CATALYTIC DEOXYGENATION OF BENZALDEHYDE OVER SUPPORTED GALLIUM CATALYSTS

Artit Ausavasukhi[a], *Daniel E. Resasco*[b], *and Tawan Sooknoi*[a]
[a] *King Mongkut's Institute of Technology Ladkrabang, BKK, Thailand.*
[b] *University of Oklahoma, Norman, OK, USA.*

Abstract

The deoxygenation of benzaldehyde was investigated over supported Ga catalysts as part of a program leading to the study of model reactions involving aldehydes, acids, furfurals, and oxygenated aromatics that may be present in pyrolysis oil (bio-oil). Ga/SiO_2 catalysts were prepared by impregnating precipitated SiO_2 supports with $Ga(NO_3)_3$ solution. The reaction conditions, H_2 concentration, Ga content, and Ga dispersion in the catalysts were varied to investigate the effect of these parameters on activity, selectivity, and stability. TPR gave evidence for a partial reduction of Ga/SiO_2 in the range 500-750 ^oC. Increasing H_2 concentration (3-100%v/v) was found to enhance activity (~50-90%) and toluene selectivity (40-75%). Reaction at low temperature (< 500 ^oC) leads to the formation of high molecular weight oxygenates and consequently rapid catalyst deactivation (< 2 h). In contrast, no benzaldehyde conversion can be observed over a physical mixture of Ga_2O_3 and SiO_2.

Introduction

Bio-oils derived from biomass have been increasingly attractive as alternative sources of fuels and chemicals. This is due to an increase in petroleum prices, government regulations on alternative energy, and commitments to greenhouse gas reduction. However, the bio-oils contains various types of oxygenates that can cause problems when used as fuels. Among these, aldehyde and carboxylic are the most unwanted components. Deoxygenation of bio-oils does not only improve it fuel properties, but also provide alternative sources of petrochemicals.

This research deals with the conversion of benzaldehyde, a model compounds representing aromatic aldehydes in bio-oil, to oxygen-free compounds. It was found that nickel [1], platinum [2], palladium [3], and copper [4] based catalysts are readily active for hydrogenation of the carbonyl compound. In addition to noble metal, Ga based catalyst is proposed for the deoxygenation of benzaldehyde to produce oxygen-free aromatics. The study on catalytic performance of Ga support SiO_2 involves effect of reaction conditions, H_2 concentration, Ga content, and Ga dispersion in the catalysts.

Experimental Details

Catalyst preparation

Spherical porous SiO_2 support was prepared by precipitation of sodium silicate solution with sodium hydroxide [5-6]. Ga supported SiO_2 (1-6 wt%) was prepared by impregnation of the SiO_2 support with $Ga(NO_3)_3$ (%loading-Ga/SiO_2), and physical mixed of the support with bulk Ga_2O_3 (*b*-

Ga/SiO_2). All the samples were then activated in air at 550 °C for 4 hours. The specific surface area measurements were performed on an Autosorb-1 using N_2 as a probe molecule using BET method

Temperature-programmed reduction

Temperature-programmed reduction (TPR) experiments were carried out using a TCD detector. The sample was treated at 550 °C for 1 hour in air and then cooled to room temperature under He flow. The flow was then switched to 10% H_2/Ar (30 ml/min) and the sample was heated up to 900 °C at a rate of 10 °C/min.

Catalytic testing

Catalytic testing of benzaldehyde conversion was performed with a continuous fixed bed reactor. Saturated vapor of benzaldehyde at 20 °C was carried by H_2 (or H_2/He mixture) at 30 mL/minute regulated by a mass flow controller. The catalyst bed was set in a quartz tube reactor (ID 6 mm) that was located inside a temperature-regulated furnace. The products were periodically collected and analyzed by online gas chromatography (GC). The preferred reaction conditions used in the experiments were as follows: temperature, 450-550 °C; total pressure, 1 atm; carrier gas, He/H_2; W/F, 100-375 g·h/mol.

Results and discussion

Catalyst characterization

The specific surface area of supported Ga catalysts both $3Ga/SiO_2$ (325 m^2/g) and *b*-$3Ga/SiO_2$ (355 m^2/g) are slightly lower than that of the SiO_2 support (370 m^2/g). This may be derived from a surface reaction of the loaded Ga with the support. However, all samples still possess high surface area.

Catalytic activity

Benzaldehyde conversion

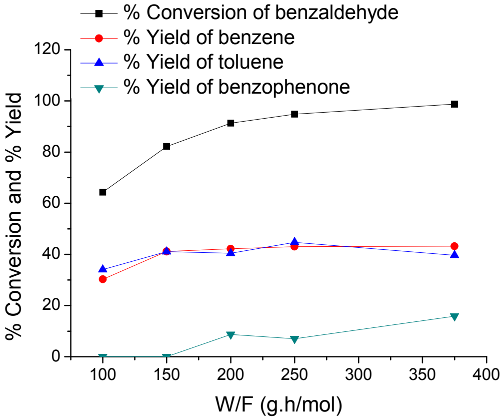


Fig. 1 Effect of W/F of benzaldehyde conversion over $3Ga/SiO_2$.

