

Furfural Upgrading by Aldol Condensation with Ketones Over Solid-Base Catalysts

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Abstract

Aldol condensation reactions between furfural and various ketones were studied in a flow reactor at 373 K and 100 psi for application to upgrading of furfural. Specific rates for the reaction of acetone and furfural were measured on MgAl_2O_4 , Al_2O_3 , $\text{CaO/MgAl}_2\text{O}_4$ and $\text{MgO/MgAl}_2\text{O}_4$ and found to be highest on $\text{CaO/MgAl}_2\text{O}_4$. While the presence of CO_2 and H_2O did not affect the stability of the $\text{CaO/MgAl}_2\text{O}_4$ catalyst, the catalyst deactivated over a period of a few hours due to the production of 2-furoic acid formed by the Cannizzaro reaction. While aldol condensation rates between furfural and either 2-pentanone and decanal approached that of acetone, rates for 4-heptanone and 2,5-heptanedione were significantly lower because the α -hydrogens of the carbonyl compounds are less easily attacked in these molecules. The selectivity to aldol products is affected by the relative rates of the aldol-condensation and the Cannizzaro reactions. Possible strategies for maximizing production of the aldol products with larger ketones are discussed.

Key Words: Furfural; Acetone; Ketones; Aldol Condensation; Cannizzaro Reaction; Base Catalysts; Calcium Oxide; Lignocellulose

Introduction

Upgrading of biomass could be an important means for producing fuels and chemicals from renewable resources in the future [a-c]. For a number of these applications, furfural and 2-hydroxymethylfurfural (HMF), formed by dehydration of C-5 and C-6 sugars, provide attractive starting points for the synthesis of interesting compounds, including those used to make novel surfactants [1, 2] and lube oils [3]. Many of these products require increasing the number of carbons in a controlled manner. One way to do this is through aldol condensation reactions with ketones [4] that in turn could be synthesized by ketonization of organic acids derived from triglycerides. For example, Fakhfakh, et al. reacted acetone with furfural to obtain products with 8 and 13 carbon atoms [5]. In another example, furfural was reacted with 12-tricosanone to form products with 28 and 33 carbons [3], which, when hydrogenated, could be used to make lubricants. Although aldol condensations can be catalyzed by either acids or bases, base catalysis provides more control since acids tend to catalyze oligomerization of furans [6] and the products formed in the reaction [7–11]. Heterogeneous catalysts are preferred over homogeneous catalysts because they are more easily separated from the products and less likely to cause corrosion of process equipment.

Although there have been a significant number of studies involving solid bases [10, 12, 13], our understanding of these catalysts and our ability to characterize them is clearly less developed compared to that for solid acids. Solution-phase concepts, such as an effective pK_b , are almost certainly as inappropriate for describing solid bases as they are for describing solid acids [14, 15]. The comprehensive review by Ono and Hattori demonstrated that many oxides have basic character but some of these are more complex than others [12, 16]. For example, while ZrO_2 has been used as a base catalyst, it has also been used as an acid catalyst [17] and for dehydrogenation of alkanes [18] and amines [19]. By comparison, Mg and Ca are not transition metals, suggesting that their oxides should be much simpler. Another issue with solid bases is that they may have low surface areas when used in bulk form. For these and other reasons, homogeneous bases, such as solution-phase NaOH, remain the primary catalysts for most aldol-condensation applications.

Most aldol condensation studies employing solid bases have focused on the reaction of small ketones, primarily acetone [20–23] or cyclopentanone [24–28]; but applications, including the production of larger molecules that could be used to make lube oils [3], may require the use of larger ketones. It is not clear how well results from acetone relate to the larger ketones. Also, few

studies have been carried out in flow reactors which allow determination of catalyst stability and of catalyst deactivation mechanisms. Therefore, in the present study, we set out to examine aldol condensation reactions of furfural with a range of carbonyl-containing reactants in a flow reactor. For simplicity, we have focused on CaO and MgO as catalysts, supported on MgAl₂O₄ to maintain a high surface area. To ensure that the MgAl₂O₄ support was uniformly covered, the CaO and MgO were added to the support by Atomic Layer Deposition (ALD). The results demonstrate that the reactivity of ketones with furfural varies dramatically with the nature of the hydrogens in the α position to the carbonyl. Catalysts were found to deactivate with time, primarily due to the presence of organic acids that form by disproportionation of furfural in the Cannizzaro reaction.

2. Experimental Section

A list of the catalysts used in this study, together with some of their properties, is shown in Table 1. The MgAl₂O₄ (Sasol, Puralox MG 26/100) was used directly without further treatment, while the Al₂O₃ (γ -Al₂O₃, Strem Chemicals, Newburyport, MA, USA) was stabilized by calcination in air at 1173 K for 24 h prior to use. For each sample, the MgO or CaO loadings were targeted to give an average film thickness of 0.3 nm, assuming that the films were uniform and had the same density as the bulk oxides.

Table 1. Samples used in this study.

Samples	BET S.A. (m ² /g)	Metal Oxide Loading (wt %)
MgAl ₂ O ₄	96	n.a.
CaO/MgAl ₂ O ₄	64	9.3 wt%
MgO/MgAl ₂ O ₄	78	9.8 wt%
imp-CaO/MgAl ₂ O ₄	68	9.3 wt%
Al ₂ O ₃	120	n.a.

n.a.: not applicable.

