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# Effect of catalyst modification on hydrodealkylation of aromatic mixtures

## *Aromatik karışımların hidrodealkilasyonuna katalizör modifikasyonun etkisi*

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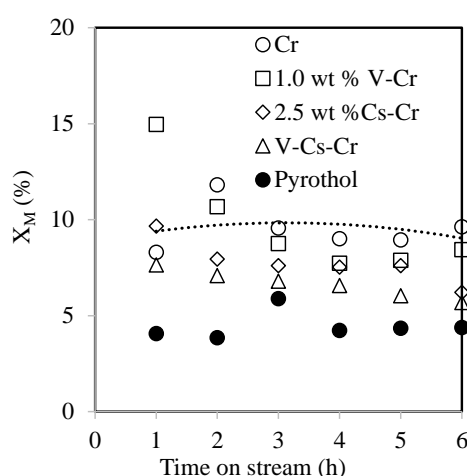
# Effect of Catalyst Modification on Hydrodealkylation of Aromatic Mixtures

## 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-Al<sub>2</sub>O<sub>3</sub> was investigated.
- ❖ The presence of *n*-decane accelerated the hydrodealkylation activity of mesitylene.
- ❖ V-Cs-Cr-Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub>) has a comparable performance with the commercial catalyst Pyrotol (Houdry, USA) in terms of stability and reactant conversions.



**Figure.** Comparison of activities and stabilities of the catalysts

## 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-Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub> katalizörünün aktivitesi ve stabilitesi, V ve Cs ile modifiye edilerek iyileştirilmiştir./ The activity and stability of the Cr-Al<sub>2</sub>O<sub>3</sub> catalyst was improved by modification of V and Cs.

## Findings

Impregnation of Cr to Al<sub>2</sub>O<sub>3</sub> was optimized, the activity and stability of the Cr-Al<sub>2</sub>O<sub>3</sub> catalyst was improved by the addition of promoters (V, Cs, Ni and Mo).

## Conclusion

The activity and stability of Cr-Al<sub>2</sub>O<sub>3</sub> 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 Cr-Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub> was investigated. The addition of n-decane to mesitylene accelerated the hydrodealkylation activity of Cr-Al<sub>2</sub>O<sub>3</sub> because of the formation of methyl- and ethyl-radicals. The catalyst modified with V and Cs (V-Cs-Cr-Al<sub>2</sub>O<sub>3</sub>) has a comparable performance with the commercial catalyst Pyrotol (Houdry, USA) in terms of stability, product selectivity, and reactant conversions.

**Keywords:** Cr-Al<sub>2</sub>O<sub>3</sub>, promoter, hydrodealkylation, hydrocracking, BTX.

## Aromatik Karışımlarının Hidrodealkilasyonuna Katalizör Modifikasyonun Etkisi

### ÖZ

Promoter ile modifiye edilmiş Cr-Al<sub>2</sub>O<sub>3</sub> yüzeyinde mezitilenin benzen, toluen ve ksilene hidrodealkilasyonu n-dekanın varlığında çalışılmıştır. Cr-Al<sub>2</sub>O<sub>3</sub> katalizörünün aktivitesine ve stabilitesine, reaksiyon sıcaklığının, WHSV, krom impregnasyonunun tür ve miktarı ve V, Cs, Ni ve Mo gibi promoterların etkisi incelenmiştir. N-dekanın mezitilene eklenmesi, metil ve etil radikallerinin ortamda bulunmasıyla, Cr-Al<sub>2</sub>O<sub>3</sub> katalizörünün hidrodealkilasyon aktivitesini artırdı. V ve Cs ile modifiye edilmiş katalizör (V-Cs-Cr-Al<sub>2</sub>O<sub>3</sub>), stabilize, ürün seçiciliği ve girdi dönüşümü için ticari Pyrotol (Houdry, USA) katalizörü ile karşılaştırılabilir performans gösterdi.