(W/F = 100-375 g.h/mol, reaction temperature 550 °C, 100 % H_2 concentration, total flow 30 mL/min, the data was shown at initial time on stream)

From Fig.1, it is found that benzaldehyde can be converted to benzene, toluene and benzophenone. Moreover, such products increase with W/F. It is expected that the formation of benzene and toluene are taken place from the parallel reaction, possibly derived from the coupled precursor, namely benzophenone.

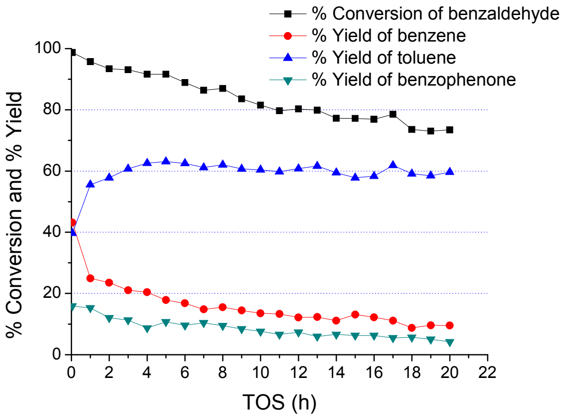


Fig. 2 Deactivation profile of benzaldehyde conversion over 3Ga/SiO_2 catalyst.

(W/F = 375 g.h/mol, reaction temperature 550 ^oC, 100 % H_2 concentration, total flow 30 mL/min)

From Fig. 2, change in product yield with time on stream can be observed along with the continual deactivation of the catalyst. This is the case for all W/F tests. Benzene and toluene are equally produced at the beginning of the reaction. Interestingly, the toluene product is initially increased with time on stream, while benzene and benzophenone are gradually reduced.

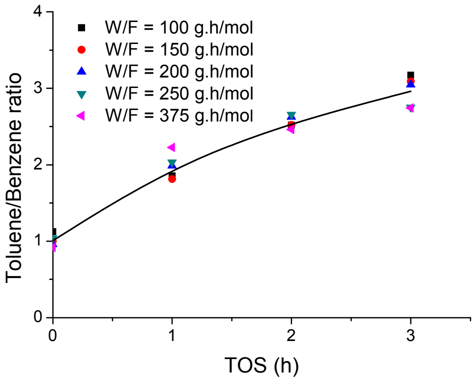
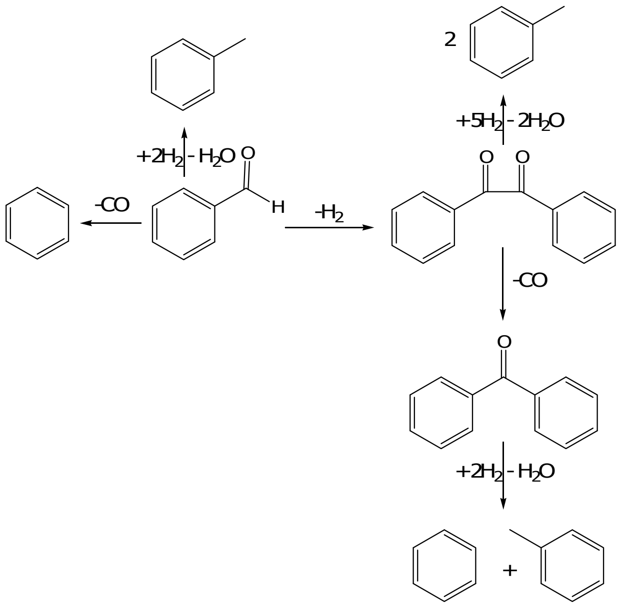


Fig. 3 Toluene/benzene ratio at different time on stream over 3Ga/SiO_2.

