Oligomerization of Propionaldehyde on Novel Basic Catalysts

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Abstract

Vapor-phase oligomerization of propanal to 2-methyl-2-pentenal and 2-ethyl-3,5-dimethylcyclo-2-pentenone over basic zeolite catalysts (NaX, KNaX, KX, and CsNaX), as well as more traditional solid basic catalysts (MgO and MgO-Al2O3 hydrotalcites), was studied in an integral flow reactor at atmospheric pressure. Conversion and carbon yield based on catalyst properties (basicity, acidity) are reported. The highest stable activity was over KX, with the highest selectivity to the primary product, 2-methyl-2-pentenal (dehydrated aldol dimer of propanal) and the second highest selectivity to the secondary product, 2-ethyl-3,5-dimethylcyclo-2-pentenone (a non-aromatic cyclic trimer), with essentially no other products. Promotion of Zeolite X with various alkali metals also affected the acid and base site strengths, which had an effect on the conversion and selectivity.

Keywords: Propanal; Aldol condensation; Solid base; Basic Zeolite; Cesium

1. Introduction

With the increased price of petroleum around the world, countries with high consumption or low reserves are interested in producing transportation fuels from other sources. Producing liquid fuels from biomass has the advantage of being local, both decreasing dependence on foreign powers as well as creating local jobs.

One popular process for biomass conversion involves the transesterification of vegetable oils, using methanol, to produce fatty acid methyl esters (FAMEs) with a glycerin (impure glycerol, 1,2,3-propanetriol) byproduct stream. Although a market for purified glycerol does exist, it will be overwhelmed if all the planned biodiesel facilities purify and sell the resultant glycerol. The result would be a precipitous drop in the price of what was intended to be a side revenue stream, resulting in negative economics for equipment installation and energy consumption of glycerol purification. An alternative market must be found for this high-volume stream, preferably with positive economics.

Thermal and catalytic decomposition of glycerol produces acrolein, which may be hydrogenated to propanal with a reactive aldehyde moiety. The well-known aldol condensation reaction, that increases hydrocarbon molecular weight via carbon-carbon bond formation, is catalyzed in solution both by acids and by bases, so it is a reasonable proposition to study the use of solid acids or solid bases to catalyze these reactions. Since solid acids tend to promote cracking, and given the appreciable activity of basic catalysts at low temperatures, solid base catalysts have been studied in this work at low enough temperatures to avoid cracking.

The dimer and trimer species resulting from the propanal condensation reaction, in which each addition of a monomer is accompanied by a dehydration step, are potentially valuable components of the gasoline pool. The dimer could be hydrogenated and deoxygenated, while the (cyclic) trimer is a highly branched molecule, potentially with a high octane number. While the intermediate dehydration steps remove one oxygen after each condensation step, the ring closure step does not eliminate an oxygen atom. This oxygen remains in a carbonyl group, but it should not be overly reactive in the fuel pool: the C-O double bond is conjugated with a C-C double bond, so it should be less reactive than unconjugated carbonyl compounds. In any case, if necessary, the carbonyl and alkene moieties in the trimer can be hydrogenated to a saturated alcohol, or even deoxygenated altogether in a subsequent step.

In this contribution, the activity, selectivity, and stability of a series of basic catalysts with or without associated mild acidity have been compared for the self-condensation of propanal. As will be seen below, the alkali-ion-exchanged zeolite X catalysts generally have both higher activity and higher stability than the classical basic catalysts. The resulting trimer/dimer ratio has been found to be a strong function of conversion, but also the catalyst type.

2. Experimental

2.1. Catalyst preparation

Several alkali-ion-exchanged zeolite catalysts were compared in the propanal condensation reactions. The NaX zeolite was used as purchased (Molecular Sieve UOP Type 13 X from Fluka, product no. 69856). From this were prepared KX and CsNaX by ion exchange.

To prepare the magnesium oxide (MgO), typically 12 grams of magnesium nitrate hexahydrate (99% A.C.S. reagent, Sigma Aldrich) and 6 g of citric acid were dissolved in approximately 60 mL of water in a thin walled mortar. This was then placed in a 500°C oven for 2 h. The resulting solids were ground lightly with a pestle.

The hydrotalcite (HT) was used as purchased (synthetic, from Sigma Aldrich).

2.2. Fresh Catalyst Characterization

Temperature programmed desorption (TPD) of adsorbed CO_2 was used to explore the basic nature of the catalysts, while TPD of adsorbed isopropyl amine (IPA) was used to explore the acidic nature of the catalysts. A mass spectrometer was used as the detector for TPD experiments.

