Deoxygenation of heptanoic acid to hexene over cobalt-based catalysts: A model study for  $\alpha$ -olefin production from renewable fatty acid

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### Deoxygenation of heptanoic acid to hexene over cobalt-based

### catalysts: A model study for $\alpha$ -olefin production from

### renewable fatty acid

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**Graphical abstract** 



### Highlights

- Strong feed adsorption leads to rapid deactivation over Co based catalyst.
- Incorporation of 0.5% wt Pt in 5% wtCo/SiO<sub>2</sub>, increases activity and stability.
- Higher olefin/paraffin ratio is obtained over Co-Pt/SiO<sub>2</sub> under atmospheric H<sub>2</sub>.
- DeCO activity/stability w/o excessive hydrogenation can be tuned over Co-Pt/SiO<sub>2</sub>.

#### Abstract

Deoxygenation of heptanoic acid, a model compound, over bimetallic cobalt (Co-Pt, Co-Au, Co-Pd, Co-Ru) supported silica catalysts, was examined for  $\alpha$ -olefin production. The catalysts were prepared by conventional impregnation of the metal precursors on silica and characterized by XRF, TEM, H<sub>2</sub>-TPR, acetic acid-TPD, and XANES. Catalytic testing was performed in a fixed-bed flow reactor under atmospheric H<sub>2</sub> pressure. Monometallic cobalt

catalysts yielded mainly 1-hexene, but rapid deactivation was observed. Incorporation of 0.5% wt secondary metal, particularly Pt, increases activity and stability under H<sub>2</sub>. A relatively higher olefin/paraffin ratio can be obtained from the reaction over 5%Co+0.5%Pt/SiO<sub>2</sub> when compared to that with higher Pt loading. The co-impregnation method offers Co-Pt catalysts with stability higher than that prepared by the sequential impregnation method. Over cobalt-based catalysts, the deoxygenation is proposed to proceed via reduction of heptanoic acid to heptanal that is an intermediate for decarbonylation to hexene; while other side reactions are suppressed.

Keywords: Deoxygenation; Heptanoic acid; Cobalt; a-olefins; bimetallic catalysts, Co-Pt

#### **1. Introduction**

Linear alpha olefins (LAOs) is one of the important intermediate chemicals widely used as plasticizers, synthetic lubricants, surfactants, synthetic drilling fluids, detergents, and comonomers [1–3]. Industrially, linear alpha olefins are commonly produced by the oligomerization of ethylene, which is derived from non-renewable feedstocks [4]. While decarbonylation of fatty acid is an attractive approach for  $\alpha$ -olefin production from renewable sources [5–7].

In general, conversion of fatty acids to olefinic or paraffinic hydrocarbons can be proceeded via catalytic decarbonylation [6,8,9] or decarboxylation [6,10–12], respectively. However, other side reactions, such as ketonization [13], and cracking [11] can be competitive. Therefore, the design of the catalyst and reaction conditions are of particular importance. Metals supported on silica catalysts, such as platinum [14–18], palladium [14,19,20] and rhodium [11,21], are normally used in a semi-batch reactor. Murzin, et al. reported that the activity of the supported metal on carbon catalysts was in the order of Pd > Pt > Rh > Ir > Ru> Os > Ni for the deoxygenation of stearic acid at 300°C and 6 bar of H<sub>2</sub> [11]. However, under

this high pressure of  $H_2$ , paraffin yields are higher than that of olefins, due to rapid hydrogenation of the olefins primarily formed. In a similar manner, the conversion of fatty acid over Pd/C, catalysts provides high paraffinic hydrocarbons in a continuous flow reactor [5].

A severe deactivation was typically observed for the conversion of fatty acid over metal catalysts [11,14,22]. This is mainly derived from the strong interaction of fatty acid over the active metal surface. Therefore, high hydrogen pressure is generally used in the reaction system [11,14,22,23]. This could prolong the catalyst stability, but the product selectivity is shifted to paraffinic hydrocarbons. Thus, minimization of (i) the hydrogenation activity of the catalyst and (ii) the feed interaction with the catalyst's surface, is the key challenge in this reaction.

With this regard, non-noble oxophillic metals (Ni, Cu, Co, and Cr over SiO<sub>2</sub> support) are good candidates due to their limited hydrogenation activity, as compared to the noble metal (Pt, Pd, etc.) [24]. Amongst those, cobalt exhibits high initial activity and selectivity to olefins. However, large cobalt particles possess a strong interaction with a carboxylic acid, which leads to successive adsorption of the feed on the active sites, resulting in a rapid deactivation.

