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Catalytic conversion of anisole over HY and HZSM-5 zeolites in the presence of different hydrocarbon mixtures

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ABSTRACT

The conversion of pure anisole (with a methoxy functionality, typical of some bio-oil components) and its mixtures with propylene, *n*-decane, benzene, or tetralin, has been investigated over zeolites in continuous flow and pulse reactors. The dominant reaction of pure anisole is transalkylation, which produces phenol, cresols, xylenols, and methyl anisoles as main products. However, in the presence of an effective hydrogen donor like tetralin important differences in product distribution are observed. In addition, while with pure anisole in the feed a fast deactivation is observed, the addition of tetralin to the feed results in lower amounts of carbon deposits and much higher catalyst stability. By contrast, less dramatic effects on stability and carbon formation were observed with most of the other co-fed hydrocarbons investigated.

1. Introduction

The unprecedented interest in renewable energy expressed in recent years by both government and industry has greatly accelerated research in this field [1]. As a result of these efforts, a significant increase in the role of renewable sources is expected for the near future [2]. In this regard, transportation is a crucial sector in which biomass-derived liquid fuels may have an important impact [3,4]. Among the various approaches for production of biomass-derived liquids investigated during the last few decades, fast pyrolysis and catalytic pyrolysis appear as potential options [5]. The products from these pyrolysis processes (so-called bio-oils) comprise different amounts of acids, esters, alcohols, furfural, aldehydes (including benzaldehyde with methyl and/or hydroxyl groups), and phenolics (phenol with methyl, methoxy and/or propenyl groups) [6–9]. Consequently, the oils directly obtained from fast pyrolysis (or even catalytic pyrolysis) processes cannot be directly used as transportation fuels without a prior upgrade. Their high oxygen and water contents cause chemical instability, immiscibility with hydrocarbon fuels, high viscosity, high acidity, and low heating value [10].

A major challenge in processing bio-oils in commercial scale is the massive production volume that will need to be handled. Therefore, it will be desirable to utilize existing refining infrastructure. For example, fluid catalytic cracking (FCC) represents a possible upgrading alternative since it is one of the largest refinery processes, it has flexibility for handling varying feedstocks, and does not require hydrogen, a valuable commodity. The primary function of the FCC process is to convert gas-oil streams containing high-boiling-point and high-molecular-weight hydrocarbons to more valuable products, such as high-octane gasoline and olefin-rich light gases, e.g. propylene. Co-processing bio-oils with conventional crude oil cuts in FCC units has been discussed in the literature [11–14].

Oxygenated aromatics deriving from lignin represent a significant fraction of bio-oil and are known to be much more refractory than other oxygenates in bio-oil [15–18]. Moreover, they tend to accelerate catalyst deactivation due to enhanced coke formation and strong adsorption on acid sites [13,14]. Bio-oil derived from lignocellulosic biomass comprises a large number of different phenolic compounds (guaiacol, vanillin, eugenol, etc.), which contain various oxygen functionalities (carbonyl, OH, methoxy). In this study, anisole was selected as a representative model compound because it is the one with only one methoxyl functional group. Rather than using real bio-oil mixtures, which would greatly complicate the analysis and interpretation of the results, we have

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studied the conversion of this methoxyl compound, which is a characteristic functionality in bio-oil. The objective of this contribution is to quantify the deactivating tendency of compounds containing methoxy groups on acidic zeolites and to explore the combined effects of these compounds with hydrocarbons representative of FCC feeds. We conducted most of our studies on HY zeolites, which are typical active components in FCC catalysts [19]. Therefore, the selected reaction conditions in this work are similar to those of FCC processes, but are not necessarily identical. This study does not attempt to simulate the FCC process, but rather investigate the chemistry of relevant molecules on relevant catalysts. A better understanding of the phenomena involved in the conversion of aromatics containing methoxy functionality and their mixtures with hydrocarbons over HY zeolites may certainly be of importance in FCC commercial units in which biomass-derived stream may be incorporated. For comparison, the behavior observed on an HZSM-5 zeolite was also investigated. The influence of feed composition on the activity, product selectivity, and catalyst stability was investigated for various hydrocarbons in a continuous flow reactor. In addition, experiments were performed using a pulse reactor to elucidate the reaction pathway for the specific mixture of anisole and tetralin, which is an effective H-donor.

2. Experimental

2.1. Catalytic measurements

The catalytic measurements were conducted on a 1/4 in. stainless steel tubular reactor. Commercial zeolites HY (Si/Al = 15 and 40) from Zeolyst International and HZSM-5 (Si/Al = 45) from Süd-Chemie were used as catalysts. Anisole, a model compound with methoxy functionality, typically present in bio-oil phenolics, was used as the main feed. Various hydrocarbons including propylene (C_3=), benzene (Bz), n-decane (n-C_{10}) and tetralin (Tet), were used as co-feeds. In each run, the catalyst sample (50 mg, 40–60 mesh) was placed at the center of the reactor and held in place with plugs of clean glass wool. The top and bottom parts of the packed bed were filled with 3 mm-diameter glass beads. The thermocouple was affixed to the outside wall of the reactor, at the height corresponding to the center of the catalyst bed. The operating conditions were as follows: atmospheric pressure, 400 °C, He carrier gas (40 mL/min), space–time (W/F) 0.42 h, with respect to the mass flow rate of anisole in both pure and mixed feeds. Prior to each run, the feed was sent through a by-pass until the concentration stabilized. At this point, the feed stream was switched to enter the reactor. The feed was introduced from a syringe pump at a liquid flow rate 0.12–0.24 mL/h and vaporized before entering the reactor. All pipelines were kept heated at 300 °C to avoid condensation of reactants. With to the procedure mentioned above, we have been able to close the carbon mass balance for every run. By comparing the total mass of the by-pass and that of the reactor outlet, based on the response from the GC-FID signals, a correspondence within 5% was obtained in every run. The products were analyzed on-line using an HP5890 gas chromatograph, equipped with an HP-5 column and a flame ionization detector (FID) detector. In parallel, the effluent was trapped in methanol, and analyzed by GC–MS (Shimadzu QP2010s) with the same HP-5 column, using reference standard compounds for identification. The GC–MS was used only for qualitative identification of the different product. All the quantitative analysis was done on the basis of the FID detector. The space–time (W/F), expressed in hours, is defined as the ratio between the mass of the catalyst and the mass flow rate of the feed.