The CaO/MgAl₂O₄ and MgO/MgAl₂O₄ samples were prepared by ALD using equipment and procedures that have been described in detail elsewhere [29, 30]. Briefly, the evacuated, MgAl₂O₄ powder was first exposed to a few torr of one of the precursors, either Bis(2,2,6,6-

tetramethyl-3,5-heptanedionato)calcium (Ca(TMHD)₂, Strem Chemicals, Inc, USA) or Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)magnesium dihydrate (Mg(TMHD)₂, Strem Chemicals, Inc, USA), for 5 min at 553 K. After evacuation of the precursor, the sample was calcined in air at 873 K in a muffle furnace for 10 min to remove the ligands. This procedure was repeated until the desired loading was achieved. Growth rates were determined gravimetrically using the data shown in Figure S1 of the Supplemental Information. Following deposition of both Ca and Mg, the sample weights increased linearly with the number of ALD cycles. Assuming the density of the films is the same as that of the bulk materials, specific growth rates can be calculated from the MgAl₂O₄ surface area and the slope of the lines in Figure S1. For Ca, which forms CaCO₃ under these conditions, the growth rate was 6.6×10^{17} Ca/m²-cycle (0.041 nm CaCO₃/cycle, equivalent to 0.019 nm CaO/cycle); for Mg, which deposits as MgO, the growth rate was 9.6×10^{17} Mg/m²-cycle (0.018 nm MgO/cycle). These values are in good agreement with previous reports from the literature, 0.044 nm CaCO₃/cycle [31] and 0.022 nm MgO/cycle [32]. After the final ALD cycle, each sample (~0.4 g) was calcined in 10-mol% O₂ in He (total flow rate 100 mL/min) at 1073 K for 3 h to stabilize the structures.

For the imp-CaO/MgAl₂O₄ sample, 2.0 g of MgAl₂O₄ powder was added to an aqueous solution consisting of 0.865-g calcium nitrate tetrahydrate (99%, Sigma-Aldrich) in 2.5-g deionized water. After holding the sample for 2 h at room temperature, it was dried in an oven at 333 K for 12 h, then calcined in 10-mol% O₂ at 1073 K for 3 h to decompose the salt.

BET surface areas were obtained using N₂ adsorption at 78 K on a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument Corporation, U.S.A.). Temperature programmed desorption/thermogravimetric analysis (TPD/TGA) experiments were carried out on 20-mg samples placed in the sample pan of a CAHN 2000 microbalance that could be evacuated with a turbomolecular pump [33]. After exposing the sample to a few torr of the adsorbate of interest, followed by 1-h evacuation, the temperature of the samples was ramped at 10 K/min while monitoring the partial pressures using a quadrupole mass spectrometer (SRI RGA-100).

Aldol condensation reactions were performed using a continuous flow reactor made from a stainless-steel tube, 200-mm long and 4.6-mm inside diameter, inserted into a vertical tube furnace [34]. The catalyst samples were placed in the stainless-steel tube and held in place with quartz-wool swabs. Stainless-steel rods, 4-mm diameter, were inserted at the two ends of the reactor to decrease the dead volume. With this configuration, the volume between the catalyst bed

and the outlet from the back-pressure regulator was ~ 0.5 mL. The liquid feed was introduced to the reactor in upward flow, using an HPLC pump (Series I+, Scientific Systems Inc., USA). The pressure in the reactor was controlled by a back-pressure regulator (U-607/608/609, IDEX Health & Science LLC., USA) at the reactor exit. In a few cases where lower flow rates were required, experiments were performed at atmospheric pressure in an identical reactor with a syringe pump (KDS 100, KD Scientific Inc, USA) to introduce the liquid feed. The furfural concentration in feed was either 1.22 mol/L or 0.12 mol/L, and the ratio of ketones or aldehydes to furfural were in the range of 0.5 to 10.

Product analysis from the reactions was performed using a GC-MS (QP-5000, Shimadzu), calibrated with standard solutions of the products. Unless otherwise stated, conversions were measured within 30 minutes of catalyst regeneration. In most experiments, n-decane was added to the furfural (5-mol% relative to the furfural) as an internal standard. The carbon balances were usually better than 93%, although lower carbon balances were observed in the reactions of 4-heptanone and 3,5-heptanedione with furfural, for reasons that will be discussed. At the beginning of each experiment, catalysts were pretreated in 30 mL/min helium (He, 99.999%, Airgas, Inc., USA) at 873 K for 30 min to remove adsorbed water and CO₂ and then cooled to room temperature.

Unless otherwise stated, all reagents were purchased and used without further purification, including furfural (99%, Sigma-Aldrich), acetone (99.8%, Fisher Chemical), 2-pentanone (98%, Sigma-Aldrich), 4-heptanone (98%, Alfa Aesar), 3,5-heptanedione (97%, TCI America), decanal (98%, Sigma-Aldrich), n-decane (99+%, Alfa Aesar), toluene (99.9%, Fisher Chemical), methanol (99.9%, Fisher Chemical), ethanol (99.9%, Decon Labs, Inc.), and benzene (99.8%, Sigma-Aldrich).

3. Results

3.1 Sample Characterization

XRD patterns of the CaO/MgAl₂O₄, imp-CaO/MgAl₂O₄, and MgO/MgAl₂O₄ samples are shown in Figure 1. In addition to the diffraction peaks for MgAl₂O₄, as-prepared CaO/MgAl₂O₄ exhibited peaks associated with CaCO₃. After calcination in O₂-He mixtures at 1073 K, the CaCO₃ peaks were replaced by those for CaO. The diffraction pattern for MgO/MgAl₂O₄ showed small peaks for MgO in the as-prepared sample and there were no observable changes after calcination, consistent with the lower stability of MgCO₃ relative to CaCO₃. Figure 1 also showed that the

diffraction pattern for imp-CaO/MgAl₂O₄ after calcination to 1073 K is essentially identical to that of the ALD-prepared sample. In previous work comparing supported oxides prepared by ALD or infiltration [35], the XRD peak intensities for the supported phase were much less for ALD-prepared materials. The explanation for this was that the thicknesses of films formed by ALD were less than the coherence length of the x-rays, while the characteristic size of the three-dimensional particles formed by infiltration were not. The fact that the XRD patterns for the CaO-based catalysts were so similar suggests that the morphology of films may also be similar.

