



Deoxygenation of benzaldehyde over CsNaX zeolites

Maria A. Peralta¹, Tawan Sooknoi², Tanate Danuthai³, Daniel E. Resasco*

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

ARTICLE INFO

Article history:

Received 2 March 2009

Received in revised form 3 July 2009

Accepted 7 July 2009

Available online 15 July 2009

Keywords:

Deoxygenation

CsNaX

Benzaldehyde

Biofuels

ABSTRACT

The deoxygenation of benzaldehyde to benzene and toluene was investigated on basic CsNaX, and NaX zeolite catalysts. It was observed that as-prepared CsNaX, containing Cs in excess, displays high activity for direct decarbonylation of benzaldehyde to benzene. However, in parallel with the decarbonylation reaction, condensation of surface products occurs. Therefore, the lower pore volume of catalyst having excess Cs leads to lower catalyst stability. Decomposition of surface condensation products results in further evolution of benzene and toluene. It is observed that gas-phase H₂ can play an important role by reducing the residence time of surface intermediates, thus decreasing the amount of condensation products that accumulate and lead to catalyst deactivation. Hydrogen transfer to the condensation surface products accelerates the decomposition of these condensation compounds primarily into toluene. NaX catalyst and washed CsNaX do not exhibit a high initial activity for direct decarbonylation, but rather operate via formation of surface condensation products which subsequently decompose yielding benzene and toluene. The residual acidity present in NaX catalysts causes a faster deactivation for this catalyst than for those containing Cs.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Production of bio-oil by fast pyrolysis of lignocellulosic biomass has received renewed attention in recent years [1–3]. The bio-oils from biomass pyrolysis typically contain a complex mixture of acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds, and heavier oxygenates [4]. To be used as a fuel, bio-oils require refining due to their high viscosity, poor heating value, corrosiveness, and chemical and thermal instability [5,6]. The upgrading of bio-oils primarily involves deoxygenation, because oxygen enhances the reactivity of the bio-oil components, resulting in the mentioned undesirable properties [7].

Deoxygenation of bio-oils has been typically attempted via metal-catalyzed hydrotreating, conducted at high pressure with large consumption of hydrogen or hydrogen-donor solvents [8–11]. Several attempts have been made to reduce hydrogen consumption and reaction severity. For example, acidic catalysts, such as zeolites or silica–alumina, have been found to promote deoxygenation of

bio-oils at relatively low pressures [12–17]. In all these studies, coke and tar were observed as undesirable by-products [18]. Basic catalysts are also active for decarbonylation and decarboxylation with relatively low hydrogen consumption, as compared to metal catalysts. We have recently demonstrated that Cs-exchanged zeolites with low Si/Al ratios (CsNaX) provide highly active basic surfaces for deoxygenation of methyl octanoate in He [19]. The highly polar environment of the zeolite micropore seems to play an essential role in the adsorption and decomposition of the adsorbed species without the need for hydrogen.

While intermolecular interactions and adsorption-site competition may greatly affect the reactivity of a given catalyst in a complex mixture such as that of bio-oils, detailed studies with model compounds are important in understanding the different reaction paths that may take place on a given catalyst. Deoxygenation of model compounds, such as acetophenone [20], aromatic ketones [21], benzophenone [22], benzaldehyde and benzyl alcohol [23] has been investigated on various catalysts. Aldehydes are particularly undesirable compounds in fuels due to their high reactivity, which greatly affects the stability of fuels.

Oxygenated aromatics such as phenols and substituted benzaldehyde compounds are found in liquid products obtained from lignin pyrolysis [24]. While some of the pyrolysis oil components may be too bulky for conversion in zeolites it is likely that future refining processes may involve separation of different fractions for conversion. Monocyclic phenolic fractions contain oxygenated aromatics such as benzaldehyde, guaiacols, vanillin, etc., for which zeolites may be adequate deoxygenation catalysts.

* Corresponding author. Tel.: +1 405 325 4370; fax: +1 405 325 5813.

E-mail address: resasco@ou.edu (D.E. Resasco).

¹ Permanent address: Institute of Research on Catalysis and Petrochemistry, Santa Fe, 3000, Argentina.

² Permanent address: Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand.

³ Permanent address: Petroleum and Petrochemical College, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand.

Accordingly, we have chosen benzaldehyde as a model compound to investigate decarbonylation over basic CsNaX at atmospheric pressure. The effect of H₂ in the feed and the role of Cs species in the catalyst activity will be discussed, together with possible reaction pathways that occur over these catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The molecular sieve (UOP type 13X, NaX) was purchased from Fluka. The Cs-containing zeolite (CsNaX) was prepared by ion-exchange of the NaX with 0.1 M Cs acetate solution at 353 K for 24 h. The mixture was filtered to separate the solid material and dried overnight at 353 K. The sample was then calcined in flow of dry air at 723 K for 2 h. To study the effect of excess Cs, the CsNaX sample was washed 7 times with deionized water to remove a significant fraction of excess Cs (washed CsNaX). For NaX, the commercial 13X was treated with 1 M NaCl, then washed and calcined at 723 K for 2 h before using. Surface areas of the CsNaX, before and after washing, and NaX catalysts were evaluated by N₂ adsorption at 77 K using Micromeritics ASAP 2000. The crystalline phase of the zeolites was verified by X-ray diffraction (XRD) using a Bruker AXS D8Discover diffractometer. Elemental analysis was performed by ICP-AES.

2.2. Temperature-programmed desorption (TPD) and pulse reaction of benzaldehyde

Desorption and decomposition of adsorbed benzaldehyde as a function of temperature were investigated by TPD, using a quadrupole mass spectrometer (MS) detector. For these experiments, the catalyst was loaded in a 1/4"-diameter quartz reactor and pretreated in flow of dry air at 748 K for 1 h. For each TPD experiment, four pulses of benzaldehyde (10 μl) were injected onto 0.1 g of catalyst at 473 K under flow of H₂. The excess benzaldehyde was flushed at the same temperature until a stable signal was observed in the MS. The reactor temperature was then linearly raised up to 1173 K at a heating rate of 10 K/min. Masses $m/z = 2, 4, 28, 44, 78, 92,$ and 106 were monitored to determine the evolution of H₂, He, CO, CO₂, benzene, toluene and benzaldehyde, respectively. Since the fragmentation pattern of benzaldehyde contains small contributions to some of the m/z values that correspond to the other compounds, corrections for these contributions were made.

For the pulse reaction experiments, three pulses of benzaldehyde (1 μl) were injected onto 0.1 g of CsNaX catalyst at 748 K, under flow of He. The evolution of products in the outlet stream was monitored by MS.

2.3. Continuous-flow reaction

The catalytic activity was measured at atmospheric pressure in a continuous-flow fixed-bed reactor, made of 1/4"-diameter quartz tube. The catalyst bed (0.020–0.050 g) was supported with quartz wool, and packed glass beads. The catalyst was pretreated under flow of pure air (30 ml/min) by heating at 5 K/min to 748 K and held at that temperature for 1 h. The catalyst was then purged with He for 30 min and cooled down to the reaction temperature (673–748 K). At that time, the carrier gas was either changed to H₂ or kept in He. Benzaldehyde vapor saturated at 273 K was introduced into the reactor by the carrier gas (H₂ or He) at a flow rate in the range 25–90 ml/min. The outlet stream was analyzed in a GC HP 5890 connected online and equipped with an HP-5 capillary column and FID detector. In addition a GC-MS (Shimadzu 2010) was used for product identification.