It must be noted that the thermal conversion (i.e. blank run with an inert Hisil silica at the same reaction temperature) was negligible for all mixed feeds investigated.

2.2. Pulse experiment

The same reactor system was modified to operate in the pulse mode. In this case, two six-port valves were placed in a heating box, connected to the reactor inlet, outlet and sample loop to switch the flow and inject the pulse of reactant. The reactor includes 2 parallel 1/4 in. stainless steel tubes, one for bypass, and the other for reaction, which are connected through 3-way valves, also placed inside the oven. The tubing was heated by heating tape to avoid condensation of the reactants.

The feed was injected from a syringe pump, evaporated in the injection port and carried by He gas flow (He #2) into the sampling valve to fill the loop. Then, by switching the six-port valve, another He gas stream (He #1) was used to push the mixture from the sample loop into the reactor and carry it directly into the GC column for analysis. The 30 mg catalyst sample (HY, Si/Al = 40 or HZSM-5, Si/Al = 45) was mixed with 70 mg Hisil silica used as diluents and packed in the reactor tube. The catalyst bed was placed between two sections of 1 mm glass beads and fixed in place with clean glass wool. Before starting the pulse reaction experiment over the catalyst, the mixture from the sample loop was sent repeated times through the bypass line until a stable pulse size was measured in the GC. Then, the 3-way valves were switch to reactor tube. The products leaving the reactor were analyzed by the same GC-FID system mentioned above. The operating conditions for the pulse experiments can be specified as follows. Pulse: 1.0 s retention time, size: 0.0033 mmol tetralin and 0.0017 anisole mmol, atmospheric pressure, 450 °C.

2.3. Catalyst characterization

The coke deposited during reaction was analyzed by temperature programmed oxidation (TPO) of 30 mg samples of spent catalyst, under a gas flow of 2% O_2/He (30 mL/min). The heating ramp was 10 °C/min. The signals of H_2O (m/z = 18) and CO_2 (m/z = 44) were continuously monitored by a mass spectrometer (MKS). To get a precise measurement of the total amount of coke deposits on the catalysts an elemental carbon analyzer was used in addition to the TPO. While the results from both techniques are essentially equivalent (±5%), those from the elemental carbon analyzer were more precise and reproducible, and those are the ones reported in this paper.

3. Results and discussions

3.1. Catalytic reactions of pure anisole over HY zeolite

The total conversion and product distribution obtained from feeding pure anisole (An) onto the HY zeolite are summarized in Table 1. The main products were phenol (Ph), cresol isomers (Cr), xylenol isomers (Xol), methylanisole isomers (MA), and trace amounts of light gases (mainly methane for pure anisole feed and C_1–C_5 hydrocarbons for mixture feeds). In line with anisole conversion results previously observed on HZSM-5 [20–22], we find here that transalkylation is the dominant reaction over HY. The transalkylation steps involved in the anisole conversion that account for the observed products, are as follows [20].

$$\mathrm{An} + \mathrm{An} \rightarrow \mathrm{Ph} + \mathrm{MA}$$

$$\mathrm{An} + \mathrm{Ph} \rightarrow \mathrm{Ph} + \mathrm{Cr}$$

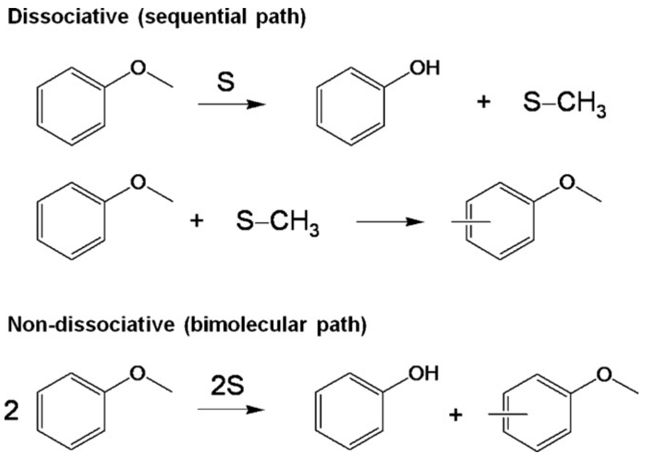
Table 1
Product distributions from conversion of anisole and anisole-tetralin mixture (~50% tetralin) over HY zeolite. Reaction conditions: $W/F = 0.42$ h (wrt. anisole for co-feed reaction), $T = 400\,^{\circ}$C, $P = 1$ atm He.