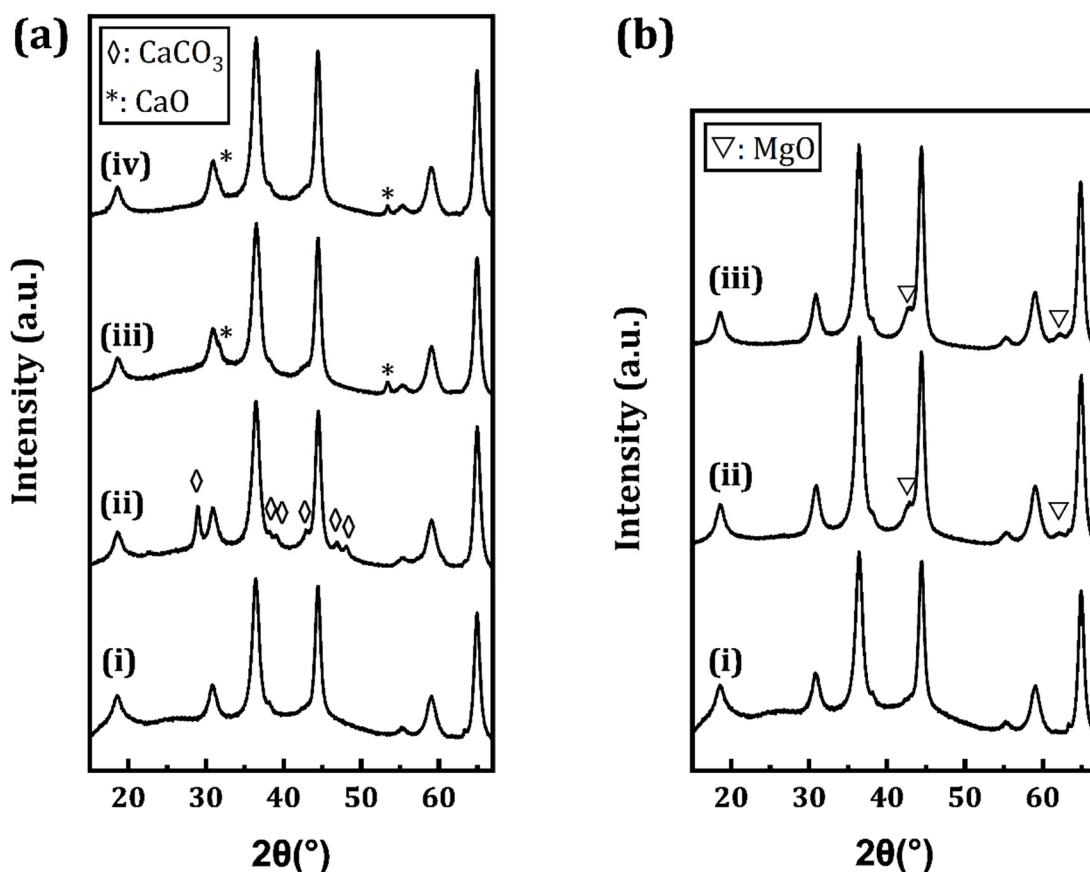


Figure 1. XRD patterns of (a) CaO on MgAl₂O₄ and (b) MgO/MgAl₂O₄. (a): (i) unmodified MgAl₂O₄; (ii) as-prepared CaO/MgAl₂O₄ before 1073 K calcination; (iii) CaO/MgAl₂O₄; (iv) imp - CaO/MgAl₂O₄. (b): (i) unmodified MgAl₂O₄; (ii) as-prepared MgO/MgAl₂O₄ before 1073 K calcination; (iii) MgO/MgAl₂O₄.

The TPD-TGA data for 2-propanol, reported in Figure 2, provide evidence that the alkaline-earth oxides exist as uniform films on the MgAl₂O₄ support. The data obtained on MgAl₂O₄, Figure 2a), shows that the 2-propanol coverage after room-temperature exposure and 1-h evacuation was approximately 580 $\mu\text{mol/g}$, or 3.6×10^{18} molecules/m². This is close to the value

expected for a close-packed monolayer, implying that the entire surface was probed by the 2-propanol. Upon ramping the temperature, some 2-propanol ($m/e = 41, 43,$ and 45) left the surface unreacted below 450 K; however, approximately half of the adsorbed species desorbed as propene ($m/e = 41$) and water (not shown) in a sharp feature at around 500 K, suggesting the MgAl_2O_4 has acidic character.

The analogous TPD-TGA results for 2-propanol on the supported MgO and CaO catalysts were quite different. The initial coverage on the $\text{MgO}/\text{MgAl}_2\text{O}_4$, $500 \mu\text{mol/g}$ in Figure 2b), was lower due to the lower specific surface area; and about half of the alcohol again left the sample unreacted below 450 K. However, the remaining adsorbed alcohol desorbed as a mixture of propene and acetone ($m/e = 43$) at about 580 K. The sharp propene feature at 500 K that was observed on MgAl_2O_4 is completely absent, implying that the substrate was effectively covered by the MgO film. The presence of acetone in the desorption products is clear evidence of the basic properties of the MgO . TPD-TGA results for the $\text{CaO}/\text{MgAl}_2\text{O}_4$ and $\text{imp-CaO}/\text{MgAl}_2\text{O}_4$ samples, Figures 2c) and d), were different from that of MgAl_2O_4 in that the propene and acetone peaks were shifted to slightly higher temperatures, ~ 620 K. The propene:acetone ratio was also slightly higher based on the ratio of peaks at $m/e = 41$ and 43 on the Ca-containing samples. The fact that the MgAl_2O_4 surface was covered so effectively by each of the alkaline earths, whether added by ALD or impregnation, implies that there must be favorable interactions between these oxides and the support which cause the oxides to form a film rather than three-dimensional particles. If large, three-dimensional particles had formed, there would have been insufficient amounts of the alkaline earths to completely cover the support.