**Anahtar Kelimeler:** Cr-Al<sub>2</sub>O<sub>3</sub>, promoter, hidrodealkilasyon, hidrokraking, BTX.

### 1. INTRODUCTION

Aromatics are important raw materials for the production of monomers for engineering plastics, polyester, and phthalates, detergents, pharmaceuticals, etc. Among them, benzene, toluene, and xylenes (BTX) are the three basic aromatic starting reactants. Dickson et al. [1] reported the global demand for benzene (48 x 10<sup>6</sup> tons) and para-xylene (43 x 10<sup>6</sup> 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 C<sub>9+</sub> 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 Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> is carried under high hydrogen atmosphere (60-70 10<sup>5</sup>

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-Al<sub>2</sub>O<sub>3</sub> 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].

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## 2. MATERIAL and METHOD

Commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 m<sup>2</sup>/g, 0.58 cm<sup>3</sup>/g, and 69 Å, respectively. After calcination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub>-KF catalyst was prepared by impregnation of 15 wt. % of CrO<sub>3</sub>. Besides, Cr-Al<sub>2</sub>O<sub>3</sub>-KF catalysts were prepared with impregnation of the solution containing CrO<sub>3</sub> both 5 wt. % and 10 wt. % (three times) and varied contact times for 2, 12, 24, 48 h with 15 wt. % of CrO<sub>3</sub>. In three times impregnation, after each impregnation of 5 wt. % and 10 wt. % of Cr, the samples were dried at 120 °C and calcined at 600 °C for 2 h. The addition of promoters to Cr-Al<sub>2</sub>O<sub>3</sub>-KF was performed with aqueous solutions of 15 wt. % CrO<sub>3</sub> containing 1 wt. % of Mo, Ni, V, and Cs using (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, H<sub>4</sub>VO<sub>3</sub>, and CsNO<sub>3</sub> salts.

To determine the hydrodealkylation and hydrocracking activities of the catalysts, a model mixture of 1,3,5-trimethylbenzene (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 cm<sup>3</sup>) were filled to 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 cm<sup>3</sup>/min of pure H<sub>2</sub> and then tested with mesitylene+n-decane(90:10) mixture in the range of 500-625 °C with 28.4 cm<sup>3</sup>/min of H<sub>2</sub> (H<sub>2</sub>/raw material (mol/mol)=5:1). Stabilization tests of catalysts were performed for 6 h with 11.4 cm<sup>3</sup>/min of H<sub>2</sub> (H<sub>2</sub>/raw material (mol/mol) =2:1). The ratio of hydrogen to liquid reactants was chosen lower for acceleration of coking. After cooling, the reaction products were separated into gas and liquid products. Liquid products were analysed by OV-101 packed column in 'Varrian 3400' gas chromatography. In addition, catalytic performances of catalysts prepared were compared to a commercial Pyrotol 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:

$$X = (1 - C_{M0})/C_{M0} \quad (1)$$

$$S = C_i / (C_{M0} - C_M) \quad (2)$$

$$\text{Stability} = X/X_0 \quad (3)$$

where, C<sub>M0</sub> and C<sub>M</sub> represent the concentrations of mesitylene at the inlet and outlet of the reactor, respectively, C<sub>i</sub> indicates concentration of products such as benzene, toluene and xylenes) at the outlet of the reactor. X and S show conversion of reactants and

selectivity of products, respectively. X<sub>0</sub> indicates an initial conversion.

A DTA/TGA instrument (Seteram) was used to determine the amount of coke formed in the catalysts. The used catalysts were heated up to 1050 °C under the air atmosphere with a ramp of 10 K/min and weight loss of samples was measured.

XRD patterns were obtained by using a Rigaku diffractometer operated at 35 kV and 15 mA employing Ni-filtered Cu K radiation (1.54 Å). The scanning range of samples is in the range of 0-70° with a step size of 2°.