Feed	Anisole		Anisole + Tetralin	
	TOS = 0.5 h	TOS = 3.0 h	TOS = 0.5 h	TOS = 3.0 h
Conversion of Anisole	83.6	13.9	100	100
Conversion of Tetralin			98.4	96.6
Weight percent at reactor outlet				
C_1–C_5	1.2	0.2	8.8	8.2
Anisole	16.4	86.1	0.0	0.0
Phenol	35.2	6.8	28.1	29.2
Methylanisoles	3.3	4.2	0.0	0.0
Cresols	26.4	1.4	12.5	13.1
Xylenols	17.5	1.3	2.8	2.8
Benzene	0.0	0.0	2.1	1.9
Toluene	0.0	0.0	3.5	3.0
Alkylbenzene	0.0	0.0	9.7	8.8
Tetralin	0.0	0.0	0.8	1.7
Naphthalene	0.0	0.0	20.0	19.9
Alkylnaphthalene	0.0	0.0	9.9	9.5
Heavies	0.0	0.0	1.8	1.9
Selectivity of anisole products (wt.%)				
Methane	1.4	1.4	2.8	1.1
Phenol	42.1	48.9	63.7	64.0
Methylanisoles	3.9	30.2	0.0	0.0
Cresols	31.6	10.1	27.4	28.7
Xylenols	20.9	9.4	6.1	6.1

$$\mathrm{An} + \mathrm{Cr} \rightarrow \mathrm{Ph} + \mathrm{Xol}$$

$$\mathrm{MA} + \mathrm{Ph} \rightarrow \mathrm{Cr} + \mathrm{Cr}$$

It must be noted that these steps are not necessarily elementary and may involve intermediate steps [20]. Two possible reaction pathways can be considered for the transmethylation steps involved in these reactions (see Scheme 1). The first one is a dissociative pathway, in which an anisole (An) molecule generates phenol (Ph) and a methyl group, which may remain on the catalyst site as a surface methoxy. In a second step, this methoxy group can be transferred to another aromatic molecule. This aromatic molecule could be An yielding MA (as shown in Scheme 1), but it also could be any of the molecules included in the secondary reactions shown above (Ph, Cr) or an aromatic molecule present in the feed, (e.g., tetralin). The second possible reaction pathway involves a non-dissociative bimolecular reaction. In this case, as shown in Scheme 1, two anisole molecules directly interact on the surface, producing Ph and MA. A similar non-dissociative bimolecular reaction could in principle be operative for the other reactions mentioned above, including the reaction with tetralin, which is discussed below.



Scheme 1. Possible reaction pathways for transalkylation of anisole.

A rather fast catalyst deactivation was observed as a function of time on stream (TOS). That is, within 3 h of reaction, the anisole conversion dropped from more than 83% to less than 14%. Both, coke formation and strong adsorption of phenolic compounds (i.e. anisole derivatives) may be responsible for the rapid catalyst deactivation [13,14]. An interesting trend in product distribution can be observed as the catalyst deactivates. Fig. 1 shows the evolution of products (in wt.%) as a function of TOS. It is first noted that phenol

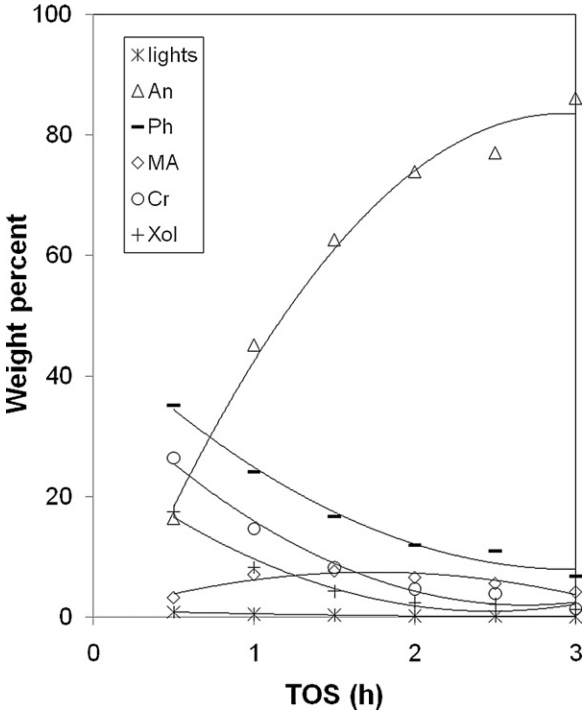


Fig. 1. Product composition at the reactor outlet as a function of time on stream during anisole conversion over the HY zeolite. Reaction conditions: $W/F = 0.42$ h, $T = 400\,^{\circ}$C, $P = 1$ atm He.

(Ph) is the most abundant product at all TOS. At the beginning of the run, the yield of cresol (Cr) and xylenol isomers (Xol) is higher than that of MA; however, this trend is reversed as the catalyst deactivates (i.e. at high TOS). A previous kinetic study [20] demonstrated that Ph and MA are the two primary products arising from anisole disproportionation. By contrast, Cr and Xol appear as secondary products derived from subsequent transalkylation steps.

The evolution of MA shows a maximum as a function of TOS. MA is only produced in the primary transalkylation while the subsequent steps only consume it. The catalyst deactivation causes and initial increase in MA due to a decreased consumption, but at long enough TOS the deactivation affects the primary step as well and the overall generation of products, including MA, decreases. This maximum was not observed for Ph, which in secondary steps, is not only consumed but also produced.