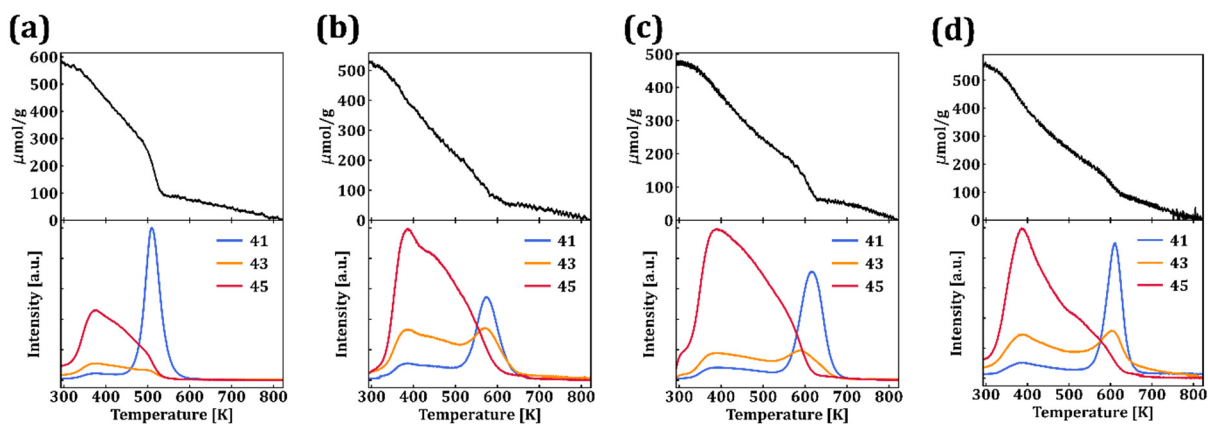
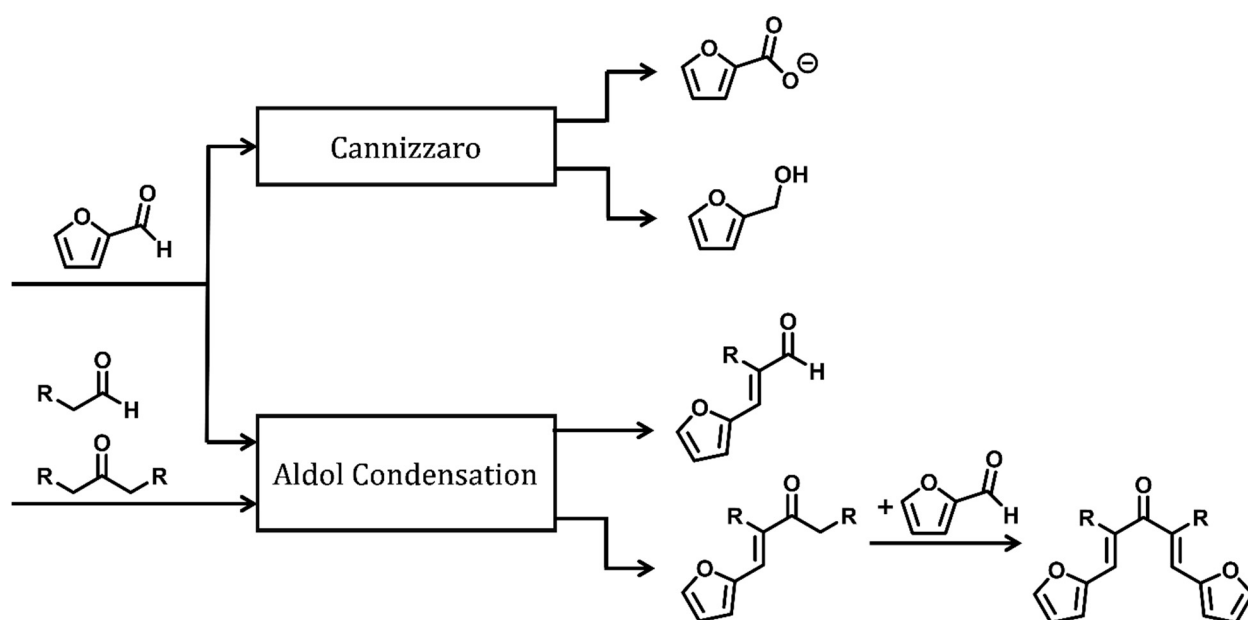


Figure 2. TPD-TGA of 2-propanol on (a) MgAl_2O_4 , (b) $\text{MgO}/\text{MgAl}_2\text{O}_4$, (c) $\text{CaO}/\text{MgAl}_2\text{O}_4$, (d) $\text{imp-CaO}/\text{MgAl}_2\text{O}_4$. The TPD peaks correspond to propene ($m/e = 41$), acetone ($m/e = 43$), and unreacted 2-propanol ($m/e = 41, 43, \text{ and } 45$).

3.2 Catalytic Performance

The reactions of interest for this study are shown in Scheme 1. Because the product of the initial aldol condensation reaction is a ketone, a second furfural molecule can react with that ketone to form a larger product. The other reaction observed in this study is the Cannizzaro reaction of two furfural molecules to form an alcohol and a carboxylic acid. This undesirable side reaction appears to be a major reason for catalyst deactivation in this process, as will be discussed later.

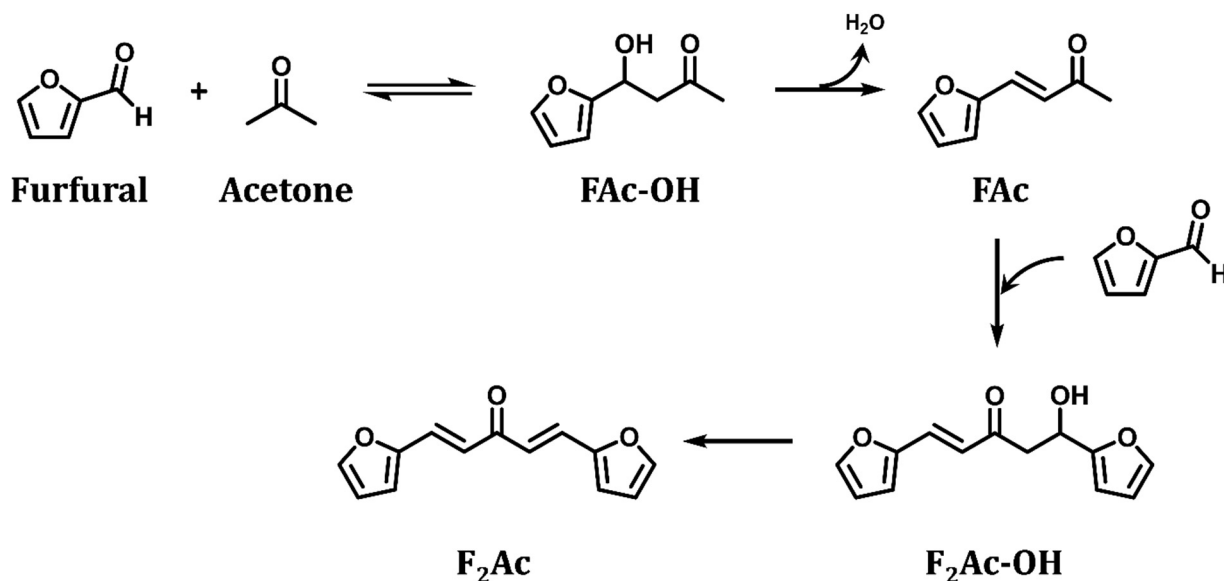


Scheme 1. Mechanism of aldol condensation of furfural with carbonyl compounds over $\text{CaO}/\text{MgAl}_2\text{O}_4$.

