Hydride transfer between a phenolic surface pool and reactant paraffins in the catalytic cracking of m-cresol/hexanes mixtures over HY zeolites

Anh T. To and Daniel E. Resasco*

School of Chemical, Biological and Materials Engineering, University of Oklahoma,
Norman, OK 73019, USA

16 April 2015

* Corresponding Author:

Daniel E. Resasco

Phone: (405) 325-4370

E-mail: resasco@ou.edu

Abstract

The effect of the presence of m-cresol on the monomolecular and bimolecular pathways of paraffin conversion has been studied over the bare surface of an HY zeolite in a micro-pulse reactor. The influence of m-cresol is interpreted in terms of the two types of sites present in pristine HY zeolites pre-treated at high temperatures. These two types of sites are described as normal Brønsted acid sites and synergistic sites. The latter have higher activity and favor the monomolecular path. They are more severely deactivated than the former by the presence of m-cresol, especially at low reactant concentrations, where the monomolecular reaction is the dominating path. At higher reactant concentrations, hydride transfer from paraffins becomes important and promotes desorption of the phenolic compounds, which hinders the deactivating effect of m-cresol and the growth of a surface phenolic pool, typically formed by condensation reactions of phenolics. Hydride transfer between the paraffinic feed and the surface carbenium ions is also reduced by the presence of m-cresol.

Keywords: HY zeolite, m-cresol, hexanes, co-feeding, phenolic pool, hydride transfer, deactivation, coke formation.

1. Introduction

Among several strategies for biomass upgrading proposed during the last few years, co-processing biomass-derived feedstocks with intermediate streams in refinery units has been considered as a techno-economically attractive option since utilizing existing refinery infrastructure would help diminishing investment costs for bio-fuel production [1-5]. Moreover, the characteristically large capacity of the refining industry, would allow processing very large volumes of biomass-derived feedstocks, such as stabilized pyrolysis-oils, which would have a significant impact in the incorporation of biomass in the transportation fuel market. Possible refinery injection points include [3-457] hydrotreating (HDT), hydrodesulfurization (HDS), and [1-23, 5, 8, 9] fluid catalytic cracking (FCC) units. This processing pathway has been proposed to be techno-economically more advantageous than those involving lignocellulosic biomass gasification or processing of vegetable oils [2-34].

In this context, the FCC process represents a promising pathway for co-feeding of biomass-derived compounds since FCC is one of the largest refinery processes, it exhibits high flexibility for handling varying feedstocks, and does not require H_2 , a valuable commodity in refinery operations. Previous studies have investigated the influence of co-processing hydrotreated pyrolysis oils with typical FCC feedstocks, such as long residue and vacuum gasoil (VGO) [1, 2, 8]. These reports have concluded that co-processing results in much lower yields of dry gas and coke compared to direct processing of the same capacity of pyrolysis oil. Analysis of the gasoline fraction showed that there were more branched paraffin and short benzene derivatives produced at the expense of linear paraffin in comparison to the reaction of the hydrocarbon feed alone. Enhanced formation of CO and CO_2 in the gas product, as well as

the reduction in the oxygen content in the liquid fractions, indicated that at least some deoxygenation of the biomass-derived products took place. At the same time, the lower H₂ production observed in these studies indicated that more efficient hydrogen transfer between hydrocarbons and oxygenates occurred compared to the reaction only involving hydrocarbons.

It is well known that the liquid product (bio-oil) derived from pyrolysis of lignocellulosic biomass comprises a large fraction of phenolic compounds including cresols, guaiacol, vanillin, and eugenol, which contain various oxygen functionalities such as hydroxyl, methoxyl, and carbonyl groups. They are known to be much more refractory to upgrading than other oxygenates in the bio-oil and, in most stabilized bio-oils, remain unconverted [10-13]. Moreover, they tend to accelerate deactivation due to enhanced coke formation and strong adsorption on acid sites of the zeolites [14-17]. Therefore, to get a full assessment of the pros and cons of the co-processing strategy a detailed investigation of the behavior of these phenolic compounds in zeolites and their influence in the deactivation of hydrocarbons cracking catalysts is necessary.

In several studies of model compound reactions over zeolites, Graca et al. [14,15,18, 19] explored the influence of the presence of phenolic compounds in hydrocarbon cracking. In these studies, either phenol or guaiacol was co-fed with n-heptane or methylcyclohexane over HY and HZSM-5 zeolites. It was found that strong adsorption of phenolic species causes severe deactivation of the cracking catalysts. Minor changes in product selectivity were observed, mostly due to the increased coke formation by phenols rather than the interaction of phenols with the hydrocarbon feeds. Minor enhancement in production of aromatics was observed in the gasoline range resulting from the dehydration and alkylation of phenol and guaiacol. It was

proposed that some hydrocarbon molecules in the gasoil feed might transfer hydrogen to the phenolic compounds, which would favor deoxygenation of these molecules [9, 19].

In a previous study, we demonstrated that hydride transfer from tetralin was able to reduce coke formation and catalyst deactivation during the conversion of anisole on acidic zeolites [20]. The coke from the reaction of phenolic compounds over zeolites is either phenolic oligomers (i.e phenolic pool) from condensation reaction or polyaromatic (or graphitic) coke from further cracking of the phenolic pool [16].

In this contribution, we have used a micro pulse reaction system to investigate the effects of the presence of m-cresol on the cracking of C6 hydrocarbons over clean surfaces of HY zeolite, especially on the hydride transfer reaction. While m-cresol is not a major component in crude bio-oil, it appears in large quantities in the stabilized bio-oil. Compounds such as syringol and guaiacol, directly formed from pyrolysis of lignin fractions in biomass, contain methoxy groups. They readily undergo transalkylation reactions leading to compounds containing hydroxyl and methyl groups, for which cresol is a representative model. n-Hexane and 2,3-dimethyl butane, which represent paraffinic hydrocarbons with different hydride transfer ability, were selected as model hydrocarbon feeds. The influence of m-cresol in the catalytic cracking reactions has been analyzed under varying conditions chosen to emphasize either the bimolecular or the monomolecular reaction pathway. The latter is dominant over clean surfaces and low feed concentrations while the former dominates over surfaces containing carbonaceous deposits and at high feed concentrations.

