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Selective Hydrodeoxygenation of Bio-Oil Derived Products:

Ketones to Olefins

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Abstract

6	The hydrodeoxygenation (HDO) of various ketones (acetone, methyl ethyl ketone and
7	cyclohexanone) to olefins via hydrogenation - dehydration was conducted in fixed bed
8	reactor at $373 - 573$ K under H ₂ . Ketone can be hydrogenated over the metal function to
9	alcohol intermediate that is subsequently dehydrated to olefin over the acidic function. A
10	preliminary study on hydrogenation of acetone to 2-propanol over metal/SiO ₂ catalysts (Cr,
11	Fe, Co, Ni, Cu and Pd) shows that Ni and Cu are active at > 373 K. Although Ni possesses an
12	activity higher than that of Cu, it promotes olefin hydrogenation and alcohol hydrogenolysis
13	at > 473 K. Hydrogenolysis of the alcohol intermediates can be reduced over Ni-Cu alloy. An
14	optimum conversion with 100% selectivity to alcohol, can be obtained at 448 and 473 K for
15	Ni and Cu, respectively. The dehydration of 2-propanol to propylene over proton zeolites
16	(ZSM-5, Y, Mordenite and β) can be achieved at > 398 K. The zeolites with three-
17	dimensional pore structure (β and Y) provide relative higher activity (> 90% conversion).
18	However, a bimolecular dehydration to ether is also promoted. Only HZSM-5 shows
19	excellence selectivity to propylene (98 %). Hydrodeoxygenation of ketones was tested with

20	(i) Double bed of 5%Ni/SiO ₂ and HZSM-5 (Si/Al~13), (ii) physical mixed bed of 5%Cu/SiO ₂
21	and HZSM-5 (Si/Al ~13) and (iii) bi-functional catalyst of 5% Cu/HZSM-5 (Si/Al ~250). It
22	was found that high alkene selectivity was readily obtained at 448 K. While, over the
23	physical mixed bed and bi-functional catalyst, the hydrogenation activity was enhanced as the
24	alcohol intermediate was removed from the system. The reactivity of ketone depends on their
25	adsorption on the metal surface and steric hindrance, i.e. acetone > cyclohexanone > methyl
26	ethyl ketone.

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28 1. Introduction

29 Nowadays, the application of pyrolysis bio-oil is limited because approximately 20-50 % oxygen is retained in the products.¹⁻³ Therefore, the upgrading of pyrolysis bio-oil is 30 necessary. Many researchers suggest that almost all oxygen can be removed by 31 32 hydrotreatment process. However, a large amount of hydrogen is consumed and the saturated oxygen-free compounds⁴⁻⁷ cannot be used as chemical feedstock. Accordingly, mild 33 hydrodeoxygenation is of interest to remove oxygen functional groups and produce olefins as 34 reactive hydrocarbon feedstock. For example, mild hydrodeoxygenation of acetone can 35 produce propylene that can be used to produce valuable C3 chemicals e.g. acrylic acid and 36 acrylates,⁸⁻¹⁰ acrylonitrile,¹¹⁻¹² pyridine¹³ propylene oxide and 1,2-propane-diol,¹⁴⁻¹⁶ and the 37 most consumed polymer, polypropylene.¹⁷⁻¹⁸ 38

Aliphatic and cyclic ketones are common oxygenate compounds found in bio-oil¹⁹⁻²³ 39 and a lot more in the upgrading of bio-oil via ketonization process.²⁴⁻²⁶ The decarbonylation 40 as done for aldehydes is impossible for the ketones. The direct reduction usually leads to 41 formation of paraffin or alcohol when drastic or mild condition is used, respectively.²⁷⁻³⁰ It 42 seems that multi-step reaction on one or more catalyst system is required. A similar idea to 43 produce acrylic acid from glycerol via an integration of dehydration-oxidation³¹ can be 44 applied for mild hydrodeoxygenation of ketones to olefins. In this case, the ketone can be 45 primarily hydrogenated to alcohol that is subsequently dehydrated to olefin. However, the 46 nature of sub-reactions is different. For example, hydrogenation is preferred at relatively low 47

temperature and high pressure while dehydration is promoted at higher temperature and lower pressure. In the catalytic point of view, the acid function should promote only dehydration of the alcohol product, but not aldol condensation of the ketone fed. In the same view, the metal function should be selective only for hydrogenation of the ketone to alcohol, not the olefin to paraffin. Accordingly, several parameters have to be adjusted and controlled including competitive adsorption of feed, intermediates and products on each individual active site.

