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A comparison of the reactivities of propanal and propylene on HZSM-5

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ABSTRACT

The reactivities of propanal and propylene have been compared over HSZM-5 zeolites (Si/Al = 45 and 25). Propanal is found to be much more reactive than propylene and to form mostly 2-methyl-2-pentenal and C_9 aromatics as early products in the reaction network. Propylene, in contrast, requires more severe conditions to form C_6 and C_7 aromatics. It is proposed that propanal undergoes acid-catalyzed aldol condensation to form 2-methyl-2-pentenal. This dimer undergoes further condensation to form the aldol trimer, which subsequently dehydrates and cyclizes into C_9 aromatics. In contrast, it is well known that propylene, like other olefins, undergoes aromatization via oligomerization and formation of a hydrocarbon pool. While in the conversion of propanal, propylene is also produced, it appears that it does not play a major role in the formation of aromatics under conditions of shorter space times and lower temperatures, at which propanal produces aromatics in significant amounts.

1. Introduction

Substantial production of oxygenates from biomass conversion and biodiesel production has generated growing interest in processes for upgrading these compounds to fuels and chemicals. Bio-oil production from fast pyrolysis of biomass has been estimated to have lower operating and capital costs compared to other biomass conversion processes [1,2]. Bio-oil contains large amounts of reactive oxygenated compounds with various functional groups including aldehydes, ketones, acids, and polyols. The composition of bio-oil varies considerably depending on feedstock and reaction conditions (a range of composition might be: 54–58% C, 5.5–7% H, 35–40% O, and 0–0.2% N) but contain large amounts of oxygenate species such as aldehydes, alcohols, and acids, and thus has a low heating value [3,4]. Furthermore, these oxygenates are thermally and chemically unstable and need to be converted to make them compatible with transportation fuels [3,4]. For instance, acetaldehyde and propanal found in bio-oils can further oxidize to form corrosive acids or participate in polymerization reactions to form heavy products during storage and transportation. While small oxygenates are liquid, they tend to have high volatility and increase the vapor pressure of fuels. In contrast to hydrotreating [3–5] that converts the light oxygenates to gases, causes losses in liquid yield, and consumes valuable hydrogen, the conversion of light oxygenates via condensation and aromatization to larger, more stable molecules appears to be an attractive opportunity to enhance the liquid quality and yield.

The complexity of bio-oil has created a great challenge in understanding reaction pathways and tailoring catalysts toward desirable fuel components. Thus, model compounds have been studied over different types of catalysts. e.g., metals, metal oxides, and zeolites. Reforming sugar/carbohydrate compounds from pretreated biomass, such as sorbitol, to produce synthesis gas and alkanes has been well demonstrated on metal catalysts by Huber and Dumesic [6]. They have also proposed a strategy for making non-oxygenated diesel compounds, C_9–C_{15}, in sequential steps: dehydration, aldol condensation, and hydrodeoxygenation. At the same time, condensation of small aldehydes, acids, or ketones to form higher boiling point *n*- and isoalkanes has been studied on metal oxide catalysts [7,8]. In contrast to noble metal and metal oxide catalysts, acidic zeolites [9–11] have the ability to directly convert oxygenates to primarily isoalkanes and aromatics in the gasoline boiling range.

HZSM-5 has been extensively studied for the conversion of methanol to hydrocarbons, in relation to the well-known MTG process (methanol-to-gasoline) [12], as well as other similar processes, such as the integrated gasoline synthesis process from Haldor Topsøe [13].

The reactions of aldehyde, ketone, acid, and furanic compounds on HZSM-5 also have been extensively investigated [9–11,14]. In these studies, substantial amounts of aromatics have been observed in the final products. In general, the most widely accepted aromatization pathway is that oxygenates are first converted to

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olefins and these are then oligomerized and dehydrocyclized to form aromatics [9]. Other studies have found that greater aromatization activity is observed with propanal compared to other C_3 oxygenates such as ketone, alcohol, acid, or ester [14–16]. Similarly, researchers from our group have found that aromatics are produced to a much greater extent when starting from methyl-octanoate than when starting from *n*-octane [17,18]. They have proposed that aromatics are produced from the direct ring closure of an oxygenated intermediate keeping the original carbon chain, rather than via cracking/oligomerization/cyclization.

Therefore, it appears important to conduct a direct side-by-side comparison of the reactivity of a simple aldehyde and the corresponding olefin to determine whether they follow different reaction paths or they go through a common path. In this contribution, we report the results of the propanal conversion to aromatics in comparison with the conversion of propylene, obtained on two HZSM-5 catalysts under identical reaction conditions.

2. Experimental details

2.1. Catalyst preparation

A commercial HZSM-5 (Si/Al = 45) zeolite was supplied by Süd-Chemie, Inc. Another ZSM-5 sample was synthesized in-house following a synthesis method described elsewhere [19]. The Si/Al ratio of the synthesized ZSM-5 sample was specified to be 25 by modifying the amount of Al in the original recipe. The proton form of the zeolite was obtained from ion-exchange with NH_4NO_3 at 80 °C for 10 h. The process was repeated to completely replace the cations in the zeolite with NH_4^+. The final synthesized HZSM-5 catalyst was obtained after drying at 100 °C for 10 h and calcining at 600 °C for 3 h in dry air. The two zeolite samples used in this work are identified as HZSM-5 (45) and HZSM-5 (25), corresponding to the commercial HZSM-5 (Si/Al = 45) and the in-house synthesized HZSM-5 (Si/Al = 25), respectively.