2.4. Hydrogen/deuterium exchange

Hydrogen/deuterium exchange over the zeolite catalysts was tested at 748 K under atmospheric pressure. First, 0.050 g of sample was pretreated in 2% O₂/He for 1 h at 748 K. Then, a flow of H₂ was introduced to the reactor at a flow rate of 50 ml/min. To analyze the H/D exchange, deuterium gas (D₂) was pulsed into the reactor using a 2 ml sample loop. A mass spectrometer was used to monitor the evolution of masses $m/z = 2, 3,$ and 4, representing the evolution of H₂, HD, and D₂, respectively.

2.5. Temperature-programmed oxidation (TPO)

The carbon deposits left on the spent catalysts after reaction were evaluated by TPO. In each case, 0.010 g of spent catalyst was loaded into a 1/4" quartz reactor. The TPO profiles were obtained at a heating rate of 10 K/min under flow of 5% O₂/He. The CO₂ produced from the oxidation of coke was further converted to methane in a methanator [25] and analyzed in an FID detector. After each TPO measurement, several 100 μl pulses of pure CO₂ were injected and the average area was used for calibration.

2.6. Temperature programmed of isopropylamine (TPD-IPA)

The zeolite acidity was quantified by the TPD of adsorbed isopropylamine (IPA) [26]. The sample (30 mg) was initially pretreated in flow of He for 1 h at 773 K. Then, the sample was cooled in He to room temperature and 10 μl pulses of IPA were injected over the sample each time until the sample was saturated. The saturation of IPA adsorption was confirmed by mass spectrometry. After removal of the excess IPA by flowing He for 3 h, the sample was linearly heated to 973 K at a ramping rate of 10 K/min. Masses $m/z = 44, 41,$ and 17 were monitored to determine the evolution of isopropylamine (IPA), propylene, and ammonia, respectively.

3. Results

3.1. Characteristics of the catalysts investigated

After ion-exchange with Cs, XRD reveals that the faujasite structure is retained for both the CsNaX and the washed CsNaX samples. Table 1 shows the elemental analysis and specific surface area (BET) for the zeolite samples. It is clear that the accessible surface area, or more precisely the accessible pore volume, decreases with increasing Cs content. This is due to the relatively large size of Cs cation, as compared to the original Na cation. It is well known that the exchangeable Cs cations are mostly located in the supercages, while the excess Cs species in the unwashed sample can be retained and dispersed as Cs carbonate, Cs oxide, Cs peroxide, or Cs superoxide [27,28]. Moreover, the oxides species associated with the excess Cs have been shown to be stronger bases than those of the zeolitic framework [28]. Therefore, since washing removes a significant fraction of such extra-framework species, not only the accessible pore volume and specific surface area are partially recovered but the overall basicity of the catalyst decreases.

Table 1
Chemical analysis and surface area of Cs and NaX catalysts.

	Si/Al ratio	Na %mol	Cs %mol	Al %mol	Na + Cs Al	BET surface area (m ² /g)
CsNaX	1.2	18.2	17.5	29.1	1.2	460
Washed CsNaX	1.2	20.8	11.2	31.2	1.0	506
NaX	1.2	35.8	–	30.6	1.2	745

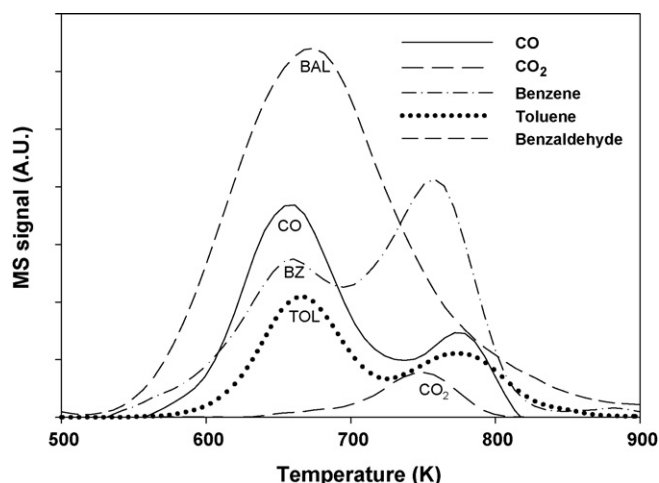


Fig. 1. Evolution of products from pre-adsorbed benzaldehyde on CsNaX as a function of temperature in a linear heating ramp, using H_2 as carrier gas.

3.2. Temperature-programmed desorption and pulse reactions

The TPD profiles of adsorbed benzaldehyde depicted in Fig. 1 show that this aromatic molecule desorbs from CsNaX at relatively high temperatures (~ 673 K). Interestingly, the evolution of the signals corresponding to CO ($m/z=28$) and benzene ($m/z=78$) was observed at 658 K, before complete desorption of benzaldehyde. This earlier desorption indicates that some of the adsorbed benzaldehyde can readily undergo decarbonylation on the CsNaX surface. Since the TPD was carried out under a flow of H_2 , production of toluene may be expected. In fact, toluene evolution ($m/z=92$) was observed although at a slightly higher temperature than benzene. This difference may imply that toluene is produced in parallel to decarbonylation but this reaction may require slightly higher temperatures. A later evolution (i.e., higher temperature) of benzene, toluene, CO and CO_2 was also observed above 750 K. It is believed that this evolution be derived from the high-temperature decomposition of benzaldehyde coupling products remaining on the catalyst surface without desorbing.

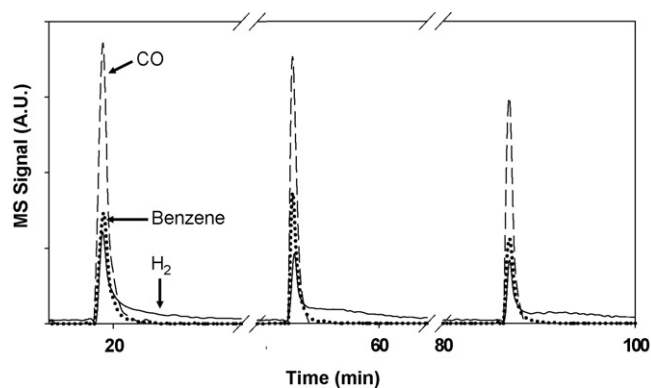


Fig. 3. Time evolution of CO, benzene, and hydrogen from consecutive pulses of benzaldehyde sent over CsNaX catalyst at constant temperature, 748 K, in He.

In agreement with the TPD results, the products evolved from pulses of benzaldehyde in the He carrier flow over CsNaX at 748 K presented in Fig. 2 give evidence of direct decarbonylation, i.e., formation of benzene and CO products. A remarkably lower activity is observed over the NaX catalyst in the pulse experiments, which illustrates the significant difference brought about by the addition of strong basic sites associated with Cs.

