ALDOL CONDENSATION OF BUTANAL OVER ALKALI METAL ZEOLITES

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Alkali metal zeolites and metal oxides were used for the aldol condensation of n-butanal to 2-ethyl-2-hexenal. The order of activity at 150 ° C and 1 atm. was: CsNaY > NaY > LiNaY > MgO > Al_2O_3. Selectivity to 2-ethyl-2-hexenal was 100% for both pure and mixed isomer feed. Infrared spectroscopic studies showed that stable catalysts were produced by propene pretreatments which blocked Lewis acid sites. Adsorption of ammonia and carbon dioxide on CsNaY during aldol condensation of n-butanal causes a decrease in rate. This result, along with the order of activity, suggests that the presence of both acid and basic sites produce higher activity than strongly basic MgO.

Keywords: Aldol condensation, zeolites, butanal, MgO, alumina, basic zeolites

1. Introduction

While the homogeneous aldol condensation reaction of aldehydes to α,β-unsaturated aldehydes has been demonstrated to be either acid or base catalyzed, heterogeneous catalysts for the aldol condensation reaction have also been reported. Isakov et al. studied the aldol condensation of n-butanal to 2-ethyl-2-hexenal over zeolites at 200 ° C in liquid-solid reaction system [1]. The aldol condensation activity was found to increase with increasing basic character, i.e. KY > NaY > HY catalysts. Because of the ability for these zeolites to catalyze this reaction, it was suggested zeolites behave as solid bases. However, no additional data was presented to suggest zeolite basic catalysis.

For homogeneous systems, the aldolization is preferred in the basic route, as demonstrated by the use of NaOH as the catalysts for the aldolization step in commercial processes [2,3]. Acid catalysis for the condensation reaction to form the enal is generally a lower activation energy process than the basic catalyzed condensation and is used commercially. Therefore, a catalyst possessing both acid and base character may be beneficial for the aldol condensation due to the bifunctionality of the catalysts.

Alkali metal zeolites are known to possess both acid and base sites. Although the acidic properties of many zeolites have been studied thoroughly, zeolites also exhibit basic character. This has not been investigated with the same vigor. A number of base catalyzed reactions have been studied [4–7]. For example, the decomposition of isopropanol over alkali metal exchanged NaY to acetone (a base catalyzed reaction) and to propylene (an acid catalyzed reaction) is strongly affected by the alkali metal content. The formation of acetone increases in the series LiY > NaY > KY > RbY > CsY, as the propylene formation decreases in this series of catalysts. In this paper, we present results for the aldol condensation of butanal over alkali metal zeolites and metal oxides. In contrast to the liquid-solid reaction system studied by Isakov, this work investigates the catalytic activity and catalyst properties under gas-solid reaction conditions. Catalyst properties were studied by differential kinetic studies, infrared spectroscopy, and temperature programmed desorption.

2. Experimental

2.A. CATALYST PREPARATION

All the catalysts were prepared by ion exchange from NaY. The zeolite Y source was batch 646-58-3 from PQ Corporation. The Si/Al ratio was 2.49 as measured by atomic absorption spectroscopy. For alkali metal zeolite, a 0.2 N alkali metal chloride solution was prepared. NaY was added to make a slurry of 1 gram of NaY per 100 ml of solution. Typical batch sizes were 5 grams of NaY and 500 ml of alkali metal chloride solution. The mixture was then heated to 90 °C and held there for 5 hours. After the 5 hours, the slurry was allowed to cool overnight to room temperature. The zeolite was recovered by filtration and washed with 3 liters of distilled water. The filtrate was tested for chloride ions by the silver nitrate test. The 3 liters of washing was sufficient to ensure that all excess chloride ions were washed out. The cake was then dried in air at 120 °C to dry powder. The degree of exchange was determined by acid digestion of the zeolite and analysis of the solution by atomic absorption. Li and Cs exchange for Na was 70%. X-ray diffraction measurements of all exchanged zeolites showed that crystallinity was preserved.