2.2. Equipment and procedures

The continuous flow reactor used in the catalytic measurements was a 1/4″ outside diameter, quartz tube fixed bed reactor. The reactor was heated in a split-tube furnace (Thermal Craft) with a digital feedback temperature controller (Omega). Before each run, the catalyst was treated *in situ* with H_2 (35 sccm) for 1 h at 400 °C. Propanal, obtained from Sigma–Aldrich, was fed into the reactor by using a syringe pump (KD Scientific) at a constant flow rate of 0.12 ml/h. Ultra-high-purity propylene was obtained from Airgas. The reactions were carried out at atmospheric pressure in flowing H_2 (35 sccm) at different space times (weight of catalyst to organic mass feed rate ratio: W/F).

In the pulse experiments, the same diameter quartz tube was used as in the continuous flow configuration. The catalyst was pretreated with the same procedure mentioned above. Liquid propanal was introduced into the reactor in 5-μl (liquid) pulses using a GC syringe (Hamilton 10 μl). Propylene was introduced into the system using a 6-port valve with a 5-ml sample loop. For temperature-programmed reaction–desorption experiments, propanal was pre-adsorbed by sending twenty 5-μl pulses at 250 °C. After flushing with He, the reactor was heated up to 600 °C with a ramp rate 10 °C/min.

2.3. Product analysis

Every 30 min on stream, products were analyzed online by GC/FID (HP6890). The products were sampled using a 6-port valve with a 250-μl sample loop heated to 290 °C. After each run, the reactor was purged with pure He for 15 min to collect the residual products that desorb from the catalyst bed. The liquid products collected in solvent methanol were then identified by GC/MS (Shimadzu Q-2010). Both GCs are equipped with HP-INNOWAX columns. In the pulse experiments, the products were analyzed by a mass spectrometer (MS) detector (MKS Cirrus 200).

2.4. Characterization

The commercial and in-house synthesized HZSM-5 samples were characterized by X-ray powder diffraction (Bruker D8 Discover) and scanning electron microscopy (SEM) to confirm the crystal structure and determine the morphology and crystallite size of the zeolites. The acidity of the HZSM-5 was determined by temperature-programmed desorption (TPD) of iso-propyl amine (IPA) in a quarter inch quartz tube reactor with 50 mg of catalyst connected to an online MS detector (MKS Cirrus 200). Before each TPD run, the sample was pretreated in He at 400 °C for 1 h and then cooled down to 100 °C. The IPA adsorption was carried out by injecting four liquid pulses of IPA (4 μl each pulse) over the sample in He at 100 °C, at 2.5 min intervals. The catalyst was then flushed in He flow for 30 min at 100 °C and the TPD was started, using a temperature ramp of 10 °C/min up to 650 °C. The MS signals of m/z 44 (IPA), 41 (propylene), 17 (ammonia), 18 (water), 16 (fragment of ammonia) were monitored. The signals were calibrated with a 5-ml loop of 2 vol.% ammonia in He.

3. Results

3.1. Characterization

The XRD pattern of the synthesized HZSM-5 sample is in agreement with those reported in the literature [12]. The SEM results show that the synthesized sample has a crystallite size of 1–2 μm, significantly larger than the commercial HZSM-5 (100–150 nm).

The TPD profiles of the commercial HZSM-5 (45) and synthesized HZSM-5 (25) in Fig. 1 show the evolution of propylene from adsorbed IPA with a maximum at about 350 °C. It has been suggested that the decomposition of adsorbed IPA is catalyzed by strong Brønsted sites and therefore the amount of propylene desorbed can be directly related to the density of Brønsted acid sites [20,21].

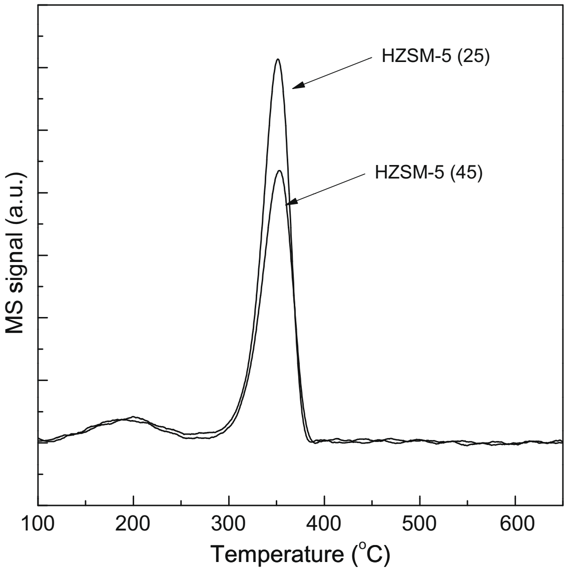

Fig. 1. Isopropylamine-TPD profiles of HZSM-5 (45) and HZSM-5 (25):propylene evolution.

Table 1
Total acid density and Si/Al of zeolites.

Zeolite	Si/Al[a]	Acidity[b] (mmol/g)
HZSM-5 (25)	25	0.421
HZSM-5 (45)	53	0.330

[a] Si/Al ratio calculated from elemental analysis in SEM by EDX.
[b] Brønsted acid density derived from IPA-TPD.

