DEOXYGENATION OF MODEL BIOFUEL COMPOUNDS OVER CsNaX ZEOLITE CATALYST

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ABSTRACT

The deoxygenation of methyl octanoate and benzaldehyde over CsNaX zeolite catalyst has been investigated as a model for reactions for production of hydrocarbon fuels from bio-oxygenates. The CsNaX zeolite used in the study was prepared by ion exchange of NaX with a $CsNO_3$/CsOH solution to a 50% exchange level. The decarbonylation activity, selectivity, and stability of the CsNaX catalyst were enhanced when methanol was co-fed for the reaction of methyl octanoate. TPD studies suggest that methyl octanoate first decomposes to an octanoate-like species. The decomposition of such species leads to the formation of heptenes and hexenes as major products. Octenes and hydrogenated products are formed in lesser amounts via hydrogenation / hydrogenolysis using hydrogen produced on the surface from methanol decomposition, but not from gas phase H_2.

INTRODUCTION

The interest in renewable fuels as replacements for fossil fuels has rapidly increased over the past few years. Among the various fuels-from-biomass investigated, fatty acid methyl-ester biofuels (FAME) obtained by trans-esterification of triglycerides from natural oils and fats with methanol and production of bio-oil by flash pyrolysis of lignocellulosic biomass have received considerable attention [1-4]. Due to the oxidation and thermal instability of these biofuels, there is continuing concern about their fungibility. Reduction of the reactive oxygen content in the fuel would improve the stability of the fuel and therefore its utilization potential. Various processes including hydrogenolysis [5,6], decarbonylation [7,8], and decarboxylation [9,10] have been proposed to transform the biofuels into a fungible hydrocarbon base fuel.

Typically, decarbonylation takes place over supported noble metal catalysts. For example, Pd/C has been found to be an effective catalyst for decarbonylation / decarboxylation [9]. However, CO produced from the reaction may competitively adsorb on the metal surface, leading to a loss in catalytic activity as conversion increases. Hence, total and hydrogen partial pressures are generally high, in order to keep the surface clean and facilitate the oxygenate-metal surface interaction, and reduce catalyst deactivation [11]

An alternative family of catalysts that may overcome some of these limitations is that of solid bases because the intermolecular interactions and adsorption site competition may greatly affect the reactivity of a catalyst. Among possible solid base catalysts, low-silica zeolites containing highly polarizable cations, such as cesium, may be good candidates.

These catalysts have been found to exhibit relatively high activity towards hydrogenation and hydrogenolysis of acrylonitrile and propionitrile [12]. Recent studies [13] suggest that, in addition to the need for high base strength, an active catalyst requires the co-existence of acid and basic sites for reactions such as hydrogenation and hydrogenolysis.

The purpose of this work is to investigate deoxygenation reactions on Cs- and NaX zeolite catalysts, using methyl octanoate as a model biofuel compound. The effects of varying reaction conditions such as temperature, hydrogen partial pressure, feed concentration, presence of competing molecules, as well as catalyst formulations were investigated in a flow reactor. In addition, temperature programmed techniques were employed to elucidate possible reaction pathways.

EXPERIMENTAL

Catalyst Preparation and Characterization

Molecular sieve (UOP type 13X, NaX) catalyst was commercially obtained from Fluka. The as-received materials were calcined at 450 ^oC. The Cs-containing zeolite (CsNaX) was prepared by ion exchange of Molecular sieve 13X with 0.1 M $CsNO_3$/CsOH (4/1 v/v) at 80 ^oC for 24 h. The solid material was filtered and left to dry at 80 ^oC overnight. The sample was then calcined at 450 ^oC for 2 h in a flow of dry air. Surface area of the CsNaX and NaX catalysts was determined by Nitrogen adsorption at 77 K using a Micromatics ASAP 2000 apparatus. X-ray diffraction (XRD, Bruker AXS D8Discover) was employed to confirm the catalyst structure.

Temperature Programmed Desorption (TPD) of Methyl Octanoate

The evolution of pre-adsorbed methyl octanoate over CsNaX catalysts was followed by temperature programmed desorption in an apparatus equipped with a mass spectrometer (MS). In each run, 50 mg of the sample was initially pretreated in a flow of 2% O_2/He for 2 h at 450 ^oC. Then, the sample was cooled in He flow to 150 ^oC. 100 μl of methyl octanoate was injected to the sample, and a He flow was introduced for 3 hours at 150 ^oC in order to remove the excess methyl octanoate. The sample was then heated up to 900 ^oC at a rate of 10 ^oC/min. Masses (*m/z*) of 2, 28, 56, and 74 were monitored to determine the evolution of hydrogen, carbon monoxide, hydrocarbons, and methyl octanoate, respectively.