The magnesium oxide (Alpha Products–99.5% pure and −325 mesh) was used without further purification. The alumina (Alpha Products–alpha phase, and 90% pure with 9% H_2O) was calcined in air at 500 °C for 4 hours to ensure that eta-alumina was formed [8]. All catalysts, except alumina, were pressed under 10,000 psi, and crushed and sieved to −45/+80 mesh size without binder. X-ray diffraction of catalysts prepared in this manner does not effect zeolite crystallinity. Alumina was pressed to 20,000 psi before crushing and sieving to −45/+80 mesh.

2.B. GASES

Helium, hydrogen, carbon monoxide, carbon dioxide, and propylene were obtained from Matheson Gas Company. Helium was 99.999% grade and passed through gas purifiers consisting of 4 A molecular sieve and drierite. Propylene was 99.0% min. grade and used without further purification. Carbon monoxide was 99.9% grade and also used without further purification. Hydrogen was 99.99% grade and was passed through an Alltech Oxy-Trap oxygen trap to ensure the absence of oxygen in the reactor system. Bone dry air was obtained by passed compressed air through a refrigeration unit, and a molecular sieve and silica gel trap.

2.C. LIQUIDS

All liquid chemicals were obtained from Aldrich and were of 99% + grade or gold label. These were used without further purification.

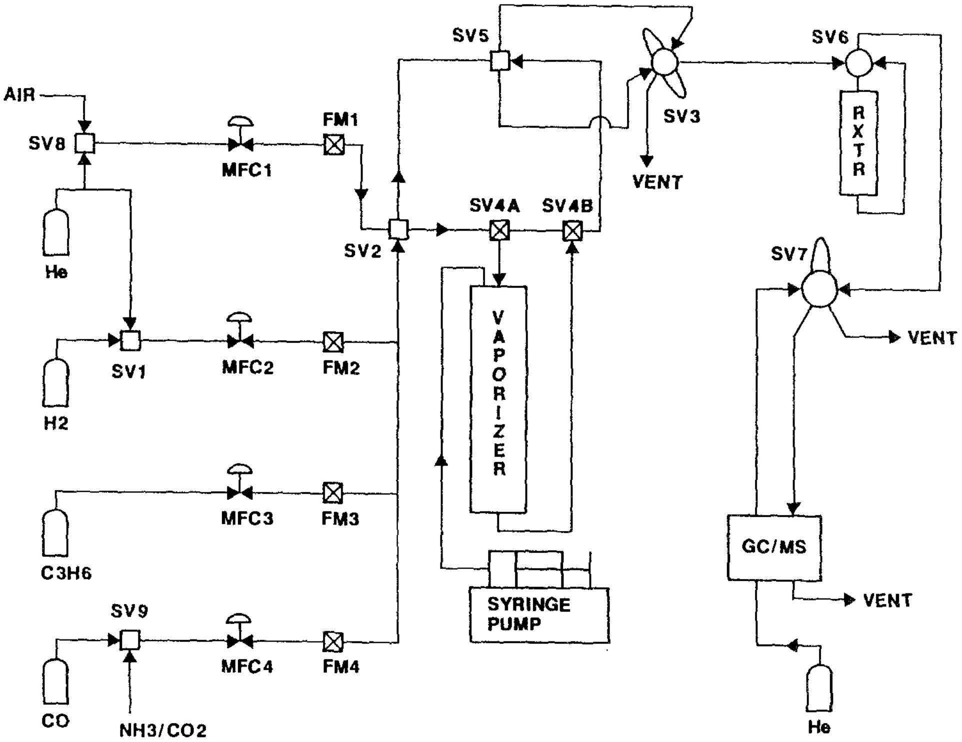

Fig. 1. Schematic diagram of reaction and temperature programmed desorption system.

2.D. REACTOR

A schematic diagram of the differential reactor system is shown in fig. 1. The aldol condensation reactions were carried out in the 3/8 inch diameter (o.d.), 9 inch long Vycor reactor. Typically, 0.1 grams of catalyst was supported by a glass wool plug in the reactor. Helium carrier gas at a flow rate of 20 ml/min passed over the catalysts. Catalyst pretreatment included heating to 150 °C, under helium, and then passing propene over the catalysts for 30 minutes, then flushing with helium to remove residual propene. Liquid feed rates were kept at 0.02 ml/hr. The vaporized liquid and helium flow through the reactor resulted in a reactor pressure of 1 psi. For other reactivity experiments, the catalyst was heated to 150 °C under helium and then the reactant stream was passed over the catalysts. Gas samples were required via a 250 microliter sample loop.