2.3. Measurement of Catalytic Activity

The gas phase down-flow reactor was built of 3/8” stainless steel tubing with an internal temperature controlling thermocouple. Quartz wool was placed at the thermocouple to form a support for the catalyst bed. After adding the catalyst (typically 300 mg), more quartz wool was placed on top of the bed.

The liquid feed was propanal (reagent grade, >97%, Sigma Aldrich). To prevent oxidation, the head space was swept with He whenever the bottle was opened. To study the effect of feed oxidation, propanoic acid (99.5+% A.C.S. from Sigma Aldrich) was used in some runs.

Liquid feed was delivered to the system at 0.5 mL/hr by a syringe pump with a needle pointing down through a septum into the reactor. The reactor effluent line was heated to 220°C and fed through a 6-port sampling valve. The vent line from the 6-port valve could be submerged in methanol to collect products for GCMS analysis on a Shimadzu GCMS-QP2010S. A sample loop was used to capture a snapshot of the effluent gas, which was fed to an Agilent 6890 for GC analysis via FID through a 30m HP5 column or a 30m Innowax column. Due to the presence of heteroatoms in the feed and product molecules, a response factor for each compound was used to determine the carbon fraction rather than using the raw FID signal.

Zeolites were pretreated by heating from ambient to 450°C at 4°C/min in a flowing air and helium mixture (air 7.0 mL/min, helium 45.6 mL/min) and held at 450°C for 1 hour. The reactor was then cooled to 300°C, the air flow was eliminated, the helium flow was set to 39.1 mL/min, and the reaction was initiated by starting the syringe pump.

MgO and HT were pretreated by heating from ambient to 500°C at 10°C/min in a flowing air and helium mixture (air 7.0 mL/min, helium 45.6 mL/min) and held at 500°C for 2 hours. The reactor was then cooled to 300°C, the air flow was eliminated, the helium flow was set to 39.1 mL/min, and the reaction was initiated by starting the syringe pump.

The chemical reaction investigated was aldol self-condensation of propanal. While aldol condensation is well-known, and some researchers have used propanal as a reactant in cross-condensation, few researchers have studied propanal self-condensation in any detail. Drawing an analogy from the reaction catalyzed by a homogeneous base, one would expect the first step our system of solid bases to be proton abstraction. The resulting carbanion donates its lone pair to the carbonyl carbon of an adjacent propanal molecule, pushing the □ electrons onto the oxygen. The negatively charged oxygen atom is then reprotonated, and the subsequent facile dehydration results in the □ □ unsaturated carbonyl compound (here called the “dehydrated dimer”).

The next reaction step to the linear trimer follows the same mechanism. For acetone self-condensation, two linear trimer species are possible, but it does not matter whether propanal or the dehydrated dimer is converted to the enolate-like species; both options produce the same linear trimer, 2,4-dimethylhepta-2,4-dienal. This molecule was not identified by GCMS, nor were there any unidentified peaks in the GC traces which could be attributed to this species. However, GCMS did identify a 9-carbon cyclic species (2,3,4,5-tetramethyl-2-cyclopentenone) similar to one which may be formed via Nazarov cyclization (2-ethyl-3,5-dimethyl-2-cyclopentenone), which is catalyzed exclusively by acids. It is believed that the actual species is indistinguishable by GCMS from the tetramethyl isomer, due to the improbability of producing an ethyl fragment from the ethyl-dimethyl isomer.

In the alkali-exchanged zeolites, the alkali metal cations act as adjacent acid sites, so the resulting enolate oxygen (with a formal -1 charge) may be stabilized by electron donation to the cation. Alternatively, when acid-base pairs are present, the oxygen of the carbonyl could adsorb onto alkali metal cations, followed by proton abstraction by the adjacent base site. As mentioned above, it does not matter which molecule acts as the enolate-like species; the same linear trimer is formed.

While the linear trimer is not observed in the GC or GCMS analysis, a cyclic trimer is observed. If the Nazarov electrocyclic ring closure is the correct mechanism, then the Lewis acidity of the alkali cations must catalyze this step of the reaction scheme. Solids with only basic character would not be expected to produce any of this trimer.

2.4 *Spent Catalyst Characterization*

Temperature programmed oxidation (TPO) experiments were conducted on the spent catalysts to determine the nature of the carbonaceous species remaining after reaction. A small amount (about 40 mg) of spent catalyst was loaded in a ¼" quartz tube. A dilute mixture of oxygen in helium was flowed over the catalyst while the temperature was increased at 10°C/min up to 900°C. The effluent gases flowed through a methanator to convert the CO2 to methane, which was then fed to an FID detector. After the TPO run, a sample loop filled with CO_2 was cycled to produce reference peaks.