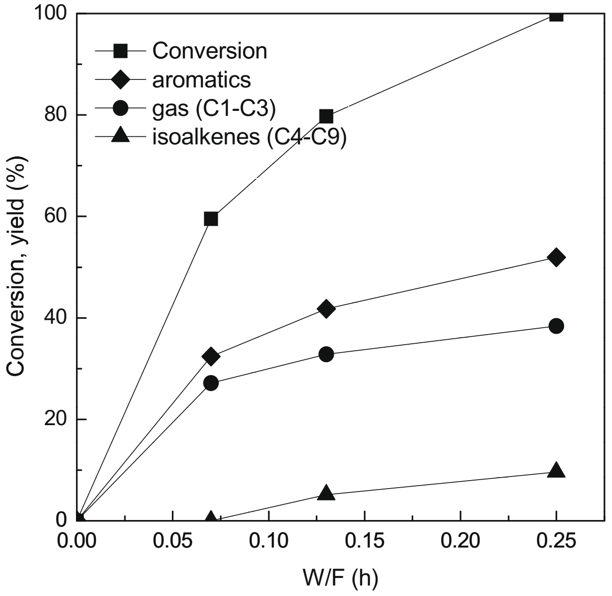

Fig. 2. Propanal conversion and product distribution as a function of space time (W/F) on HZSM-5 (45) at 400 °C.

The calculated Si/Al ratios of the samples were obtained from elemental analysis in SEM by EDX. The summary of the physical properties of the HZSM-5 (45) and HZSM-5 (25) samples are shown in Table 1.

3.2. Conversion of propanal and propylene in a steady flow reactor

Propanal was converted to aromatics (C_6–C_9), gas (C_1–C_3), and isoalkenes (C_4–C_9) on HZSM-5 (45) at 400 °C. The variation of product yields with space time (W/F) are shown in Fig. 2 over the range of 0.07–0.25 h for data taken after 1 h on stream. In this range, the propanal conversion ranged from 59.5% to 99.8%. Aromatics and gas (C_1–C_3) yields increased more rapidly compared to the isoalkenes (C_4–C_9) yield as W/F increased. In fact, aromatics were always observed as major products even at the shortest W/F studied. In this range of W/F, the highest yield of aromatics was 51.9% obtained at 0.25 h W/F. The second major products were gases (C_1–C_3) of which the majority was propylene. The isoalkenes (C_4–C_9) were always relatively minor products.

A separate experiment under the same conditions as those used for propanal conversion was conducted feeding 2-methyl-2-pentene to determine its propensity for further reaction and aromatics formation. The results showed that this isoalkene is reactive, forming only propylene and other isoalkenes, but did not form aromatics. These results are summarized in Table 2.

Conversion of propylene was performed at the same temperature, 400 °C, as the propanal experiments but to longer space times, up to W/F = 4 h. However, the level of conversion with this feed was much lower and only traces of aromatics were obtained (<1%), as shown in Table 3. This result indicates that these reaction conditions are insufficient for the reaction to proceed through the intermediate steps typically observed at higher temperature, in which aromatization occurs via oligomerization of olefins. In order to obtain significant yields of aromatics from propylene, a

Table 2
Product distribution from propanal and 2-methyl-2-pentene reaction experiments.

Feed	Propanal	2-Methyl-2-pentene
Conditions	W/F = 0.2 h HZSM-5 (45) 400 °C	W/F = 0.2 h HZSM-5 (45) 400 °C
TOS (min)	60	60
Conversion	94.4	96.0
Gas (C_1–C_3)	37.8	44.6
Isoalkenes (C_4–C_9)	5.5	51.4
Aromatics	51.1	
C_6 (benzene)	0.1	–
C_7 (toluene)	10.3	–
C_8 (xylene)	13.1	–
C_9 (MEB and TMB)	20.2	–
C_{10+}	7.3	–

Table 3
Product distribution from propanal and propylene reaction experiments.

Feed	Propanal				Propylene			
Conditions	W/F = 0.07 h HZSM-5 (45) 400 °C		W/F = 0.13 h HZSM-5 (45) 400 °C		W/F = 4 HZSM-5 (45) 400 °C		W/F = 4 h HZSM-5 (25) 500 °C	
TOS (min)	60	150	60	150	60	150	60	150
Conversion	52.5	39.4	76.3	56.8	42.4	41.0	65.6	64.4
Gas (C_1–C_3)	27.0	22.5	32.2	29.9	–	–	38.4	36.6
Isoalkenes (C_4–C_9)	0	0	3.4	1.0	41.8	40.6	9.7	10.6
Aromatics	25.9	16.8	40.7	25.8	0.7	0.5	17.5	17.2
C_6 (benzene)	0.0	0.0	1.0	0.0	0.3	0.3	3.5	3.5
C_7 (toluene)	4.2	2.4	6.9	4.2	0.2	0.1	9.0	9.0
C_8 (ethyl-benzene)	0.8	0.5	1.3	0.9	–		0.2	0.2
C_8 (p-xylene)	2.7	1.5	3.8	2.4	0.2	0.1	1.3	1.3
C_8 (m-xylene)	2.3	1.4	3.9	2.5	–		2.6	2.5
C_8 (o-xylene)	2.1	2.2	1.5	2.3	–		1.0	0.9
C_9	11.2	7.1	15.5	10.6	–		–	–
C_{10+}	2.5	1.7	6.3	2.9	–		–	–
C_9/others	0.93	0.89	0.84	0.86				