## 3. RESULTS AND DISCUSSION XRD

The XRD patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Cr-Al<sub>2</sub>O<sub>3</sub>-KF catalysts were reported previously [19]. Namely, the main diffraction lines of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were observed at about 32, 37, 47 and 67°, indicating the phase of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Modification of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with KF insignificantly affected the pattern of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The impregnation of Cr led to an appearance of peaks at about 24, 36, 41, 50, 56 and 61 ° due to formation of Cr<sub>2</sub>O<sub>3</sub>. The Pyrothol catalyst showed similar XRD pattern to Cr-Al<sub>2</sub>O<sub>3</sub> because its content is similar to Cr-Al<sub>2</sub>O<sub>3</sub>. The increase of Cr loading into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-KF led to an increase in the intensity of Cr<sub>2</sub>O<sub>3</sub> 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.

### Activity Results of Catalysts

#### *The effect of n-decane on mesitylene hydrodealkylation over Cr-Al<sub>2</sub>O<sub>3</sub> catalysts*

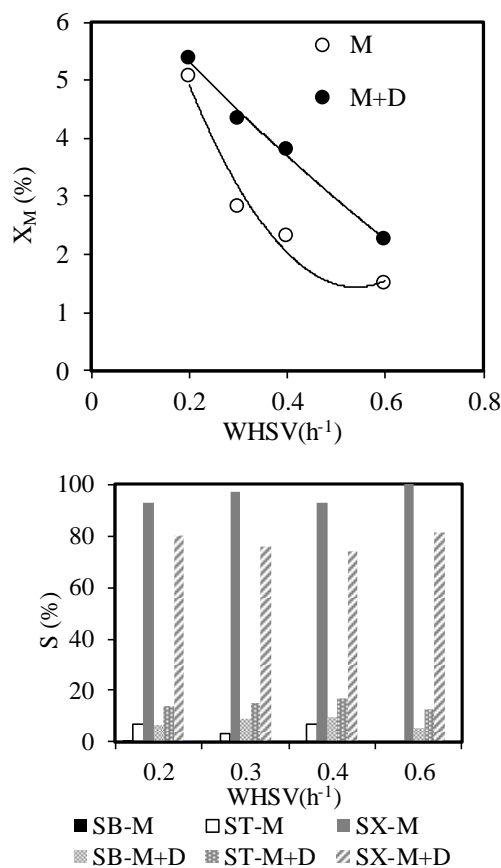
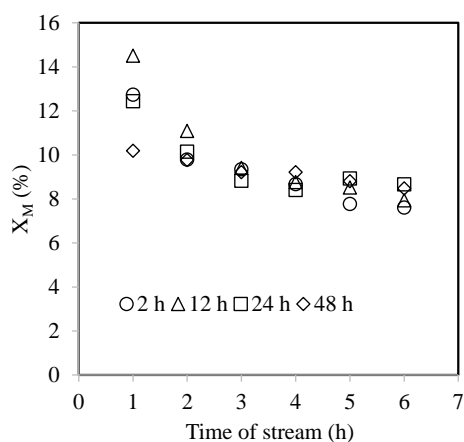
The hydrodealkylation of mesitylene in the presence of n-decane over Cr-Al<sub>2</sub>O<sub>3</sub>-KF was studied and the results obtained were illustrated in Fig. 1. Mesitylene conversion with adding of n-decane increased. While benzene and toluene selectivities increased particularly by adding of n-decane, xylene selectivities decreased as a result of consecutive reactions. Similar findings were reported by Alibeyli et al. [18] that non-aromatics 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-Al<sub>2</sub>O<sub>3</sub> occur.