In this work, we thus further investigate the effects of cobalt particle size and incorporated secondary metals (Ru, Pd, Pt, and Au). This aims to modify the feed adsorption *vs.* hydrogenation over the cobalt active site in the deoxygenation of heptanoic acid (a model compound of fatty acids) to  $\alpha$ -olefins under atmospheric H<sub>2</sub> flow. The interaction of the feed on the active sites under H<sub>2</sub> is evaluated by acetic acid-temperature-programmed desorption (acetic acid-TPD). The electronic property of the cobalt active sites is studied by X-ray absorption near edge structure (XANES) and temperature-programmed reduction (TPR). Deoxygenation activity to the corresponding  $\alpha$ -olefins with minimal hydrogenation of the  $\alpha$ -olefins produced, is deliberately tuned. Besides, methods of bimetallic catalyst preparation (co-and sequential impregnation) are verified.

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#### 2. Experimental procedure

Silica (99.0%; Fluka) was calcined before use, in a muffle furnace at 600°C for 1 h with a heating rate of 5°C/ min. Co/SiO<sub>2</sub> (2, 5, 10, 15% wt) and 5%Co-X%M/SiO<sub>2</sub> (X = 0.25, 0.5, 0.75 and M = Pt, Pd, Au, Ru) were prepared by impregnation (IMP) and co-impregnation (CIP). For IMP, solution of cobalt precursor (Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O; Carlo) or a mixture of Co and M precursors (Pd(OAc)<sub>2</sub>, [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>, AuCl<sub>3</sub>.3H<sub>2</sub>O; Sigma-Aldrich, Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>; Ramken) was sprayed on the calcined silica. After that, the solid was dried in an oven at 70°C for 24 h and then calcined in a tube furnace at 600°C for 1 h with a heating rate of 5°C/min. The sequential impregnation method was used to prepare 5%Co+0.5%Pt/SiO<sub>2</sub> (SIP). Briefly, the 5%Co/SiO<sub>2</sub> (IMP) was repeatedly impregnated by the solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>. The solid was dried in an oven at 70°C for 6 h and calcined at 600°C for 1 h.

Specific surface area, chemical composition, and morphology of the catalyst were determined by nitrogen gas adsorption, wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF), and transmission electron microscopic (TEM), respectively. The reducibility of the incorporated metals was examined by a temperature-programmed reduction (H<sub>2</sub>-TPR), equipped with a thermal conductivity detector (VICI). The H<sub>2</sub> consumption was calculated using CuO as a standard. The adsorption of acetic acid on the catalysts was studied by temperature-programmed desorption (acetic acid-TPD) under He and H<sub>2</sub>. A portion of samples (~20 mg) was flushed with He at 300°C for 1 h (50 mL/min) to remove the absorbed moistures, and then treated with acetic acid vapor at 140°C for 30 min using a bubble flow vapor generator (glacial acetic acid) at room temperature. After the adsorption, the excess acetic acid was flushed with He or H<sub>2</sub> at 140°C. The acetic acid-TPD signal was then detected from 140°C to 900°C under He or H<sub>2</sub>. *In situ* XANES experiments were performed at BL2.2: TR XAS, Synchrotron Light Research Institute (SLRI), Thailand. An energy-dispersive monochromator and position-sensitive detector were employed to perform XANES

measurement [25]. The Co K-edge XANES was collected using the integration time of 2000 ms with an average of 10 scans. The oxidation state of cobalt composition was estimated by Linear Combination Fitting (LCF) of XANES spectra over Athena software using Co foil, CoO, and Co<sub>3</sub>O<sub>4</sub> as a standard. A thermogravimetric analyzer (Pyris) was used to quantify coke content on the used catalysts.

Deoxygenation of heptanoic acid was investigated at atmospheric pressure in a fixedbed flow reactor made with a quartz tube (6.3 mm O.D.). The catalyst was primarily activated at 600°C (heating rate of 5°C/min) for 1 h under the stream of air (100 mL/min). N<sub>2</sub> was purged for half an hour, and then the gas stream was switched to H<sub>2</sub> (100 mL/min) at the same temperature for 3 h. After reduction, the furnace was cooled down to the designed reaction temperature (350 – 425°C) and solution of reactant (10% wt./wt. heptanoic acid (Carlo) in octane (Sigma-Aldrich)) was fed to the reactor by a syringe-pump. The reaction was carried out for 6 h on stream under the stream of H<sub>2</sub> (100 mL/min). The gas sample was collected in a gas sampling loop, then periodically injected into GC column (MXT-1, 60 m length, 0.25 mm internal diameter, 0.5 µm film thickness) equipped with a flame ionized detector (FID).