2. Experimental

a. Materials

Hexane isomers used in this study include n-hexane (n-C6, 99% pure) from Sigma Aldrich and 2,3-dimethylbutane (23DMB, 99%+) from Tokyo Chemicals Inc. m-Cresol (99%+) from SAFC and 1-hexene (99%+) from Sigma Aldrich were used for the co-feeding experiments. These hydrocarbons and m-cresol were used for the reaction without further purification. The catalyst was dealuminated HY zeolite with Si/Al = 40 (CBV780) obtained from Zeolyst International. The catalyst was pelletized to 90 – 250 μm particles for the reaction. Brønsted acid site (BAS) density of the catalyst was quantified as 0.07 mmol/g using temperature programmed desorption of isopropyl amine (IPA-TPD) technique [16].

b. Catalytic measurements

Conversion of hexane isomers in Helium (He) carrier gas over the zeolite was evaluated on a micropulse reactor. For the reactions of n-C6 at different feed concentrations, 100 mg of catalyst was pretreated under 200 sccm He flow at 600 °C for 1 hour. After pretreatment, the He flow rate was lowered to 20 sccm and reactor temperature was adjusted to 500 °C for the reaction. When the reactor temperature was stable, a pulse of the reactant diluted in He was sent over the catalyst bed. The products were analyzed on-line by using an HP5890 gas chromatograph (GC), equipped with an HP-PLOT/ Al_2O_3 /"S" column and a flame ionization detector (FID) directly connected to the reactor outlet. Reactions were carried out with different concentrations of n-C6, i.e. 3.7, 10 and 30 mol% of n-C6 in He. Because volume of the pulse was kept constant (500 μl), when n-C6 concentration was varied, the amount of n-C6 in a pulse also changed (i.e. 0.5, 1.4 and 4.1 μmol , respectively). During the 1-h period between each pulse, the catalyst was exposed to continuous flow of He. Experimental procedure for 23DMB reactions was also similar, except that the catalyst was pretreated at 500 °C for 5 hours and the reaction was carried out at 450 °C. In the reaction of mixed feed, the concentrations of paraffin

were identical to that in the pure feed and the mass ratio of hexanes/m-cresol or hexanes/1-hexene was kept constant at 95/5, no matter what concentration of paraffin in He was. Therefore, when the concentration of paraffin increased, the concentration and amount of olefins or m-cresol in a pulse also increased. For co-feeding 1-hexene, mixtures of hexanes and 1-hexene were prepared and injected. When co-feeding m-cresol, it was injected separately from the hydrocarbons, using an injection port operating at higher temperature. Conversion runs with pure m-cresol at the same concentrations (low and high) as those used in the mixed feed were also carried out to compare aromatic production and coke formation with the mixed feeds.

To quantify the extent of non-catalytic thermal conversion, pulse of each of the reactant was injected over an inert bed (acid-washed glass beads, 100 μm in diameter) under the same reaction conditions as used with the catalyst. In all cases, contribution of thermal conversion was lower than 0.2% and was subtracted from the total conversion in each of the conversion values reported below. Each experiment was carried out in duplicate. The differences were always less than 10% and in most cases less than 5%. Therefore, each of the reported values is the average of the two measurements. Products were identified and quantified by using mixtures of reference compounds of calibrated concentrations.

c. Temperature programmed oxidation (TPO) of the spent catalyst

TPO experiment was used to quantify coke amount on the catalyst after the reaction. The same reactor tube containing spent catalyst was installed in the TPO system, connected with a Cirrus mass spectrometry (MS) to measure evolution of CO_2 ($m/z = 44$) during the TPO process. To oxidize the carbonaceous deposits, a stream of 20 sccm of He/O_2 (5% volume of O_2) was used. Following reaction and after the furnace temperature was stable at 50 $^\circ\text{C}$, the reactor was heated linearly with a 10 $^\circ\text{C}/\text{min}$ ramp up to 700 $^\circ\text{C}$ and held at this temperature until the CO_2

signal reached the baseline. Since the oxygen was used in surplus, the deposits were oxidized completely to CO₂ and only trace amount of CO was observed. To quantify the amount of carbonaceous deposit, the CO₂ signal was calibrated with 100 µl CO₂ pulses.

3. Results

a. Conversion of hexane isomers at different C6 reactant concentrations

The evolution of n-C6 and 23DMB conversion with the sequential number of pulses in a He carrier over the HY zeolite is shown in Figures 1 (a) and (b), respectively, for different feed concentrations. The reaction temperatures were 450 °C for 23DMB and 500 °C for n-C6 due to the higher reactivity of the former compared to the latter. In both cases, the conversion observed in the few initial pulses was much higher than the constant value reached after about the 5th pulse. In a recent study [21], we have explained this activity enhancement of the fresh catalyst in terms of the generation of synergistic sites created on the zeolite upon high temperature pretreatment. These synergistic sites deactivate fast due to strong adsorption of hydrocarbon species. Hence, after each pulse, the enhanced conversion dropped until all of the synergistic sites were covered and only the activity of the normal BAS remained. The deactivation of the normal BAS was negligible after each pulse. As shown in Figures 1 (a) and (b), increasing reactant concentration resulted in very small changes in conversion for both synergistic sites and normal BAS. In the data shown below, we refer to conversion and product distribution obtained after the 8th pulse as representative of normal BAS.

Regarding product distribution, it was observed that cracking of n-C6 mainly yielded C2–C5 olefins (C2= to C5=) and C1–C5 paraffins (C1 to C5), with small amounts of hexenes (C6=) and light aromatics (i.e., benzene, toluene, ethylbenzene and xylenes). Isomerization products (C6 isomers) were not observed in the reaction of n-C6. However, in the conversion of 23DMB,

which is a better hydride donor [22-25], isomerization became an important contribution. Even though the overall conversion was not greatly affected by changes in reactant concentration (Figure 1), the product selectivity changed considerably, as shown in Figures 2 and 3, as well as in Figures S1 and S2 of the Supplementary Information.

Figure 2 summarizes the variation of the olefin to paraffin molar ratio in the products (O/P ratio) with both, the number of pulses and reactant concentration. A clear decrease in the O/P ratio is observed with increasing either the number of pulses or the reactant concentration with both feeds (n-C6 and 23DMB). Likewise, as shown in Figure 3, the selectivity to aromatic products also decreased with increasing number of pulses or reactant concentration. The O/P ratio and selectivity to aromatics were always higher during the reaction of n-C6 than that of 23DMB. Also, they were always higher for the 1st pulse (synergistic sites) than for the 8th pulse (normal BAS). In the n-C6 conversion, as the reactant concentration increased, a decrease in C3-C5 olefin selectivity and an increase in C3-C5 paraffin selectivity (see Figure S1) are responsible for the observed decrease in O/P ratio. A similar trend was observed in the conversion of 23DMB (Figure S2). Significant increases in the selectivity to C6 isomers with reactant concentration were also observed.