Temperature Programmed Desorption (TPD) and Temperature Programmed Reaction (TPRx) of methanol

Methanol was chosen as a probe for the zeolite surface and as a co-reactant to help reduce the rate of catalyst deactivation during the conversion of methyl octanoate. Therefore, the desorption and decomposition of methanol over CsNaX and NaX catalysts was investigated by TPD and TPRx techniques in the same apparatus described in the previous section. In each run, 50 mg of the sample was initially pretreated in a flow of 2% O_2/He for 2 h at 450 ^oC. Then, the sample was cooled in He flow to room temperature. In the desorption experiment, 10 μl of methanol was repeatedly injected over the sample at room temperature until reaching saturation, as indicated by a constant pulse size MS signal. After the removal of the excess methanol by flowing He for 3 h at room temperature, the sample was then heated to 900 ^oC at a rate of 10 ^oC/min. For the TPRx experiment, methanol was continuously fed through the sample bed at a flow rate of 1 ml/hr. The sample was linearly heated from room temperature to 700 ^oC at a heating rate of 10 ^oC/min.

Masses (*m/z*) of 2, 28, 31, and 45 were monitored to determine the evolution of hydrogen, carbon monoxide, methanol, and dimethylether, respectively.

Catalytic activity measurements

The reaction was carried out at atmospheric pressure, in a fixed bed flow reactor made with 1/4" quartz tube. Prior to the reaction, the catalyst samples were pretreated *in situ* under flow of 2% O_2/He at 450 ^{o}C for 2 h. Then, the catalyst bed was cooled to the reaction temperature (425 ^{o}C) under flow of He (25 ml/min). The 10 %wt methyl octanonate in methanol solvent was introduced into the reactor using a syringe pump via a heated vaporization port. Alternatively, in some runs, nonane was used as a solvent instead of methanol. Unreacted feed and products were quantified using an online GC-FID equipped with a capillary HP-5 column, following a temperature program to optimize product separation.

Temperature Programmed Oxidation (TPO) of coke deposits after reaction

Temperature programmed oxidation (TPO) was employed to investigate and quantify the nature and amount of coke deposited on the spent catalysts. 30 mg of the sample was packed in the 1/4" quartz tube reactor. The temperature was ramped to 900 ^{o}C with a heating rate of 10 ^{o}C/min and the TPO profiles were recorded under flow of 2% O_2/He. The CO_2 produced by the oxidation of the coke deposits was converted to methane over a methanation catalyst (15% Ni/Al_2O_3) in the presence of hydrogen at 400 ^{o}C. The corresponding methane was then analyzed online by an FID detector. The amount of oxidized coke was calibrated using 100 μl pulses of pure CO_2 injected to the same system.

RESULTS AND DISCUSSION

Catalytic Activity of the Deoxygenation of methyl octanoate

Effect of Solvents

The reaction of 10%wt methyl octanoate in different solvents (nonane and methanol) was carried out to investigate the effect of solvent. It can be seen from Figure 1 that, the reaction using nonane, a non-polar solvent, gives a high activity at the beginning of the reaction. However, rapid deactivation of the catalyst is observed shortly after an hour on stream. This is presumably because the adsorption of methyl octanoate on the highly basic sites in zeolite is much stronger than that of the hydrocarbon solvent. This results in saturation of the feed in the zeolite micropores and the adsorbed methyl octanoate may well react with itself (self-condensation) forming high molecular weight oxygenates. Such compounds cannot readily diffuse out of the zeolite pores and may well inhibit further feed from adsorption and reaction. Hence, a rapid deactivation was observed after a short period of time on stream. Consistent with this view, the major product from the reaction is mainly 8-pentadecanone, a coupling product of methyl octanoate. Deoxygenated products, namely octene, heptene and hexene, are also observed but with lower selectivity (Figure 2a)

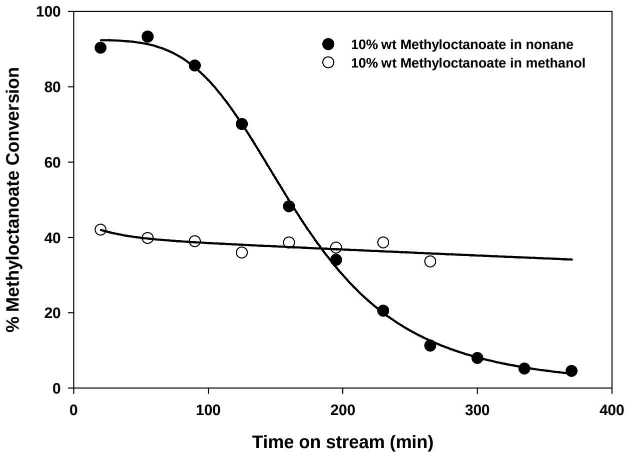


Figure 1 Conversion of 10 %wt methyl octanoate over CsNaX using nonane and methanol as solvent as a function of time on stream. Reaction Conditions: 425 ^oC, 1 atm, W/F = 198 g*h/mol, 25 ml/min of He.