### 3. Results & discussion

### 3.1 Catalyst characterization

Metal loadings and surface area of the catalysts are summarized in Table 1. The observed metal loadings are in agreement with the desired catalyst preparation. Comparing with SiO<sub>2</sub> support (319 m<sup>2</sup>/g), a proportional decrease in surface area (226-286 m<sup>2</sup>/g) is observed with the increase in metal loadings, presumably due to a partial surface/pore blockage by the loaded metal species.

Table 1 Metal loadings, surface area, H<sub>2</sub> consumptions and metal dispersion of the catalysts.

Enatr y	Catalysts	Ele analys	mental sis (XRF)	S <sub>BET</sub>	H <sub>2</sub> consumptio n	Metal <sup>b</sup> conten t	Dispersio n <sup>°</sup>	
-		Co (%wt. )	Secondar y metal (%wt.)	(m <sup>2</sup> /g )	mmol/g	(%wt. )	(%)	
1	SiO <sub>2</sub>	-	-	319	-			
2	2%Co/SiO <sub>2</sub>	1.9	-	286	0.5	2.4	22.5	
3	5%Co/SiO <sub>2</sub>	4.8	-	277	1.3	5.5	6.7	
4	10%Co/SiO <sub>2</sub>	9.2	-	236	2.2	9.8	2.4	
5	15%Co/SiO <sub>2</sub>	13.7	-	225	3.2	14.1	2.4	
6	5%Co+0.5%Pd/SiO 2	4.4	0.6	252	1.1	4.7	n/a	
7	5%Co+0.5%Au/SiO 2	4.6	0.5 <sup>a</sup>	254	1.3	5.6	n/a	
8	5%Co+0.5%Ru/SiO 2	4.5	$0.7^{a}$	251	1.4	6.0	n/a	
9	5%Co+0.5%Pt/SiO <sub>2</sub> (CIP)	4.4	0.5	253	1.3	5.6	n/a	
10	5%Co+0.5%Pt/SiO <sub>2</sub> (SIP)	4.9	0.5	227	1.3	5.8	n/a	
11	5%Co+0.25%Pt/Si O <sub>2</sub>	4.6	0.2	249	1.2	5.3	n/a	



<sup>*a*</sup> SEM-EDX <sup>*b*</sup> Calculated from  $H_2$  Consumption, <sup>*c*</sup> Calculated from  $H_2$  Chemisorption



Figure 1 Temperature programmed reduction profiles of catalysts.

The reducibility of the catalysts can be deduced from the H<sub>2</sub>-TPR, as shown in Figure 1. The hydrogen consumption is also collected in Table 1. For all cobalt catalysts (Figure 1, a-d), the only peak at ~340°C is observed and attributed to the reduction of  $Co_3O_4$  to CoO species and CoO to metallic Co [26]. When cobalt loading is increased from 2% to 15% wt., the H<sub>2</sub> consumption is increased proportionally (Table 1, entry 2-5 and Figure S1 supporting information). The higher reduction temperature (320-340°C) for 10% and 15 % wt. Co/SiO<sub>2</sub>,

compared with those for 2% and 5% wt. Co/SiO<sub>2</sub> (300-320°C), suggests a larger cobalt particle at high loadings [27,28], as confirmed by TEM (Figure 2). It can be seen that the average cobalt particle size is approximately 18, 27, 41, and 52 nm for 2%, 5%, 10%, and 15% wt. loadings, respectively.



**Figure 2** TEM images and particle size distribution histograms of reduced catalysts: a) 2%Co/SiO<sub>2</sub>, b) 5%Co/SiO<sub>2</sub>, c) 10%Co/SiO<sub>2</sub>, d) 15%Co/SiO<sub>2</sub>.

Upon incorporation of the secondary metals, the H<sub>2</sub> consumption of bimetallic Co catalysts (1.1-1.4 mmol/g) is similar to that of monometallic Co (~1.3 mmol/g). This is because the only small amount of the secondary metals is incorporated (~0.5 %wt.). However, the reduction peaks of the bimetallic catalysts (Figure 1, e-h) generally shift to lower temperatures, as compared to the monometallic cobalt catalyst. The first reduction at ~120°C is assigned to the reduction of Co-Pt mixed oxide, presumably forming a bimetallic Co-Pt. While, the second and third peaks (130 and 240°C) suggest the reduction of Co<sup>3+</sup> to Co<sup>2+</sup> and Co<sup>2+</sup> to Co<sup>0</sup>, respectively [29]. The presence of Pt facilitates the reduction of nearby cobalt oxide particles presumably via hydrogen spilled-over [30,31]. Hence, the incorporated Pt significantly decreases the reduction temperature of cobalt, as observed.