It is interesting to note that, in addition to CO and benzene the basic CsNaX catalyst produces smaller amounts of H_2 and of toluene. In particular, H_2 is continuously evolved in significant concentration even after decarbonylation has been completed, i.e., after benzene and CO evolution ceased. Therefore, the only source of H_2 is the dissociation of the aldehydic H in ($O=C-H$) since the aromatic H cannot be readily dissociated over basic zeolites. In fact, TPO gives evidence that the coke produced over these catalysts is rather soft and can be oxidized at significantly low temperature (Table 2), which is an indication of the low extent of dehydrogenation of the carbonaceous deposits. The late desorption of H_2 after the benzaldehyde pulse is also observed in subsequent pulses. As the catalyst deactivates the ratio of the late-to-early hydrogen evolution is even higher, as illustrated in Fig. 3. These observations suggest that, in addition to decarbonylation that produces CO and benzene, coupling of benzaldehyde with other carbona-

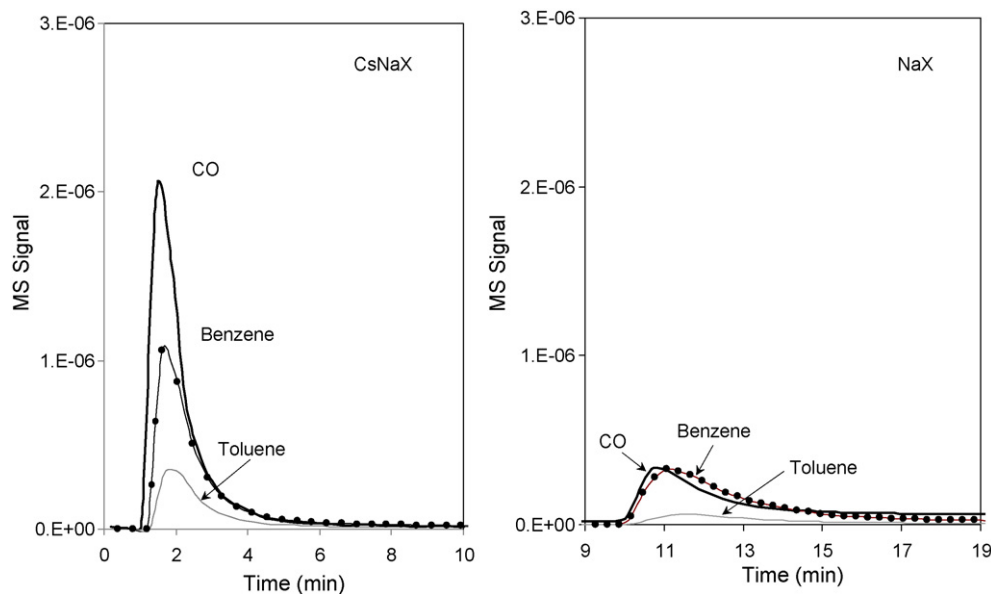
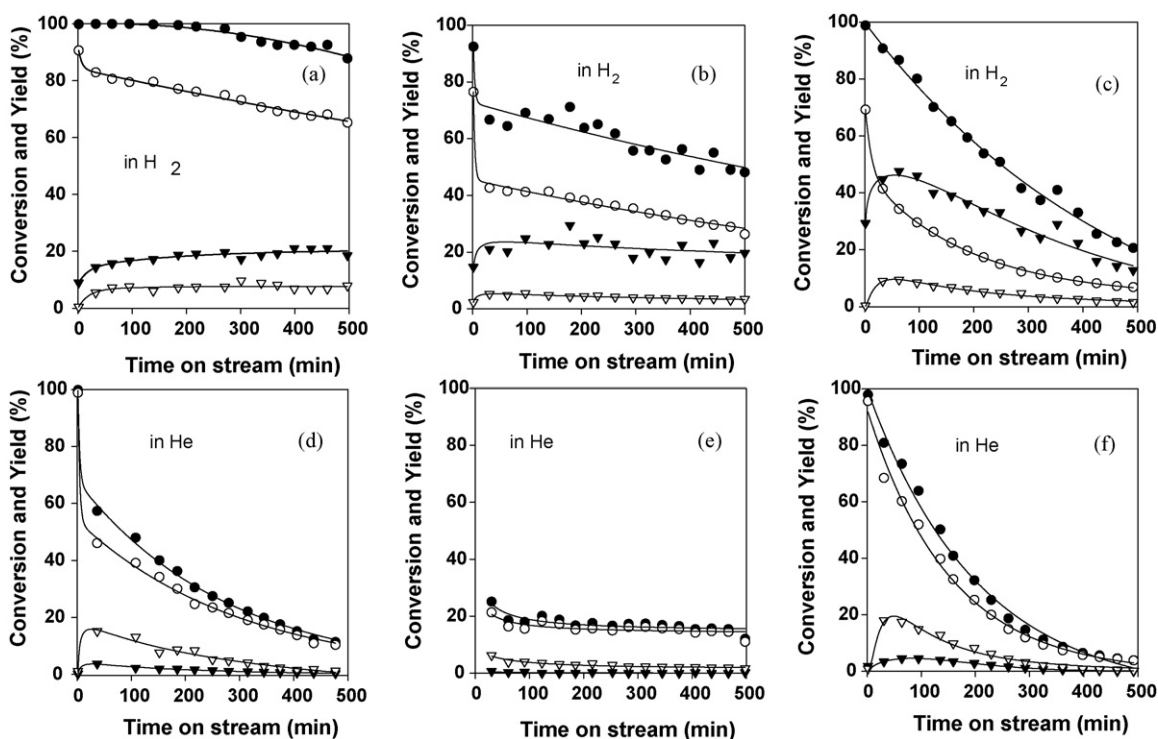


Fig. 2. Time evolution of CO, benzene, and toluene after a pulse of benzaldehyde sent over CsNaX (left) and NaX (right) catalysts at constant temperature, 748 K, using He as carrier gas.

Table 2

Amount of carbon deposited during benzaldehyde reaction after 500 min on stream under different experimental conditions.

Run No.	Catalyst	Temperature (K)	Carrier gas	W/F (g h/mol)	Amount of carbon deposited (%wt)	Max. temp. (K)
1	CsNaX	673	H ₂	2355	6.6	678
2	CsNaX	748	H ₂	2355	1.1	696
3	CsNaX	748	H ₂	942	3.9	685
4	CsNaX	748	He	942	8.8	724
5	NaX	748	H ₂	942	12.6	682

**Fig. 4.** Conversion and product distribution from the flow reaction of benzaldehyde over Cs and NaX catalysts at 748 K at W/F=942 g h/mol using different carrier gases; (a and d) CsNaX, (b and e) washed CsNaX, and (c and f) NaX. Conversion (●), benzene (○), toluene (▼), and 2-ring compounds (▽).