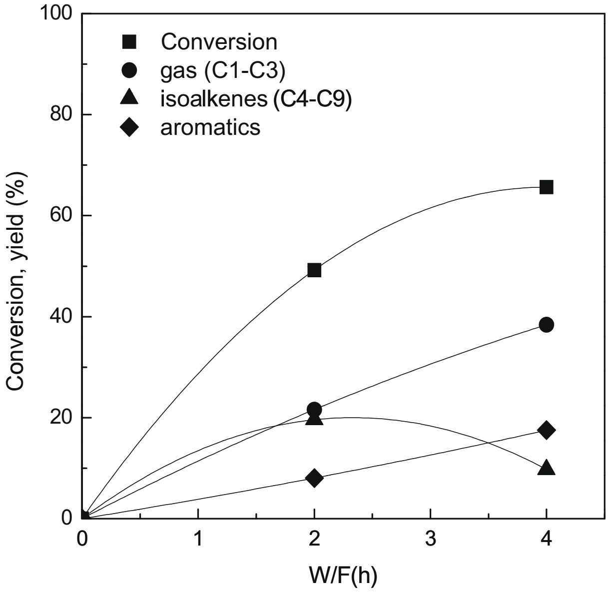

Fig. 3. Propylene conversion vs. W/F on HZSM-5 (25) at 500 °C.

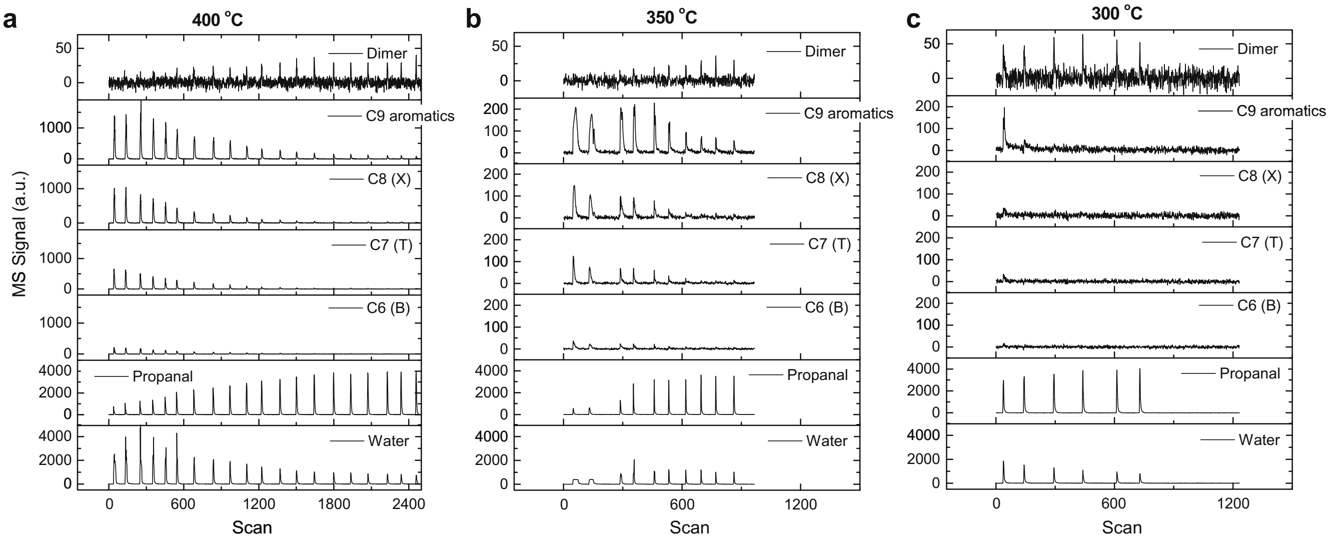

Fig. 4. Propanal pulse reaction series on HZSM-5 (45) at different temperatures: (a) 400 °C; (b) 350 °C; (c) 300 °C.

synthesized HZSM-5 with a higher acid density (Si/Al = 25) was used and operated at a higher temperature of 500 °C and longer W/F. Table 3 shows that the propylene conversion under these severe conditions and with a much more active catalyst can reach a similar range to that obtained with propanal conversion. Only in this case, does the aromatics yield from propylene becomes significant. These results are summarized in Fig. 3. At short W/F, in contrast to the behavior observed with propanal, the major products are alkenes and light gases C_1–C_2. At longer W/F, yields of both aromatics and light gases continued to increase while the yield of alkenes reached a maximum and then declined. This trend suggests that the alkenes were consumed to produce more aromatics as well as cracking products. Although the particle size of the synthesized high acid density zeolite was considerably larger than the commercial (0.5–1 μm vs. 200 nm), this behavior has been extensively reported in the literature for the aromatization of hydrocarbons and is consistent with those results operating via the well-known hydrocarbon pool [22,23]. An interesting point is that aromatics formation with propanal was much higher than that from propylene. For example, at a similar conversion level (∼60%), only 10% aromatic yield was obtained in comparison to 30% obtained with propanal. Understandably, at the severe conditions used in the propylene experiments, the extent of cracking is much greater.