Similarly, 5%Co+0.5%Pd/SiO<sub>2</sub> contains three reduction peaks at 115, 135, and 280°C (Figure 1f) [32]. Even though Co-Pd mixed oxide is reduced at a lower temperature compared with Co-Pt, the reduction of the remaining cobalt species in this sample requires a higher temperature. This indicates the lower activity of Pd for H<sub>2</sub>-spilled-over, as compared to the Pt. Unlike 5%Co+0.5%Pt/SiO<sub>2</sub> and 5%Co+0.5%Pd/SiO<sub>2</sub>, 5%Co+0.5%Ru/SiO<sub>2</sub> shows two reduction peaks at 155 and 245°C, referring to the reduction of the Co-Ru mixed oxide to bimetallic Co-Ru and the remaining  $Co^{2+}$  to  $Co^{0}$ , respectively [33]. On the other hand, 5%Co+0.5%Au/SiO<sub>2</sub> shows only a single reduction peak at 300°C. It is suggested that Au may well promote the reduction of  $Co^{3+}$  to metallic Co in a single step.

#### 3.2 Catalysts activity

#### Effect of temperature over 5%Co/SiO<sub>2</sub> catalysts

The conversion of heptanoic acid using 5% Co/SiO<sub>2</sub> as a catalyst is enhanced (total yield from 22% to 56%) upon increasing the reaction temperature (from  $350^{\circ}$ C to  $425^{\circ}$ C), as shown in Figure 3. 1-Hexene can be observed as the main product; while, minors include heptanal, 7-tridecanone and other lighter hydrocarbons. Yields of all products are also increased with temperature, except for heptanal that may well undergo decarbonylation to hexene at high temperature [33,34]. Unlike other report on transfer hydrogenation of fatty acid over cobalt catalysts [35], heptanol was not detected. This was presumably because a higher temperature was used in this study; while other report in the liquid phase was tested at relatively lower temperature (~200°C) in the presence of isopropanol as hydrogen donor. However, at 425°C hexene was decreased; while, methane and 7-tridecanone were notably enhanced. This suggests that, at high temperatures, hydrogenolysis of the light hydrocarbons and ketonization of heptanoic acid could be promoted over the cobalt catalyst [36–38]. Besides, methane could be formed by the hydrogenation of CO and CO<sub>2</sub> produced by decarbonylation and decarboxylation of heptanoic acid, respectively [33,36]. In a different manner from the reaction over noble metal catalysts i.e. Pd/SiO<sub>2</sub> [39] and PdSn/SiO<sub>2</sub> [40], higher selectivity of linear  $\alpha$ -olefin were obtained in this study without iso-olefins. This could attribute to the weaker adsorption of olefinic product over Co, as compared to that over Pd. Hence further hydrogenation and/or double bond/skeleton isomerization of the initially formed linear olefins are suppressed in this work.



**Figure 3** The effect of the reaction temperature on the conversion of heptanoic acid (total yields) and yield of products from the deoxygenation of heptanoic acid over 5% Co/SiO<sub>2</sub>. (*Conditions:* 10%wt. heptanoic acid in octane, contact time 20 g-h.mol<sup>-1</sup>, activation temperature 550°C and reduction temperature 500°C, reaction temperature 350 - 425°C, 1 atm, and 100 mL/min of H<sub>2</sub>. The activity is at 30 min on stream.)