Coke formation on the spent catalyst after 10 pulses was measured by TPO and summarized in Table 1. It is interesting to note that, even though the amount of reactant increased 8 times when the concentration of hexanes in He was increased from 3.7 to 30 mol%, the coke amounts after 10 pulses of the reactants were essentially the same. The reaction of 23DMB, which was conducted at lower temperature with a better hydride donor, resulted in lower coke formation than during the reaction of n-C6.

b. Effect of co-feeding 1-hexene at different C6 reactant concentrations

Figure 4 compares the paraffin conversion (at the 8th pulse, i.e. normal BAS) obtained when co-feeding small amounts of 1-hexene (5 wt% in n-C6 or 23DMB) with that obtained with pure paraffin feed. At low hydrocarbon concentrations, the paraffin conversion in the mixed feed was almost the same as that obtained with pure feed. However, when the n-C6 concentration increased to 30 mol%, the conversion in the mixed feed greatly increased, while paraffin conversion in the pure feed remained essentially unchanged (Figure 4 a). The same remarkable increase was also observed with 23DMB (Figure 4 b).

c. Effect of co-feeding m-cresol at different C6 reactant concentrations

Figures 5 and 6 show the effects of co-feeding m-cresol along with the hexane isomers at different feed concentration for n-C6 and 23DMB, respectively. For the reaction of n-C6 at low reactant concentration (i.e. corresponding to 3.7 mol%), co-feeding m-cresol caused significant deactivation, especially to the synergistic sites, as evidenced by the fast decrease in the enhanced conversion typically observed during the first few pulses. When m-cresol was co-fed, the conversion during the initial pulses dropped dramatically to the level of the normal BAS (Figure 5a) in marked contrast with the behavior exhibited with the pure paraffin feeds, in the absence of m-cresol. The deactivation of these normal BAS (after the 5th pulse) was less severe and the difference in conversion over the normal BAS between the pure feed and the mixed feed did not vary with pulse number. Interestingly, when the feed concentration increased, the deactivation by m-cresol was less severe for both the synergistic sites and the normal BAS. That is, the drop in conversion when co-feeding m-cresol was less as the reactant concentration increased. At the

highest reactant concentration, (i.e corresponding to 30 mol% n-C6), the deactivating effect of m-cresol was practically negligible (Figure 5c).

As shown in Figure 6, the reaction of 23DMB and its mixtures with m-cresol showed the same trend with increasing reactant concentration as n-C6. At low 23DMB concentrations, co-feeding m-cresol caused considerable deactivation, but when the reactant concentration increased the deactivation was less severe. Interestingly, a comparison of the conversion evolution at a given reactant concentration shows that the deactivating effect of m-cresol is less severe for the 23DMB conversion than for n-C6, particularly on the synergistic sites. Moreover, a lower reactant concentration was needed to neutralize the deactivating effect of m-cresol in the reaction of 23DMB (10 mol%, Figure 6b) than in the reaction of n-C6 (30 mol%, Figure 5c).

Co-feeding m-cresol also affected the selectivity to different pathways in the reaction of C6 paraffins. The O/P ratio in the reaction of the mixed feed was compared with that obtained with the pure paraffin feeds. In Figure 7, the differences $(O/P)_{\text{mixed feed}} - (O/P)_{\text{pure feed}}$ are plotted for the reactions of n-C6 and 23DMB over the normal BAS (at the 8th pulse). It can be observed that co-feeding m-cresol resulted in a decrease in O/P ratio, as shown by the negative differences shown in Figure 7. The effect is particularly pronounced at low reactant concentration.

The significant drop in O/P ratio when co-feeding m-cresol at low reactant concentrations could be due to a different degree of deactivation in the monomolecular protolytic cracking and protolytic dehydrogenation paths, since bimolecular hydride transfer is minimized at low reactant concentrations. Additional data showing differences in product selectivity for the reaction over the normal BAS (Figures S3 and S4 in the Supplementary Information) provide additional clues about the changes in reaction pathways. The observed trend shows that in the reaction of n-C6 at low concentrations, selectivity to light paraffins (C1 to C3) is higher and selectivity to light

olefins (C₂= to C₄=) is lower in the mixed feed (Figure S3). These changes lead to the observed decrease in the O/P ratio, as shown in Figure 7. These trends suggest that deactivation by m-cresol suppresses the protolytic dehydrogenation pathway more effectively than the protolytic cracking since the light paraffins are mostly formed from the protolytic cracking pathway. Meanwhile, in the reaction with 23DMB, the selectivity to C₆ isomers increased significantly compared to other products in the mixed feed (Figure S4). In reaction of 23DMB, isomerization is a major reaction pathway but further cracking of the C₆ isomers also produce smaller products. The observed change in product selectivity indicates that co-feeding m-cresol suppresses the secondary cracking of the C₆ isomers, leading to increased selectivity to these products and a drop in selectivity to other products.

Thus, co-feeding m-cresol in general decreased the O/P ratio in the products due to deactivation of the protolytic cracking and protolytic dehydrogenation paths of the paraffin. The reduction of O/P ratio was more pronounced for the reaction of n-C₆ since deactivation by m-cresol was more severe in the reaction of n-C₆ than that of 23DMB.

In parallel to the behavior shown in Figures 5 and 6, the differences in O/P ratio greatly diminished when the reactant concentration increased. This result is clearly linked to the lower extent of catalyst deactivation taking place with increased paraffin concentration, as mentioned above. However, a more careful analysis of the change in product selectivity (Figures S3 and S4) also reveals other effects of m-cresol on paraffin reaction pathways other than the deactivation of active sites. One might expect that when deactivation is suppressed by increasing reactant concentration, the losses in protolytic cracking and dehydrogenation activities would also diminish. However, even though the differences in the O/P ratio decreased as reactant concentration increased, changes in the product selectivity were also evident in the drops in

protolytic cracking (in 23DMB reaction) and protolytic dehydrogenation (in n-C6 reaction) pathways. For instance, the selectivity to C6 isomers in the mixed feed was always higher than that in the pure 23DMB conversion, regardless what reactant concentration was used. Also, the selectivity difference regarding C2= was always negative for the n-C6 reaction while those for C1 and C2 were always positive. Hence, co-feeding m-cresol still caused deactivation to the protolytic cracking and dehydrogenation path of paraffins.

Besides, as discussed below, the phenolic pool formed by condensation of m-cresol and its phenolic derivatives can have a hydride acceptor role. At high reactant concentration, when the contribution of hydride transfer is more significant, the presence of the phenolic pool reduces hydride transfer between paraffins, but enhances the β -scission cracking path since the carbenium ion of the parent paraffin can still be formed by transferring a hydride to the phenolic pool. Therefore, the drops in protolytic cracking and dehydrogenation contributions to the product are compensated by an enhancement in β -scission cracking, which is evident by the change in selectivity to olefinic C3= and C4= products. When the reactant concentration increased, the differences in selectivity to these products became less negative and more positive, respectively, which indicates that more olefins were produced in the mixed feed from β -scission cracking. Furthermore, the more negative differences in C4 and C5 selectivity indicate decreases in hydride transfer when comparing hydrocarbons in the mixed feed to the pure paraffin feed.