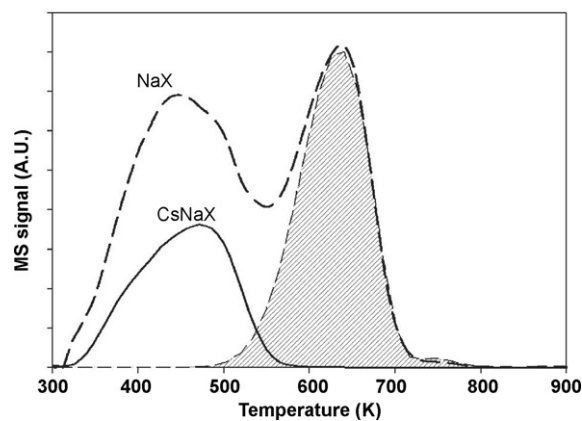
aceous species may also occur at the catalyst surface. The larger is the extent of this coupling the larger is the relative amount of H₂ evolved, leaving heavier carbonaceous fragments on the surface.

3.3. Catalytic activity measurements in continuous flow

The effect of having Cs in excess or exchanged in the zeolite was primarily investigated in the reaction studies over washed CsNaX and NaX samples, as shown in Fig. 4. As shown in the top row of Fig. 4 for the runs conducted under H₂, the activity, as well as the benzene/toluene ratio is significantly higher on the unwashed CsNaX catalyst than on the washed CsNaX. This difference suggests that the presence of excess Cs species provides stronger basic sites, as previously proposed [19,28], which increase the reaction rate and favor the formation of benzene. It can be noticed that the yield of toluene remains similar for both catalysts, while the benzene yield decreased with time on stream as the catalyst deactivates. This trend suggests that the basicity plays an important role in the direct decarbonylation of benzaldehyde to benzene and CO. The somewhat better stability observed in the washed sample may be derived from a relatively higher pore volume (BET surface ~506 m²/g, as compared with 460 m²/g for the unwashed sample) as the excess Cs species are removed.

The catalytic behavior of the NaX catalyst is clearly different from that of the two Cs-containing catalysts. In addition to a more rapid deactivation, the yield of benzene is lower than that of toluene (benzene/toluene ratio is <1). TPD of isopropylamine indicates that

the NaX possesses residual (Lewis) acidity (Fig. 5). This acidity is revealed by the rather strong isopropylamine adsorption that results in desorption at about 650 K, only observed for the NaX catalyst. It is worth noting that no Hoffmann reaction of isopropylamine with Brønsted acid sites to propylene and ammonia has been observed over this catalyst. That is, only Lewis acid sites associated with Na⁺ are responsible for the observed chemisorption. In contrast, physisorbed isopropylamine desorbing at lower temper-

**Fig. 5.** Evolution of $m/z = 44$ (isopropylamine) during the TPD of isopropylamine over CsNaX and NaX.

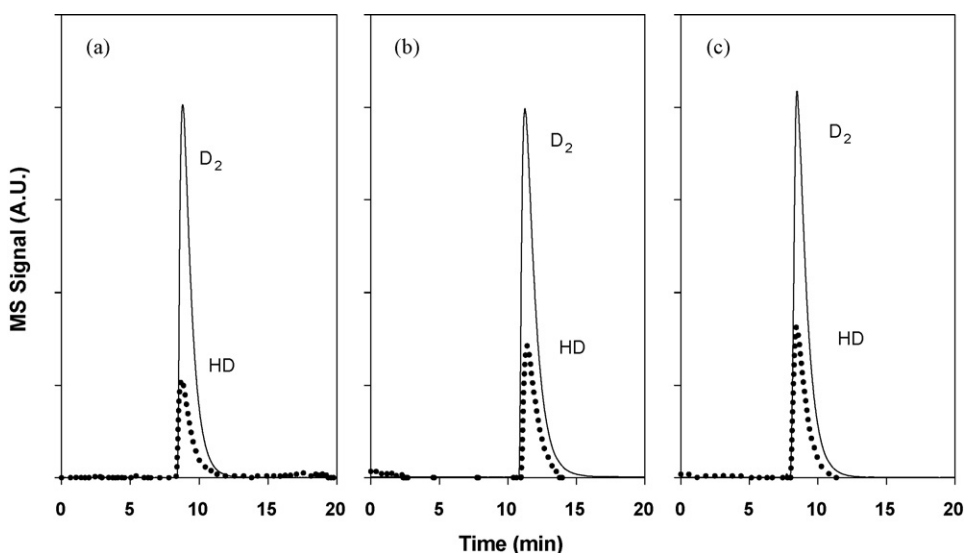


Fig. 6. Pulse reaction of deuterium under a flow of hydrogen at 748 K over various catalysts: (a) CsNaX, (b) washed CsNaX, and (c) NaX.

atures (~450 K) was detected for both CsNaX and NaX catalysts. The amounts adsorbed correspond with the surface area of the catalysts (NaX > CsNaX). Therefore, it is possible that an important fraction of the catalytic activity of NaX derives from its Lewis acidity, rather than its basicity. Together with the difference in selectivity (toluene > benzene), the enhanced amount of coke formation observed on this catalyst is in agreement with the Lewis acid sites playing a role in the reaction.

The effect of co-feeding H_2 is also illustrated in Fig. 4 in which the evolution of activity at 748 K at a $W/F=942$ is compared, with H_2 or He as carrier gas. It can be seen that when the carrier gas is H_2 , a higher activity and lower rate of deactivation are observed, compared to the runs in which He is used as the carrier gas. Moreover, in the absence of H_2 , the yield of toluene went to zero relatively rapidly. By contrast, although the catalyst is severely deactivated, the yield of benzene is much higher than that of toluene. This result suggests that the decarbonylation to benzene is not readily affected by H_2 while the production of toluene requires H_2 . The fact that the presence of H_2 significantly affects the catalyst stability leads to the

conclusion that H_2 can participate in reactions of hydrogen transfer over Cs and NaX. On these zeolite catalysts H_2 may be heterolytically dissociated, thus accelerating the rate of hydrogen transfer. Consistent with the lower deactivation rate observed in the presence of H_2 , a higher amount of heavy deposits were found by TPO after reaction with He than with H_2 (Table 2).

To compare the hydrogen transfer capacity of the different catalysts, we conducted H–D exchange by injecting pulses of D_2 over the catalyst in flow of H_2 . The comparison of the three alkali zeolites is made in Fig. 6. It is clearly shown that HD ($m/z=3$) is produced when a pulse of D_2 is sent over CsNaX, washed CsNaX and NaX under a flow of H_2 . This confirms that gas-phase H_2 can participate in hydrogen transfer at 748 K over these catalysts. This hydrogen transfer may play a role in reducing the life of reaction intermediates on the surface, thus helping to keep the surface clean. It should also be noted that a relatively higher activity for HD formation over NaX, as compared to those over washed CsNaX and CsNaX, can be attributed to the higher pore volume/surface area of NaX. This kind of H/D exchange would facilitate the reactions of hydrogen transfer