In this work, a catalytic system designed for mild hydrodeoxygenation of ketone to 54 55 olefin was investigated. Hydrogenation of ketone to alcohol was accomplished over metal catalysts (Ni, Cu, Fe, Co, Pt and their alloys) at low temperature.³²⁻³⁵ The alcohol produced 56 was then dehydrated over acidic catalysts (y-Al₂O₃, HZSM-5, HY and H-Beta).³⁶⁻³⁹ 57 Hydrogenation and dehydration were separately studied in order to understand the role of 58 each catalytic function. The integrated hydrogenation-dehydration over double bed, physical 59 60 mixed bed and bi-functional catalyst bed were then optimized to allow only essential amount of hydrogen consumption in the first stage. The olefins were selectively obtained and the 61 62 reactivity of different ketones were compared and discussed.

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64	2. Experimental	procedure

65	As zeolites with various Si/Al are used in this study, the Si/Al of a particular sample
66	is designated as a number in the parenthesis; i.e. a HZSM-5 sample with Si/Al~13 is referred
67	to as HZSM-5 (13). HZSM-5 (13) and HZSM-5 (250) were obtained from Zeochem $^{\ensuremath{\mathbb{R}}}$ and
68	HZSM-5 (180) were obtained from Zeolyst [®] . NH4 ⁺ -Beta (14), H-Mordenite (15), NH4 ⁺ Y
69	(3.5) and HY (100) were supplied by Tohso. The NH_4^+ -zeolites were converted to H^+ -zeolites
70	by calcination at 773 K under flow of air zero (60 mL/min) for 5 h with a heating rate of 2
71	K/min. Metal supported catalysts were simply prepared by incipient wetness impregnation.
72	Metal nitrate precursors (Cu(NO ₃) ₂ .3H ₂ O by Ajax Fine Chem, Ni(NO ₃) ₂ .6H ₂ O,
73	Cr(NO ₃) ₃ .9H ₂ O Fe(NO ₃) ₃ .9H ₂ O, and Co(NO ₃) ₂ .6H ₂ O by Carlo Erba [®]) were dissolved in
74	deionized water (~0.01 M) and slowly drop onto support (SiO ₂ ; Carlo Erba and Zeolites)
75	until wet. The sample was dried at 333 K in an oven for 15 min, and then the loading was
76	repeated until desired metal content was reached. The samples were kept to dry at 333 K
77	overnight and calcined in air zero (60 ml.min ⁻¹) at 723 K for 5 h, then pelletized to the size of
78	600–850 μm.

Elemental composition was determined by X-ray fluorescence spectrometer (XRF; Siemens). Specific surface area (BET) of catalysts was measured using nitrogen adsorption analyzer (Quantachrome) at 77 K and 0.05–0.30 P/P₀. Residue retained in the used catalysts was analysed by thermo-gravimetric analysis (Perkin Elmer) under air-zero or N₂ stream from 323 - 1173 K at rate of 10 K/min. Reducible metal oxide species in the catalysts was 84 analyzed by temperature programmed reduction (TPR). The catalysts were treated in air-zero at 723 K for 5 hours prior to heating from 323 - 1173 K in 10% H₂/Ar. The hydrogen 85 consumption was recorded with an on-line thermal conductivity detector (VICI).⁴⁰⁻⁴¹ Copper 86 dispersion on support was also analyzed by selective surface TPR technique. Briefly after 87 typical TPR, the sample was *in situ* treated with N₂O at 333 K for 2 hours. Then, the surface-88 oxidized sample was subjected to a secondary TPR.⁴² Moles of surface copper can be 89 calculated as described by Sagar et al.43 Acidity of HY and Cu/HY was quantified by NH3-90 TPD. 1 % NH₃/He was pre-adsorbed at 323 K. TPD was carried out in He at 10 K.min⁻¹ from 91 323 – 973 K.⁴⁴ 92