The aromatic product distribution at 60 min and 150 min time on stream (TOS) for both the propanal and propylene experiments are summarized in Table 3. The conditions were adjusted so that in both cases the conversions were in about the same range. It is clearly seen that propanal yields larger amounts of heavier aromatics and much lower amounts of C_6 (benzene) and C_7 (toluene) compared to those from propylene. That is, C_8 (xylene), C_9 (trimethylbenzene (TMB) and methylethylbenzene (MEB)), and C_{10+} aromatics were observed as products from propanal but not from propylene at this conversion level. Because the distribution of aromatics produced from propanal appears to be different than those produced from propylene, transient pulse reaction experiments were performed for both propylene and propanal at the reaction conditions used in their respective steady flow experiments in order to better see the evolution of the product distributions through to the formation of the aromatics.

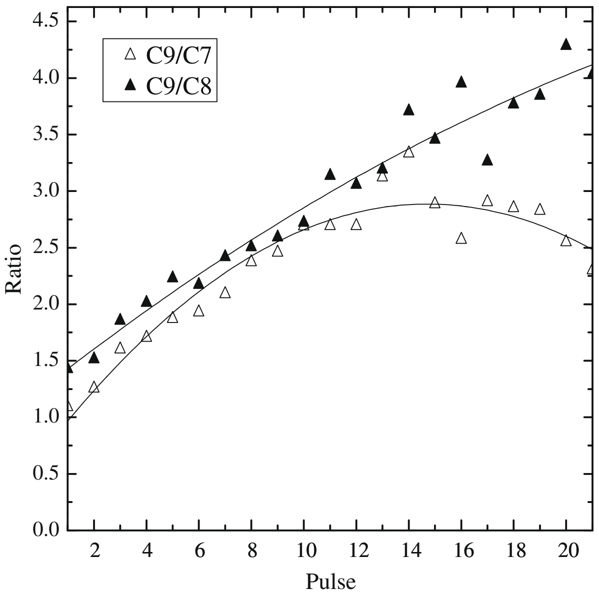

Fig. 5. Aromatics ratios for propanal pulse reaction series on HZSM-5 (45) at 400 °C.

One difference in reaction conditions between experiments feeding propanal or propylene is the presence of water. The conversion of propanal, either via dehydration or aldol pathways, results in the formation of an equimolar amount water. In pyrolysis, it is also known that substantial amounts of water are produced and may be expected to be present in catalytic conversion of bio-oil and its oxygenate fractions. Therefore, the effect of water on the catalysis may be an important consideration. An experiment was conducted with propanal as the feed in which water was injected part way through the run, injected for a period of time, and then stopped while the experiment was continued. The result showed that during the period when water was being injected, activity was reduced. After the water addition was stopped, the activity returned to a comparable level as if the water had never been injected.

3.3. Transient conversion of propanal

The pulse reactor was loaded with 10 mg of HZSM-5 (45) and pretreated at 400 °C in He at a flow rate of 30 sccm. Propanal was introduced into the reactor at 400 °C by injecting consecutive 5-μl pulses until the catalyst was deactivated. This point was

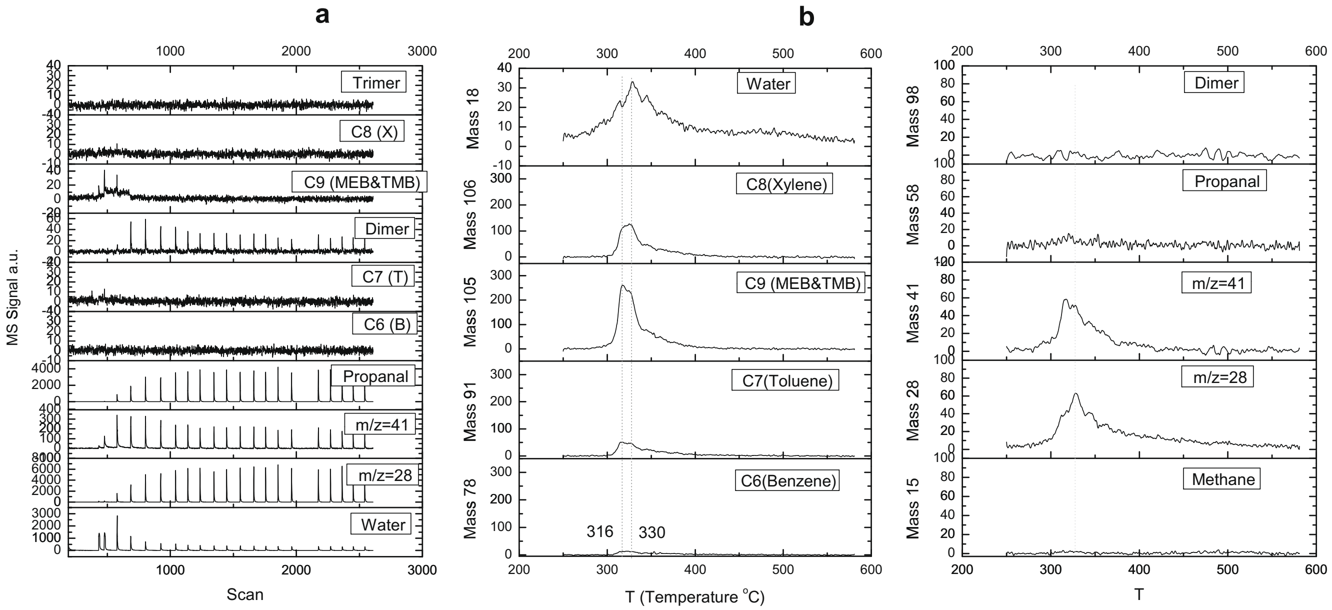

Fig. 6. TPD of propanal on HZSM-5 (45). (a) Isothermal propanal pulses at 250 °C; (b) TPD from 250 °C to 600 °C at 10 °C/min ramp rate.