Reaction products were analyzed by a Hewlett-Packard 5980 A/5970 B gas chromatograph and mass selective detector controlled by a Hewlett-Packard 59770 C Chemstation. Compounds were identified by comparison with retention times and mass spectra of standards solutions.

3. Results and discussion

3.A. REACTIVITY

N-butanal, i-butanal, propene hydroformylation mixtures, and n/i-butanal mixtures were passed over the catalysts. The hydroformylation gas mixture was 3 : 3 : 1 propene, hydrogen, carbon monoxide with a total flow of 45 ml/min. The results are summarized in table 1. All catalytic reaction experiments were conducted at 150 °C and 1 atm.

For all the zeolite and alumina catalysts under propene hydroformylation

Table 1
Summary of catalytic activity and selectivity

Catalyst	$C_3H_6/CO/H_2$	n-butanal [1,2]	i-butanal	$n/i = 1$
LiNaY	hexenes [3]	9.30E(-5)	hexenes	no data
NaY	hexenes	1.09E(-4)	hexenes	no data
CsNaY	hexenes	1.99E(-4)	hexenes	1.0E(-4)
Al_2O_3	hexenes	3.33E(-5)	hexenes	no data
MgO	no reaction	4.04E(-5)	no reaction	1.0E(-4) [4]

[1] All rates are steady state values and in moles 2-ethyl-2-hexenal formed/g-catalyst-hr.
[2] Catalysts were pretreated with propene for 30 minutes at 150 °C.
[3] Rate data was not determined since the hexene rate was always decaying.
[4] Propanal formation rate, moles propanal/g-catalyst-hr.

conditions, the formation of hexenes was observed initially. The hexene formation decayed to zero within 12 hours. Elimination of the hydrogen and carbon monoxide in the reactant feed did not alter the hexene formation rate, indicating that hexene was produced via propylene dimerization. Hexene formation rate data was not determined due to high initial activity, and inability to reach a steady state.

The addition of n-butanal to the propene hydroformylation mixture did not alter the hexene formation rate. Prior to the detection of 2-ethyl-2 hexenal, hexenes were observed for roughly 12 hours over alumina, 8 hours over LiNaY, 4 hours over NaY, and only 2 hours over CsNaY. Based on the activity and length of time required to decay, The order of acidity can be listed as: Al_2O_3 > LiNaY > NaY > CsNaY ≫ MgO. The enal reaction rate increased as the hexene formation rate decreased.

A steady state aldol condensation rate was obtained over all the catalysts which had been pretreated with propene at 150 ° C for 30 minutes. Catalysts pretreated by heating the catalysts under helium at 150 ° C, and then introducing aldehyde, deactivated within 12 hours. The reactivity data presented in table 1 are for propene pretreated catalysts only. (The role of propene will be discussed below.)

N-butanal reacts selectively to yield 2-ethyl-2-hexenal. The order of activity is: CsNaY > NaY > LiNaY > MgO > Al_2O_3. The selectivity decreased at higher temperatures; larger molecular weight products were detected above 180 ° C. These mass spectra were not fully interpreted; however, the compounds were most likely higher aldol condensation products (trimers, etc.).

I-butanal was unreactive over all the catalysts. Hexenes were detected initially and gradually decayed below detection limits. The lack of aldol condensation product is predictable. The aldol condensation reaction requires the presence of alpha hydrogens in the aldol intermediate in order for the condensation (water removal) to occur. The aldol intermediate for i-butanal self condensation does not contain alpha-hydrogen.

