Production of linear alkane *via* hydrogenative ring opening of a furfural-derived compound in supercritical carbon dioxide†

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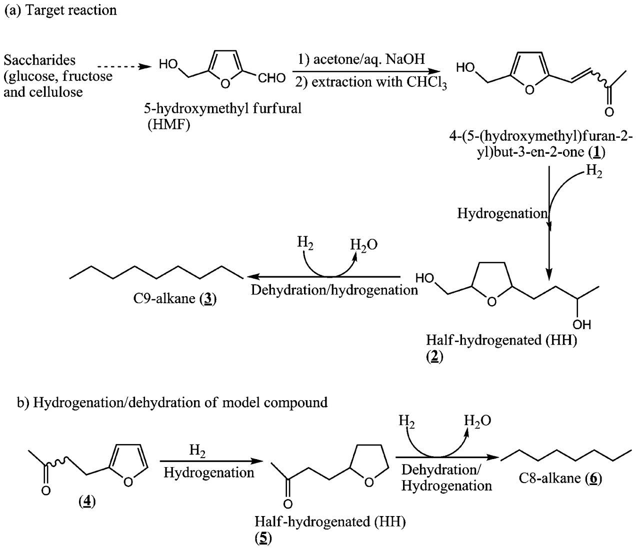
A simple method has been described to accomplish the formation of linear alkane with >99% selectivity in supercritical carbon dioxide under very mild conditions using Pd/Al-MCM-41 catalyst. The linear alakne was formed through the hydrogenation and dehydration/hydrogenation of 4-5-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one, which is an aldol condensation product of 5-hydroxymethyl furfural and acetone.

The need for more research into alternative energy sources has become obvious because of the increasing demand for energy and decreasing resources. Indeed, it is expected that energy demand would grow more (especially in the transportation sector) in coming years from several rapidly developing nations. At present, there is a renewed interest in the field of renewable energy to avoid the undesirable effects of pollution, which comes from burning of fossil fuels and from nuclear waste. Biomass is one of the suitable renewable energy sources, with development of new technologies for the generation of bio-energy. It would offer a great potential through the long-term storage of carbon and also is considered part of a closed carbon cycle. It can reduce the greenhouse gas emission in comparison with fossil fuel. Utilization of biomass has extreme importance for sustainable developments.[1,2]

Several methodologies has been described to obtain bio-oils by pyrolysis,[3,4] bio-diesel from vegetable oil,[5] polyols from cellulose,[6] biomass-derived sorbitol[7] and liquid hydrocarbon from the carbohydrates.[8] Among them, production of liquid fuel from the gasification of biomass is an important technology. However, those processes involve harsh reaction conditions, a tedious fermentation/distillation step, which requires high energy consumption, and catalytic instability due to a large amount of coke formation.

5-Hydroxymethylfurfural (HMF) is a valuable and versatile key intermediate formed during the thermal decomposition of saccharides (a component of biomass) like glucose, fructose and cellulose. Scheme 1a shows the probable reaction pathway of alkane formation *via* hydrogenation and dehydration/hydrogenation of compound **1** obtained by aldol condensation between HMF and acetone. Recently, Huber *et al.*[9] described the synthesis of liquid alkane (the major constituent of petroleum) from HMF. Their process consisted of (i) aldol condensation between HMF and acetone using Mg–Al oxide catalyst at room temperature, (ii) hydrogenation of the condensation product over Pd/Al_2O_3 catalyst at 120 °C and 5.5 MPa of H_2 in a batch reactor followed by (iii) ring opening *via* dehydration/hydrogenation (250–265 °C, 5.2–6.0 MPa, Pt/SiO_2–Al_2O_3 catalyst) using aqueous phase reforming process (APR). Depending on the nature of the aldol condensation product, a mixture of alkanes was formed.



Scheme 1 Possible reaction path of hydrogenation and dehydration/hydrogenation of HMF, an acetone aldol condensation compound in $scCO_2$.