determined by observing the increase in the unreacted propanal peak size until it remained constant. The online MS detector was set to monitor the following signals: *m*/*z* 18 (water), *m*/*z* 28 (C_2 and CO), *m*/*z* 41 (propylene and fragment from the dimer), *m*/*z* 58 (propanal), *m*/*z* 78 (C_6–B), *m*/*z* 92 (C_7–T), *m*/*z* 98 (C_6 dimer: 2-methyl-pentenal), *m*/*z* 105 (C_9: TMB and MEB), *m*/*z* 106 (C_8: xylene), *m*/*z* 138 (C_9 Trimer: dimethyl-heptenal). A reference sample containing all the aromatics in equal volumes, showed that the MS responses for C_8 and C_7 were somewhat higher than C_9, but no attempt at calibration was made. The products obtained were consistent with the flow reactor results mentioned above. As shown in Fig. 4a, the largest signals were primarily C_9 (TMB and MEB) and C_8 (X), less C_7 (T), and traces of C_6 (B). As the number of propanal pulses increased, catalyst deactivation was evidenced by a decrease in the size of the product peaks and an increase in the propanal peak. The water signal was reduced but did not completely disappear. In addition, the dimer (D) product was detected only in the last few pulses as deactivation proceeded, although the signal was small. The products from the first pulse showed a mixture of aromatics from C_6–C_9 with the C_8 (X) and C_9 aromatics more pronounced compared to C_6 (B) and C_7 (T). As deactivation proceeded, it appears that C_9 and the dimer were the only significant products observed at lower conversion. It also was observed that the ratio of C_9–C_8 aromatics increased as the catalyst deactivated, as shown in Fig. 5. This trend suggests that aldol dimerization and then aromatization of an aldol trimer may be the initial pathway for aromatics formation under these mild conditions, as has been shown on other acidic systems [24,25]. When C_9 (TMB) was pulsed into the system at this temperature, a mixture of aromatics: C_7 (T), C_8 (X), C_9 (TMB), but no C_6, was observed. With increasing number of pulses of TMB, deactivation occurred accompanied by a decrease in the amount of lighter aromatics. This experiment also showed that at 400 °C in this system, there are certainly cracking reactions taking place.

The same experiments were performed at lower temperatures, 350 °C and 300 °C with the results shown in Fig. 4b and c. Much lower signals for products and much higher propanal signals show the decreased conversion obtained at the lower temperatures. A significantly higher C_9 aromatics signal was observed compared to those for C_8 (X), C_7 (T), C_6 (B), with a much higher ratio than at 400 °C. As the catalyst deactivates, the C_9 aromatics again become the dominant aromatic product. At even lower temperatures, i.e. 300 °C, C_9 aromatic appeared as the only major aromatic product but rapid deactivation occurred. In contrast to the results obtained at higher temperature, the dimer product was observed

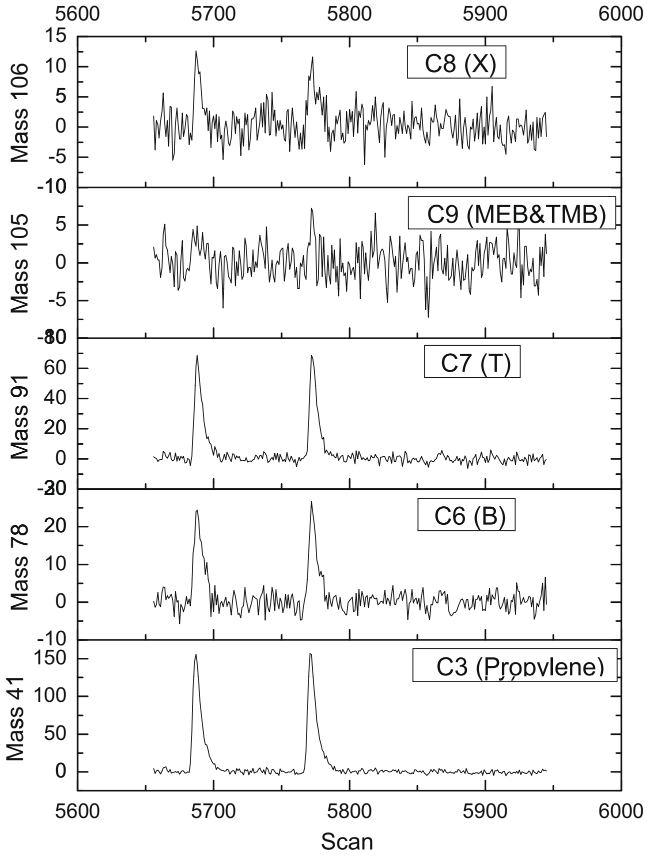

Fig. 7. Propylene pulse reaction series on HZSM-5 (25) at 500 °C.