#### *The effect of impregnation conditions on the stability of Cr-Al<sub>2</sub>O<sub>3</sub>*

The effect of impregnation time and impregnation stages on the catalytic performance of Cr-Al<sub>2</sub>O<sub>3</sub> was studied and the results obtained were shown in Fig. 2. After 6 h-operating time, the mesitylene conversion on the Cr-Al<sub>2</sub>O<sub>3</sub> prepared with 48 h-impregnation varied from 10% to 8.5 %, indicating its high stability. In contrast, Cr (2 h)-Al<sub>2</sub>O<sub>3</sub>-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-Al<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub> 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 Cr<sub>2</sub>O<sub>3</sub> and these interactions might affect homogeneously distribution and oxidation states (Cr<sub>2</sub>O<sub>3</sub>, CrO, etc.) of Cr.

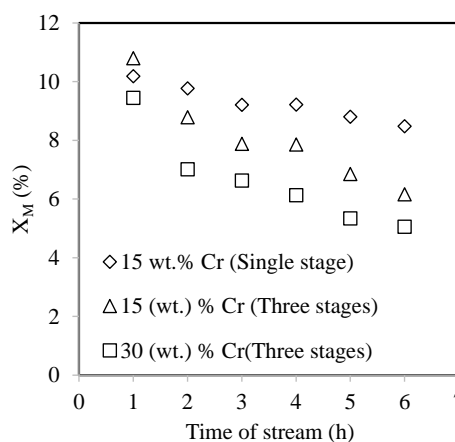
For different impregnation times, selectivity results of BTX and stability of catalysts are listed in Table 1. For incorporating time of Cr to Al<sub>2</sub>O<sub>3</sub>-KF, the stability of catalysts for 12 h and 48 h is better than those of 2 h based on toluene (S<sub>T</sub>/S<sub>T0</sub>) and benzene (S<sub>B</sub>/S<sub>B0</sub>) formation. These findings might be due to more homogeneously dispersion of Cr on Al<sub>2</sub>O<sub>3</sub>-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 Al<sub>2</sub>O<sub>3</sub>-KF showed that gradual impregnation of chrome 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, homogeneously dispersion of Cr on the surface of Al<sub>2</sub>O<sub>3</sub> insignificantly improved either catalytic activity or catalyst stability.



**Fig 1.** Conversion of mesitylene and selectivity of BTX as a function of WHSV in the presence of n-decane over Cr-Al<sub>2</sub>O<sub>3</sub> at 600 °C. M: Mesitylene; D: N- decane; B: Benzene; T= Toluene; X: Xylene.

*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



**Fig. 2.** Conversion of mesitylene as a function of time-on-stream over Cr-Al<sub>2</sub>O<sub>3</sub> catalysts prepared with different contact times and different amounts of Cr to Al<sub>2</sub>O<sub>3</sub>-KF under atmospheric pressure for H<sub>2</sub>/raw material (mol/mol) =2 at 625 °C.

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 adding 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 reaction: 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 as stated above, their activities relatively increased above 600 °C. Tsutsui et al. [27] reported that V and Mo alumina catalysts show considerable stable activity for 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. Conversion curves for mesitylene over catalysts containing Ni and V decreased rapidly with time on