Theoretically, aldol condensation reaction between the butanal isomers is allowed, and 2 products are possible: the self condensation product of n-butanal, 2-ethyl-2-hexanal, and the attack of the n-butanal alpha-carbon at the carbonyl carbon of i-butanal would yield 2-ethyl-4-methyl-2-pentenal. A 1 : 1 stoichiometric mixture of n/i-butanal reacted over CsNaY produced only the n-butanal product at half the rate of reaction measured for pure n-butanal feed. MgO under the same conditions, did not convert n-butanal to 2-ethyl-2-hexenal. Only propanal was detected at the same rate as 2-ethyl-2-hexenal over CsNaY. Propanal was not observed during the pure feed experiments. It was not determined whether n-butanal or i-butanal was the source of propanal. It is interesting that the zeolite catalysts prohibits the cross condensation product. Certainly, the molecular size of the reactants and products are smaller than CsNaY pore dimensions.

3.B. ROLE OF PROPENE PRETREATMENT

Infrared spectroscopy and temperature programmed desorption were used to elucidate the role of propene adsorption as a required catalyst pretreatment. Fig. 2 presents the JR results from three experiments on CsNaY which had been evacuated and heated to 225 ° C for 10 hours. Spectrum A resulted following contact with propene at 150 ° C, then evacuating. The only distinct absorption occurs at 1643 cm^{-1}, with a broad shoulder down to approximately 1560 cm^{-1}. The 1643 cm^{-1} band is assigned to the C=C stretching mode of propene adsorbed on the catalysts. Spectrum B resulted from pyridine adsorbed at 150 ° C, then evacuated. The presence of bands at 1541 cm^{-1}, and 1453 and 1439 cm^{-1}, indicates both Bronsted and Lewis acid sites, respectively. The strong 1487 cm^{-1} is a common mode of absorption for both acid types. Spectrum C was taken following pyridine absorption onto a propene treated CsNaY catalysts. The 1541 and 1487 cm^{-1} are both present. However, the Lewis acid sites bands have been removed, indicating that propene is effectively blocking Lewis acid sites.

This information on the acid sites can be used to account for the deactivation of catalysts which were not propene pretreated. Catalyst deactivation on helium pretreated catalysts may be caused by aldehyde (reactant and product) adsorption and decomposition at Lewis acid sites. These reaction products can ultimately fill the zeolite cages and prevent further reaction to aldol condensation products.

Fig. 3 shows the same set of experiments as discussed in fig. 2 for CsNaY which was evacuated at 500 ° C for 10 hours. Several differences are exhibited between the low and high temperature pretreatments. Spectrum 3A contains absorption frequencies at 1426, 1609 and 1692 cm^{-1}. The stronger, broad band

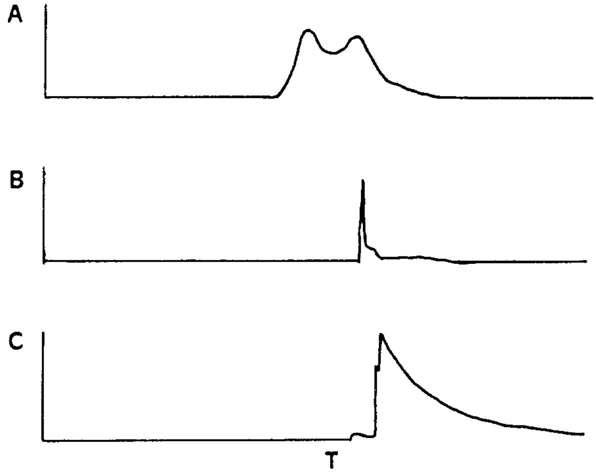

Fig. 2. FTIR of CsNaY heated to 225 ° C under vacuum, then: A. Propene adsorbed at 150 ° C; B. Pyridine adsorbed at 150 ° C; C. Propene adsorbed followed by pyridine.