3. Key results

Relative activities of all catalysts studied appear in Figure 1. Basic zeolites are generally superior to the traditional solid bases in terms of activity per gram and longevity, except for the case of NaX which deactivates rapidly. Other authors discussing solid bases only provide data up to one hour Time On Stream (TOS), or do not report what the TOS is.

In addition to the longevity, another remarkable feature of the zeolites is their resistance to poisoning by the oxidized feed, apart from NaX, whose conversion is reduced from 65% with clean feed at 0.75 h TOS to only 19% conversion (a 70% drop) at 1 h TOS with the oxidized feed. In contrast, the KX catalyst exhibits similar initial activity (41% at ~1 h TOS) in both cases, although KX deactivates more quickly than with clean feed. In contrast to both of the other alkaline zeolites, CsNaX exhibits both augmented activity and better stability with PA in the feed (Figure 2). While not having as high of an activity compared to the zeolites, MgO shows measurable activity for several hours TOS when clean feed is used. However, MgO is completely deactivated within an hour when PA is present, while most of the zeolites continue with appreciable activity beyond five hours, even under the least favorable conditions (with PA for NaX and KX, without PA for CsNaX.

Figure 3 shows the ratio of trimer yield to dimer yield as a function of conversion for all catalysts. The CsNaX clearly shows a higher tendency to produce trimer than the other catalysts. The MgO, HT, and KX all fall roughly along the same line, while the NaX data fall between the other catalysts.

4. Acknowledgements

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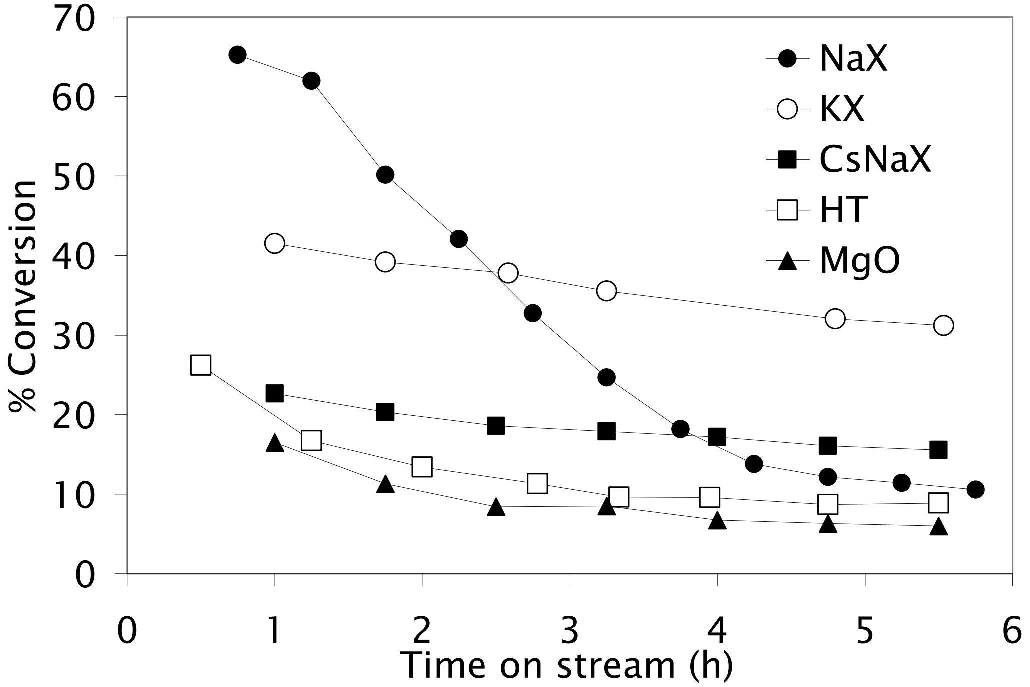

Figure 1. Conversion over base catalysts as a function of time on stream. Reaction conditions: 300°C, 1 atm, 0.5 mL/hr clean propanal; 0.3 g catalysts; W/F = 0.745 hr.