#### Effect of cobalt loading on the silica support

With the same contact time based on cobalt, the conversion at 1 h on stream is decreased (from 84.7% to 49.0%) when cobalt loading is increased (from 5% wt. to 15% wt.), as shown in Table 2, entry 2-4, and Figure 4. This is presumably due to a lower dispersion of cobalt particles at higher loading, as seen from Table 1 (entry 2-5) and Figure 2. However, 2%Co/SiO<sub>2</sub> gives lower conversion despites its higher metal dispersion (~22% dispersion). This could be derived from the severe deactivation of this catalyst, as observed in Figure S2 (supporting information). The hexene/hexane ratio is generally improved (21.1 to 53.0, Table 2) with cobalt loading (5%-15%), possibly due to the suppression of hydrogenation activity when Co dispersion is decreased (from 6.7% to 2.4%). It is also seen that over 15%Co/SiO<sub>2</sub>, the yield of 7-tridecanone is notably high (Figure 4). This is presumably because, at high Co loading, some of the non-reduced cobalt oxides may well be retained even after reduction at 600°C. In line with this view, a high reduction temperature (>600°C) was particularly observed in this sample (Figure S3 in supporting information). Such non-reduced cobalt oxide species presenting in 15%Co/SiO<sub>2</sub> can readily promote the ketonization of heptanoic acid to 7-tridecanone, as observed [38].

Entr	Catalysts	Contact time (g.h/mol )	ion (%)	%Yield						Hexane in	
y		by Co weight by	Convers	$C_1-C_5$	Hexene	Hexane	iso-C <sub>6</sub>	Heptene	Heptanal	7- tridecano	Hexene/
1	2%Co/SiO <sub>2</sub>	1.64 82	57.2	13. 3	29. 4	1.3	0.0	2. 4	4.2	6.5	22. 6
2	5%Co/SiO <sub>2</sub>	1.62 33	84.7	19. 1	46. 4	2.2	2.2	3. 6	3.5	7.7	21. 1
3	10%Co/SiO <sub>2</sub>	1.65 17	78.6	9.5	53. 7	1.4	4.8	3. 5	0.6	5.0	38. 4
4	15%Co/SiO <sub>2</sub>	1.63 11	49.0	6.1	26. 5	0.5	0.6	1. 9	2.6	10. 8	53. 0
5	5%Co+0.5%Pt/SiO <sub>2</sub>	1.69 34	100. 0	11. 2	54. 4	17. 9	14. 3	2. 2	0.0	0.0	3.0
6	5%Co+0.5%Au/Si O <sub>2</sub>	1.69 34	69.1	13. 2	39. 1	1.5	1.8	2. 8	3.1	7.5	25. 7
7	5%Co+0.5%Pd/SiO 2	1.69 34	75.7	9.1	36. 6	3.3	1.5	2. 3	15. 3	7.6	11. 0
8	5%Co+0.5%Ru/Si O <sub>2</sub>	1.68 34	57.5	8.7	37. 2	1.0	1.2	2. 1	3.0	4.3	35. 9
9	5%Co+0.5%Pt/SiO <sub>2</sub> (c-SIP)	1.69 34	100. 0	16. 2	52. 5	15. 0	11. 6	2. 6	2.1	0.0	3.5
10	5%Co+0.5%Pt/SiO <sub>2</sub> (nc-SIP)	1.69 34	100. 0	3.3	6.9	71. 9	14. 6	0. 0	3.2	0.0	0.1
11	5%Co+0.25%Pt/Si O <sub>2</sub>	1.70 34	95.7	14. 9	52. 4	11. 0	10. 4	2. 6	2.9	1.5	4.8
12	5%Co+0.75%Pt/Si O <sub>2</sub>	1.68 34	100	11. 4	52. 2	17. 4	14. 1	2. 0	2.9	0.0	3.0

Table 2 Deoxygenation of heptanoic acid and product distribution of various catalysts

(Condition: 10%wt. heptanoic acid in octane, reaction temperature 400 °C, activation temperature 600 °C and reduction temperature 600 °C, 1 atm, and

100 mL/min of  $H_2$ . The activity is at 1 h on stream. (5%Co+0.5%Pt/SiO<sub>2</sub> (nc-SIP) is not in situ calcined).





#### Catalyst deactivation

Although 5%Co/SiO<sub>2</sub> provided high activity amongst other loadings, the deactivation was notably observed. All the product yields are decreased, except for 7-tridecanone, as shown in Figure 5. The cause of catalyst deactivation could be the results of (i) strongly adsorbed heptanoic acid or (ii) coke formation on the Co surface. To verify the nature of adsorbed species, TGA of the used catalysts shows only major weight loss ~10% at 330°C, in addition to ~2% wt. absorbed moisture (50-100°C), as depicted in Figure S4 (see supporting information). This low temperature weight loss may be due to the decomposition of adsorbed heptanoic acid on the cobalt surface rather than the coke deposition. To validate this assumption, the heptanoic acid was paused after 6 h on stream. Subsequently, the catalyst bed