3.2.1 Reactions of Acetone and Furfural

The reaction of furfural and acetone, shown in Scheme 2, served as a more detailed illustration of aldol condensations for these reactants. Furfural and acetone first form the 8-C product, 4-(furan-2-yl)-4-hydroxybutan-2-one (FAC-OH), which rapidly dehydrates into 4-(2-furyl)-3-buten-2-one (FAC). FAC can then react with another furfural molecule and form the 13-C product, 1,5-di(furan-2-yl)-5-hydroxypent-1-en-3-one (F₂Ac-OH), which subsequently

dehydrates into 1,4-pentadien-3-one, 1,5-di-2-furanyl (F₂Ac). F₂Ac-OH was not observed in our study, indicating that the dehydration step is fast in this case.



Scheme 2. Mechanism of aldol condensation of furfural with acetone. FAc-OH: 4-(furan-2-yl)-4-hydroxybutan-2-one. FAc: 4-(2-Furyl)-3-buten-2-one. F₂Ac-OH: 1,5-di(furan-2-yl)-5-hydroxypent-1-en-3-one. F₂Ac: 1,4-pentadien-3-one, 1,5-di-2-furanyl.

Furfural conversion rates for the reaction of acetone and furfural at 373 K are shown for each of the catalysts in Figure 3. In these experiments, the acetone:furfural mole ratio was 10 and the pressure was 100 psi in order to ensure the reaction occurred in the liquid phase. The amounts of catalyst and feed flow rates were tuned to keep the furfural conversion below 20% and conversions were measured within 30 minutes of introducing the feed so as to avoid the effects of deactivation. Under these conditions, the product selectivities were found to be similar for each of the catalysts, with the concentrations of 8-C products being higher than that of the 13-C product by at least a factor of 6. The two CaO-based catalysts showed the highest rates, with the ALD-prepared sample, CaO/MgAl₂O₄, showing slightly higher rates compared to the sample prepared by impregnation, imp-CaO/MgAl₂O₄. Somewhat lower rates were found on MgO/MgAl₂O₄, followed by much lower rates on MgAl₂O₄ and Al₂O₃.

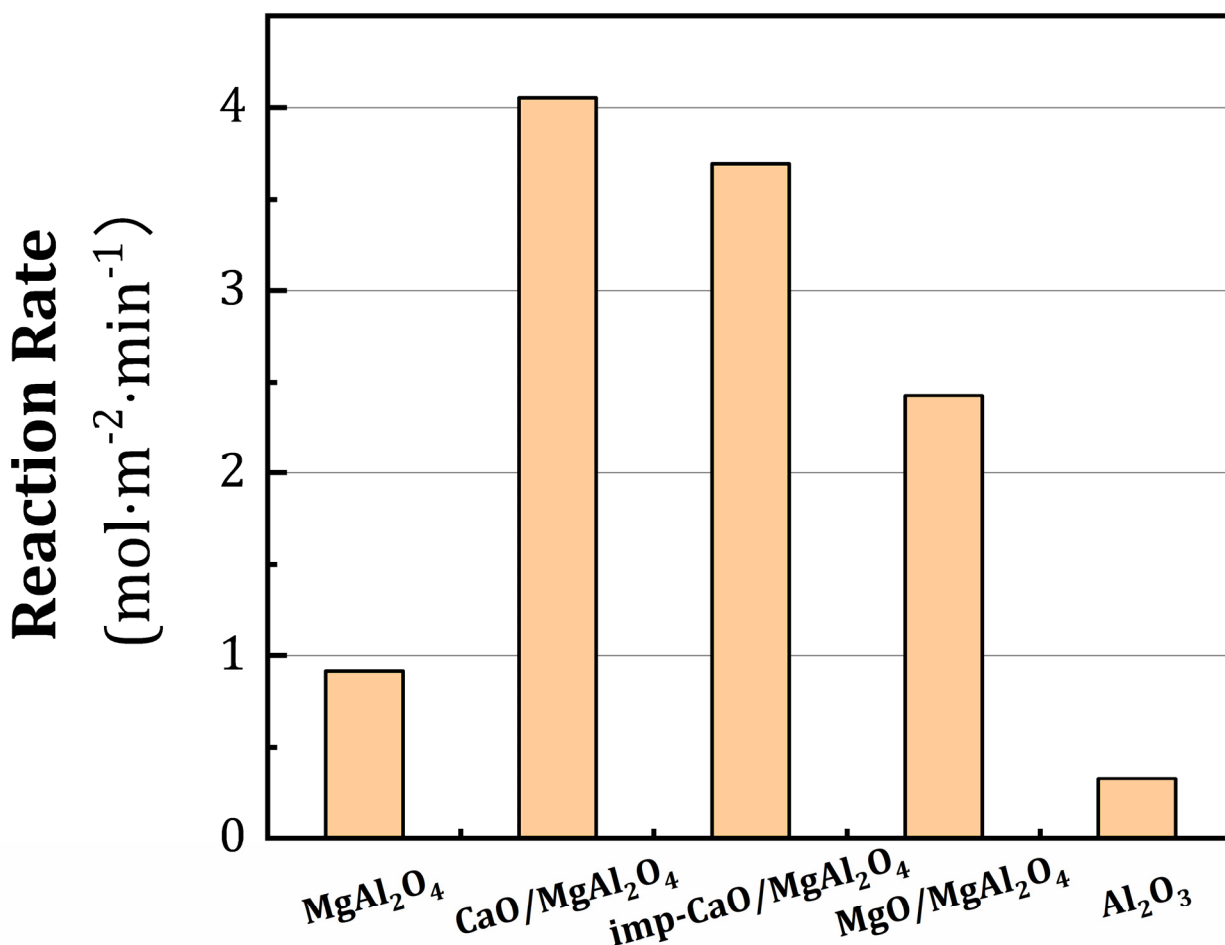


Figure 3. Aldol reaction rates of furfural with acetone on various supports based on the catalysts surface area. Reaction rate is expressed in the consumption of furfural. Conditions: 373 K, 100 psi, 1.22 mol/L furfural in acetone, acetone: furfural mol % = 10:1. The amounts of catalysts and the liquid flow rate were tuned to ensure a conversion < 20%.