Coke analysis of the spent catalysts was carried out after 10 pulses of the pure m-cresol and its mixture with hexanes. The results are summarized in Figure 8 for the reactions corresponding to paraffin concentrations of 3.7 mol% and 30 mol%. The amount of m-cresol in the pure m-cresol feed was the same as that of m-cresol in the mixed feed, corresponding to 5wt% m-cresol in C6. The concentration of the feed was adjusted according to the paraffin

concentration. At low feed concentration (Figure 8a), m-cresol was entirely trapped by the catalyst, in both cases, with the mixed feed and the pure m-cresol feed. Due to the additional carbon fed with the C6 paraffins, the coke deposited from the mixed feed was higher than that from the pure m-cresol feed. However, at high C6 feed concentration (30 mol% paraffin in He) the results show the opposite trend (Figure 8b). That is, when m-cresol was co-fed with paraffins, the coke amount was lower compared to the pure m-cresol reactions, even though much higher amounts of carbon were sent in each pulse. In the reaction of pure m-cresol, almost but not all m-cresol was trapped in the catalyst bed (i.e. over 92%). Due to the larger amount of carbon fed in each pulse, the coke amount was higher than that in the runs at low feed concentrations. However, not all the carbon sent in a pulse was trapped and the remaining fraction leaving the catalyst was in the form of cracked aromatic products. In fact, as previously shown [16], at higher reaction temperatures the fraction converted into coke from m-cresol was less than at low reaction temperatures because the surface phenolic pool was cracked more effectively into aromatic products. As m-cresol was co-fed with n-C6 and 23DMB, the coke amount dropped by about 10% and 6%, respectively, compared to the reaction with pure m-cresol.

d. Conversion of m-cresol in mixed and pure feeds

The previous section describes the effects of m-cresol in the conversion of paraffins. It is also important to investigate the effect of the presence of paraffin in the conversion of m-cresol. As shown in our recent study [16], m-cresol conversion over fresh zeolite surfaces produces mainly aromatics (benzene, toluene and xylenes) via formation and cracking of a surface phenolic pool. Table 2 summarizes the observed aromatic products leaving the reactor after the

8th pulse from the reaction of pure hydrocarbons, m-cresol and their mixtures. As expected, no aromatic was produced in the conversion of pure m-cresol at low reactant concentration (i.e. corresponding to 3.7 mol% hydrocarbon) since all of the material was trapped (Figure 8a). And the aromatic production from the reaction of m-cresol/hydrocarbon mixtures was slightly lower than that in the reaction of pure hydrocarbons. This slight difference might be due to the deactivation of m-cresol to hydrocarbon conversion at low reactant concentration as shown earlier (section 3c).

In the conversion of pure m-cresol at high reactant concentration (i.e. corresponding to 30 mol% hydrocarbon), small amount of aromatic was produced from cracking of the phenolic pool. And the aromatic production from the reaction of pure hydrocarbons also increased due to more reactant was fed, even though the selectivity to aromatic products decreased (Figure 3). For the reaction of the mixed feed, even though the aromatic production was higher than that in the conversion of pure m-cresol, but it was lower than the combined aromatic yields from the reaction of the pure hydrocarbons and pure m-cresol.

4. Discussions

The main pathways for paraffin conversion over zeolites have been studied extensively in the literature [21-34]. They are (i) the protolytic cracking of a C–C bond in the pentacoordinated carbonium ion formed when the catalyst protonates the paraffin, (ii) protolytic dehydrogenation of the carbonium ion, and (iii) hydride transfer with a surface carbenium ion. The first two pathways are monomolecular reactions occurring on pristine BAS bearing the H⁺, while the third pathway occurs with the involvement of a carbenium ion in the transition state. Besides hydride transfer with the paraffinic feed, i.e. route (iii), other reactions involving the participation of

carbenium ions include isomerization, β -scission, and desorption to regenerate the BAS. The various conversion pathways of n-C₆ are shown in Scheme 1.

In paraffin conversion over zeolites, the monomolecular and bimolecular pathways always co-exist and compete with each other in the chain reaction mechanism, and their contribution vary, depending on reaction conditions [26, 27, 35]. In order to compare the contribution of monomolecular protolytic cracking and bimolecular hydride transfer (or β -scission) pathways, the ratio of olefin to paraffin (O/P) in the products has been commonly used [31, 36]. Likewise, the (C₁ + C₂)/iso-butane ratio has also been widely used to quantify the relative contributions of the protolytic cracking and β -scission cracking routes [37]. The kinetic chain length, defined as the ratio of overall rate to the rate of initiation, has also been often used [27, 35] to quantify the significance of the chain propagation mechanism via hydride transfer or disproportionation between the paraffinic feed and the surface carbenium ion. Regardless of the criterion used, the conclusion is always that the reaction conditions determine which pathway dominates [24, 26, 27, 31, 38]. That is, the monomolecular pathway is favored at high reaction temperatures, low paraffin concentrations, and low conversions with low olefin product concentration. In contrast, the bimolecular hydride transfer reaction is favored at lower reaction temperatures with high paraffin and olefin product concentration. In addition, the structure of the paraffin has a strong effect on the hydride transfer ability. Branched paraffins, having tertiary carbons, are better hydride donors than linear ones because the tertiary carbenium ion is more stable than the secondary, resulting in lower activation barriers and longer life-time of the carbenium ion on the catalyst surface, with a higher possibility for hydride transfer reaction to occur [25].

As shown in Scheme 1, the protolytic dehydrogenation path is followed by β -scission or desorption yields olefin products, while the protolytic cracking and hydride transfer produce paraffins. Hence, the ratio between these two types of product (O/P) can be used to evaluate the relative contribution of each different pathway:

$$\frac{\text{Protolytic dehydrogenation} + \beta\text{-scission}}{\text{Protolytic cracking} + \text{hydride transfer}} \sim \frac{\text{Olefins}}{\text{Paraffins}}$$

As shown in section 3a, increasing reactant concentration reduces the O/P product ratio, mostly due to decrease in the C3= to C5= selectivity and increase in the C3 to C6 selectivity. Meanwhile, the C1 and C2 selectivity almost did not change or was slightly reduced. Since protolytic cracking preferentially produces small paraffins (C1 and C2) rather than larger ones [31], these changes reflect an enhanced contribution of the hydride transfer pathway when the reactant concentration increases.

Carbenium ions play an important role in the bimolecular reactions by promoting the chain propagation reaction via hydride transfer [24]. At the same time, since they occupy BAS, they also inhibit monomolecular protolytic cracking. Abbot et al. [24] and Zhao et al. [27] observed that when co-feeding small amount of olefins, conversion of hydride donor such as branched paraffin (i.e, 2-methylpentane or 2,3-dimethylbutane) was enhanced, while conversion of poor hydride donor such as n-hexane did not change or slightly decreased. In section 3b, we also observed an enhanced paraffin conversion when co-feeding small amounts of 1-hexene at high hexanes concentration (i.e. 30 mol%), at which contribution of the hydride transfer mechanism is important. However, it is interesting to note that co-feeding 1-hexene did not enhance 23DMB conversion at low concentration (i.e. 3.7 mol%), even though 23DMB is a better hydride donor than n-C6. The high O/P ratio in the reaction of 23DMB (ca. 2) might

indicate that, at this low concentration, the hydride transfer mechanism may not be significant. In turn, protolytic dehydrogenation of the tertiary carbon and demethylation to methane may be the dominant pathways [21]. That is, not only the structure of the paraffin molecule, but also the concentration is an important parameter that determines the relative contribution of the hydride transfer pathway.