3.2. Effect of mixing anisole with different hydrocarbons over zeolites

To compare the effect of co-feeding hydrocarbons on the reaction of anisole, reactions with mixed feeds were performed at the same $W/F(\mathrm{An}) = 0.42$ h with respect to the mass rate of anisole (F(An)). The total W/F was in fact lower for the mixture because the total feed rate of the mixture (F) was higher than the feed rate of anisole alone (F(An)), which was kept constant. As seen in Table 1, the anisole conversion of the feed containing 50% tetralin was enhanced dramatically to ∼100% (i.e. W/F became in excess) even though the total W/F was lower and the W/F(An) was the same as in the case of pure An. We have previously reported the results obtained with pure tetralin feeds over HY zeolite under the same conditions used in this contribution [23]. In that study, we reported that light hydrocarbons, benzene, toluene and alkylbenzenes, such as ethylbenzene and xylenes, were produced by cracking. Naphthalene, resulting from the dehydrogenation of tetralin was also observed as an important product. In the same study, we measured the H-transfer ability of different hydrocarbons by using 1-tetralone as an indicator. In that contribution, tetralin was identified as a good H-donating molecule [23].

In addition to the changes in activity and stability, significant changes in product distribution were observed with the mixed feed in comparison to the reaction with the pure anisole. For example, the amount of methylanisoles, cresols, and xylenols obtained with pure anisole were significantly higher than those obtained with the mixed feed. At the same time, no changes in product distribution were observed as a function of TOS during the reaction. As we have recently discussed [23], tetralin is an effective H-donor in H-transfer reactions, and it is conceivable that a similar effect is responsible for the enhancement observed here.

A similar set of experiments was conducted with different co-fed hydrocarbons (∼50% hydrocarbon–50% anisole). The effect of the presence of different hydrocarbons in the mixture is illustrated with the different deactivation profiles shown in Fig. 2 together with the profile obtained with anisole alone (dashed line). The addition of tetralin greatly increased the anisole conversion on the HY zeolite. Since the conversion was 100% during the entire reaction time it is not possible to evaluate the deactivation, but it is clear that the activity remained very high during the 3 h of the experiment. It is suggested that H-transfer from tetralin, a good H-donating compounds [23], influences the adsorbed species in two possible ways: (1) promotes desorption of surface species; and (2) minimizes the rate of H-transfer from coke precursors. As a result, reduction of coke deposition is expected.

At the same time, tetralin itself can directly react with anisole through a bimolecular interaction. Consequently, the observed beneficial effect of tetralin the addition on anisole conversion may result of a combination of effects.

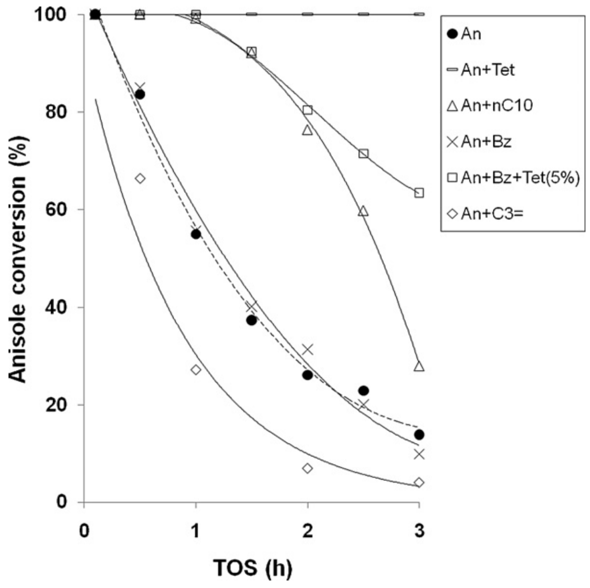


Fig. 2. Anisole conversion over HY zeolite with different co-fed hydrocarbons as a function of time on stream. Pure anisole feed is indicated with a dashed line. Reaction conditions: $W/F = 0.42$ h (wrt. anisole for co-feed reactions), co-feed concentration = ∼50%, $T = 400\,^{\circ}$C, $P = 1$ atm He.

In contrast, when benzene was used in the mixture instead of tetralin, the deactivation profile followed the same trend as that observed with pure anisole. Benzene is not a H-donor molecule and therefore it is not surprising that it showed no enhancement in either anisole conversion or catalyst stability. Interestingly, as shown in Fig. 2, adding only 5% of tetralin into the anisole/benzene mixture had a significant positive impact on anisole conversion. The addition of n-decane had a noticeable effect, although not as pronounced as that obtained with tetralin. Our previous study has shown that the H-transfer from n-decane is minimal [23]. Therefore, the improvement in catalytic activity upon the addition of n-decane can be ascribed to a dilution of the oxygenated aromatics (anisole or its products, phenol, cresol, etc.) on the surface, which prevents condensation of these compounds and minimizes catalyst deactivation. Finally, co-feeding propylene had a negative effect on anisole conversion; it is evident that propylene itself can participate in coke formation [24,25] and accelerates catalyst deactivation. While to make a conclusion regarding commercial applications, much longer times on stream will need to be evaluated, the 3 h reaction period used in this comparison is long enough to illustrate the dramatic differences observed with the different co-feeds.