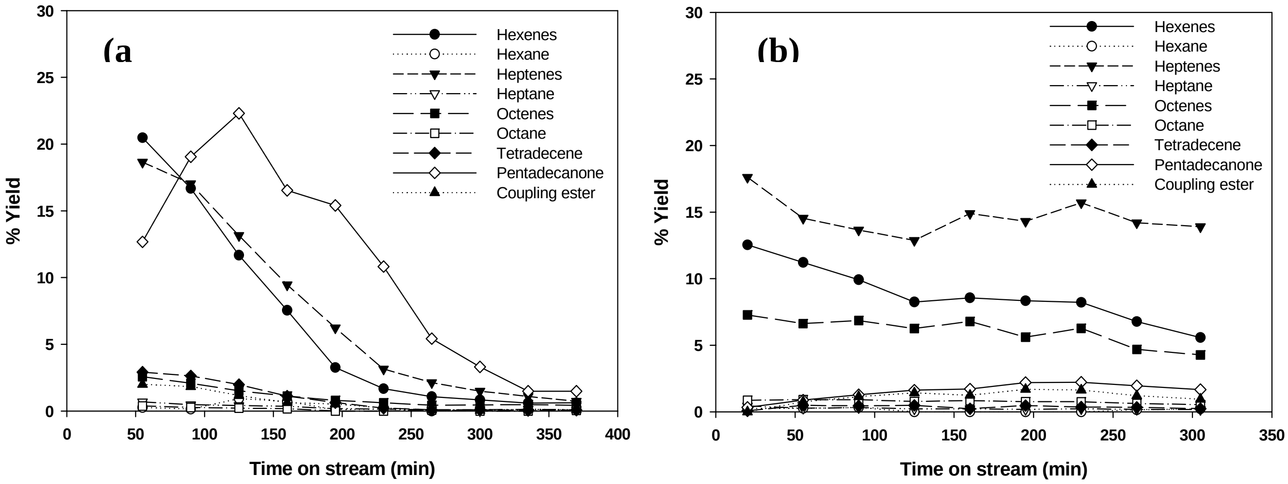


Figure 2. Product distributions from the reaction of 10% wt methyl octanoate using (a) nonane and (b) methanol as solvent as a function of time on stream. Reaction Conditions: 425 ^oC, 1 atm, W/F = 198 g*h/mol, 25 ml/min of He.

However, when methanol was used as a solvent, a reaction with relatively lower activity but high stability was observed (Figure 1). The explanation is that methanol is highly polar and can competitively interact with the zeolite basic sites. This leads to the decomposition of methanol to give formaldehyde, carbon monoxide and hydrogen. These products can remain on the surface and inhibit the co-adsorption and self-condensation of methyl octanoate. Accordingly, such “virtual” pressure of hydrogen and other methanol products would prevent the formation of higher molecular weight oxygenates resulting in better catalytic stability. The results of decomposition of methanol over CsNaX by TP reaction are shown in Figure 3. It is interesting that a high H_2/CO is pronounced only at 300-400 ^oC. This indicates that, at this temperature, methanol would primarily decompose to formaldehyde that can readily remain on the surface. As the temperature is increased, the adsorbed formaldehyde can decompose to carbon monoxide and hydrogen as shown by a constant H_2/CO at higher temperature. This adsorbed formaldehyde is likely to be responsible for the reduced activity, but increased stability of the catalyst in the presence of methanol.