Aromatics are produced on cracking catalysts through a series of reactions such as oligomerization of olefins, dehydrogenation, and cyclization [39, 40]. Dehydrogenation occurs via hydride transfer followed by proton transfer (or desorption) to form olefins. These paths contrast with the protolytic dehydrogenation described previously, which occurs via protonation of paraffin by an acid site followed by dehydrogenation and carbenium ion formation. Continuous dehydrogenation forms polyolefins, which can cyclize to naphthenic products. Further dehydrogenation of naphthenic products forms aromatics. The aromatic products can also undergo alkylation, hydride transfer, and cyclization reactions, eventually forming polyaromatic hydrocarbons (i.e. coke) that absorb strongly on the catalyst surface [39, 40]. Even though contribution of hydride transfer reaction increases with paraffin concentration, it occurs mostly between paraffinic feed and the surface carbenium ion, yielding paraffin products. As a result, the possibility of carbenium ions going through proton transfer to form olefins and further dehydrogenation to form polyolefins, in fact, decreases owing to hydride transfer from the paraffinic feed. As a result, with an enhanced contribution of hydride transfer, the production of aromatics and formation of coke are reduced, as experimentally observed here (Fig. 3). The selectivity to aromatics was lower in the reaction of 23DMB than n-C6 since contribution of hydride transfer is higher for the reaction of the better hydride donor at lower temperature. Also,

as a result of enhanced contribution of the hydride transfer reaction, selectivity to coke is also reduced, as shown in section 3a.

a. Effects of concentration to the paraffin cracking activity

Catalytic cracking and dehydrogenation of paraffins over the BAS are first-order dependent on reactant concentration (or partial pressure) [26, 27, 41]. Hence, the conversion of the feed in the first-order reaction does not depend on the reactant concentration, but rather on the residence time of a pulse. In these pulse experiments, the carrier gas flow rate, and hence the residence time of a pulse, was kept constant. Therefore, the conversion should be similar when the reactant concentration was varied as shown in the Figure 1 for both the BAS and the synergistic sites. However, if one takes into account deactivation of the synergistic sites, which caused by strong adsorption of hydrocarbon species [21], increase of hydrocarbon concentration means higher amount the reactant was sent in a pulse and hence, the hydrocarbons that adsorbed and deactivated the synergistic sites should increase. However, the results in Figure 1 showed that deactivation behavior was similar for all feed concentrations. This interesting behavior can be explained by the enhanced contribution of hydride transfer with increasing paraffin concentration, which reduced selectivity to aromatic, coke formation and possibly other heavy hydrocarbon fragments that adsorbed strongly on the synergistic sites. The role of hydride transfer in coke reduction and catalyst decay prevention was also presented in the cracking of n-hexane and 2-methylpentane [25] or n-pentane and isobutane [27] in which coke formation in a better hydride donor (i.e. iso-paraffin) was less than that in the poor hydride donor (i.e n-paraffin). Besides, higher dehydrogenation activity of the synergistic sites also promotes formation of the carbenium ions, which enhances paraffin conversion at high concentration when contribution of hydride transfer reaction is important as discussed earlier.

b. Role of hydride transfer from the paraffins to relieve the deactivation effect of m-cresol

Strong adsorption and coke formation of m-cresol (and phenolic compounds in general) on zeolite have been major reasons for accelerated catalyst deactivation [9, 17-20]. Graca and coworkers [9, 18, 19] proposed that molecular adsorption of phenolic compounds on both the BAS and Lewis acid sites (LAS) at early time on stream, which enhances coke formation and reduces micropore volume, causes fast deactivation to the cracking activity of paraffins even with small amount. In our recent studies on the conversion of m-cresol over zeolites using the pulse reaction system [16, 20], significant trapping of the feed was also observed which resulted in fast catalyst deactivation. The structure of carbonaceous deposits derived from phenolic compounds was described as either strongly adsorbed individual phenolic molecules or a surface pool of oligomeric species formed via condensation of the phenolic compounds [16, 42, 43]. This is different from the graphitic nature of coke typically formed in reactions of hydrocarbon, which has polyaromatic structure and is formed via a series of intermolecular reactions such as oligomerization of olefins, H-transfer, cyclization and alkylation on the BAS [39].

For the catalyst in this study, even though the synergistic sites have much higher activity than the BAS, the number of these sites only accounts for a small fraction of the total acid sites. The higher heats of paraffin adsorption on zeolites pretreated at high temperatures indicate that the synergistic sites created by this pretreatment adsorb hydrocarbons more strongly than normal BAS [44, 45]. Because of the strong adsorption of hydrocarbon species they deactivate rapidly, even in the reaction of pure paraffins. However, it appears that this deactivation is reversible, since the enhanced activity for hydrocarbon cracking can be recovered by thermal treatment of the spent catalyst at high temperature [21]. As m-cresol was co-fed, strong adsorption and coke formation of phenolic species on these sites might cause deactivation more detrimental,

especially at low reactant concentration. Even though the BAS also trapped the phenolic compounds strongly, amount of m-cresol in a pulse was so small comparing to the number of the BAS (i.e. $n_{\text{cresol}}/n_{\text{Bronsted acid site}}$ is about 0.02) that accumulation of phenolic pool during pulses did not cause continuous decrease in the conversion over the BAS. Nevertheless, the constant difference in the conversion of paraffin between the pure feed and the mixed feed after the 5th pulse at low reactant concentration might indicate that deactivation by m-cresol still occurred and it was due to competitive adsorption of m-cresol.

The reduction of deactivation effect by m-cresol when the reactant concentration increased is in fact an interesting result. Because with the mass ratio of m-cresol to paraffin in the mixed feed kept constant (i.e. 5 wt%), when the feed concentration in He increased, m-cresol concentration in the pulse also increased. That is, larger amount of m-cresol was sent in a pulse at higher reactant concentration. Therefore, more coke formation, which might result in more deactivation, should be expected. However, the opposite results suggested that, at high reactant concentration, the enhancement of hydride transfer from the paraffin might relieve the deactivation effect of m-cresol. Less deactivation in the reaction of 23DMB with m-cresol comparing to that of n-C6 with m-cresol (section 3c) can further confirm this hypothesis because contribution of hydride transfer in the reaction of 23DMB, which is a better hydride donor, at lower temperature is higher than that in the reaction of n-C6. Furthermore, the reduction in coke formation from m-cresol when it was co-fed with paraffin at high concentration (Figure 8b) is also consistent with the observed reduction of the deactivation effect.