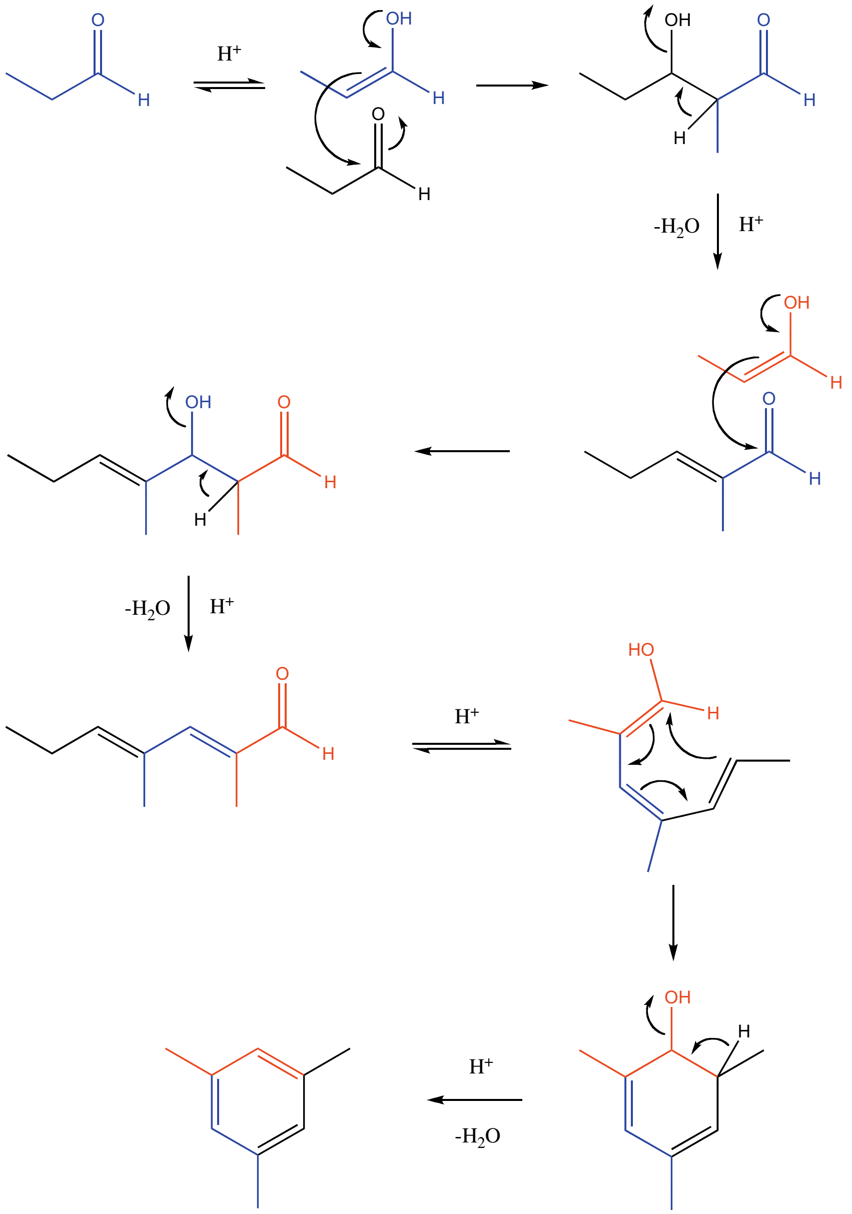

Fig. 8. Proposed mechanism for TMB formation via the aldol pathway.

with the first pulses but not in the subsequent ones. The results at lower temperatures also suggest that as the conversion is lowered and the contribution from cracking decreases, the observed products are those expected as initial products from the aldol pathway, while the lighter aromatics may result mostly from secondary cracking reactions of heavier aromatics.

A temperature-programmed reaction–desorption experiment was conducted under the pulse reactor conditions. First, 20 pulses of propanal (5 μl) were injected over the catalyst while keeping the temperature at 250 °C; then, the temperature was increased with a linear heating ramp of 10 °C per min. During the isothermal period at 250 °C shown in Fig. 6a, the dimer and C_9 aromatics were the only products observed until the catalyst deactivated. With later pulses, while the dimer continued to appear, production of aromatics rapidly decreased, as shown by the disappearance of the C_9 aromatic peak. This trend suggests that while the weaker acid sites and even the Lewis acids may catalyze the aldol condensation of propanal to form the dimer (2-methyl-pentenal), stronger Brønsted acid sites, which are the first to deactivate, are required for the cyclization and dehydration steps required to produce C_9 aromatics.

After the isothermal pulse injections, He was allowed to flow for 10 min before the temperature ramp was started. As shown in Fig. 6b, water along with significant amounts of C_9 aromatic appeared concurrently during the 316–330 °C range. Smaller peaks of C_8 (X) and C_7 (T) were also observed. This evolution of products suggests that some adsorbed intermediates are converted to the C_9 aromatics at higher temperature. The fact that water was produced along with the formation of the C_9 aromatics points at the participation of a step involving the dehydration of an oxygenated intermediate. This is consistent with an aldol pathway forming a cyclic trimer oxygenate, which could be a precursor to aromatics.