was flushed with steam at the reaction temperature (400°C) for another 6 h (6-12 h on stream in Figure 5) before the feed was re-introduced. It can be seen that, from 12-15 h on stream, the activity is recovered with similar product distribution. This experiment clearly shows that steaming can displace the feed that is adsorbed on the surface of catalysts. If the coke deposit is the cause of the catalyst deactivation, the activity shall not regain after steaming. Accordingly, the observed deactivation appears to derive from the strong adsorption of heptanoic acid on the cobalt active site. In a supportive manner, a significantly stronger TPD signal was observed (Figure S5) over 5%Co/SiO<sub>2</sub>, as compared to the parent support, after these samples was pre-adsorbed with acetic acid (a smaller carboxylic acid probe). Such signals are derived from ketonization of the chemisorbed acetic acid as reported previously [41]. This suggests that the presence of Co promotes both chemisorption and ketonization of carboxylic acid at elevated temperature.



Figure 5 Conversion of heptanoic acid and yield of products from the deoxygenation of heptanoic acid over 10%Co/SiO<sub>2</sub>. (*Conditions: 10%wt. heptanoic acid in octane, contact time 17* 

g-h/mol, activation temperature 600°C and reduction temperature 600°C, reaction temperature 400°C, 1 atm, and 100 mL/min of H<sub>2</sub>. ; (•) conversion ; (×) C1 ; (\*) C2 ; (◊) C3 ; (Δ) C4 ; (-) C5 ; (•) Hexene ; (□) Hexane ; ( $\mathcal{O}$ ) iso-C6 ; (+) Heptene ; ( $\blacktriangle$ ) Heptanal ; (•) 7-tridecanone)

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#### Effect of secondary metal incorporated into 5% cobalt catalysts

To improve catalyst stability, 0.5% wt. secondary metals (Pt, Pd, Ru, and Au) were incorporated in 5%Co/SiO<sub>2</sub>. As seen from Figure 6, the stability 5%Co+0.5%Au/SiO<sub>2</sub> is not modified because desorption/decomposition of the carboxylic acid is not facilitated even under H<sub>2</sub> (see Figure 7c), as compared to that observed with 5%Co/SiO<sub>2</sub> (Figure 7a). It is worth noting here that the peak area of acetic acid-TPD would refer to the amount of chemisorbed acetic acid on the catalyst. While the peak temperature would suggest the desorption/ decomposition of such chemisorbed acetic acid. Accordingly, the catalyst exhibiting signal at lower temperature and/or with smaller peak area, would be generally less adsorptive for carboxylic acid. Accordingly, similar product distribution to 5%Co/SiO<sub>2</sub> was observed over 5%Co+0.5%Au/SiO<sub>2</sub> (Table 2, entry 6). The stability of 5%Co+0.5%Pd/SiO<sub>2</sub> is not improved, despite a facile H<sub>2</sub> spilled-over from Pd to Co surface, as implied by the lower reduction temperature for this sample (Figure 1). This could be the result of the strong interaction with the carboxylic acid over Co-Pd/SiO<sub>2</sub>, as deduced from the high decomposition temperature of the adsorbed acetic acid (Figure 7d). A noticeable yield to heptanal was obtained over this catalyst (Table 2, entry 7), suggesting that the bimetallic Co-Pd also promotes the reduction of heptanoic acid to heptanal. Although, in the case of 5%Co+0.5%Ru/SiO<sub>2</sub>, the high selectivity of hexene was obtained (Table 2, entry 8), the catalyst is rapidly deactivated, possibly due to the CO poisoning (that is produced from the decarbonylation of heptanal), as reported in the literature [42,43].



**Figure 6** Catalytic performance on deoxygenation of various cobalt/metal bimetallic supported on silica catalysts. (*Condition 10%wt. heptanoic acid in octane, contact time 34 g-h/mol, reaction temperature 400°C, activation temperature 600°C and reduction temperature 600°C, 1 atm, and 100*  $mL/min of H_2$ )



**Figure 7** Acetic acid decomposition of 5%Co/SiO<sub>2</sub> and 5%Co/metal bimetallic catalysts: helium atmosphere (solid lines) and hydrogen atmosphere (square dot).