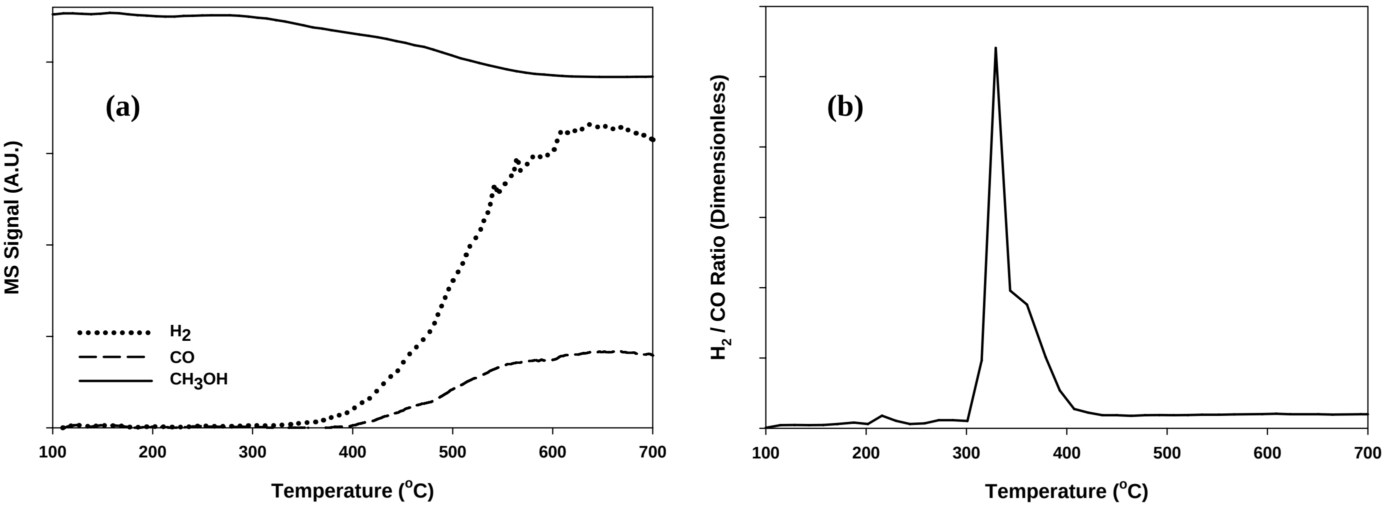


Figure 3. (a) Temperature Programmed Reaction of continuous flow methanol over CsNaX (b) H_2/CO signal of continuous flow methanol over CsNaX.

It is also suggested that the “virtual” pressure of hydrogen can further facilitate the decarbonylation of the ester. Hence, various deoxygenated products are obtained from the reaction using methanol as a solvent (Figure 2b). It is worth noting that the decarbonylation of methyl octanoate over CsNaX requires no additional hydrogen despite the fact that decarbonylated and hydrogenated products are largely obtained. This is because methanol does not only act as reaction media, but it is also serving as a hydrogen source for necessary reactions.

Proposed Reaction Pathways

Although it is certain that the reaction of methanol indeed takes place, the methanol conversion is relatively small (~5%) and product selectivities based on methanol are not considered. Only the carbon yield based on methyl octanoate has been taken into account. It can be seen from Table 1 that heptenes and hexenes are mainly produced from catalytic decarbonylation of methyl octanoate over CsNaX. Octene and larger coupling products, together with small amounts of alkanes and oxygenates, are also observed.

Table 1 Product distribution from decarbonylation of different feeds over CsNaX using methanol as solvent Reaction Conditions: 425 °C, 1 atm, W/F = 396 g*h/mol, 25 ml/min of He.

	10 %wt Methyl octanoate in Methanol
Conversion	62.3
Yield (%)	
Hexenes	19.3
Haxane	0.3
Heptenes	26.1
Heptane	0.8
Octenes	6.7
Octane	1.0
Octanal	0.4
Methyl octanonate	37.7
Oxygenates	3.4
Octanonic acid	2.2
Tetradecene	0.6
Pentadecanone	0.9
Coupling ester	0.8

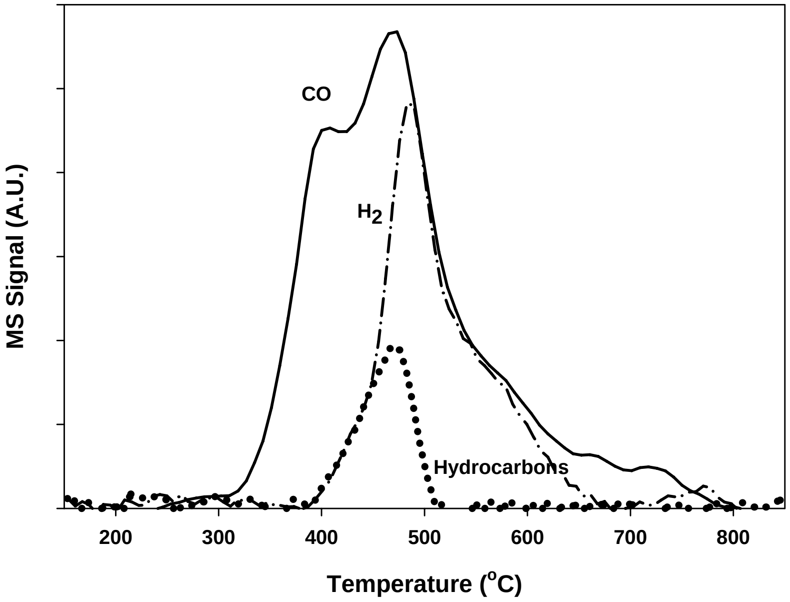
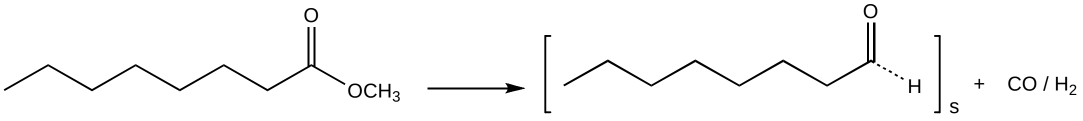