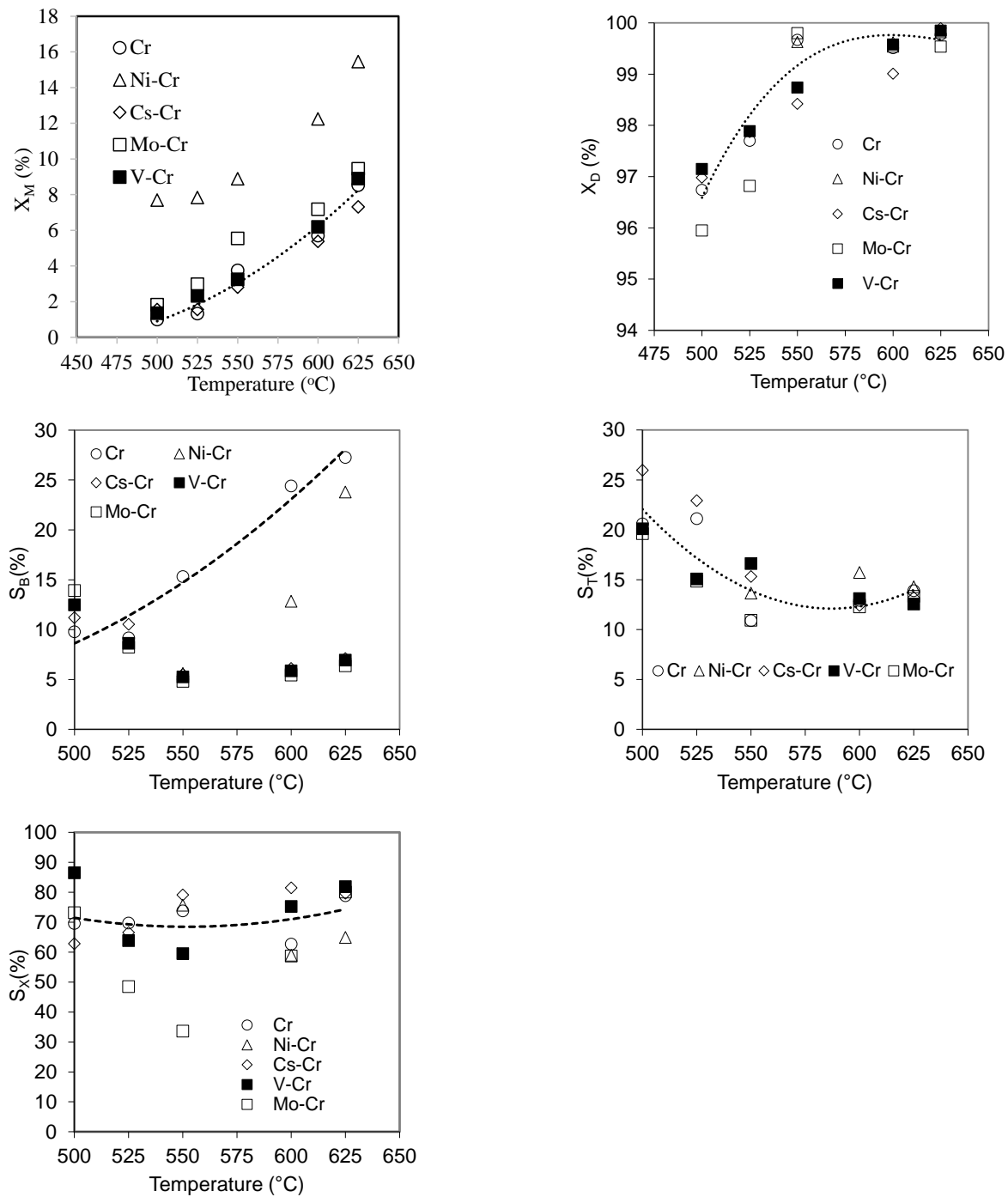
stream as seen in Fig. 4. Contrary to the deactivation of V-Cr-Al<sub>2</sub>O<sub>3</sub>, it showed remarkable high initial activity. Cr-Al<sub>2</sub>O<sub>3</sub> and Cs-Cr-Al<sub>2</sub>O<sub>3</sub> catalysts showed lower initial activity, but almost no loss of activity with time on stream. The stability of promoted catalysts evaluated by the conversion of mesitylene versus time on the 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 Cs-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 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> catalyst (V-Cs-Cr-Al<sub>2</sub>O<sub>3</sub>) containing both 1.0 wt. % V and 2.5 wt. % Cs was 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. 6. 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>. Cs-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.