In sharp contrast, Co-Pt/SiO<sub>2</sub> provides an improved stability, presumably because Pt can facilitate desorption of the heptanoic acid from Pt-Co surface, as seen from acetic acid-TPD in Figure 7b. It is clear that no acetic acid desorption/decomposition was detected at a temperature higher than 300°C, over Co-Pt/SiO<sub>2</sub> under H<sub>2</sub>, while some adsorbed species were retained over other catalysts. This suggests that H<sub>2</sub> can assist the desorption of carboxylic acid more efficiently over Co-Pt/SiO<sub>2</sub>, possibly due to an improved H<sub>2</sub> spilled-over on the catalyst surface. In line with this view, the in situ TR-XANES measurement of Co-Pt catalysts under H<sub>2</sub> from 50 to 600°C revealed that the Co species could be more readily reduced, as compared to 5%Co/SiO<sub>2</sub> catalyst. It can be seen from the linear combination fitting of XANES spectra in Figure 8 that the metallic Co species could be formed in 5%Co+0.5%Pt/SiO<sub>2</sub> at a relatively much lower temperature (~100°C), as compared to 5%Co/SiO<sub>2</sub> catalyst (~200°C). The complete reduction of 5%Co+0.5%Pt/SiO<sub>2</sub> can be observed at 300 °C; while, less than 15% metallic Co is present in 5%Co/SiO<sub>2</sub> at this temperature (Figure 8). This emphasizes that the addition of Pt clearly facilitates the reduction of Co species. Vajda, et al. reported that the addition of 25% wt. Pt into Co would result in a higher fraction of CoO in the catalyst, as compared to the bulk Co oxides [44]. Similarly, ~20%CoO was observed in 5%Co+0.5%Pt/SiO<sub>2</sub>, but Co<sub>3</sub>O<sub>4</sub> was solely contained in 5%Co/SiO<sub>2</sub>. In consistence with this result, the reduction peak (TPR) of 5%Co+0.5%Pt/SiO<sub>2</sub> shifts to the low temperature (Figure 1e).



Figure 8 Fraction of Co components from linear combination fitting of a) 5%Co/SiO<sub>2</sub> and b) 5%Co+0.5%Pt/SiO<sub>2</sub> catalysts under reduction condition from 50 to 600°C using CoO and Co<sub>3</sub>O<sub>4</sub> bulk standards.

Even though 5%Co+0.5%Pt/SiO<sub>2</sub> shows similar hexene selectivity (~54%, Table S1, entry 5) as compared to 5%Co/SiO<sub>2</sub>, hexane and *iso*-C6 selectivities are particularly increased (from 2.6 and 2.5 to 17.9 and 14.3%, respectively). This could be attributed to the fact that the incorporated Pt could promote hydrogenation of hexene to hexane, decarboxylation of heptanoic acid to hexane, and also isomerization of hexane to *iso*-C6 [16]. In accordance, hexane and *iso*-C6 are obtained only at high contact time (Figure 9). While hexene, heptanal, and 7-tridecanone are observed initially ( $\leq$ 12 g·h/mol). The major product, hexene, can be produced via the decarbonylation of heptanoic acid [45]. While 7-tridecanone can be alternatively produced via ketonization of heptanoic acid. The C1-C5 hydrocarbons, minor products, were derived from cracking of the C6-C7 obtained initially. The overall reaction pathway for the deoxygenation of heptanoic acid over 5%Co+0.5%Pt/SiO<sub>2</sub> catalyst can be proposed in Figure S6.



**Figure 9** a) Contact time using 5%Co+0.5%Pt/SiO<sub>2</sub> as a catalyst for the heptanoic acid conversion b) Zoom in other product yields. (*Condition: 10%wt. heptanoic acid in octane, reaction temperature 400°C, activation temperature 600°C and reduction temperature 600°C, 1 atm, and 100 mL/min of*  $H_2$ . ; (•) conversion ; (×) C1 ; (\*) C2 ; ( $\Diamond$ ) C3 ; ( $\Delta$ ) C4 ; ( $\Diamond$ ) C5 ; ( $\bigcirc$ ) Hexene ; (•) Hexane ; ( $\square$ ) iso-C6 ; (+) Heptene ; ( $\blacktriangle$ ) Heptanal ; (•) 7-tridecanone)

As the Pt loading is increased (0.25-0.75% wt.), C1-C5 and 7-tridecanone yields were suppressed, as compared to the 5%Co/SiO<sub>2</sub> (Table 2, entry 2, 5, 11, 12, and Figure 10), presumably due to the increased electron density of bimetallic Co-Pt, which minimizes the cracking and ketonization activity. In addition, the stability is improved with the Pt loading, as seen in Figure 10. This is presumably because the increased Pt content in the bimetallic Co-Pt surface would increase the H<sub>2</sub> spilled-over, which assists the desorption of heptanoic acid from the bimetallic surface. In a supportive manner, the reduction of the bimetallic catalysts was shifted to lower temperature along with the increase in Pt loading (see Figure S7). However, as Pt loading is increased to 0.75% wt., hexane and *iso*-C6 yields are slightly increased, causing the decrease in hexene/hexane ratio as Pt readily promotes decarbonylation and hydrogenation (Table 2, entry 11, 5 and 12).