In this work, we have attempted to build up a simple and convenient method of linear alkane formation from HMF in supercritical carbon dioxide ($scCO_2$). The motivation behind this work is to propose an advanced process of alkane synthesis from HMF in mild reaction conditions. Our method can be distinguished from the previous method in that a single linear alkane (Scheme 1a, **3**; Scheme 1b, **6**) was formed with high selectivity.

Supercritical carbon dioxide ($scCO_2$) is a well-established ecologically benign, energy conserving, waste reducing (economical) and highly efficient reaction medium for metal-catalyzed

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Table 1 Effects of the nature of catalyst on hydrogenation and dehydration/hydrogenation in $scCO_2$

Entry	Catalyst	Substrate[a]	Conv. (%)	Selectivity (%) HH (**5**)	Alkane (**6**)
1	Pd/Al-MCM-41	**4**	>99.0	0.0	>99.0
2	Pd/Al_2O_3	**4**	>99.0	37.5	62.5
3	Pd/SiO_2–Al_2O_3	**4**	>99.0	9.2	90.8
4	Pd/C	**4**	>99.0	100.0	0.0
5	Pd/Zeolite Y	**4**	68.2	0.0	>99.0
6	Pt/C	**4**	0.0	0.0	0.0
7	Rh/C[b]	**4**	>99.0	79.5	0.0
8	Pd/Al-MCM-41	**1**	>99.0	0.0 (**2**)	>99.0 (**3**)

Entries 2, 4, 6, and 7 are commercial catalysts from Aldrich; entries 3 and 5 are ion-exchanged Pd on commercial supports. Reaction conditions: Temp. = 80 °C, P_{CO_2} = 14 MPa, P_{H_2} = 4 MPa, time = 20 h. [a] Substrate = compound **4** from Scheme 1b and **1** from Scheme 1a. [b] ~20% unknown compound.

Table 2 Recycling of Pd/Al-MCM-41 catalyst

Run	Conv. (%)	Selectivity (%) HH (**5**)	alkane (**6**)
1	>99.0	0.0	>99.0
2	>99.0	0.0	>99.0
3	98.9	0.0	>99.0
4	96.5	0.0	>99.0

Substrate = compound **4** from Scheme 1b; reaction conditions: Temp. = 80 °C, P_{H_2} = 4 MPa, P_{CO_2} = 14 MPa and reaction time = 20 h.

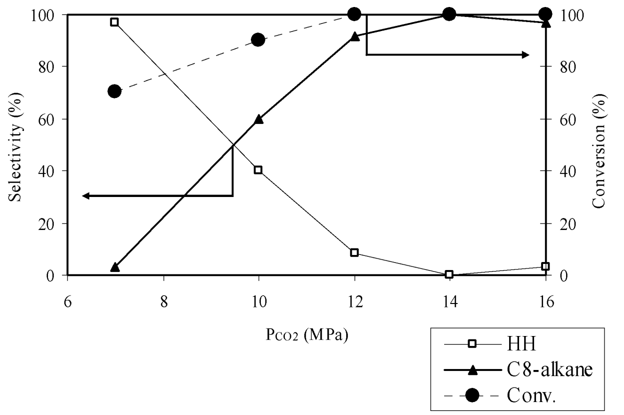

Fig. 1 Effect of CO_2 pressure on conversion and selectivity of alkane formation from compound **4** of Scheme 1b; reaction conditions: Temp. = 80 °C, time = 20 h, P_{H_2} = 4 MPa; HH = compound **5** and C8-alkane = compound **6** (Scheme 1b).

reactions.[10] It can dissolve a large amount of reactant gasses, which can allow kinetic control of reactions as opposed to limiting reaction rates by the transport of the gaseous reactant across the gas/liquid interface.

Initially, we have optimized the reaction conditions for the ring opening with a model compound (Scheme 1b; **4**; 95%; predominantly *cis*; Aldrich) *via* hydrogenation and dehydration/hydrogenation in $scCO_2$ using various catalysts under the same reaction conditions (T = 80 °C, P_{CO_2}= 14 MPa, P_{H_2}= 4 MPa, time = 20 h). Table 1 shows the results of different noble metal catalysts over a variety of supports. Except Pd, no alkane formation was detected with other catalysts. Hence, it could be suggested that the nature of the metal plays a crucial role in the ring opening under the described reaction conditions.