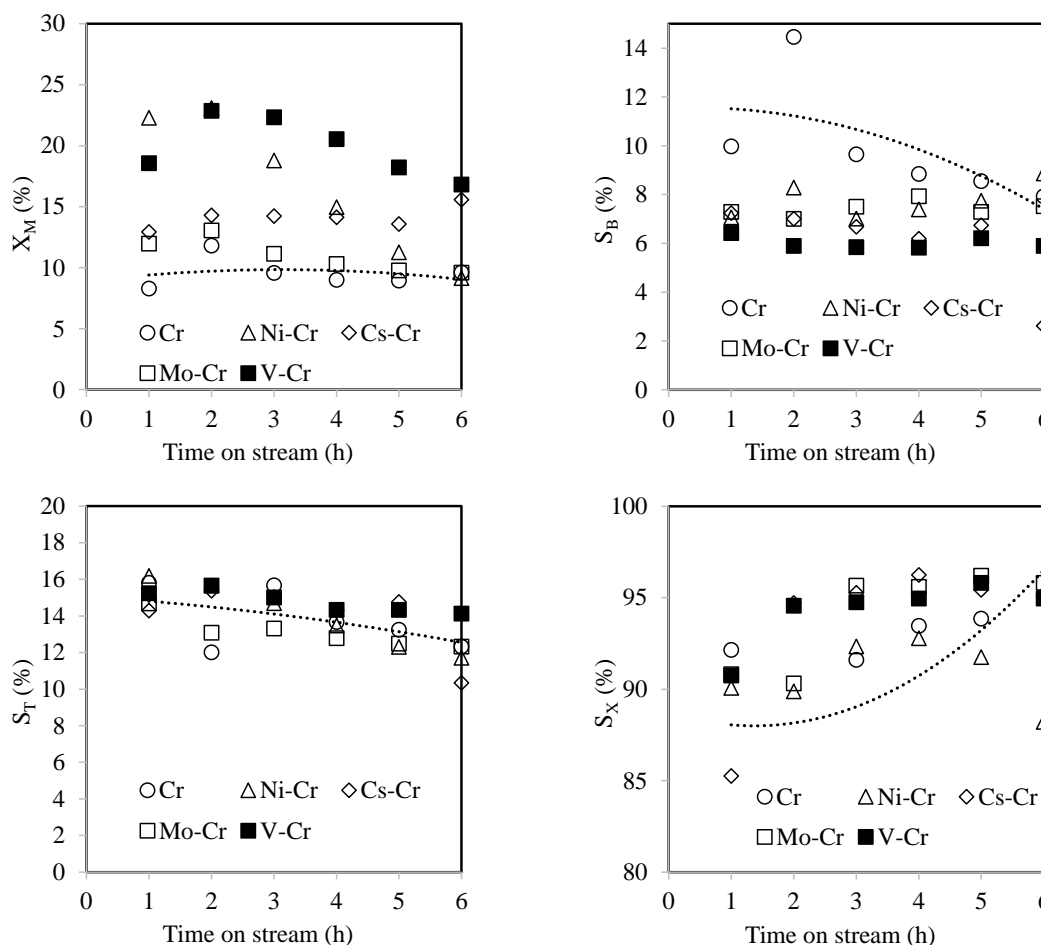
**Table 1.** Selectivity variations of BTX with time on the stream for hydrodealkylation of mesitylene in the presence of n-decane over Cr-Al<sub>2</sub>O<sub>3</sub>-KF catalysts.

Samples	t (h)	S <sub>Benzene</sub> %	S <sub>B</sub> /S <sub>B0</sub> <sup>b</sup>	S <sub>Toluene</sub> %	S <sub>T</sub> /S <sub>T0</sub> <sup>b</sup>	S <sub>Xylenes</sub> %	S <sub>X</sub> /S <sub>X0</sub> <sup>b</sup>
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	71.1-77.0	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