Important role of hydride transfer ability of hydrocarbon to catalyst deactivation during anisole conversion was also reported in our previous study [20]. Due to its strong adsorption and coke formation tendency, anisole conversion dropped remarkably with reaction time on stream

as the catalyst was deactivated. When anisole was co-fed with a good hydride donor such as tetralin [46], catalyst activity enhanced significantly, and catalyst deactivation could not be observed during the same time on stream period with pure anisole reaction. TPO analysis of the spent catalysts also showed that coke amount in the reaction of anisole and tetralin mixture was lower comparing to the reaction of pure anisole, even though more material was sent through the catalyst bed in the case of the mixed feed. Furthermore, co-feeding tetralin to anisole reduces the H/C ratio in the coke compared to that from the reaction with pure anisole. We proposed that hydride transfer from tetralin promotes desorption of the surface species and minimize coke formation from anisole. In this study, as hydride transfer reaction was enhanced either by increasing paraffin concentration or using a better hydride donating paraffin, similar effect was also observed.

Furthermore, co-feeding anisole with benzene [20], which is not a hydride donating molecule, did not change catalyst activity and stability comparing to the reaction of pure anisole. And co-feeding anisole with a poor hydride donor such as n-decane only increased the activity slightly comparing to pure anisole conversion. The reason for slight conversion increase was explained by dilution effect from n-decane that prevented condensation of anisole into coke, because the paraffin concentration in this case was small (i.e. 2-3 mol% in He). Perhaps, one might think that similar effect might play an important role in this study. However, the mass ratio between hydrocarbon and m-cresol was always kept constant at 95/5 in all cases. Hence, the relief of deactivation effect should be due to enhanced hydride transfer from the hydrocarbons.

c. Interaction of paraffin and phenolic compound via hydride transfer

As discussed previously, increased paraffin concentration in the feed enhanced hydride transfer between the paraffin feed and the surface carbenium ion, leading to higher selectivity to paraffin products. When m-cresol was co-fed with paraffins at high reactant concentration, the fact that selectivity to paraffin products (C4 and C5) decreased more than when it was co-fed at low reactant concentration might indicate that the phenolic pool formed by m-cresol [16] interfered with the hydride transfer reaction between the paraffin feed and the surface carbenium species. The interference of the phenolic pool to the hydride transfer reaction of hydrocarbon can be visualized in Scheme 2. In the chain propagation mechanism, the reaction of the surface carbenium ions proceeds via either desorption or β -scission to produce olefin or hydride transfer with the feed to produce paraffins. The phenolic pool, in this case, might act as a hydride acceptor, which competes with the hydride transfer step between hydrocarbons. This interference leads to reduction of the hydride transfer reaction between hydrocarbons, and hence decreases the selectivity to paraffins. Nevertheless, conversion of the feed does not drop because the carbenium ion of parent paraffin is still formed and continues to react via β -scission cracking, which produces more olefins such as C3= and C4=. This effect increases the overall O/P ratio in the products.

In summary, there are two possible effects of m-cresol that might change the contribution of different paraffin reaction pathways, which makes the variation of O/P ratio in the products more complicated. Deactivation by competitive adsorption of m-cresol decreases the contribution of protolytic cracking and protolytic dehydrogenation paths, leading to reduction of the O/P ratio (as shown in section 3c). Intervention of the phenolic pool as a hydride acceptor suppresses hydride transfer between hydrocarbons while increases selectivity to β -scission cracking leading to increase in the O/P ratio. Overall change of the O/P in the products should

be the combination of these two effects, which compensate each other. At low reactant concentration, where contribution from hydride transfer is insignificant, the former effect is dominant, leading to considerable drop in the O/P ratio. When reactant concentration increases, the role of hydride transfer reaction becomes more important. And the effect of co-feeding m-cresol to hydride transfer step is more pronounced, resulting in less difference in the O/P ratio.

Hydride transfer from the paraffin to the phenolic pool did not only alter the relative contributions of each paraffin reaction pathway, but also affected the extent of m-cresol conversion. In previous work [20], we showed that hydride transfer from tetralin enhances desorption of phenolic compounds in the anisole conversion and minimizes hydride transfer from the coke precursor, leading to inhibition of coke formation and catalyst deactivation. Here, we wanted to investigate whether hydride transfer from paraffins has a similar effect on the conversion of m-cresol. Then, the evolution of phenolic products during m-cresol conversion was monitored chromatographically, using an HP-1 column. No phenolic products were detected during the reaction of m-cresol and its mixtures with the two hydrocarbons at low concentrations. This result is consistent with the quantitative observation confirmed by TPO analysis (Figure 8a) that all m-cresol was trapped in the catalyst bed forming coke, even when it was co-fed with hydrocarbons. In contrast, in the reaction of the mixture of m-cresol and hydrocarbon at high concentration (i.e. 30 mol% of hydrocarbon in He), small amounts of phenolic products were detected, including cresol isomers, xylenols and other heavier phenolic products. These products were not observed in the reaction of pure m-cresol or pure hydrocarbon at the same condition (i.e high reactant concentration). The amount of detected phenolic products, estimated by comparing the GC-FID area of those products with that of m-cresol in the feed, was about 1.5% to 2%. The evolution of phenolic compounds is consistent

with the observed decrease in coke formation when m-cresol was converted in the presence of hydrocarbons at high concentration, even though the released amount was smaller (10% and 6% for the co-feeding experiment with n-C₆ and 23DMB, respectively). This difference is only a semi-quantitative measure of the enhancement of phenolic compound desorption by hydride transfer from the hydrocarbon. The release of phenolic compounds via hydride transfer with hydrocarbon is illustrated in Scheme 3. Similar to the case of an acid-catalyzed cleavage of ether bonds [47], the proton from a BAS attacks the lone pair of the O atom in the surface pool. This must be an easy step since the pool adsorbs strongly on the catalyst surface and most probably is covering the acid sites. This interaction may weaken the ether bond and the hydride transfer from the hydrocarbon promotes the cleavage of this weakened bond, thus forming the phenolic compounds experimentally observed. Obviously, the hydride from hydrocarbon is not an efficient reagent for cleaving the phenolic fragment from the pool. Therefore, the amount of phenolic compounds coming off is very small, as mentioned above. Yet, it still has a considerable effect on the rate of deactivation, since via hydride transfer, surface carbenium ions are still formed and the catalytic cracking reactions are still able to proceed.