The presence of tetralin not only enhanced anisole conversion, but also influenced product distribution, as shown in Fig. 3. For instance, the degree of the secondary reaction of phenol alkylation can be measured by the ratio (Cr + Xol)/Ph. For the pure anisole feed, this ratio was about 1.2 at the start of the reaction and decreased to about 1.0 as the catalyst deactivated, since the contribution of the secondary reactions became less prominent (Fig. 4a). Similar behavior is observed when the anisole feed was mixed with propylene, n-decane or benzene than for pure anisole (Fig. 4c and d). By contrast, the ratio was less than about 0.5 for the anisole/tetralin mixture and it remained unchanged as a function of TOS (Fig. 4b). The reduced phenol alkylation in the presence of tetralin was compensated by an increase in the alkylation of tetralin. In fact, the alkylnaphthalenes/naphthalene ratio gradually increases with the concentration of anisole in the feed as compared with that of pure tetralin (Fig. 5). This trend demonstrates that anisole can transfer its methyl group from the methoxyl group to naphthalene, which is a product of tetralin dehydrogenation.

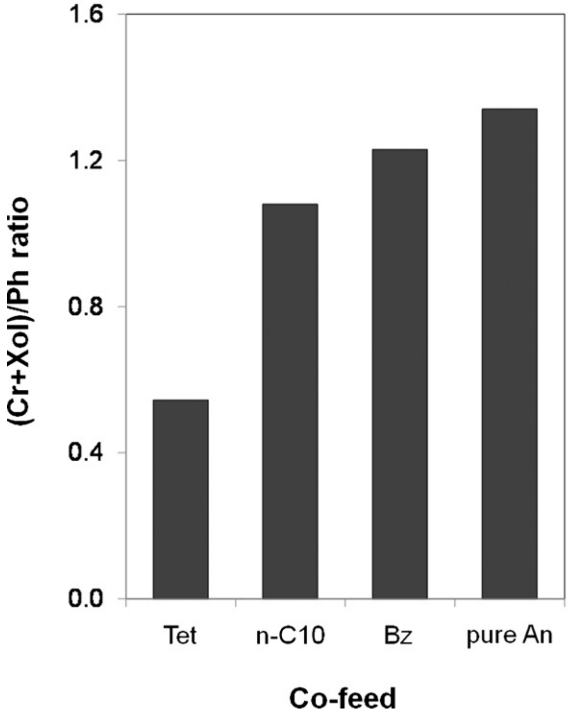


Fig. 3. Degree of phenol alkylation (i.e. (Cr + Xol)/Ph yield ratio) for pure anisole and mixture feed reactions over the HY zeolite. Reaction conditions: $W/F = 0.42$ h (wrt. anisole), $T = 400\,^{\circ}$C, $P = 1$ atm He, co-feed concentration = ~50%, TOS = 0.5 h.

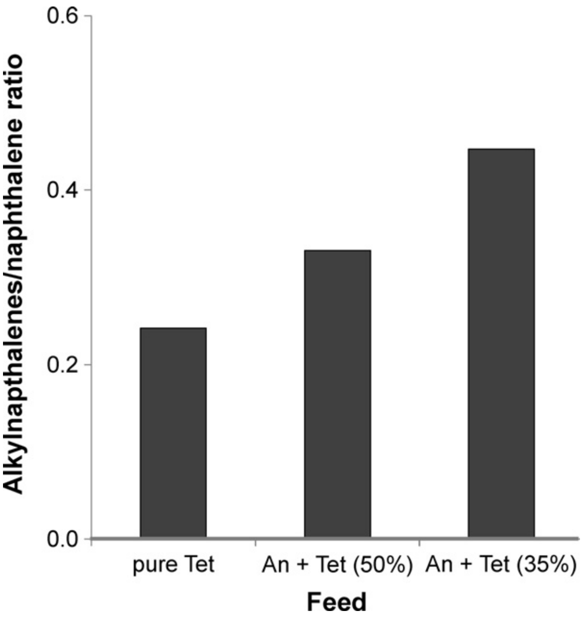


Fig. 5. Alkylnapthalenes/naphthalene product ratio for pure tetralin and mixture feed reactions over the HY zeolite. Reaction conditions: $W/F = 0.42$ h (wrt. anisole), $T = 400\,^{\circ}$C, $P = 1$ atm He, TOS = 0.5 h.