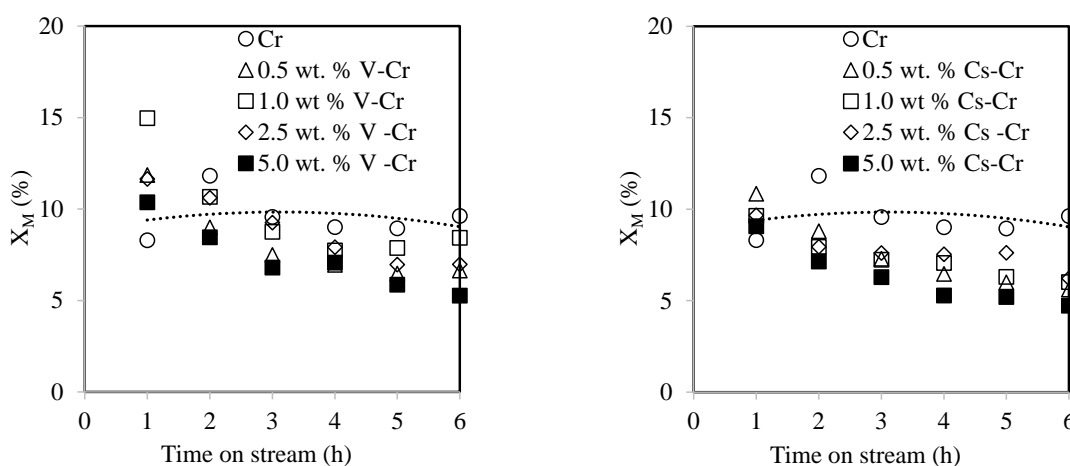
<sup>a</sup>15 wt % Cr and 30 wt % Cr were impregnated to Al<sub>2</sub>O<sub>3</sub>-KF with three steps. <sup>b</sup>S<sub>B</sub>/S<sub>B0</sub>, S<sub>T</sub>/S<sub>T0</sub>, S<sub>X</sub>/S<sub>X0</sub>: ratio of product selectivity in the end of 6 h to initial product selectivity benzene, toluene and xylenes, respectively.



**Fig. 3.** Effect of temperature on catalytic performance of promoted Cr-Al<sub>2</sub>O<sub>3</sub> catalysts. Reaction conditions: WHSV= Q<sub>0</sub>/V<sub>catalyst</sub>=0.4 h<sup>-1</sup>, pressure: atmospheric pressure, H<sub>2</sub>/raw material (mesitylene+ n-decane=90:10 mol/mol)= 5.0 mol/mol (Q<sub>0</sub>= initial flow rate of liquid reactants).