**Figure 10.** Effect of Pt loading (wt%) over 5%Co/SiO<sub>2</sub> for deoxygenation of heptanoic acid. (*Condition: 10%wt. heptanoic acid in octane, contact time 34 g-h/mol, reaction temperature 400°C, activation temperature 600°C and reduction temperature 600°C 1 atm, and 100 mL/min of H<sub>2</sub>)* 



**Figure 11.** Catalytic performance of deoxygenation of heptanoic acid using Co-Pt bimetallic catalysts. (*Condition: 10%wt. heptanoic acid in octane, contact time 34 g-h/mol, reaction temperature 400°C, activation temperature 600°C and reduction temperature 600°C 1 atm, and 100 mL/min of H\_2, (5%Co+0.5%Pt/SiO<sub>2</sub> (nc-SIP) is not in situ calcined))* 

When the 5%Co+0.5%Pt/SiO<sub>2</sub> was prepared by sequential impregnation (SIP), lower stability with similar product distribution was observed, as compared to the catalyst prepared by co-impregnation. (Figure 11, Table 2, entry 5 and 9). Such lower stability might be the result of the lower fraction of bimetallic Co-Pt prepared by the sequential impregnation method (SIP), as compared to the co-impregnation (CIP). This is deduced from an early reduction temperature of Pt species in 5%Co+0.5%Pt/SiO<sub>2</sub> (c-SIP), while the reduction of  $Co^{2+}$  to  $Co^{0}$  is observed at a higher temperature. (Figure S7). Such phenomenon suggests a disaggregation of Pt from the Co particles upon reduction, presumably due to poor mixing of Pt and Co precursors during SIP preparation. The disaggregation of the Pt particle becomes more severe when the catalyst is reduced without calcination. The H<sub>2</sub>-TPR of 5%Co+0.5%Pt/SiO<sub>2</sub> (nc-SIP) shows a small peak at 128°C indicating the reduction of platinum (II) nitrate and higher reduction temperature peaks of  $Co^{3+}$  to  $Co^{2+}$  and  $Co^{2+}$  to  $Co^{0}$  at 178 and 314°C (Figure S7). Accordingly, a high activity (Figure 11) with exceptionally high hexane selectivity (Table 2, entry 10) was observed in the non-calcined catalyst, 5%Co+0.5%Pt/SiO<sub>2</sub> (nc-SIP). This is because the isolated Pt successively promotes the decarboxylation of heptanoic acid yielding hexane and its isomers.

#### 4. Conclusion

 $\alpha$ -Olefin (1-hexene) can be selectively produced from deoxygenation of heptanoic acid, a fatty acid model compound, over supported cobalt-based catalysts. Cobalt particle size plays a significant role in the catalytic activity (optimum at ~30 nm), despites that deactivation is observed for all catalysts. The strong feed adsorption on the Co active sites leads to the catalyst deactivation. The incorporation of secondary metals, namely Au, Pd, Ru, facilitates the reduction of cobalt oxides. However, the catalyst stability is not readily improved even under H<sub>2</sub>. In sharp contrast, bimetallic 5%Co+0.5%Pt/SiO<sub>2</sub> provides a higher stability presumably due to a weaker interaction of the carboxylic acid with the Co-Pt bimetallic surface. The *in situ* TR-XANES shows a lower edge energy of Co when Pt is incorporated. This indicates a higher electron density of Co-Pt bimetallic catalyst, leading to a lower reduction temperature (H<sub>2</sub>-TPR) and a facile desorption of carboxylic acid (Acetic acid-TPD). The 5%Co+0.5%Pt/SiO<sub>2</sub> shows hexene selectivity, similar to 5%Co/SiO<sub>2</sub>; however, hexane and *iso*-C6 are particularly increased, especially upon the increase in contact time and Pt content. An appreciated decarbonylation activity without excessive hydrogenation of the olefin produced, results in selective conversion of fatty acid to a desirable  $\alpha$ -olefin. The preparation of Co-Pt catalysts by co-impregnation (CIP) provides a higher  $\alpha$ -olefin selectivity, as compared to that by sequential impregnation (SIP).

### CRediT author statement

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#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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