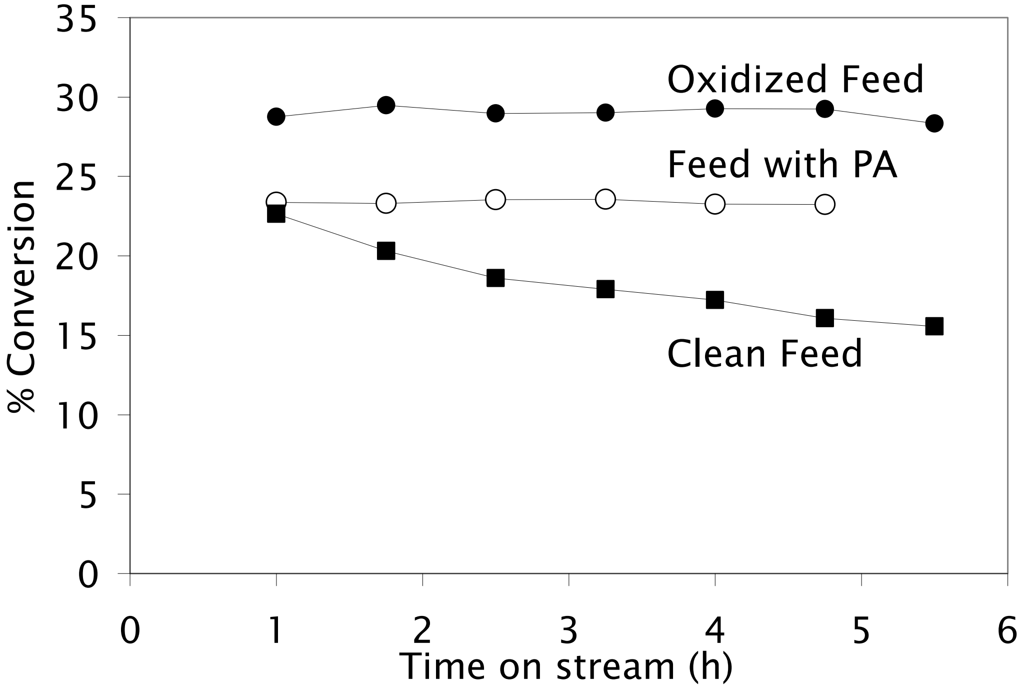

Figure 2. Conversion over CsNaX as a function of time on stream. Reaction conditions: 300°C, 1 atm, 0.5 mL/hr propanal; 0.3 g catalysts; W/F = 0.745 hr

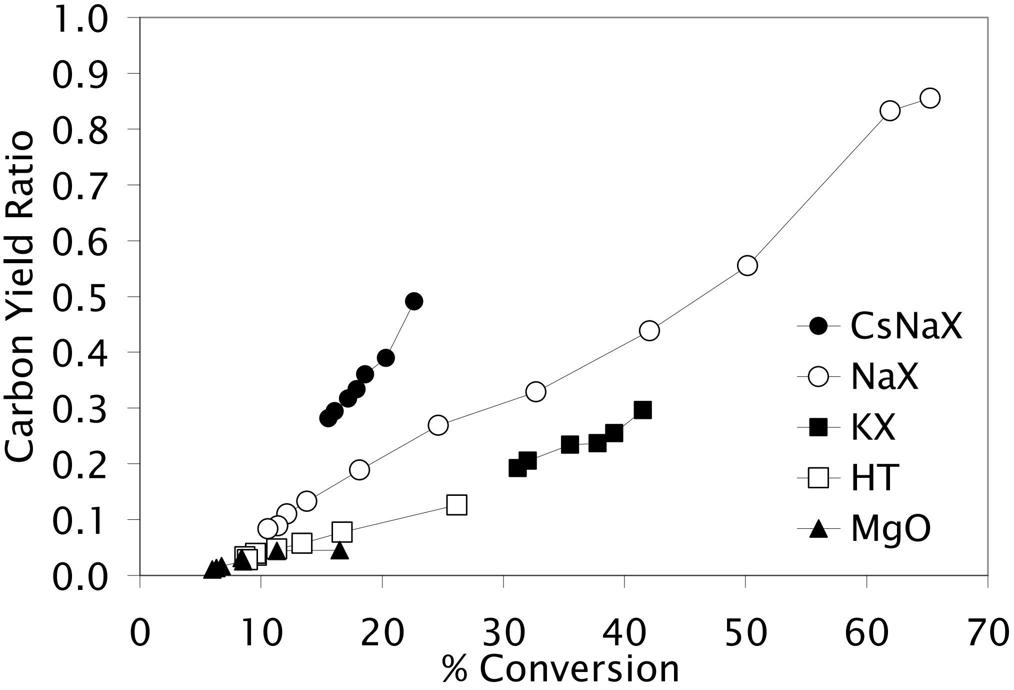

Figure 3. Ratio of trimer yield to dimer yield over base catalysts as a function of conversion. Reaction conditions: 300°C, 1 atm, 0.5 mL/hr clean propanal; 0.3 g catalysts; W/F = 0.745 hr.