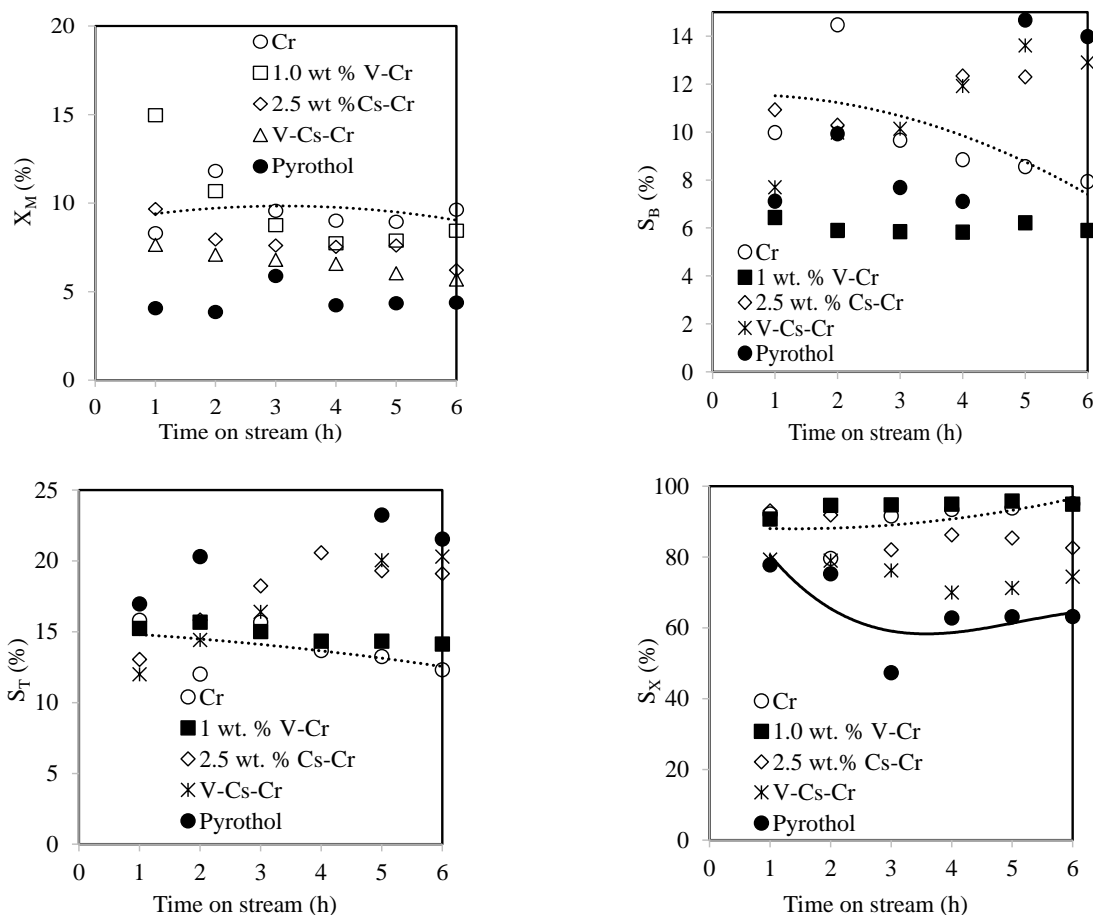


**Fig. 4.** Effect of time on stream on catalytic performance of promoted Cr-Al<sub>2</sub>O<sub>3</sub> catalysts. Reaction conditions: WHSV=0.4 h<sup>-1</sup>, pressure: atmospheric pressure, H<sub>2</sub>/raw material (mesitylene+ n-decane=90:10 mol/mol) = 2.0 mol/mol.



**Fig. 5.** The effect of Cs and V content on activity and stability of Cr-Al<sub>2</sub>O<sub>3</sub>-KF catalyst Reaction conditions: T= 650 °C, WHSV=0.4 h<sup>-1</sup>, P= atmospheric pressure, H<sub>2</sub>/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<sup>-1</sup>, P: atmospheric pressure, T=650 °C, H<sub>2</sub>/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-Al<sub>2</sub>O<sub>3</sub> > 21.6 % for Mo-Cr-Al<sub>2</sub>O<sub>3</sub> > 15.8% for V-Cr-Al<sub>2</sub>O<sub>3</sub> > 11.8% for Cs-V-Cr-Al<sub>2</sub>O<sub>3</sub> > 10.7 % for Cs-Cr-Al<sub>2</sub>O<sub>3</sub> > 9.8% for Pyrothol. Cs-V-Cr-Al<sub>2</sub>O<sub>3</sub> and Cs-Cr-Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub> catalyst and the addition of promoters (Ni, Mo, V, and Cs) on the activity and stability of Cr-Al<sub>2</sub>O<sub>3</sub> catalyst for hydrodealkylation 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-Al<sub>2</sub>O<sub>3</sub> and V-Cr-Al<sub>2</sub>O<sub>3</sub> catalysts, the highest stability and the lowest coke

content were determined on Cr-Al<sub>2</sub>O<sub>3</sub> containing 2.5 wt. % Cs after 6 h-time on stream. V-Cs-Cr-Al<sub>2</sub>O<sub>3</sub> 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.

#### AUTHORS' CONTRIBUTIONS

**Ayten ATEŞ:** / Performed the experiments, analyse the results and wrote the manuscript.

**Hasip YENİOAVA:** Conceptualization and analyse the results

**Rafiq ALİBEYLİ:** Analyse the results and wrote the manuscript.

#### CONFLICT OF INTEREST

There is no conflict of interest in this study.

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