During these studies, the rates on each the catalysts were found to decrease by about 10% per hour. The mechanism for deactivation appears to be poisoning of the catalysts by formation of 2-furoic acid by the Cannizzaro reaction. The evidence for this is as follows. First, ~0.2 % furfuryl alcohol, the other product formed in the Cannizzaro reaction, was observed in the product stream at high furfural conversions. Second, while intentional exposure of the CaO/MgAl₂O₄ catalyst to CO₂ or water in the feed had no effect on the rate of deactivation, adding 5% acetic acid to the furfural dramatically increased the rate of deactivation, as shown in Figure S2. The catalyst effectively acted as a trap, adsorbing the acid from the feed stream. Purification of the furfural, in the absence of added acetic acid, by passing it over a bed of CaO at room temperature prior to

feeding it to the reactor had no effect on the deactivation rate, implying that impurities in the feed were not to blame. Third, the deactivated catalyst could be regenerated by simply heating it to 873 K in flowing He, whereas humin formation with polyaromatics would be expected to require oxidation for regeneration. Reaction and 2-propanol TPD results for the catalyst following several regeneration cycles are shown in [Figure S???](#) The importance of the Cannizzaro reaction in deactivation of base catalysts has been reported previously [ref].

Additional evidence that poisoning of the catalyst is due to exposure to an organic acid is shown by the TPD results on the $\text{CaO/MgAl}_2\text{O}_4$ sample in Figure 4. The data in Figure 4a) was obtained following room-temperature exposure to acetic acid. Following evacuation, no unreacted acetic acid was observed leaving the surface. The peaks at 630 K correspond to acetone ($m/e = 43$, 58) and CO_2 ($m/e = 44$), formed by the ketonization reaction. TPD data obtained on the sample after deactivation during reaction of furfural with acetone, Figure 4b), show desorption in a similar temperature range. Although the desorption products were more complex, products containing furan rings ($m/e = 39$) and CO_2 ($m/e = 44$) could be identified.

Although we did not see evidence for humin formation with acetone and furfural at 373 K, there was evidence for the polymerization of the reactants at higher temperatures. In reaction experiments performed at 423 K and 100 psi on the $\text{CaO/MgAl}_2\text{O}_4$ catalyst, the back-pressure regulator became blocked within a few hours of operation. This implies that high-molecular-weight products were formed at these higher temperatures. Therefore, all subsequent rate measurements were performed at 373 K.

Because there are reports that higher pressures can affect the rates and catalyst stabilities [34, 36, 37], the effect of varying the pressure between 100 and 500 psi was investigated with the $\text{CaO/MgAl}_2\text{O}_4$ catalyst at 373 K, with results reported in Figure S3. Figure S3(a) shows that the conversions and selectivities were unaffected by pressure; the catalyst deactivation rates also did not change with pressure, as indicated by Figure S3(b).

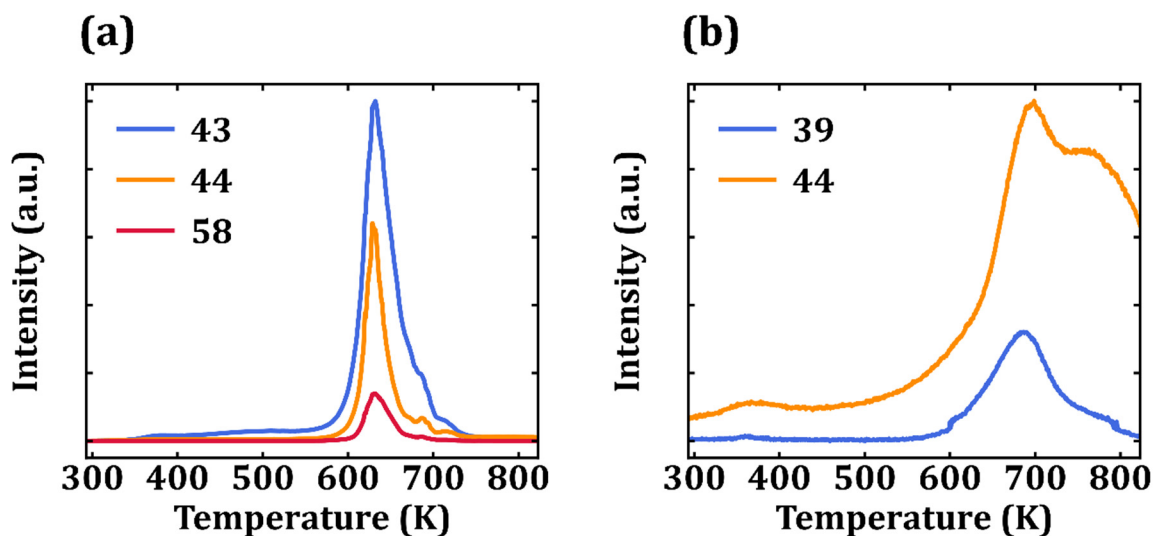


Figure 4. TPD of (a) acetic acid on fresh $\text{CaO/MgAl}_2\text{O}_4$, (b) used $\text{CaO/MgAl}_2\text{O}_4$. The TPD peaks correspond to acetone ($m/e = 43, 58$), CO_2 ($m/e = 44$), and furan ring fragment ($m/e = 39$).