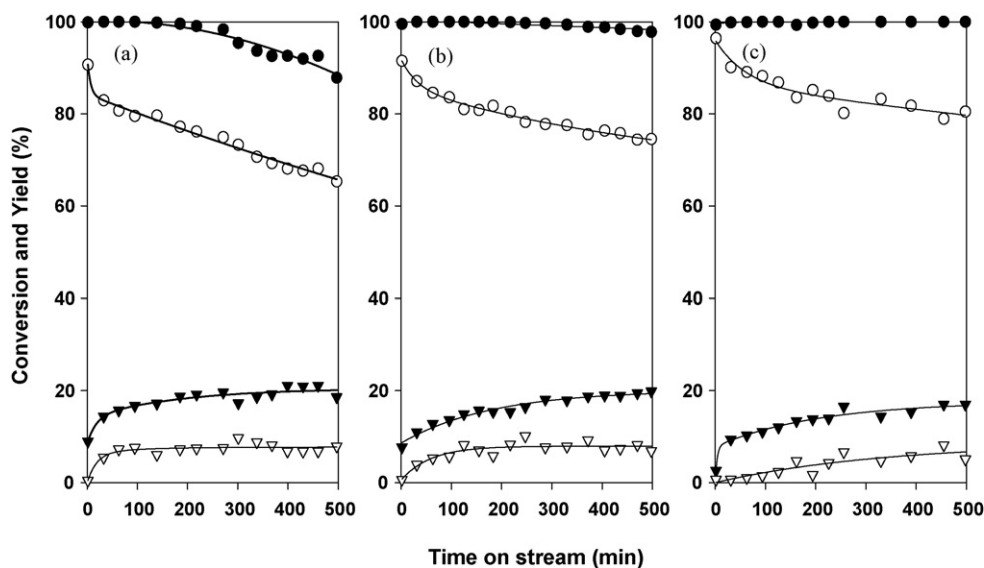


Fig. 7. Conversion and product distribution as a function of time on stream for the flow reaction of benzaldehyde over CsNaX catalyst using H_2 as carrier gas at 748 K for various W/F : (a) 942 g h/mol, (b) 2355 g h/mol, and (c) 7066 g h/mol. Conversion (●), benzene (○), toluene (▲), and 2-ring compounds (▽).

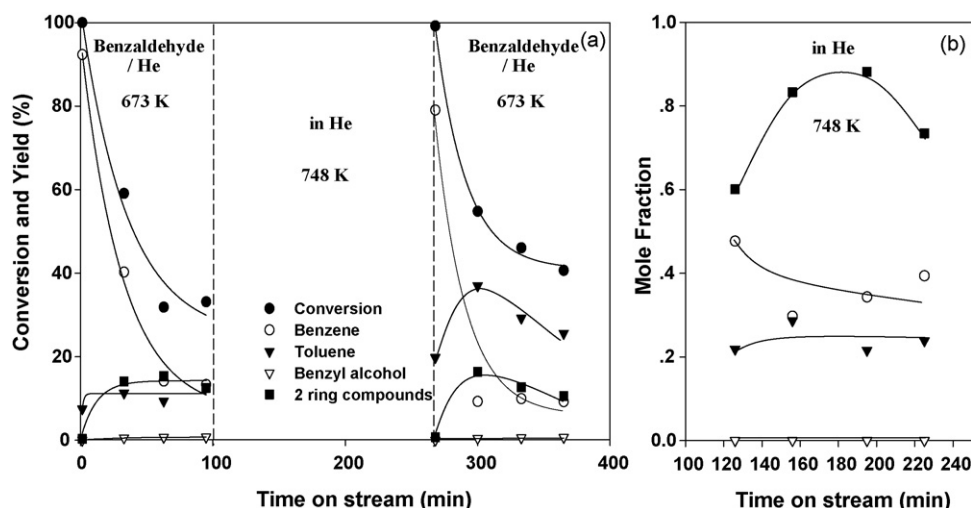


Fig. 8. (a) Conversion and yield from the reaction of benzaldehyde in flow of He over CsNaX at 673 K followed by heating in He at 748 K, and restarting the reaction at 673 K, $W/F=942$ g h/mol. (b) Product distribution during the heating period of spent catalyst at 748 K in He. Conversion (●), benzene (○), toluene (▲), benzyl alcohol (▽), and 2 ring compounds (■).

and thus the formation of toluene from the carbonaceous deposits adsorbed on the zeolite. Then, the higher H/D exchange activity of NaX zeolite is consistent with the higher yield of toluene on this catalyst, as observed in Fig. 4c.

The product distribution from benzaldehyde conversion on CsNaX at 748 K is shown in Fig. 7 as a function of time on stream for the different space times (W/F). It can be seen that the initial benzaldehyde conversion is 100% for the three space times shown in this figure; that is, in all three cases, there is excess catalyst, indicating that the constant conversion does not indicate absence of catalyst deactivation. While the disappearance of benzaldehyde from the gas phase is complete, the accumulation of carbonaceous species on the surface is clearly apparent from the changes in product selectivity over time. Benzene and toluene are the main products in all cases, while bicyclic condensation products (diphenyl methane, benzophenone and other bicyclic compounds) are observed in lower concentrations. It is observed that while the conversion remains at 100%, the yield of benzene decreases with time on stream as well as with decreasing W/F . In contrast, the yield of toluene is low at the beginning of the reaction but gradually increases with time on stream. At the same time, toluene production decreases with W/F .

The TPO results of spent catalysts (Table 2) describe the coke formation tendencies for the different catalysts and conditions. First, it is interesting to note that, contrary to typical coke formation, on this system, coke forms less at the higher temperature (6.6 and 1.1% for $T=673$ and 748 K, respectively). This trend indicates that at lower temperatures (673 K), condensation of heavy compounds dominates the carbon accumulation process. At higher temperatures (748 K) a fraction of these condensation compounds decompose as illustrated in the TPD experiment (Fig. 1) reducing the accumulation of carbonaceous species. Second, the nature of the carrier gas seems to play an important role on carbon deposition. Under the same conditions and reaction time, the amount of C deposited when the carrier gas is He is much higher than when it is H_2 (3.9, and 8.8 wt% C, respectively). Third, when no Cs was present in the catalyst and the catalyst was just NaX, the amount of coke was much higher. That is, after the same time on stream under identical reaction conditions, the amounts of carbon deposits were 12.6 wt% on NaX and only 3.9 wt% on the CsNaX catalyst. Fourth, while the conversion was 100% in both cases for most of the time on stream, the run at the higher W/F produced significantly more coke than the one at lower W/F , i.e., 3.9% and 1.1 for $W/F=942$ and

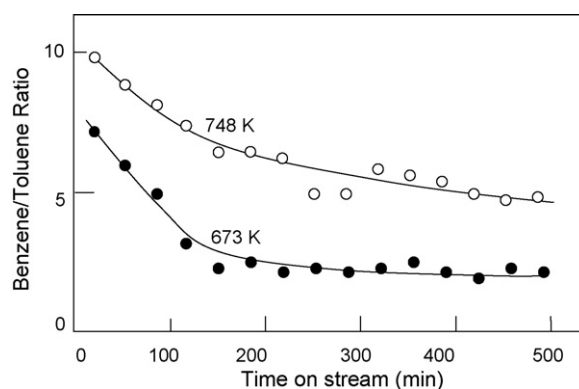


Fig. 9. Benzene/toluene product ratio as a function of time on stream in the flow reaction of benzaldehyde at 748 and 673 K under H_2 .

2355 g h/mol, respectively. This indicates that the feed, rather than the product is responsible for the carbon deposition. While in both cases, there was catalyst in excess, the one with the higher W/F had a larger fraction of the bed exposed to the product rather than the feed, and consequently in average formed less coke per mass of catalyst.