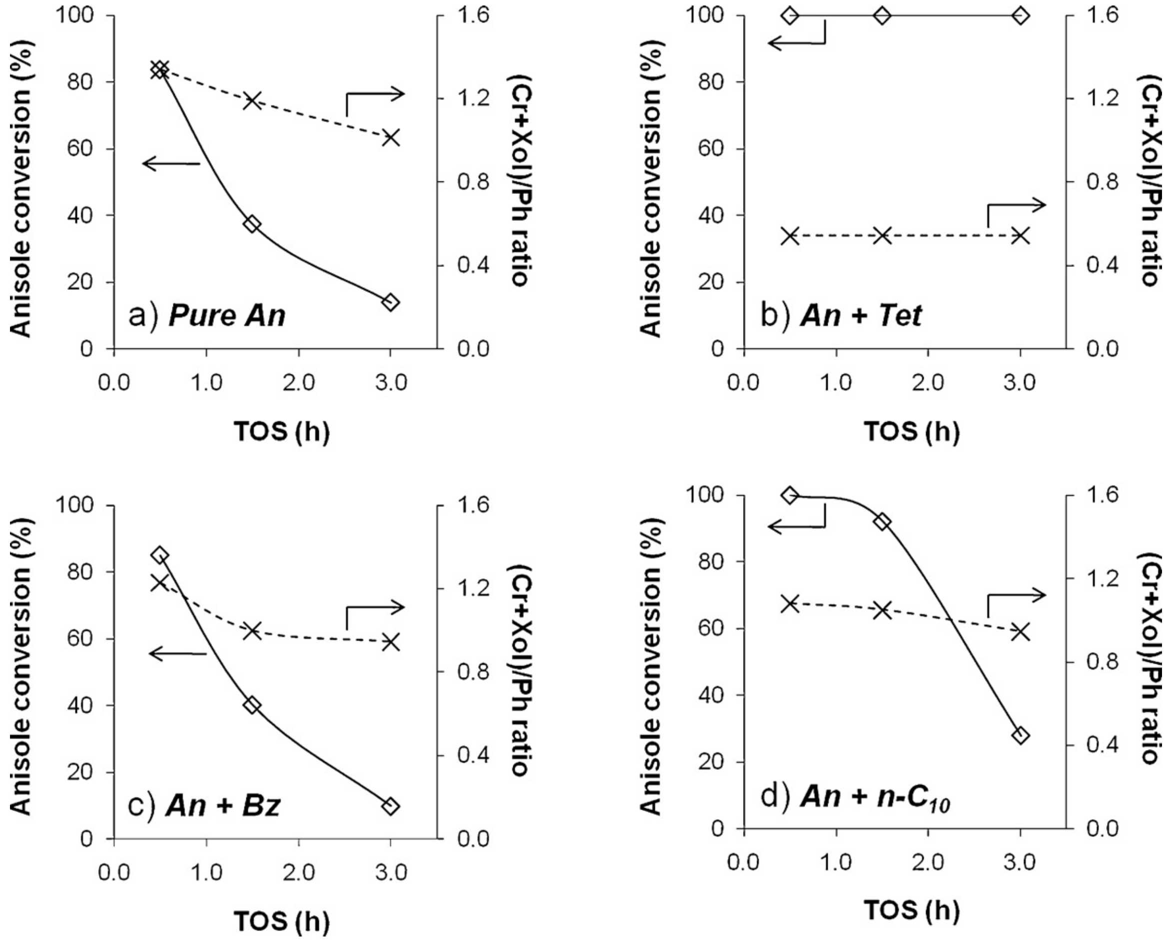


Fig. 4. Relationship between conversion of anisole and degree of phenol alkylation as a function of time on stream. Reaction conditions: $W/F = 0.42$ h (wrt. anisole), $T = 400\,^{\circ}$C, $P = 1$ atm He, co-feed concentration = ~50%, TOS = 0.5 h.

3.3. Reaction pathways

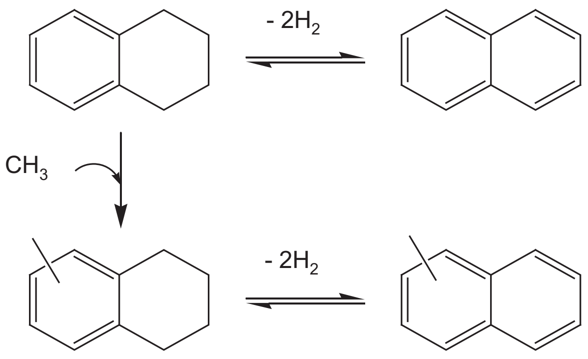
As mentioned above two possibilities can be considered for the transmethylation of aromatic molecules containing a methoxy group, a dissociative sequential pathway and a non-dissociative bimolecular pathway.

To check whether these paths occur to a significant extent the following experiment was devised. After stabilizing the reactor and the detector, a pulse of anisole was first fed to the reactor followed by a pulse of tetralin sent 4–5 s later. Since the two reactants are not simultaneously present on the catalyst, it is anticipated that only if the dissociative (sequential) pathway is operative transmethylation will be observed. That is, the anisole from the first pulse, can dissociate and leave a methyl group on the surface, this group can subsequently react with tetralin sent in the subsequent pulse.

Methylation preferentially occurs on activated aromatic rings. The aromatic ring in tetralin is highly activated and therefore it has the tendency to accept a methyl group. At the same time, tetralin is a hydrogen donor and can easily dehydrogenate to naphthalene. Since the hydrogenation/dehydrogenation reactions can be equilibrated at the high temperature of the experiments, while alkylation involves tetralin, only alkylnaphthalene and naphthalene are observed in the products, as illustrated in Scheme 2.

Accordingly, the ratio of methylnaphthalene-to-naphthalene represents the degree of transalkylation to tetralin. As shown in Fig. 6, this ratio greatly increased with the addition of anisole since with pure tetralin, alkylation can only occur from cracking fragments. The significant increase observed during the sequential pulses (An → Tet) compared to pure tetralin supports the concept of the dissociative mechanism. It is conceivable that, while the separation time between the anisole and tetralin pulses was very short (4 s), a significant fraction of the methyl group may leave the surface under the continuous flow of He; therefore, the degree of tetralin alkylation in the sequential pulse experiment (i.e. An → Tet) is always lower than that for the mixed pulses (i.e. An + Tet), in which the surface methyl groups can be consumed immediately, as also shown in Fig. 6.