Reactions with ketones significantly larger than acetone require the use of a solvent; therefore, the reaction of acetone and furfural was investigated in a range of solvents. Table 3 reports the rates of furfural conversion together with the products formed when the reactions were carried out with a fixed residence time on the $\text{CaO/MgAl}_2\text{O}_4$ catalyst at 373 K and 100 psi. The higher conversion when acetone was used as both the solvent and the reactant is simply due to the higher concentration of this reactant. The higher furfural conversion with methanol is due to the parallel reaction of furfural with methanol to form 2-furaldehyde dimethyl acetal. The acetalization of ethanol and furfural was also observed. While acetalization complicates the overall process, it did not prevent the formation of the aldol products. More importantly for this study, the conversions and selectivities to the 8-C (F_{Ac}-OH and F_{Ac}) and 13-C (F₂Ac) products were similar for the solvents that are non-reactive, benzene and toluene. Since the larger ketones are readily soluble in toluene, toluene was used in all studies with larger ketones, unless otherwise stated.

Table 3. The conversions and selectivities of furfural to aldol products (FAc-OH, FAc, and F₂Ac) and side products (acetals). Reaction conditions: 0.1 g CaO/MgAl₂O₄, 373 K, 100 psi, 0.5 mL/min solution (1.22 mol/L furfural), acetone: furfural mol % = 10:1 (acetone as solvent) or 1: 2. Data obtained at 0.5 h on stream.

Solvent	Conversions of Furfural (%)	Selectivity of Furfural (%)			
		FAc-OH	FAc	F ₂ Ac	Acetals
Methanol	37	5	16	53	27
Ethanol	19	12	23	33	32
Benzene	19	13	25	62	0
Toluene	20	6	37	57	0
Acetone	74	11	82	7	0

Finally, to better understand the reaction sequence in Scheme 2, the conversions and product distributions for the reaction of acetone and furfural (mole ratio of 2:1) in toluene over CaO/MgAl₂O₄ were measured as a function of reactor space time, with results shown in Figure 5. (In this plot, the 8-C products have been combined.) Both the acetone and furfural concentrations decreased continuously with contact time, as expected. While the concentration of 8-C products goes through a maximum at intermediate space times, the rapid rise in the concentration of F₂Ac indicates that FAc is more reactive than furfural, making F₂Ac the preferred product, even at moderate conversions.

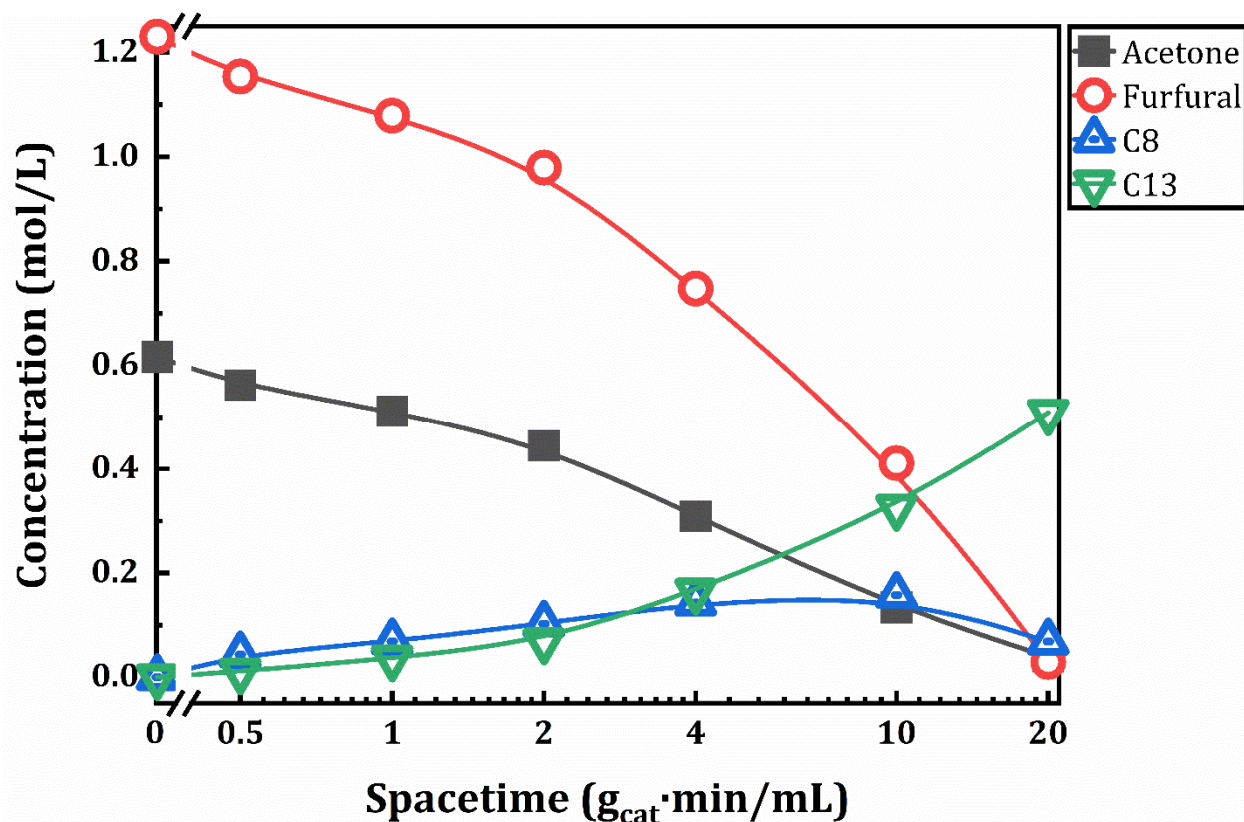


Figure 5. Concentrations of reactants (acetone and furfural) and products (C8, C13). Reaction conditions: 373 K, 100 psi, 0.5 mL/min solution (1.22 mol/L furfural in toluene), acetone: furfural mol % = 1: 2. Data obtained at 0.5 h on stream.

