S<sub>X</sub>/S<sub>Xo</sub>: ratio of product selectivity in the end of 6 h to initial product selectivity benzene, toluene and xylene, respectively.

Conversion curves for mesitylene over catalysts containing Ni and V decreased rapidly with time on stream as seen in Fig. 4. Contrary to the deactivation of V-Cr-Al<sub>2</sub>O<sub>3</sub>, it showed remarkable high initial activity. Cr-Al<sub>2</sub>O<sub>3</sub> and Cs-Cr-Al<sub>2</sub>O<sub>3</sub> catalysts showed lower initial activity, but almost no loss of activity with time on stream. The stability of promoted catalysts evaluated by the conversion of mesitylene versus time on stream followed the trend: Cs-Cr-Al<sub>2</sub>O<sub>3</sub> < Cr-Al<sub>2</sub>O<sub>3</sub> < Mo-Cr- 
Al<sub>2</sub>O<sub>3</sub> < V-Cr-Al<sub>2</sub>O<sub>3</sub> < Ni-Cr-Al<sub>2</sub>O<sub>3</sub>. According to this trend, the effect of V and Cs concentrations on activity and selectivity of Cr-Al<sub>2</sub>O<sub>3</sub> were investigated in detail. Fig. 5 shows deactivation curves of catalysts containing Cs in the various concentrations with time on stream for hydrodealkylation of mesitylene. All Cr-Cr-Al<sub>2</sub>O<sub>3</sub> catalysts almost showed the same activity. The catalyst containing 2.5 wt % Cs showed relatively stable activity. When the influence of vanadium content on the deactivation behavior of Cs-Cr-Al<sub>2</sub>O<sub>3</sub> was studied, it was found that V-Cr-Al<sub>2</sub>O<sub>3</sub> catalysts showed higher hydrodealkylation activity than Cs-Cr-Al<sub>2</sub>O<sub>3</sub> and the highest initial mesitylene conversion was found on the catalyst containing 1 wt. % V as seen in Fig. 5.

The Cr-Al<sub>2</sub>O<sub>3</sub>-KF catalysts (V-Cs-Cr-Al<sub>2</sub>O<sub>3</sub>) containing both 1 wt. % V and 2.5 wt. % Cs were prepared and its activity, selectivity and stability were compared with Cr-Al<sub>2</sub>O<sub>3</sub>-Pyrotol, V-Cr-Al<sub>2</sub>O<sub>3</sub> (1 wt. % V), and Cs-Cr-Al<sub>2</sub>O<sub>3</sub> (2.5 wt. %). The results obtained are compared in Fig. 5. The stability of the catalysts decreased in the sequence of Pyrotol >Cs-V-Cr-Al<sub>2</sub>O<sub>3</sub> >Cr-Al<sub>2</sub>O<sub>3</sub> >Cs-Cr-Al<sub>2</sub>O<sub>3</sub> > V-Cr-Al<sub>2</sub>O<sub>3</sub>. Cr-V-Cr-Al<sub>2</sub>O<sub>3</sub> catalyst is almost as stable as the commercial Pyrotol catalyst tested under the same conditions for hydrodealkylation of mesitylene. However, V-Cr-Al<sub>2</sub>O<sub>3</sub>, Cs-Cr-Al<sub>2</sub>O<sub>3</sub> and Cr-Al<sub>2</sub>O<sub>3</sub> showed higher mesitylene conversion than commercial Pyrotol catalyst. Based on selectivity results, Cs-V-Cr-Al<sub>2</sub>O<sub>3</sub> and Cs-Cr-Al<sub>2</sub>O<sub>3</sub> showed higher benzene and toluene selectivities and lower xylenes selectivities than Cr-Al<sub>2</sub>O<sub>3</sub> and V-Cr-Al<sub>2</sub>O<sub>3</sub>. Similar to the conversion of mesitylene, the Cs-V-Cr catalyst has comparable BTX selectivity values to the Pyrotol catalyst.
Fig. 3. Effect of temperature on catalytic performance of promoted Cr-Al₂O₃ catalysts. Reaction conditions: WHSV= Q₀/Vcatalyst =0.4 h⁻¹, pressure: atmospheric pressure, H₂/raw material (mesitylene+ n-decane=90:10 mol/mol)= 5.0 mol/mol (Q₀= initial flow rate of liquid reactants).
Fig. 4. Effect of time on stream on catalytic performance of promoted Cr-Al₂O₃ catalysts. Reaction conditions: WHSV=0.4 h⁻¹, pressure: atmospheric pressure, H₂/raw material (mesitylene+ n-decane=90:10 mol/mol) = 2.0 mol/mol.

Fig. 5. The effect of Cs and V content on activity and stability of Cr-Al₂O₃-KF catalyst. Reaction conditions: T=650 °C, WHSV=0.4 h⁻¹, P= atmospheric pressure, H₂/raw material (mesitylene+ n-decane=90:10 mol/mol): 2.0 mol/mol.
Fig. 6. Comparison of stabilities and activities of the catalysts. Reaction conditions: WHSV=0.4 h⁻¹, P: atmospheric pressure, T=650 °C, H₂/raw material (mesitylene+ n-decane =90:10 mol/mol)= 2.0 mol/mol.

Coke content of catalysts
Coke amount of all catalysts were determined with DTA-TGA. According to DTA results, coke characterization of all catalysts is the same and it can be burned completely at 400-700 °C with air. Coke content of catalysts obtained from TGA curves can be listed as following: 33.4 % for Ni-Cr-Al₂O₃ > 21.6 % for Mo-Cr-Al₂O₃ > 15.8% for V-Cr-Al₂O₃ > 11.8% for Cs-V-Cs-Cr-Al₂O₃ > 9.8% for Pyrothol. Cs-V-Cs-Al₂O₃ and Cs-Cr-Al₂O₃ catalysts have lower coke contents, which is comparable with Pyrothol catalyst and are in accordance with their stability results in Figs 4-6.

4. CONCLUSION
Effect of the preparation conditions of Cr-Al₂O₃ catalyst and the addition of promoters (Ni, Mo, V, and Cs) on the activity and stability of Cr-Al₂O₃ catalyst for hidrodealkylation of mesitylene in the presence of n-decane was studied. The highest activity, selectivity, and stability were found on the catalyst containing 15 wt. % of Cr impregnated at the single-stage with 48 h impregnation. Whereas the highest mesitylene conversion was obtained with Ni-Cr-Al₂O₃ and V-Cr-Al₂O₃ catalysts, the highest stability and the lowest coke content were determined on Cr-Al₂O₃ containing 2.5 wt. % Cs after 6 h-time on stream. V-Cs-Cr-Al₂O₃ catalysts showed comparable activity, selectivity, and stability to commercial Pyrothol catalyst.

DECLARATION OF ETHICAL STANDARDS
The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

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