When the reaction was carried out at the lower temperature (673 K) in He, the initial conversion was still 100% at the beginning, as shown in Fig. 8a. However, after 100 min on stream there was significant deactivation. Most interestingly, by heating under a He flow at 748 K for 3 h, the initial activity was recovered (i.e., 100% conversion). Fig. 8b shows that during this heating in He, bicyclic compounds together with small amounts of benzene and toluene are evolved from the spent catalyst. This evolution indicates that carbonaceous species are retained on the catalyst surface during reaction and they desorb, or more precisely decompose, at high temperature cleaning the surface with its activity recovered. As shown on the right panel of Fig. 8a, the conversion gets back to 100% after heating in He, but the evolution of the product distribution with time on stream during the second reaction cycle is somewhat different from the first one. On the regenerated catalyst (not shown), the selectivity towards benzene drops much faster than on the fresh catalyst while the selectivity to toluene is much higher and goes through a maximum with time on stream.

Fig. 9 shows the evolution of the benzene/toluene product ratio as a function of time on stream for two reaction runs conducted in H_2 at 748 and 673 K. It is clearly seen that the benzene/toluene ratio increase with reaction temperature, but decreases as the catalyst deactivates. That is, benzene seems to be produced in line with the total overall conversion, while the selectivity to toluene increases as the catalyst deactivates or when the W/F is lowered, as shown in Fig. 7.

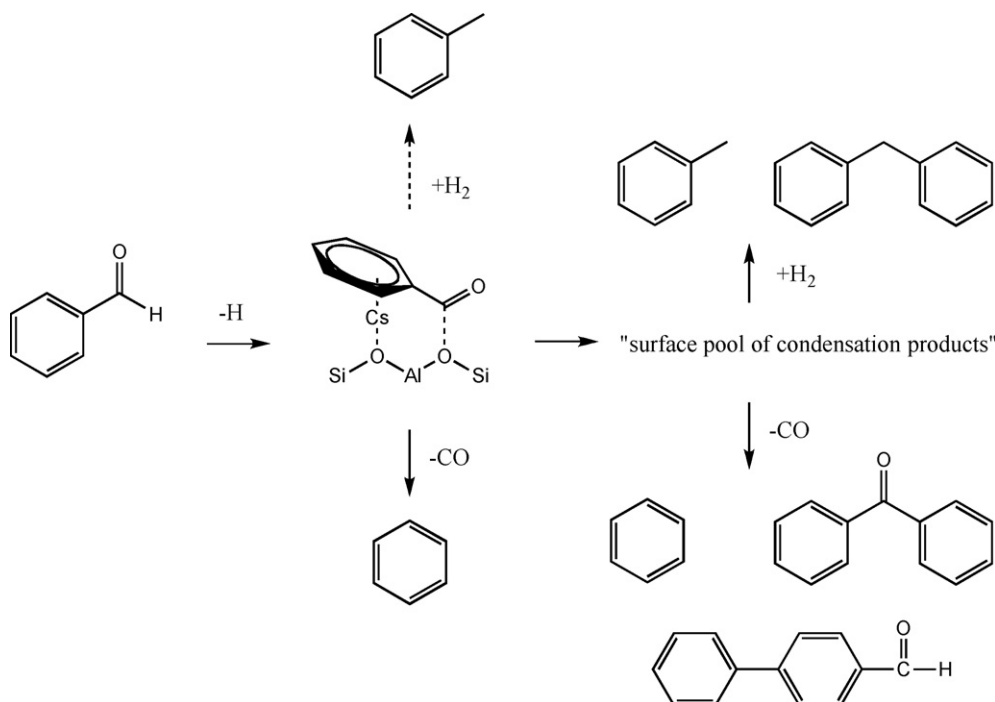
4. Discussion

4.1. Activity of CsNaX

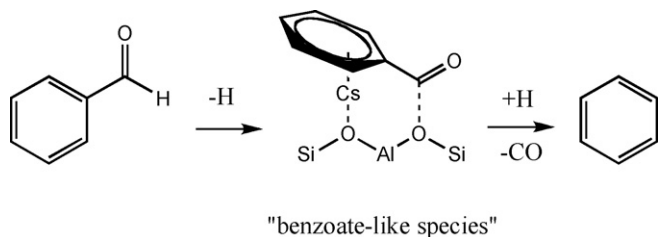
The rapid catalyst deactivation and the high temperatures needed to desorb and decompose the adsorbates indicate that

action of a soft Cs cation and the electron in the aromatic ring can readily weaken the benzylic C–C bond, leading to the decomposition of this “benzoate-like species” at high temperature to form benzene and CO (direct decarbonylation), as observed.

In addition to the decarbonylation to benzene and CO, such benzoate-like species can also couple with other adjacent adsorbates, forming a surface pool of condensation products, which remain on the surface forming a pool of compounds that are too heavy to desorb. Coupling of benzaldehyde has been previously reported over catalysts containing both basic and acid sites. For example benzyl benzoate was identified when benzaldehyde made contact with alkali earth oxide catalysts at temperatures below 473 K [33–35]. Over CsNaX, the evolution of benzene and CO_2 at around 773 K and also toluene and CO at around 793 K (Fig. 1) may be attributed to the decomposition of such aryl benzoate species.



benzaldehyde can adsorb strongly on the CsNaX surface. This strong adsorption dominates the activity and selectivity of these catalysts. Having a strongly electrophilic group, benzaldehyde is expected to attach to the highly basic sites of CsNaX. We speculate that the adsorbed benzaldehyde may form a “benzoate-like species” as suggested in earlier reports [29,30]. For example, spectroscopic data have indicated that the dissociative adsorption of benzaldehyde over Y_2O_3 takes place at the aldehydic hydrogen [30] and that “benzoate-like species” are bound to the surface oxygen. This type of adsorption intermediate can exist on CsNaX, in a manner similar to methanol/formaldehyde adsorbed over alkali exchange zeolites [31] or benzaldehyde adsorbed on the polar surface of ZnO [32].



The formation of “benzoate-like species” is in line with the observed H_2 evolution in the pulse experiments (Fig. 2). The inter-

The TPD data indicates that the surface pool of condensation products can be decomposed into benzene through decarbonylation or decarboxylation, and into toluene when H_2 is present. The bicyclic compounds observed in lower quantities may also be the result of the decomposition of these condensation products. Consistent with this view, the bicyclic compounds are observed in parallel with toluene (Fig. 7). In addition, the yield of toluene does not decrease significantly when the catalyst deactivates. Thus, it is unlikely that toluene is a primary product from the hydrogenolysis of the adsorbed benzaldehyde, but it rather decomposes from the surface pool of condensation products.

From the proposed scheme, the direct decarbonylation of adsorbed benzaldehyde would be competitive with the formation of the surface pool of condensation products. Although these heavy surface compounds can also decompose to yield benzene, toluene, and the observed bicyclic compounds, they appear to preferably remain on the surface deactivating the catalyst and eventually forming a non-decomposable coke.

The enhanced H_2 /benzene evolution ratio observed when sequential benzaldehyde pulses were injected, compared to the evolution from the first pulse (Fig. 3) suggests that the benzaldehyde from the gas phase not only couples with other co-adsorbed molecules to form bicyclic compounds, but it also couples with the condensation products remaining on the surface from the previous

pulse. This process of sequential condensation leads to deactivation and formation of a more refractory product, which may not easily leave the surface and so the density of available sites for benzaldehyde adsorption continually decreases with time on stream. This causes the catalyst to deactivate unless the decomposition of such species competitively takes place.