The catalytic testing was conducted in a fixed bed flow reactor (6 mm i.d. Pyrex[®]). The catalysts were primarily activated at 723 K (2 K.min⁻¹) under stream of air zero (30 ml.min⁻¹) for 5 h. Subsequently the metal supported catalysts were treated in H₂ at 723 K for 2 h. The system was cooled down to the reaction temperature (373 - 573 K) and the ketone feed was introduced by a syringe pump at a rate of 0.07-0.7 g.h⁻¹. The reaction was carried out for 9 h on stream and the products were analyzed by an on-line GC-FID every 70 minutes. A Hayesep[®] P (1/8" X 8') was used as separating column.

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101 **3. Result and discussion**

102 **3.1 Catalyst characterization**

103	Metal content and surface area of all catalyst samples are tabulated in Table S1
104	(supplementary information). All catalysts possess relatively high surface area. The copper
105	dispersion on SiO_2 decrease from 95 to 24 % when loading was increased from 5 - 15%
106	(Table 1). However, the dispersion for 2% Cu/SiO ₂ cannot be accurately calculated,
107	presumably due to an incomplete surface oxidation by $N_2 O$ and a deviated hydrogen
108	consumption measurement when the Cu loading is relatively small. The relatively lower Cu
109	dispersion is observed when zeolites are used as support (54 - 65 %). This is possibly
110	because, with this technique, part of the surface Cu oxide may well become exchangeable Cu
111	cation that cannot be easily reduced. The presence of exchangeable copper cation in HY can
112	be evidenced from an obvious increase in weak acidity, as compared to that in the parent HY
113	(Table 1).

Figure 1 shows that at 2 wt% loading on silica, high temperature is required for reduction of Cr >Co~Fe >Ni >Cu oxides, respectively.⁴⁵ Broad reduction peaks at the shoulder of CuO and NiO at 650-800 K are attributed to various metal support interactions including copper or nickel silicate.⁴⁶⁻⁴⁷ While, cobalt oxide reduction appears as two peaks at 548 and 643 K, corresponded to $Co_3O_4 \rightarrow CoO$ and $CoO \rightarrow Co$, respectively.⁴⁸⁻⁴⁹ For iron oxide, the first reduction peak of iron corresponds to two overlap stage Fe₂O₃ \rightarrow Fe₃O₄ and

Fe₃O₄ \rightarrow FeO (603 K).⁵⁰ While, fully reduction of FeO to Fe cannot be observed up to 1173 K. The formation of Fe₂SiO₄ is expected as a cause of incomplete reduction.⁵¹ The TPR profile of chromium oxide corresponds to the reduction of dichromate and poly chromate to Cr₂O₃ (700 K).⁵² However, chromium (III) is very stable and cannot be reduced in this temperature range.⁵³ When nickel and copper are mixed on silica, the complete alloys are obtained at every composition as seen by single hydrogen consumption peak in Figure S1 (supplementary information).

The copper loaded HY (100) and HZSM-5 (250) show two reduction peaks at 470 K, corresponding to CuO aggregates on the surface (Figure 2). The higher temperature peak (520 K) is defined as highly dispersed copper oxide in the pore of zeolites.⁵⁴⁻⁵⁵ It is noted that higher Cu dispersion is observed on HY, as compared to HZSM-5, presumably due to a better diffusion of Cu precursor in the larger pore (peak at ~520 K).