3.4. Transient conversion of propylene

For the propylene pulse experiments, the same reactor system described above was used. The first experiment was conducted with 200 mg of the commercial HZSM-5 (45) at a temperature of

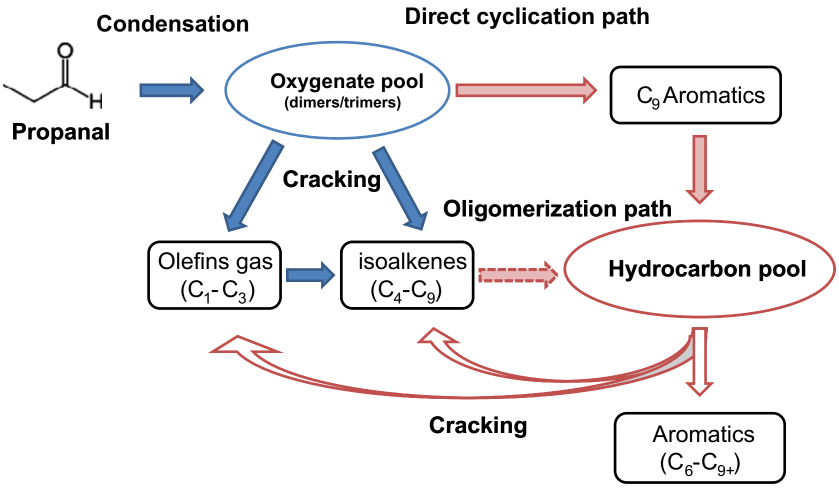

Fig. 9. Proposed pathway for aromatics formation from propanal.

500 °C. No conversion to aromatics was observed under these conditions. In the second experiment, 200 mg of the synthesized HZSM-5 (25) and a temperature of 500 °C were employed. As shown in Fig. 7, propylene was converted to C_6 (B) and C_7 (T) aromatics as the major products and only a small amount of C_8 (X) and C_9 aromatics were observed. This result is consistent with those observed in the flow reactor described above. This result further confirms that the initial aromatic formed from propylene conversion is C_6 (B), but that propylene does not convert to aromatics at 400 °C on HZSM-5 with a Si/Al of 45, in marked contrast with propanal.

4. Discussion

It is well established that aromatization of propane proceeds via alkene intermediates yielding benzene as a primary aromatic product [22,23]. Other aromatics and light alkanes are the products of subsequent alkylation, diproportionation, and cracking reactions from a surface hydrocarbon pool [26,27]. The results observed in this contribution for propylene conversion are in good agreement with these concepts. However, the results from the propanal conversion studies show much higher aromatization activity at milder reaction conditions and a significant difference in the initial aromatic product distribution compared to the results observed with propylene under the conditions at which aromatization occurs. This is an important difference that has not been previously pointed out. 2-Methyl-2-pentene has a structure similar to those isoalkenes that might be derived from the hydrolysis of the aldol dimer (2-methyl-2-pentenal) of propanal. As shown in Table 2 above, no aromatics were produced from this isoalkene when it was fed by itself. This evidence suggests that aromatics are not predominantly produced from isoalkenes C_4–C_9 but instead from a surface oxygenate pool.

The C_9 aromatic, TMB, is an interesting aromatic product to consider because it could, in principle, be produced from either alkylation of benzene or direct cyclization of a propanal trimer formed via an aldol condensation pathway. The fact that no C_9 aromatic was observed as a major product from a propylene feed at the conditions studied indicates that this alkylation pathway is not significant. By contrast, TMB along with EMB were observed as the major initial aromatic products from propanal, especially at low conversion of propanal either at low W/F, after some deactivation, or at lower temperatures. This result holds even in the presence of significant amounts of propylene formed from the propanal feed.

The reaction pathway involving condensation followed by cyclization of the aldol trimer is proposed in the scheme shown in Fig. 8. It can be suggested that the ring closure involves the highly active hydrogen in position alpha to the carbonyl. After the ring closure, the carbonyl group can tautomerize to the enol form and further dehydrate to TMB and EMB on an acid site in the zeolite. These first aromatic products can then undergo the typical secondary reactions on acid sites, such as dealkylation and disproportionation, producing light products and other aromatics. The overall proposed pathway for propanal conversion is shown in Fig. 9.

5. Conclusion

The conversion of propanal at 400 °C has been investigated on an HZSM-5 zeolite and compared to the well-known behavior of propylene, which was also studied on a second, higher acidity, HZSM-5. While C_9 aromatics are the major products formed initially from propanal, propylene does not produce significant aromatics and is much less reactive under these conditions. It is suggested that the ring closure of propanal-derived products involves tautomerization of a polyunsaturated aldehyde (Trimer) to an enol form, followed by 1,6-cyclization and subsequent dehydration to TMB and EMB on acid sites. These aromatics can then undergo secondary reactions such as dealkylation, disproprotionation and cracking. This pathway for aromatics formation is much more effective than the conventional acid-catalyzed alkane/alkene conversion on zeolites. In addition, it takes place at milder conditions than those required from alkane/alkenes, with consequently lower rates of deactivation and less undesirable cracking.

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