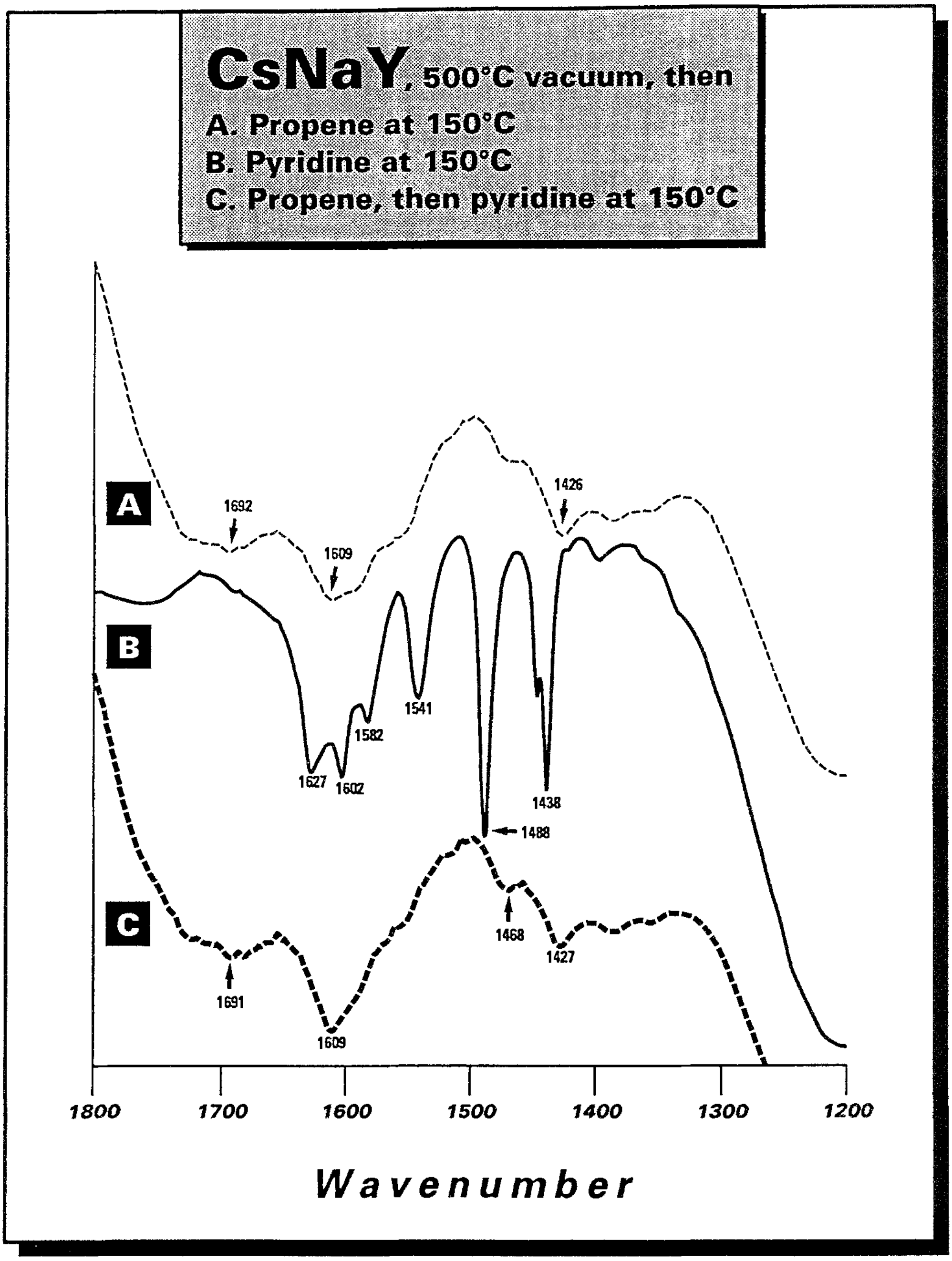

Fig. 3. FTIR of CsNaY heated 500 °C under vacuum, then: A. Propene adsorbed at 150 °C; B. Pyridine adsorbed at 150 °C; C. Propene adsorbed followed by pyridine.

around 1600 cm^{-1} suggests the formation of coke. Spectrum 3B shows a strong 1439 cm^{-1} band. The higher temperature pretreatment creates a higher concentration of Lewis acid sites. Pyridine adsorbed after propene adsorption (spectrum 3C) shows that no Bronsted or Lewis acidity remains. The reaction products of propene on this CsNaY effectively block or consume the acid sites.