From the results (Table 1) it is also evident that the Pd/Al-MCM-41 (Si/Al = 10; 1.0 wt% Pd) solely produced **6** (Scheme 1b) with >99% selectivity. Thus, we have continued with the Pd/Al-MCM-41 catalysts to study the effect of different reaction parameters. A positive effect of temperature on the conversion and selectivity of the reaction was observed. As expected, a low temperature of 30–50 °C initiates low conversion, but maximum selectivity (>99%) of **6** (Scheme 1b) with highest conversion (>99%) was obtained at 80 °C (ESI, Fig. S1†). As the density of the medium changes with temperature, which significantly controls the path of the reaction, and hence a mild reaction condition is effective for the linear alkane formation in $scCO_2$.

Interestingly, CO_2 pressure has a distinct effect on the conversion and selectivity (Fig. 1) of the ring opening of **4**. At the lower pressure of 7 MPa, the conversion was ~70% and compound **5** (Scheme 1b) was formed with 95% selectivity. However, with increasing CO_2 pressure, the conversion was increased along with the change in product distribution in which the selectivity of **5** decreased and the product **6** reached the maximum selectivity of >99% at 14 MPa of CO_2. Most likely, the increased conversion resulted from the transition of the biphasic medium (>10 MPa) to a single phase medium (as observed from the phase behavior studies; ESI, Fig. S2†) and enhanced the availability of the reactant. However, above 14 MPa of CO_2 pressure, a drop in conversion from 100% to 98.2% was observed. It seems that the decrease in conversion might be related to the deactivation of the catalyst or dilution effect. However, it was found that the catalyst can be recycled successfully (described later; Table 2). Hence, dilution of the reactant could explain the decrease in conversion with further increase of CO_2 pressure at a constant volume.

Fig. 2 shows the effect of reaction time on the hydrogenation and dehydration/hydrogenation of compound **4** at fixed pressure of CO_2 (14 MPa) and H_2 (4 MPa). The conversion increased with time and reached to the maximum (>99%) within 15–20h. Consequently, the product selectivity of **6** also changed. In the

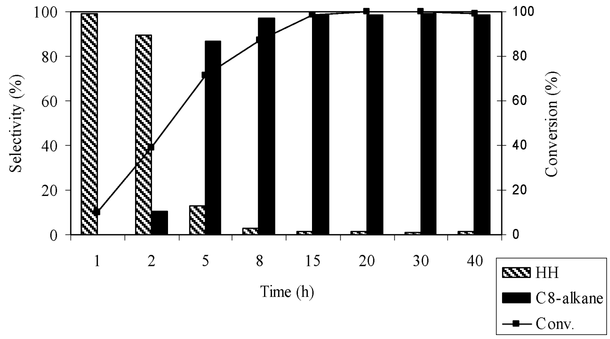

Fig. 2 Effect of reaction time on hydrogenation and dehydration/hydrogenation of compound **4** (Scheme 1b). Reaction conditions: Temp. = 80 °C, P_{H_2} = 4 MPa, P_{CO_2} = 14 MPa; HH = compound **5** and C8-alkane = compound **6** (Scheme 1b).

beginning (1–2 h), **5** was the major product, but it started to decrease gradually with the formation of **6**. Therefore, it could be suggested that a longer reaction time is necessary for the formation of linear alkane under the studied reaction conditions (temp. = 80 °C; $P_{H_2} = 4.0$ MPa and $P_{CO_2} = 14$ MPa) using Pd/Al-MCM-41 catalyst. Interestingly, from the course of the reaction it was clear that the hydrogenation of **4** to **5** was very fast and reached highest selectivity of **5** within 1 h. On the contrary, the formation of **6** *via* dehydration/hydrogenation was slow. This process started from 2 h of reaction time and attained the highest selectivity during 15–20 h in the present reaction conditions.