The continuous reduction in the number of active sites may explain the change in product selectivity with time on stream, even when the total conversion remains at 100% as a result of the presence of excess catalyst (Fig. 7). The yield of benzene is initially high because the direct decarbonylation readily occurs at the beginning of the reaction where most of the active sites are available. Once the surface pool of condensation products is formed and remains on the surface, the direct decarbonylation of benzaldehyde to benzene is reduced. However, benzene can still be produced from the decomposition of the surface pool of oxygenated aromatic condensation products, but to a relatively lower extent. The net result is then a reduction in the yield of benzene with time on stream.

In contrast, the formation of toluene does not decrease as pronouncedly. This is because the pool of condensation products is most probably the only source of toluene, as no evidence for the formation of benzyl alcohol, an intermediate for toluene formation via hydrogenation–hydrogenolysis of benzaldehyde [36,37] was observed. At longer times on stream, the size of the pool of condensation products increases and more toluene is produced even though the overall catalytic activity decreases.

Operating at 100% conversion and with catalyst in excess (i.e., large W/F), the concentration of benzaldehyde on the surface is essentially zero at the end of the catalyst bed, leading to a lower formation of condensation products. Accordingly, while the yield of benzene increases with W/F those of toluene and bicyclic compounds are somewhat suppressed (Fig. 7). As benzaldehyde is strongly adsorbed on CsNaX, the apparent activity remains at 100% for long time on stream although the number of available active sites is actually decreasing. Consistent with this observation, high molecular weight deposits leading to coke were lower at high W/F (see Table 2).

4.2. Effect of Cs cation and excess Cs species

One might anticipate that excess Cs in the CsNaX catalyst might play a role in the hydrogenation activity to increase toluene formation. It turns out that this is not the case. Both, the catalyst with the excess Cs removed (washed CsNaX) and even the one free of Cs (NaX) also give higher toluene yield (lower benzene/toluene ratio) in the presence of H_2 compared to those under He (Fig. 4). This difference suggests that the excess Cs species and the Cs cation are not responsible for the hydrogenation activity of these catalysts. On the other hand, the high rate of hydrogen transfer reactions seems to derive from the zeolite itself, as confirmed by the D_2 exchange experiments (Fig. 6). Such high H transfer can help the decomposition of the surface pool of condensation products to produce toluene, and other hydrogenated bicyclic compounds.

Although excess Cs species and Cs cations do not readily enhance the activity towards hydrogenated products, they play a clear role in the decarbonylation activity, as observed in Fig. 4. For washed CsNaX (a relatively weaker basic catalyst), the decarbonylation activity is reduced, together with the benzene/toluene ratio. This suggests that the excess Cs species is an active site for direct decarbonylation of benzaldehyde, in particular. That is, the higher basicity of the catalyst with Cs in excess correlates well with the higher activity for direct decarbonylation of benzaldehyde to benzene, while the overall activity is more in line with the pore volume and surface area.

In addition, when excess Cs is removed from the pores, diffusion of the high molecular weight compounds may be improved,

leading to a better catalyst stability, as observed. It is worth noting that in the reaction with He, a rapid deactivation is observed over unwashed sample (Fig. 4d), while a high stability is obtained over the washed CsNaX (Fig. 4e). This indicates that the excess Cs species do not only promote the direct decarbonylation but also the formation of the surface pool of condensation products.

Over NaX, a very rapid deactivation, as compared to the catalyst with Cs, was observed (Fig. 4c and f), suggesting a successive formation of surface pool of condensation products over this catalyst. This enhanced condensation may be related to the residual Lewis acidity of NaX as shown by IPA-TPD (see Fig. 5) and previously discussed [19]. Hence, the formation of larger aromatic compounds is expected and the decomposition of these species is more difficult, leading to faster deactivation. TPO results support the concept that more high molecular weight deposits are formed over NaX than over CsNaX (Table 2). Since basic sites are probably less in NaX, the direct decarbonylation is not as prominent. As a result, the benzene/toluene ratio is markedly reduced as both are produced from the decomposition of the surface pool of condensation products.

4.3. Effect of hydrogen

In addition to the effect of temperature, the presence of H_2 in the gas phase affects the decomposition of the oxygenated condensation products, and hence the stability of the catalysts. In the runs using He as a carrier gas (Fig. 4), the direct decarbonylation of benzaldehyde can be promoted forming mostly benzene at the beginning of the reaction. This is because the decarbonylation of the “benzoate-like species” requires no hydrogen. However, as the surface pool of condensation products are formed, they cannot readily be decomposed in the absence of hydrogen and a rapid deactivation is observed.

Although the reaction is taking place in He, small amounts of toluene can be obtained. This is because there is some hydrogen present on the surface resulting from the condensation of the oxygenated aromatics, as evidenced in the pulse experiment (Fig. 2). This hydrogen could be transferred to the oxygenated condensation products to produce toluene, but certainly to a much lower extent than when H_2 is present in the feed. In addition, higher amounts of bicyclic compounds are observed in the reaction using He, supporting that more oxygenated condensation products are accumulated in the absence of H_2 , which is consistent with the higher amounts of heavy deposits found over the catalyst after reaction with He as a carrier gas, as compared to that with H_2 (Table 2). Finally, if toluene is produced from the surface pool of condensation products, the higher yield of toluene observed with NaX is consistent with the higher rate of hydrogen transfer observed for NaX, as compared with CsNaX (see Fig. 6).

4.4. Effect of temperature

As stated above, the formation of a pool of condensation products reduces the direct decarbonylation activity and causes catalyst deactivation. The decomposition of this species would determine the catalyst activity and stability. At the low temperature range (i.e., 673 K), the decomposition of the surface condensation products takes place to a much lower extent than at 748 K. Hence, there are relatively less available active sites for direct decarbonylation. Since direct decarbonylation solely produces benzene, the benzene/toluene ratio can be used to estimate the relative activity for the direct decarbonylation compared to the decomposition of the surface condensation products. It is clear that the reaction at 673 K results in a lower benzene/toluene ratio, as compared to that at 748 K because surface condensation products still remain on the surface, hindering the direct decarbonylation. As illustrated in Fig. 9, this condition results in much lower benzene/toluene ratio since

the products are mostly derived from the decomposition of surface condensation products.

In contrast, high temperatures (748 K) facilitate the decomposition of the surface condensation products, leaving more available active sites for benzaldehyde adsorption and reaction. This is demonstrated by the activity recovery observed after stopping the feed of the reaction conducted at 673 K and heating up to 748 K in He (see Fig. 8). The surface condensation products retained during the reaction at 673 K are decomposed into benzene, toluene, and bicyclic compounds as the temperature is increased. Therefore, it appears that the main effect of operating at higher temperatures is to decrease the accumulation of the surface condensation products. In support of this concept, the TPO measurements of spent catalysts clearly show that a significantly higher amount of carbon deposits is formed over the catalyst after reaction at 673 K than after reaction at 748 K (see Table 2).