3.2.2 Reactions of Furfural with other Ketones and Aldehydes

For synthesis of compounds to be used in lube-oil applications, it is necessary to examine larger ketones and aldehydes. Reactions were again carried out at 373 K and 100 psi over the CaO/MgAl₂O₄ catalyst, using toluene as the solvent. The results are summarized for several representative molecules in Table 4. These data show that the furfural conversion rates measured under conditions of differential conversion varied dramatically with the position of the carbonyl group. Rates with 4-heptanone, which has n-propyl groups on each side of the carbonyl carbon, were at least 20 times lower than those for acetone, which has methyl groups on each side. This understates the difference between 4-heptanone and acetone, since 85% of the furfural that reacted in the presence of 4-heptanone formed furfuryl alcohol through the Cannizzaro reaction, rather than the desired aldol product. We were able to increase production of the aldol products with 4-heptanone by increasing the concentration of the ketone, as shown in Figure S4a). As demonstrated

by Figure S4b), the reaction is approximately first-order in the ketone concentration [38]. Interestingly, rates with 2-pentanone, which has an n-propyl group on one side of the carbonyl and a methyl group on the other, were also approximately half that of acetone. Finally, the low rates with 4-heptanone are not simply due to the size of the molecule, since rates for decanal approached those for acetone.

It appears that rates for the Cannizzaro reaction are unchanged by the nature of the ketone, becoming dominant when the aldol condensation rates are low. Based on the data in Table 4, the fraction of furfural that formed furfuryl alcohol roughly followed the decrease in the reactivity of the ketone or aldehyde. This is also observed in the reaction of n-heptanone. In that case, the rate of catalyst deactivation, shown in Table S1, decreased with increasing concentration of 4-heptanone. Because the Cannizzaro reaction is responsible for deactivation of the catalyst, this parallel reaction sets a limit on what aldol reactions can be performed. It is not possible to simply increase the residence time of the reaction to increase rates for aldol reactions with furfural, because it will simply be consumed by the other reaction path.

Table 4. The consumption rate of furfural and the product selectivities on CaO/MgAl₂O₄. Conditions: 373 K, 1 bar, 1.22 mol/L furfural in toluene, ketones: furfural mol% = 1: 2, aldehydes: furfural mol% = 1: 1. The reactions were conducted in differential conditions with conversions < 20%.

Linking Molecules	Furfural Consumption Rate	Selectivity of Furfural (%)	
	mmol/(h·g _{cat})	Aldol Products	Furfuryl Alcohol
Acetone	7.1	97	3
2-Pentanone	2.2	89	11
Decanal	3.8	98	2
4-Heptanone	0.31	15	85
2,5-Heptanedione	0.34	30	70

The reason for the lower rates with the larger ketones is not due to the thermodynamic stability of the enol forms but rather to the fact that the α -hydrogens of the carbonyl compounds

are more easily attacked when the carbonyl group is near the ends of the hydrocarbon chain. This is demonstrated by the data in Table 5, which compares the relative thermodynamic stabilities of the enols to the relative aldol condensation rates on CaO/MgAl₂O₄ and in NaOH-methanol solutions. The enol form of acetone has the lowest thermodynamic stability among the carbonyl compounds we tested, even though its reaction rate was the highest. 4-Heptanone and 2,5-heptandione have more stable enol forms than acetone, but their rates on CaO/MgAl₂O₄ were at least 20 times slower than acetone. Comparing decanal with the long-chain ketone or diketone, decanal exhibited much higher aldol condensation rates.

Table 5. Comparison of different carbonyl compounds in terms of thermodynamic stability of enol form, aldol condensation rate of heterogenous catalysts CaO/MgAl₂O₄ and of homogenous catalysts NaOH/methanol.

Enolization Reactions	Thermodynamic Stability ¹	Heterogenous Rate ²	Homogenous Rate ³
			n.m. ⁴

¹ Data obtained from computation and listed in more details in Table S2. [38]

² Obtained from Table 4.

³ See Table S3 for the numerical values.

⁴ Not measured.

Discussion

Aldol condensation reactions are potentially attractive for increasing the molecular weight of biomass-derived molecules in a controlled manner. While the reaction has been demonstrated with smaller ketones on both homogeneous and heterogeneous base catalysts, there has been relatively little work with larger ketones that would be needed to produce lube oils and some other high-molecular-weight products. The lower reactivity of larger ketones for aldol condensation reactions is well known but low reaction rates can be compensated for by longer reaction times.

What the present work demonstrates is that conversion of the furfural to 2-furoic acid and furfuryl alcohol, along with the poisoning by the parallel Cannizzaro reaction limits what one can achieve by increasing the residence time. This is likely a problem for both homogeneous and heterogeneous catalysts.

In this study the use of a flow reactor was key for identifying the importance of the Cannizzaro reaction and the subsequent deactivation of the catalyst by 2-furoic acid. While laboratory studies of liquid-phase reactions are typically carried out in batch reactors, it is difficult to measure rates under differential conditions in a batch reactor. Monitoring changes in the catalyst activity is also difficult in a batch reactor.

It is important to ask how one can maximize the production of aldol products with furfural. Based on our observation that increasing the ketone:furfural ratio increases the fraction of the furfural that goes toward the aldol product, the furfural reaction order for the Cannizzaro reaction must be higher than its reaction order for the aldol-condensation reaction. While there are limits to how high the ketone concentration can be, it may be possible to keep the furfural concentration low. For example, this could be accomplished in a semi-batch reactor by slowly feeding furfural to the ketone or in a flow reactor with recycle.

Under the reaction conditions of the present study, the $\text{CaO/MgAl}_2\text{O}_4$ catalyst appears to be very stable. The deactivation that occurs by adsorption of the acid is easily reversed by heating in an inert environment. The presence of water and CO_2 do not appear to affect the activity. High surface areas can be achieved through the use of a support.

For reasons discussed in the Introduction, the work reported here focused on alkali-oxide catalysts but other solid bases are able to carry out aldol condensation reactions. While both the aldol-condensation and the Cannizzaro reactions are base-catalyzed, it is possible that the relative rates of these two reactions could be different for different bases or that other bases would be less susceptible to poisoning by the acid. Changing the ratio of rates for those two reactions should be a major goal for producing useful chemicals from furfural.

Conclusion

In this work, we have demonstrated that supported, CaO films can be active for the base-catalyzed reactions of furfural and ketones. The specific rates for the aldol reactions are highest for smaller ketones and aldehydes which have α -hydrogens next to the carbonyl compounds that

are more easily attacked. The selectivity to the desired aldol products is largely controlled by the ratio of rates for the aldol-condensation and Cannizzaro reactions and catalyst poisoning is due to production of 2-furoic acid in the Cannizzaro reaction.

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Conflict of interest

The authors declare no conflict of interest

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