Interesting differences are observed when the results obtained on HY are compared to those obtained over an HZSM-5 zeolite of similar Si/Al ratio. When the sequential anisole/tetralin pulses were sent over the catalysts, the degree of tetralin alkylation (as measured by the alkylnaphthalene/naphthalene ratio) was almost identical for both HZSM-5 and HY. As discussed above, only the dissociative reaction pathway is operative in this case since anisole and tetralin are not simultaneously present over the catalysts. This reaction mode shows no significant differences between the two zeolites, with comparable number of acid sites. In contrast, in the mixed feed pulse experiments the extent of alkylation was much lower for HZSM-5 than for HY. Certainly, the differences in structure show a greater effect for the bimolecular path. The HZSM-5 zeolite has 10-membered ring aperture channels, with the diameter of 5.6 Å, whereas HY has 12-membered ring aperture channels with the diameter of 7.4 Å and much larger void spaces in the supercages [26]. The more open structure of HY is favorable for the bimolecular re-arrangements required for the non-dissociative path, which results in an extra contribution towards the alkylation rate via the non-dissociative bimolecular path. By contrast, it has been long recognized that the much more restrictive pores in HZSM-5 inhibit bimolecular encounters [27]. More recent molecular dynamics studies of aromatics in MFI structures support this concept [28]. Similarly, one can predict that tetralin and anisole can diffuse with significant hindrance into the small channel of HZSM-5 and, as a result, the bimolecular reactions would be inhibited, making the dissociative reaction pathway dominant.



Scheme 2. Alkylnaphthalene formation by methylation of tetralin.

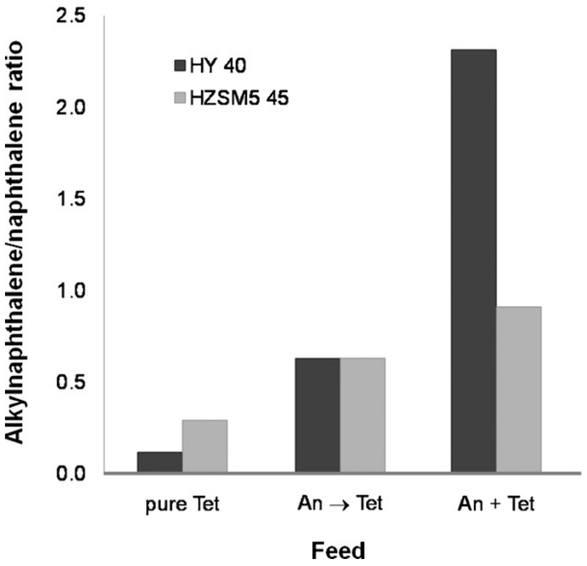


Fig. 6. Alkylnapthalenes/naphthalene product ratio (at the 5th pulse) for pure tetralin and mixture feeds over the HY and HZSM5 zeolites in pulse experiment. Reaction conditions: $T = 450\,^{\circ}$C, $P = 1$ atm He. Pure Tet: pure tetralin, catalyst/feed ratio = 70 (g/g); An + Tet: mixture of anisole and tetralin (30 wt.% tetralin), catalyst/feed ratio = 70 (g/g tetralin); An → Tet: pulse tetralin right after anisole injection, catalyst/feed ratio = 70 (g/g tetralin) and 150 (g/g anisole).

3.4. Coke formation during reaction of pure anisole and mixtures

Table 2 compares the amount of C (wt.%) deposited on the HY zeolite during 3 h TOS from the different feed mixtures. The amounts deposited during this period from pure anisole and pure tetralin feeds are 11.8 and 3.0 wt.% C, respectively. Interestingly, the addition of tetralin to anisole results in a reduction in C deposits. The extent of this reduction depends on the concentration of co-fed tetralin. That is, the amount of C deposits dropped from 11.8 to 8.8 and 6.0 wt.% C as the concentration of tetralin increased from 0% to 35% and 50%, respectively. It must be noted that, as shown

Table 2
Comparison of amount of carbon deposited on spent catalysts from the reactions of different mixture feed over the HY zeolite. Reaction conditions: $W/F = 0.42$ h (wrt. anisole for cofeed reaction), $T = 400\,^{\circ}$C, $P = 1$ atm He. TOS = 3 h.

Feed	C (wt.%)	$\mathrm{mg_{carbon}/g_{anisole}}$	$\mathrm{mg_{carbon}/g_{total\ feed}}$
Pure An	11.8	16.5	16.5
Pure Tet	3.0	–	4.1
An + Tet (50%)	6.0	8.4	4.2
An + Tet (35%)	8.8	12.3	8.0
An + n-C_{10}	10.6	14.8	7.4
An + Bz	11.6	16.2	8.1
An + C_3=	15.9	22.3	11.1

Table 3
Amounts of carbon formed on the spent HY zeolite. Reaction conditions: $W/F = 0.42$ h (wrt. anisole for co-feed reaction), $T = 400\,^\circ$C, $P = 1$ atm He. TOS = 3 h.

Feed	C (wt.%)	$mg_{carbon}/g_{total\ feed}$	A_{H_2O}/A_{CO_2}
Pure Tet	3.0	4.1	0.26
An + Tet (50%)	6.0	4.2	0.28
Pure An	11.8	16.5	0.56

in Table 2, the same trend is observed whether the amount of C deposits is compared to either the total amount of anisole or the total amount of feed passed over the catalyst

We rationalize the reduction in C deposits by an enhanced H-transfer, which as previously shown [29], inhibits coke formation that results in catalyst deactivation, in line with the higher stability shown in Fig. 2 when tetralin is added to the feed.