This also implies that by simply heating the spent catalyst at high enough temperatures, at least partial regeneration may be possible. This type of regeneration may be preferred over oxidative regeneration, since oxidation of coke may cause irreversible structural collapse of the alkaline zeolites, which are usually sensitive to water, produced during combustion. However, regeneration by heating in inert gas may only be effective when the pool of condensation products is not so excessively large that hampers gasification and produces hard coke.

5. Conclusion

The deoxygenation of benzaldehyde can be effectively carried out at atmospheric pressure on basic CsNaX catalysts, either in the presence of an inert gas or H₂. The direct decarbonylation of benzaldehyde to benzene can be readily promoted over highly basic catalyst containing Cs in excess. In parallel with direct decarbonylation, the condensation of surface products also occurs. Toluene is a result of the decomposition of species from this surface pool. H₂ can be dissociated on the zeolite surface with and without Cs at the reaction temperature. The role of H₂ is to clean the surface by reducing the residence time of surface intermediates, decreasing non-decomposable pool of condensation products that accumulate and lead to catalyst deactivation. After heterolytic dissociation, H₂ from the gas phase participates in hydrogen transfer reactions with the surface pool of condensation products, decomposing them and forming primarily toluene. The presence of excess Cs species increases the basic character of the catalyst, which correlates with the higher activity in direct decarbonylation of benzaldehyde to benzene. At the same time, the lower pore volume of catalyst with Cs in excess leads to lower catalyst stability.

Acknowledgements

This work was financially supported by the Oklahoma Secretary of Energy and by the Oklahoma Bioenergy Center. One of the authors

(T.S.) thanks the Fulbright Thai visiting program for support, and (T.D.) thanks the Thailand Research Fund for a scholarship.

References

- [1] H.B. Goyal, D. Seal, R.C. Saxena, *Renewable and Sustainable Energy Reviews* 12 (2008) 504–517.
- [2] Ozlem Onay, *Fuel Processing Technology* 88 (2007) 523–531.
- [3] J. Piskorz, D.S. Scott, D. Radlien (Eds.), *Pyrolysis Oils from Biomass: Producing Analyzing and Upgrading*, American Chemical Society, Washington, DC, 1988, pp. 167–178.
- [4] C. Amen-Chen, H. Pakdel, C. Roy, *Biomass and Bioenergy* 79 (2001) 277–299.
- [5] Y.H.E. Sheu, R.G. Anthony, E.J. Soltes, *Fuel Processing Technology* 19 (1988) 31.
- [6] E.G. Baker, D.C. Elliott, in: A.V. Bridgwater, J.L. Kuester (Eds.), *Research in Thermochemical Biomass Conversion*, Elsevier, Applied Science, London, 1988, p. 883.
- [7] F.A. Agblevor, S. Besler, *Energy and Fuels* 10 (1996) 293.
- [8] W. Craig, E. Coxworth, in: C. Ganger (Ed.), *Proceedings of the Sixth Canadian Bioenergy R&D Seminar*, Elsevier Applied Science, London, 1987, p. 407.
- [9] R. Maggi, B. Delmon, in: A.V. Bridgwater (Ed.), *Advances in Thermochemical Biomass Conversion*, Elsevier Applied Science, London, 1993, p. 1185.
- [10] R. Maggi, A. Centeno, B. Delmon, in: P. Chartier (Ed.), *Proceedings of the 9th European Bioenergy Conference*, Elsevier, Oxford, 1996, p. 327.
- [11] P. Grange, A. Centeno, R. Maggi, B. Delmon, in: A.V. Bridgwater, E.N. Hogan (Eds.), *Proc EU–Can Workshop Therm Biomass Process 2nd 1995*, CPL Press, Newbury, 1996, p. 186.
- [12] J.D. Adjave, N.N. Bakhshi, *Fuel Processing Technology* 45 (1995) 161.
- [13] S.P.R. Katikaneni, J.D. Adjave, N.N. Bakhshi, *Energy & Fuels* 9 (1995) 1065.
- [14] P.T. Williams, P.A. Horne, *Fuel* 74 (1995) 1839.
- [15] J.D. Adjave, N.N. Bakhshi, *Fuel Processing Technology* 45 (1995) 185.
- [16] J.D. Adjave, S.P.R. Katikaneni, N.N. Bakhshi, *Fuel Processing Technology* 48 (1996) 115.
- [17] F. Janssen, *Catalysis Science Series 1* (1999) 15.
- [18] S. Vitolo, B. Bresci, M. Seggiani, M.G. Gallo, *Fuel* 80 (2001) 17–26.
- [19] T. Sooknoi, T. Danuthai, L.L. Lobban, R.G. Mallinson, D.E. Resasco, *Journal of Catalysis* 258 (1) (2008) 199–209.
- [20] M. Bejblova, P. Zamostny, L. Cerveny, J. Cejka, *Collection of Czechoslovak Chemical Communications* vol. 68 (2003) 1969.
- [21] R. Abu-Reziq, D. Avnir, J. Blum, *Journal of Molecular Catalysis A: Chemical* 187 (2002) 277.
- [22] M. Bejblova, P. Zamostny, L. Cerveny, J. Cejka, *Applied Catalysis A: General* 296 (2005) 169–175.
- [23] M. Albert Vannice, Deepak Poondi, *Journal of Catalysis* 169 (1997) 166.
- [24] Zheng Ji-lu, *Journal of Analytical and Applied Pyrolysis* 80 (2007) 30–35.
- [25] S.C. Fung, C.A. Querini, *Journal of Catalysis* 138 (1992) 240.
- [26] D.J. Parrillo, A.T. Adamo, G.T. Kokotailo, R.J. Gorte, *Applied Catalysis* 67 (1990) 107.
- [27] M. Lasperas, H. Cambon, D. Brunel, I. Rodriguez, P. Geneste, *Microporous Materials* 1 (1993) 343.
- [28] P.E. Hathaway, M.E. Davis, *Journal of Catalysis* 116 (1989) 263.
- [29] C.A. Kautstaal, P.A.J.M. Angevaere, V. Poncet, *Journal of Catalysis* 143 (1993) 573–582.
- [30] S.T. King, E.J. Strojny, *Journal of Catalysis* 76 (1982) 274–284.
- [31] M. Hunger, U. Schenk, M. Seiler, J. Weiktamp, *Journal of Molecular Catalysis A: Chemical* 156 (2000) 153.
- [32] J.M. Vohs, M.A. Barteau, *Journal of Physical Chemistry* 93 (1989) 8343.
- [33] T. Seki, H. Kabashima, K. Akutsu, H. Tachikawa, H. Hattori, *Journal of Catalysis* 204 (2001) 393.
- [34] H. Tsuji, H. Hattori, *Catalysis Today* 116 (2006) 239.
- [35] K. Tanabe, K. Saito, *Journal of Catalysis* 35 (1974) 247.
- [36] A. Saadi a, Z. Rassoul a, M.M. Bettahar, *Journal of Molecular Catalysis A: Chemical* 164 (2000) 205–216.
- [37] D. Haffad, U. Kameswari, M.M. Bettahar, A. Chambellan, J.C. Lavalley, *Journal of Catalysis* 172 (1997) 85–92.