As the ring-opening reaction of furan was facilitated by the combination of acid and metal catalysts, Al has been incorporated into the Si support to increase the acidity, because the acidity of the support is directly related to the framework Al.[11,12]

As mentioned before, in comparison with the other catalysts, highest activity was achieved from the Pd/Al-MCM-41 and it might be associated with the highly dispersed Pd particles[12] as determined by the transmission electron microscopic image (TEM) of the catalyst (ESI, Fig. S3†) or support. However, understanding of the heterogeneous catalyzed reaction depending on the nature of the active site, particle size and support in $scCO_2$ is a difficult and complicated issue.

After optimization, the same reaction conditions were repeated on **1** (aldol condensation product of HMF and acetone). As a result, the successful formation of the product **3** (Scheme 1a) with >99% selectivity (Table 1; entry 8) was evident. Regarding the parameters affecting selectivity, the hydrogenation and dehydration/hydrogenation of **1** follows a similar trend to that of **4** in $scCO_2$ under similar reaction conditions.

It is well known that catalyzed ring opening of a heterocyclic compound and the removal of the heteroatom, such as sulfur, is an important part of the petroleum industry. To achieve the ring-opening product and the removal of heteroatom, the same methodology was further extended to the nitrogen and sulfur-containing compounds such as imidazole and thiophene (ESI, Table S1†), respectively. Unfortunately, ambiguous results were obtained by this method. Depending on the catalysts, imidazole shows 70 to 95% conversion, but the detection of the ring-opening product was greatly hampered by its volatile nature. For thiophene, the catalyst was deactivated easily because of sulfur and no reaction took place. The deactivation of the catalyst was again confirmed by inactivity during the ring opening of **4** in the presence of thiophene (ESI, Table S1; last entry†). Therefore, hydrogenation of these compounds requires modification of the reaction conditions as well as improvement in the product collection and identification, which might be a topic of future study.

In conclusion, we have developed a ring-opening method for the product of the aldol condensation between HMF and acetone, under very mild reaction conditions. This process has the potential to avoid the undesired coke formation as the catalyst exhibited long-term stability under the studied reaction conditions. Furthermore, we expect that it is possible to improve the catalyst efficiency to achieve high selectivity of the desired compound within a short reaction time.

Experimental

Aldol condensation

Aldol condensation between 5-hydroxymethyl furfural (HMF) and acetone was carried out at 25–40 °C without using any solid catalysts. Different ratios of acetone and HMF (mole ratio varies from 10 : 1 to 1 : 1) were placed in a bottle with the addition of 0.3 ml of 0.1 M NaOH under constant stirring for 4–6 h. A bright yellow intermediate was formed and extracted with 2 ml of $CHCl_3$ to remove the water (from NaOH solution). Finally, after the purification by chromatographic column separation and evaporation of the solvent, the product was separated and subjected to ^{13}C and ^{1}H NMR analysis to confirm the formation of desired structure. Both of the spectra show all the desired 9 peaks to ensure the formation of the intermediate (**1**; Scheme 1a). The product is stable and can be stored for a long period of time.

Ring opening by dehydration/hydrogenation

The synthesized pure intermediate was hydrogenated in $scCO_2$ in the presence of Pd catalyst at 80 °C. 0.2 g of the catalyst along with 0.5–1 g of the compound was introduced into a stainless steel batch reactor. Then, the reactor was sealed and flashed two times with 2 MPa of CO_2 to remove air. After flushing, the reactor was placed into the oven with a fan heater to maintain the constant temperature. Hydrogen was first loaded into the reactor followed by the liquid CO_2 using a high pressure liquid pump (JASCO), and compressed to the desired pressure. The reaction mixture was stirred continuously with the help of a Teflon-coated magnetic bar during the reaction. After the reaction, the reactor was cooled in ice and depressurized very carefully. The liquid mixture was identified by ^{13}C and ^{1}H NMR and analyzed quantitatively. The path of the reaction was followed by analysis of the product by NMR (Fig. 2). Due to the limitations of the experimental facility to scale up the process to the industrial level, we performed the reaction in the small scale.

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