In a previous study [16], we observed that aromatics are the dominant products observed in the conversion of m-cresol over zeolites in a pulse reactor. We proposed that formation of aromatic proceeds via the formation of oligomeric phenolic species (i.e. phenolic pool), which is formed by condensation reactions of phenolic compounds and remains adsorbed on the catalyst surface. At high reaction temperatures, rearrangement of the phenolic pool via cracking and hydride transfer produces aromatics and a more graphitic carbonaceous residue. Since hydride transfer from paraffin promotes the desorption of phenolic species, formation of the surface pool is suppressed in the presence of hydride donor reactants. As a result, a lower amount of

aromatics is produced during cracking of the phenolic pool in the presence of high paraffin concentration, as shown in section 3d. In the reaction of the mixed feeds, aromatics were produced from both direct cracking of hydrocarbons and cracking of the phenolic pool. Since no deactivation of hydrocarbon conversion was observed when m-cresol was co-fed at high reactant concentrations, aromatic production from hydrocarbon should be equivalent to that of the pure feeds. Hence, the drops in aromatic production in the mixed feed compared to that in the sum of the pure hydrocarbon and m-cresol feeds (Table 2) should be due to a lower extent of cracking of the phenolic pool. The overall scheme summarizing the interaction of the phenolic pool and the paraffin via hydride transfer is shown in scheme 4.

5. Conclusions

The influence of m-cresol in the catalytic cracking reaction of paraffins has been analyzed under chosen conditions that emphasize either the bimolecular or the monomolecular reaction pathway. It was found that co-feeding small amounts of m-cresol at low reactant concentrations causes severe deactivation of the synergistic sites. By contrast, the reaction over the normal BAS is only slightly reduced by simple competitive adsorption. Interestingly, when the paraffin reactant concentration increases, the deactivating effect of m-cresol is significantly diminished. Enhanced hydride transfer from the paraffin at higher reactant concentration, as evidenced by changes in product distribution and response to added olefins, is responsible for the inhibition of deactivation. Co-feeding m-cresol also affects the contribution of the different paraffin reaction pathways. That is, competitive adsorption inhibits the protolytic cracking and protolytic dehydrogenation paths. Meanwhile, the surface pool formed by condensation of phenolic compounds acts as a hydride acceptor that competes with hydride transfer between hydrocarbons while still promotes the β -scission cracking. As a result, variations in product

distribution from paraffin cracking when co-feeding m-cresol can be explained in terms of the relative contribution of each pathway. The importance of each pathway can be adjusted by varying the reaction parameters. Hydride transfer from hydrocarbons also promotes desorption of the phenolic compounds and suppresses the formation of the phenolic pool, resulting in less aromatic and coke formation from m-cresol conversion.

6. Acknowledgements

Financial support from the Department of Energy under Grant DE-EE0006287 of the Bioenergy Technology Office CHASE program is gratefully acknowledged. A Phillips66 scholarship for ATT is gratefully acknowledged.

References

- [1] F.M. Mercader, M.J. Groeneveld, S.R.A. Kersten, N.W.J. Way, C.J. Schaverien, J.A. Hogendoorn, *Appl. Catal., B: Environ.*, 96 (2010) 57.
- [2] G. Fogassy, N. Thegarid, G. Toussaint, A.C. van Veen, Y. Schuurman, C. Mirodatos, *Appl. Catal., B: Environ.*, 96 (2010) 476.
- [3] A.A. Lappas, S. Bezergianni, I.A. Vasalos, *Catal. Today*, 145 (2009) 55.
- [4] T.L. Marker, *Opportunities for Biorenewables in Oil Refineries*, UOP LLC, 2005, pp. 60.
- [5] G.W. Huber, A. Corma, *Angew. Chem. Int. Ed.*, 46 (2007) 7184.
- [6] V.N. Bui, G. Toussaint, D. Laurenti, C. Mirodatos, C. Geantet, *Catal. Today*, 143 (2009) 172.
- [7] A. Pinheiro, D. Hudebine, N. Dupassieux, C. Geantet, *Energ. Fuel.*, 23 (2009) 1007.
- [8] F.M. Mercader, M.J. Groeneveld, S.R.A. Kersten, C. Geantet, G. Toussaint, N.W.J. Way, C.J. Schaverien, K.J.A. Hogendoorn, *Energ. Environ. Sci.*, 4 (2011) 985.
- [9] I. Graca, F.R. Ribeiro, H.S. Cerqueira, Y.L. Lam, M.B.B. de Almeida, *Appl. Catal., B: Environ.*, 90 (2009) 556.
- [10] J.D. Adjaye, N.N. Bakhshi, *Biomass Bioenerg.*, 8 (1995) 131.
- [11] J.D. Adjaye, N.N. Bakhshi, *Fuel Process. Technol.*, 45 (1995) 161.
- [12] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, J. Bilbao, *Ind. Eng. Chem. Res.*, 43 (2004) 2610.

- [13] A.G. Gayubo, A.T. Aguayo, A. Atutxa, R. Aguado, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.*, 43 (2004) 2619.
- [14] I. Graca, J.D. Comparot, S. Laforge, P. Magnoux, J.M. Lopes, M.F. Ribeiro, F.R. Ribeiro, *Appl. Catal., A: Gen.*, 353 (2009) 123.
- [15] I. Graca, J.D. Comparot, S. Laforge, P. Magnoux, J.M. Lopes, M.F. Ribeiro, F.R. Ribeiro, *Energ. Fuel.*, 23 (2009) 4224.
- [16] A. T. To, D. E. Resasco, *Appl. Catal., A: Gen.*, 487 (2014) 62.
- [17] A. Ausavasukhi, Y. Huang, A.T. To, T. Sooknoi, D.E. Resasco, *J. Catal.*, 290 (2012) 90.
- [18] I. Graca, A. Fernandes, J.M. Lopes, M.F. Ribeiro, S. Laforge, P. Magnoux, F. Ramoa Ribeiro, *Appl. Catal., A: Gen.*, 385 (2010) 178.
- [19] I. Graca, J.M. Lopes, M.F. Ribeiro, F. Ramoa Ribeiro, H.S. Cerqueira, M.B.B. de Almeida, *Appl. Catal., B: Environ.*, 101 (2011) 613.
- [20] T. Prasomsri, A.T. To, S. Crossley, W.E. Alvarez, D.E. Resasco, *Appl. Catal., B: Environ.*, 106 (2011) 204.
- [21] A.T. To, R.E. Jentoft, W.E. Alvarez, S.P. Crossley, D.E. Resasco, *J. Catal.*, 317 (2014) 11.
- [22] J. Abbot, B.W. Wojciechowski, *J. Catal.*, 113 (1988) 353.
- [23] J. Abbot, B.W. Wojciechowski, *Can. J. Chem. Eng.*, 66 (1988) 825.
- [24] J. Abbot, B.W. Wojciechowski, *J. Catal.*, 115 (1989) 1.
- [25] P.V. Shertukde, G. Marcelin, G.A. Sill, W. Keith Hall, *J. Catal.*, 136 (1992) 446.
- [26] W.O. Haag, R.M. Dessau, R.M. Lago, *Stud. Surf. Sci. Catal.*, 60 (1991) 255.
- [27] Y.X. Zhao, G.R. Bamwenda, W.A. Groten, B.W. Wojciechowski, *J. Catal.*, 140 (1993) 243.
- [28] J. Abbot, *J. Catal.*, 126 (1990) 628.
- [29] H. Krannila, W.O. Haag, B.C. Gates, *J. Catal.*, 135 (1992) 115.
- [30] F.C. Jentoft, B.C. Gates, *Top. Catal.*, 4 (1997) 1.
- [31] A. Corma, A.V. Orchillés, *Microporous Mesoporous Mater.*, 35–36 (2000) 21.
- [32] S. Kötter, H. Knözinger, B.C. Gates, *Microporous Mesoporous Mater.*, 35–36 (2000) 11.
- [33] W.O. Haag, R.M. Dessau, in: G. Ertl (Eds.), *8th International Congress on Catalysis*, Berlin, 2-6 July 1984, p. 305.
- [34] R.D. Cortright, J.A. Dumesic, R.J. Madon, *Top. Catal.*, 4 (1997) 15.
- [35] K.A. Cumming, B.W. Wojciechowski, *Catal. Rev.*, 38 (1996) 101.
- [36] A. Corma, V. González-Alfaro, A.V. Orchillés, *Appl. Catal., A: Gen.*, 187 (1999) 245.
- [37] A.F.H. Wielers, M. Vaarkamp, M.F.M. Post, *J. Catal.*, 127 (1991) 51.
- [38] Y.X. Zhao, B.W. Wojciechowski, *J. Catal.*, 142 (1993) 499.
- [39] M. Guisnet, P. Magnoux, C. Canaff, *Stud. Surf. Sci. Catal.*, 28 (1986) 701.
- [40] M. Guisnet, P. Magnoux, *Appl. Catal., A: Gen.*, 212 (2001) 83.
- [41] T.F. Narbeshuber, A. Brait, K. Seshan, J.A. Lercher, *J. Catal.*, 172 (1997) 127.
- [42] P.D. Chantal, S. Kaliaguine, J.L. Grandmaison, *Appl. Catal.* 18 (1985) 133.
- [43] Y.T. Cheng, G.W. Huber, *ACS Catal.* 1 (2011) 611.
- [44] J.A. van Bokhoven, M. Tromp, D.C. Koningsberger, J.T. Miller, J.A.Z. Pieterse, J.A. Lercher, B.A. Williams, H.H. Kung, *J. Catal.* 202 (2001) 129.
- [45] R.D. Shannon, K.H. Gardner, R.H. Staley, G. Bergeret, P. Gallezot, A. Auroux, *J. Phys. Chem.* 89 (1985) 4778.