Figure 4. TPD profile of adsorbed methyl octanoate on CsNaX zeolite catalyst

From Figure 4, TPD of methyl octanoate revealed no evolution of the methyl octanoate. Instead, formaldehyde, hydrogen, carbon monoxide and hydrocarbons are evolved above ~300 ^oC. This suggests that methyl octanoate is strongly adsorbed on the basic sites arising from the negative framework charge countered by the large cesium cation. Due to the highly polarizable nature of methyl octanoate, the interaction between carbonyl ester with the basic framework oxygen would readily weaken the carboxylic C-O bond, leading to the decomposition of the ester into formaldehyde and "aldehyde-like species" at high temperature (>350 ^oC). The formaldehyde formed would be partly evolved and some would rapidly decompose into carbon monoxide and hydrogen, in a manner similar to methanol



It is very interesting that no hydrogen is evolved until ~500 ^oC, while hydrocarbons are readily produced. The fact that formaldehyde and carbon monoxide are evolved without hydrogen, leads to the speculation that surface hydrogen would be readily consumed for hydrocarbon formation.

It is proposed that decomposition of such "aldehyde-like species" leads to the formation of two major hydrocarbon products, heptene and hexene. A β-hydrogen elimination [14] and subsequent decomposition to form an olefin, carbon monoxide and hydrogen would give *heptene* as major product of the reaction. This reaction may well be referred to as a reversible reaction of the typical hydroformylation [15]. The decomposition of the cyclic-like intermediate can lead to the formation of more electrophillic acetaldehyde (enol-form) and hexane. The acetaldehyde may be evolved as a product or undergo further aldol condensation/alkylation to form C3-C5 oxygenates, as observed in small amounts by GC-MS

Hydrogen is not essentially required for the formation of heptene and hexene. However, it is largely consumed by the formation of octene and alkanes (Table 1). It is quite plausible to suggest that the formation of octene is derived from additional hydrogenation activity of the cesium exchanged zeolite. As discussed earlier, the basic sites, due to the highly polarizable cesium cation, can readily decompose methanol/formaldehyde, creating a "virtual" hydrogen pressure on the surface. Hence, the adsorbed "aldehyde-like species" would be hydrogenated forming primarily octanol, which may then rapidly undergo dehydration to form octene.

The small amounts of octane, heptane and hexane are further evidence that suggest the hydrogenation activity of CsNaX (Table 1). However, the hydrogenation of octene, heptene and hexene to form octane, heptane and hexane occur to a much lesser extent, as compared to that of the aldehyde-like species to form octanol. This is because olefins are less adsorptive on the basic sites, as compared to the more electrophillic aldehyde-like species. These hydrogenated products can be promoted in the reaction using methanol as a solvent, as discussed earlier.

CONCLUSIONS

It can be concluded that the decarbonylation activity of methyl octanoate can occur at high rate and for a long time on stream over CsNaX catalyst when co-feeding methanol.

Methyl octanoate strongly adsorbs on CsNaX, basic sites and cannot be desorbed unless decomposed. When a less adsorbable solvent, nonane, is used, CsNaX rapidly deactivates. When methanol is present, the catalyst stability is greatly enhanced due to the presence of decomposed fragments of methanol on the surface. The TPD results suggest that the decarbonylation of methyl octanoate proceeds via primary decomposition at the methoxyl group, presumably producing an octanoate-like species as intermediate. The direct decomposition of this species gives heptenes and hexenes as main products. Octenes and other hydrogenated products are formed by hydrogenation / hydrogenolysis, in which the surface hydrogen produced from the methanol decomposition plays an important role.

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