The strength of propene adsorbed onto CsNaY was investigated by tempera-

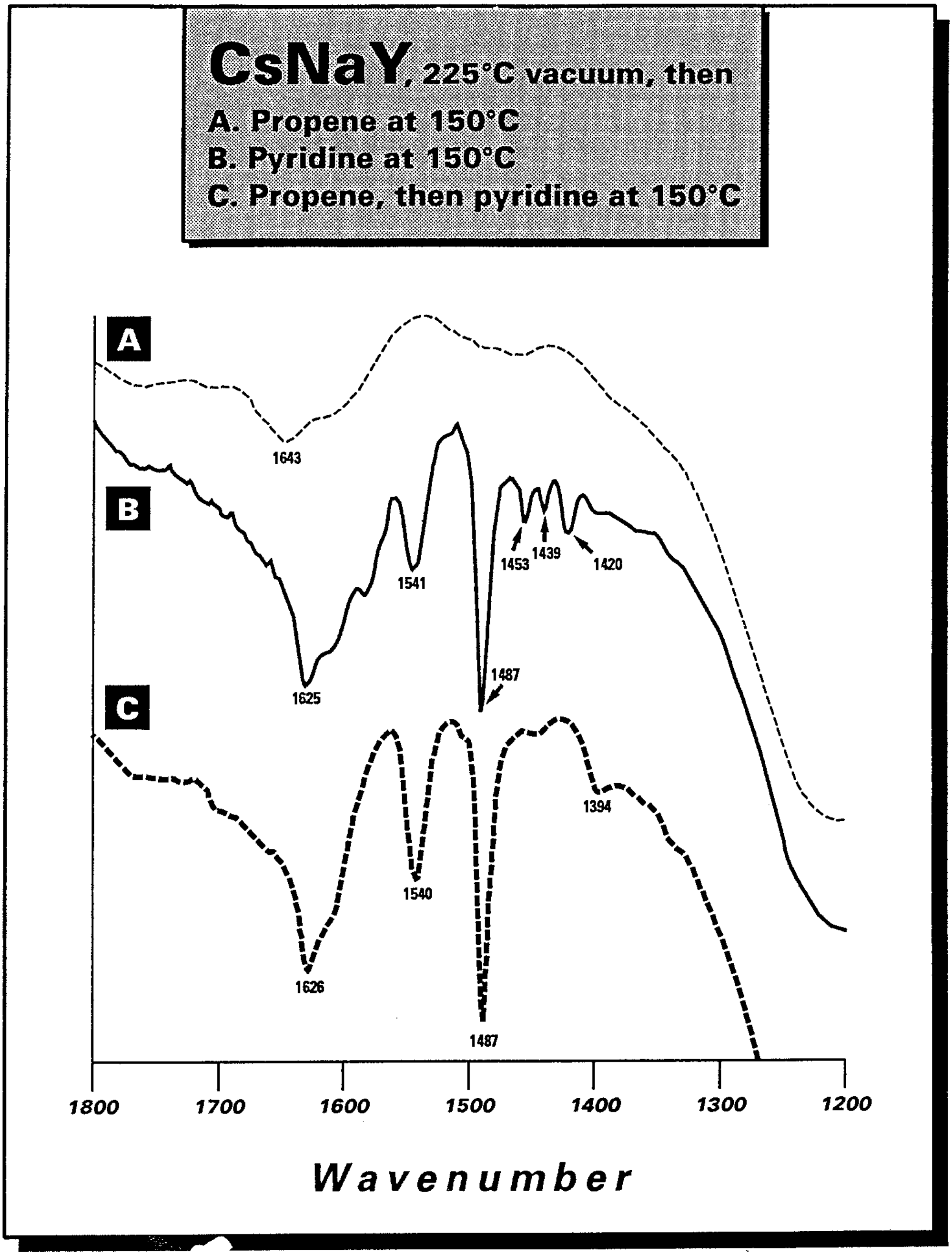

Fig. 4. Temperature programmed desorption of adsorbed propene and n-butanal from CsNaY showing relative positions and intensities for ethyl cyclohexene (A), 4-hepanone (B), and 2-ethyl-2-hexenal (C).