This concept is further supported by the almost insignificant effect on coke formation observed when other hydrocarbons with lower H-transfer capacity are used as co-feed. In fact, the amount of C deposited when incorporating *n*-decane and benzene to the anisole feed was about the same as that deposited when anisole was used as a pure feed. Moreover, when a coke-forming molecule such as propylene was used, the C deposits increased to 15.9 wt.% C. That is, the trends in coke formation are consistent with the observed deactivation patterns (Fig. 2).

To gain further insight about the nature of the coke deposits, the evolution of H_2O and CO_2 during the TPO of the coked catalysts was monitored and quantified in a mass spectrometer. The integrated intensity ratios between the H_2O and CO_2 signals are reported in Table 3. It is apparent that the reaction under pure anisole produced a coke richer in H compared to that obtained under either pure tetralin or the anisole/tetralin mixture. This difference suggests that, in the absence of tetralin, anisole adsorbs strongly on the HY zeolite and forms carbonaceous deposits with a much lower extent of dehydrogenation [13,14]. So, the deactivation due to anisole can be described as a molecular condensation process on the active surface, rather than the typical formation of polyaromatic coke. By contrast, in the presence of tetralin, elimination of anisole and its surface derivatives from the surface is assisted via H-transfer from tetralin. The coke thus formed is primarily arising from tetralin and from those species, which cannot be eliminated from the surface via H-transfer. They become more dehydrogenated than the adsorbed anisole species, as suggested by the low H_2O/CO_2 ratio observed during TPO (Table 3).

3.5. *Recovery of anisole conversion by flushing the spent catalysts with tetralin*

Two additional experiments were conducted to shed further light on the role of tetralin in inhibiting deactivation by anisole (Fig. 7). In the first experiment, a flow of pure anisole in He carrier was continuously fed for 2 h into the reactor at a $W/F = 0.42$ h and $T = 400\,^\circ$C. After stopping the flow of anisole (in He), pure tetralin (in He) was injected at the same W/F during 1 h. Finally, the feed of pure anisole (in He) was restarted at the same initial conditions. It is observed that during the first 2 h of reaction, the conversion of anisole dropped from ∼80% to ∼20%. However, after passing pure tetralin (in He) for 1 h, the anisole conversion was observed to recover to about 40%. After re-injection of the pure anisole feed, the catalyst started deactivating again. The partial recovery of the catalyst activity by passing tetralin suggests that at least some of the catalyst sites deactivated by anisole (or its derivatives) can be regenerated in the presence of tetralin. That is, unlike the typical deactivation by coke, the strong adsorption of aromatic oxygenate compounds (e.g. anisole and phenol) can be partially reversible by H-transfer from tetralin.

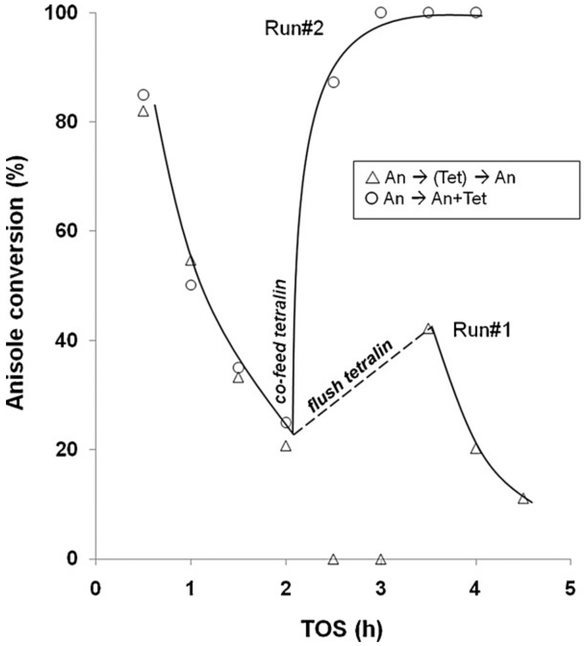


Fig. 7. Effect of co-fed tetralin on anisole conversion over the HY zeolite. Reaction conditions: $W/F = 0.42$ h (wrt. anisole for co-feed reaction), co-feed concentration = ∼50%, $T = 400\,^\circ$C, $P = 1$ atm He.

In the second experiment in this series, pure anisole (in He) was fed into the reactor for 2 h, under the same conditions as in the other sequence. However, in this case, after the first anisole reaction period, a 50/50 tetralin/anisole mixture was co-fed while the anisole conversion was being measured. As shown in Fig. 7, a remarkable increase in anisole conversion that went from ∼20% to ∼100% was observed as a function of time on stream, exceeding even the initial conversion observed under pure anisole. In this case, the role of tetralin is not only helping remove fragments that deactivate the surface, but also starting the non-dissociative bimolecular transalkylation, which is very significant on the open structure of HY zeolite.

4. Conclusion

The conversion of anisole on HY zeolite produces phenol, cresols, xylenols and methylanisoles as main products during several transalkylation steps. Catalyst deactivation is significant under the reaction conditions and it is caused by strong adsorption of phenolic compounds and coke formation. The latter is an irreversible process, whereas the former is reversible and can be minimized by incorporation of molecules such as tetralin with high H-transfer capacity. Co-feeding tetralin or other H-donors has a beneficial effect on anisole conversion and reduces coke formation. Other hydrocarbons with a weaker H-transfer capacity have lower (e.g., *n*-decane), negligible (e.g., benzene), or even detrimental effect on activity (e.g., propylene).

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