- [46] T. Prasomsri, R.E. Galiasso Tailleur, W.E. Alvarez, T. Sooknoi, D.E. Resasco, Appl. Catal., A: Gen., 389 (2010) 140.
- [47] R.L. Burwell Jr., Chem. Rev., 54 (1954), 615

Figure

Figure 1. Evolution of conversions with pulse number in the reactions of (a) n-C6 at 500 °C and (b) 23-DMB at 450 °C over HY zeolite at different reactant concentrations in He

Figure 2. O/P ratio in the products (C1 – C6) in the conversions of (a) n-C6 at 500 °C and (b) 23DMB at 450 °C over HY zeolite with different reactant concentrations in He

Figure 3. Selectivity to aromatic products in the conversions of (a) n-C6 at 500 °C and (b) 23DMB at 450 °C over HY zeolite with different reactant concentrations in He

Reactant concentration (mol%)	Reactant amount in each pulse (μmol)	Coke amount ($\mu\text{mol C}$) after 10 pulses	
		n-C6 reaction at 500 °C	23DMB reaction at 450 °C
3.7	0.5	0.9	0.7
30	4.1	0.9	0.7

Table 1. Coke amount ($\mu\text{mol C}$) in the spent catalysts after 10 pulses of hydrocarbons

Figure 4. Conversion of the paraffins at the 8th pulse in the pure feed and their mixture with 1-hexene over HY zeolite with different reactant concentrations: (a) pure n-C6 and mixed feed at 500 °C and (b) pure 23DMB and mixed feed at 450 °C

Figure 5. Evolution of n-C6 conversion with pulse number in the reaction of pure n-C6 and its mixture with m-cresol over HY zeolite at 500 °C with different n-C6 concentrations in He: (a) 3.7 mol%, (b) 10 mol% and (c) 30 mol%

Figure 6. Evolution of 23DMB conversion with pulse number in the reaction of pure 23DMB and its mixture with m-cresol over HY zeolite at 450 °C with different 23DMB concentrations in He: (a) 3.7 mol%, (b) 10 mol% and (c) 30 mol%

Figure 7. Difference in the O/P ratios in the cracked products (C1 – C6) between the mixed feed and the pure feed in the reaction of n-C6 and its mixture with m-cresol at 500 °C (n-C6); and 23DMB and its mixture with m-cresol at 450 °C (23DMB) over HY zeolite with different hydrocarbon (HC) concentrations. Data at the 8th pulse.

Figure 8. Coke amount after 10 pulses of m-cresol or its mixtures with hydrocarbons over 100mg of HY zeolite at different reactant concentrations in He, corresponding to: (a) 3.7 mol% hydrocarbon and (b) 30 mol% hydrocarbon

* *mixed feed: hydrocarbon/m-cresol (95/5 wt/wt)*

** *only cresol: m-cresol with the same amount in the mixed feed*

Dashed lines: total amount of C in 10 m-cresol pulses

Feeds	(a) 3.7 mol% hydrocarbon				(b) 30 mol% hydrocarbon			
	<i>Pure Hydro-carbon</i>	<i>Pure m-Cresol</i>	<i>Sum of pure feeds*</i>	<i>Mixed feed **</i>	<i>Pure Hydro-carbon</i>	<i>Pure m-Cresol</i>	<i>Combined from pure feeds*</i>	<i>Mixed feed **</i>
Type of hydrocarbon	Production of Aromatics (BTX)				Production of Aromatics (BTX)			
n-C6 T_r = 500 °C	1.15	0	1.15	1.05	5.91	16.52	22.43	19.87
23DMB T_r = 450 °C	0.52	0	0.52	0.50	0.72	8.19	8.91	7.71

Table 2. Aromatic production at the 8th pulse (1/1,000 μmol) for the reaction of pure hydrocarbon (either n-C6 or 23DMB), pure m-cresol and their mixtures over HY zeolite corresponding to different hydrocarbon reactant concentrations in He: (a) 3.7 mol% (b) 30 mol% hydrocarbon.

* *Sum of aromatic production from the reactions of pure feeds*

** *mixed feed: hydrocarbon/m-cresol (95/5 wt/wt)*

Scheme 1. Reaction pathways of n-C6 over zeolite

Scheme 2. Interference of the phenolic pool to hydride transfer between hydrocarbons

Scheme 3. Formation of phenolic compounds via hydride transfer between hydrocarbon and the surface phenolic pool

Scheme 4. Interaction of the m-cresol and paraffin conversion pathways via hydride transfer