ture programmed desorption. CsNaY was heated to 150 ° C under He, then exposed to a flow of propene for 30 minutes. The catalysts were linearly ramped at 5 K/min and 60 K/min. The only desorbed species observed was cyclohexene, or 2,3-dimethyl-1, 3-butadiene (the mass spectra of these molecules are virtually identical) at 350 ° C. This desorption temperature is well above the aldol condensation reaction temperature of 150 ° C. Therefore, some propene must remain on the catalyst surface during aldol condensation reaction. No pure propene was desorbed–only dimer products which also requires hydrogen production (not detectable by the HP 5970 B MSD). Hexene production requires desorption from Lewis acid sites with hydrogen abstraction from adsorbed propene to produce surface hydroxyl groups.

To confirm the propene strength of adsorption relative to n-butanal, a TPD experiment was conducted with propene pretreated CsNaY followed by n-butanal adsorption. Fig. 4 shows the results. The three products observed were assigned to be ethyl-cyclohexene, 4-heptanone, and 2-ethyl-2-hexenal as shown in curves A, B and C, respectively. All products were desorbed below 350 ° C. Mechanisms for the production of these molecules have not been determined. However, one can postulate the necessary reaction steps from aldol condensation intermediates in order to achieve these products. The presence of ethyl-cyclohexene requires the removal of both oxygen atom from an aldol intermediate. Adsorption of the aldol at the carbonyl at a weak acid site may facilitate protonation. Then, double dehydration followed by ring closure to obtain ethyl-cyclohexene. Adsorption of an aldol at the carbonyl as a carboxylate, and then decarboxylation would yield 4-heptanol. Dehydrogenation of 4-heptanol would then give 4-heptanone. The base NaY material contains approximately 500 ppm Fe which could perform this dehydrogenation. An alternative mechanism for 4-heptanone formation is direct carboxylate ketonization rather than dehydrogenation.

Desorption of n-butanal without propene pretreatment gave the same product distribution. Therefore, there appears to be no reaction between aldehyde and olefin on the zeolite. Also, above 350 ° C, small quantities of heavier products were observed with m/z of 145, 133, and 131.

3.C. CATALYST POISONING

The trend of increasing activity with increasing cation size suggests that basic sites may play a role in the aldol condensation reaction. It is known from other studies that the basic catalysis activity increases down the alkali metal group. The basic site has been assigned as the AlO_4 group which would be more accessible with decreasing electronegative cations. At the same time, however, if only base catalysis was necessary, MgO would be expected to be more active than CsNaY since it is known to have a higher concentration of base sites [8]. We did not perform analyses to determine the acid and base site concentrations which would provide a definitive measure of relative activities for these catalysts. As previously mentioned, the acid catalyzed dehydration of the aldol intermediate is a lower activation energy pathway. MgO was the least reactive for hexene formation, indicating low acid site concentration. Therefore, it was hypothesized that acid and base catalyzed sites are active on CsNaY. To test this postulate, CsNaY was pretreated with NH_3 and CO_2 so that acid and base sites, respectively, would be blocked. For each gas, the steady state aldol condensation rate was reduced by two-thirds. The fact that these gases had equal effects on the rate supports the bifunctional catalysts hypothesis.

4. Conclusions

The following conclusions can be made:

1. Alkali metal zeolites can be used as selective catalysts for butanal aldol condensation reactions to produce α,β-unsaturated, aldehydes. Under pure n-butanal and mixed normal and iso feeds, 2-ethyl-2-hexenal was the sole, steady state product.

2. Strong Lewis acid sites are present on CsNaY and can be effectively blocked by propene adsorption. Weakly adsorbed propene can be displaced by butanal adsorption, as evidenced by the formation of hexenes, to allow the aldol condensation reaction to proceed. However, the propene is more strongly adsorbed than butanal and its reaction products.

3. Poisoning experiments suggests that both acid and base sites are active for the aldol condensation reaction. Evidently, this bifunctionality makes the CsNaY a more active catalyst than strongly basic MgO.

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