(W/F = 100-375 g.h/mol, reaction temperature 550 ^oC, 100 % H_2 concentration, total flow 30 mL/min)

For all W/F tests, the toluene/benzene ratio is initially unity and gradually increased with time on stream (Fig. 3). This is presumably explained that benzaldehyde can be readily coupled to form aromatic diketone [7]. This intermediate consecutively undergoes ring contraction liberating CO (from a carbonyl group) to form benzophenone. This benzophenone can be hydrogenolysed to form benzene and toluene as observed. At initial conversion, the decarbonylation activity of the diketone was active to generate benzophenone and readily cleave to form equal molar of benzene and toluene. However, as the catalyst is deactivated, aromatic diketone is accumulated on the surface. This diketone can be directly hydrogenolysed to toluene. This leads to the observed increase in toluene/benzene ratio with time on stream. The schematic diagram shows the formation of product proposed. (Scheme I)



Scheme I

Effect of Temperature

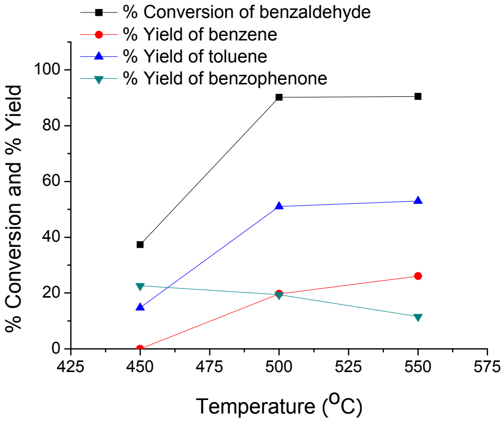


Fig. 4 The effect of reaction temperature on benzaldehyde conversion over 3Ga/SiO_2

(W/F = 250 g.h/mol, Reaction temperature 450-550 °C, 100 % H_2 concentration, Total flow 30 mL/min, the data was shown at 1 hour on stream)

From Fig.4, it is found that reaction at low temperature (450 °C) gives a low benzaldehyde conversion. A higher benzaldehyde conversion was rapidly increased, when the temperature was risen.

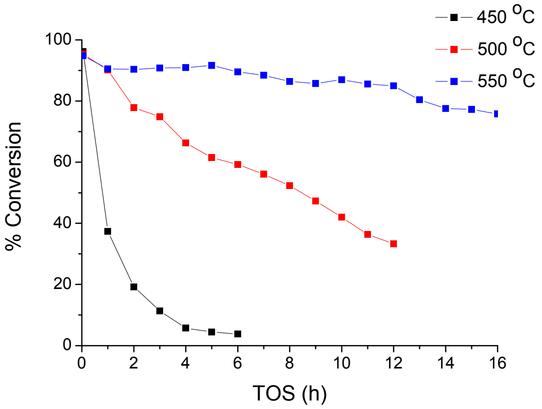


Fig. 5 Deactivation profile of benzaldehyde conversion with various reaction temperature over 3Ga/SiO_2.

(W/F = 250 g.h/mol, reaction temperature 450-550 °C, 100 % H_2 concentration, total flow 30 mL/min)

In addition, it was found that (Fig. 5), a rapidly deactivation can be obtained at low temperature (450 °C). It is consistent with the proposed reaction pathway that, at low temperature, the coupling can be promoted but the decarbonylation/hydrogenolysis activity are readily reduced. This leads to the formation of high molecular weight oxygenates and consequently a rapid catalyst deactivation (< 2 h). As the temperature was increased, such high molecular weight oxygenates can be decarbonylated/hydrogenolysed to lighter aromatic products (benzene and toluene). According, the catalyst stability can be improved.

Effect of H_2 concentration

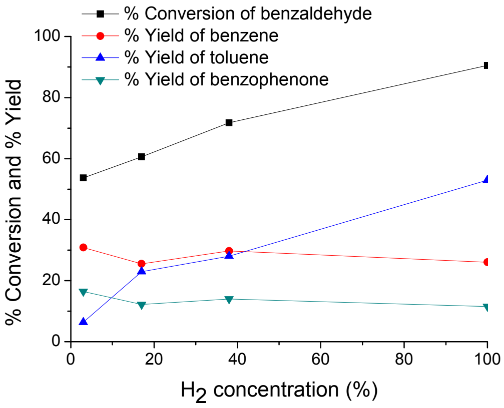


Fig. 6 The effect of H_2 concentration on benzaldehyde conversion over $3Ga/SiO_2$

(W/F = 250 g.h/mol, reaction temperature 550 °C, 3-100 % H_2 concentration, total flow 30 mL/min, the data was shown at 1 hour on stream)

From Fig. 6, the high benzaldehyde conversion was increased with H_2 concentration. This is evidenced that H_2 can play important role on hydrogenolysis of the diketone and also the benzophenone. As H_2 is increased, the high molecular weight oxygenates can be removed leaving more available sites for benzaldehyde activation. Moreover, it is interesting to note that at relatively low H_2 concentration (< 17 %), the selectivity of toluene/benzene ratio < 1. This is clearly explained that the hydrogenolysis activity was diminished due to the low H_2 concentration. Only decarbonylation can be promoted but in much lower extent, as compared to that in the presence of H_2.

Effect of Ga content

From Fig. 7, the conversion of benzaldehyde is increased with Ga content. It is worthy noting that the selectivity of benzene and toluene is similar for 1 and 3 wt% Ga loading. However, it is clearly seen that the toluene/benzene ratio is more than 1 in the case of 6 wt% Ga loading ($6Ga/SiO_2$). This is because the high Ga content can increasingly promote the hydrogenolysis activity leading to the high yield of toluene, as shown.

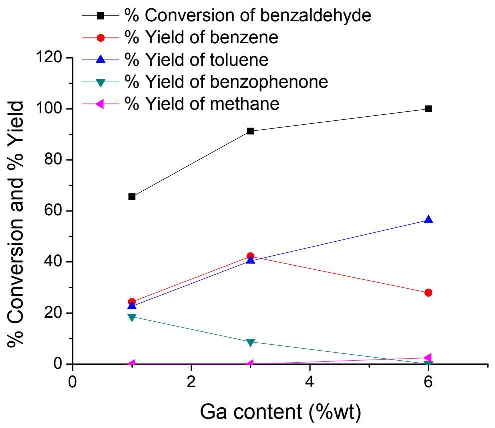


Fig. 7 Effect of Ga content of benzaldehyde conversion.

(Ga loading = 1-6 wt%, W/F = 200 g.h/mol, reaction temperature 550 ^oC*, 100 %* H_2 *concentration, total flow 30 mL/min, the data was shown at initial conversion)*

Effect of Ga cluster

From Table 1, it was found that there is no benzaldehyde conversion over *b*-3Ga/SiO_2. This is presumably because the bulk Ga_2O_3 cannot be readily reduced at reaction temperature. Consequently, the hydrogenation activity was diminished. This suggestion is consistent with the H_2-TPR (Fig. 8). It was found the *b*-3Ga/SiO_2 can be reduced at higher temperature (~730 ^oC), as compared to 3Ga/SiO_2 which prepared by $Ga(NO_3)_3$ impregnation (~630 ^oC).

Table 1. Effect of Ga cluster on benzaldehyde conversion over 3Ga/SiO_2.

Catalyst	**% of Ga content**	**% Conversion**	**% Yield***		
			Benzene	**Toluene**	**Benzophenone**
3Ga/SiO_2	3 wt%	91.31	42.18	40.45	8.68
b-Ga/SiO_2	3 wt%	no conversion	-	-	-
reduced-*b*-Ga/SiO_2	3 wt %	29.04	7.59	10.33	11.41

(W/F = 200 g.h/mol, Reaction temperature 550 ^oC*, 100 %* H_2 *concentration, Total flow 30 mL/min, Ga content = 3 wt%, the data was shown at initial time on stream)*

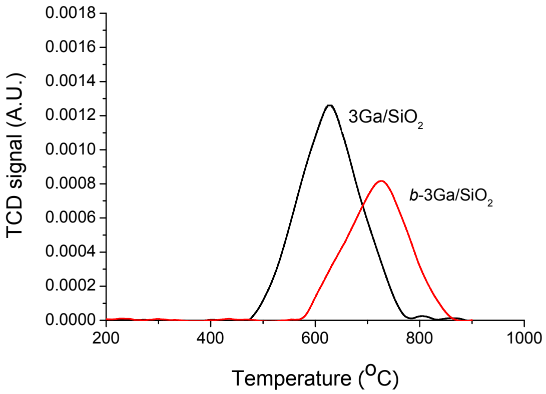


Fig. 8 TPR profile of the $3Ga/SiO_2$ and *b*-$3Ga/SiO_2$ catalyst

It was believed that the higher reduction temperature of *b*-$3Ga/SiO_2$ is due to the larger cluster size of Ga_2O_3 particle, as compared to the Ga species prepared by impregnation. The lower reduction temperature peak obtained from $3Ga/SiO_2$ indicates the well-dispersed Ga_2O_3 particles in this sample.

When *b*-$3Ga/SiO_2$ was then reduced at 700 °C for 2 hours under 100 % H_2, and then cooled to 550 °C under 100% H_2. The activity of this activated catalyst is dramatically increased (Table 1). It is suggested that cluster size of Ga species play role on hydrogenation/hydrogenolysis activity.

Conclusions

The benzaldehyde conversion over Ga supported silica at atmospheric pressure and 450-550 °C produced benzene, toluene, and benzophenone. Stability and selectivity of the products depends largely on the hydrogenolysis and decarbonylation activity of the catalyst. The deactivation of the decarbonylation activity leads to high toluene/benzene yield. While the hydrogenolysis activity can particularly enhance the toluene/benzene ratio. Inadequate H_2 concentration and temperature leads to a rapid catalyst deactivation due to the formation of high molecular weight oxygenates. Increase in Ga content result in a higher hydrogenolysis activity and stability.

Acknowledgements

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