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133 **3.2 Hydrogenation**

134	Since the successive hydrogenation of olefin product is not preferred, different metal
135	catalysts are tested for selective hydrogenation of ketone. As seen in Table 2, the initial
136	activated temperature for hydrogenation of acetone and propylene for various metal catalysts
137	are compared. The initial activated temperature reported in this study refers to the
138	temperature at which >3% conversion is obtained over the catalyst at the same contact time
139	(30 g.h.mol ⁻¹). It is clear that chromium and iron are inactive for hydrogenations at low
140	temperature. This is presumably due to an incomplete reduction of the metal phase under the
141	condition investigated (723 K). However, 10%Fe/SiO ₂ shows some activity for
142	hydrogenation of acetone and propylene at temperature higher than 473 and 573,
143	respectively. Co, Ni, Pd ⁵⁶⁻⁵⁷ catalysts are active for both acetone and propylene
144	hydrogenation. Hydrogenolysis can also be promoted over these metals at relatively higher
145	temperature. For acetone hydrogenation, the activity appears to be in the order of $Ni > Pd$
146	>Co. In the opposite view, Pd is more active than Co and Ni for propylene hydrogenation.
147	Copper seems to be the best choice for mild hydrogenation of acetone. Ketone can be
148	hydrogenated (< 373 K) to alcohol without paraffin productions. The alloy with Ni (NiCu)
149	significantly reduces both hydrogenation of propylene and hydrogenolysis acivity, as
150	compared to the Ni alone. This is attributed an increase in oxophillicity of the surface when
151	Cu is alloyed. ⁵⁸ Hence, the interaction of C=C would be readily modified. In addition, the Cu
152	alloying would strongly affect a structure sensitive reaction, such as hydrogenolysis. Both Ni

155	As Ni and Cu selectively promote hydrogenation of ketone with minimal activity for
156	olefin hydrogenation, these catalysts are particularly studied for acetone hydrogenation at 373
157	- 573 K as shown in Figure 3. It can be seen that for both metals, acetone conversion
158	increased with temperature until the thermodynamic limitation ⁵⁹⁻⁶¹ is reached for the reaction
159	conditions used in this study. The maximum conversion was obtained at 448 K for nickel and
160	473 K for copper. It is clear that the nickel is more active than the copper. 100% Selectivity
161	to 2-propanol is obtained over the nickel catalyst at 373 - 448 K. However, hydrogenolysis to
162	methane can be observed at $>$ 473 K. Accordingly, the conversion obtained at this
163	temperature is slightly higher than the equilibrium conversion of acetone to 2 -proanol ⁶¹ .
164	Meanwhile, C-O single bond breaking is unusual over copper; hence, excellent selectivity to
165	2-propanol was obtained over the copper at temperature up to 573 K. Figure S2
166	(supplementary information) emphasizes the thermodynamic limitation for acetone
167	hydrogenation over copper catalyst. Although higher rate can be obtained at higher reaction
168	temperature (473 K), the conversion levels at ~ 50%. At lower temperature (~ 448 K), the
169	conversion can be boosted up at higher contact time. It is worth noting that 2-propanol is the
170	only product over the copper catalyst despite the contact time has reached equilibrium. For
171	further investigation, the contact time in this work was tested within 80 g.h.mol ⁻¹ .

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172	Effect of nickel and copper loading on SiO_2 was studied (5-40 wt%) as shown in
173	Figure 4. When the metal loading is increased, acetone conversion is enhanced due to an
174	increase in number of active sites. The turnover frequency for all Cu/SiO ₂ catalyst is roughly
175	2.1-2.8 x 10^{-3} sec ⁻¹ , as shown in Table S2 (supplementary information). However, the
176	normalized rate (mole of feed converted per hour over mole of the metal loaded) is decreased
177	due to agglomeration of the metal particles, which notably reduces the active metal surface
178	(Table 1). In case of nickel catalyst, the increased metal particle size also leads to an increase
179	hydrogenolysis activity, as seen from Figure 4a. The Ni catalysts with $> 10\%$ loading yield
180	significant amount of methane (~30%). Meanwhile, copper retains its excellent selectivity
181	towards C=O hydrogenation. This suggests that only η -1 adsorption mode is allowed for C=O
182	on Cu surface. ⁵⁸ Hence, 100% selectivity to 2-propanol is obtained over Cu catalyst up to
183	40% loading.

184 As methane was produced over the nickel catalyst at > 473 K, copper was mixed into 185 the Ni catalyst to retard the methane formation. Theoretically, nickel and copper are miscible in wide range of component 62 , as evidenced by TPR (Figure S1). It is clear from Figure 5 that 186 the conversion is generally decreased with copper content in the alloy. A synergistic effect 187 observed at $\sim 25\%$ Cu is presumably due to a better dispersion of the metal phase. At 473 K, 188 no methane is observed from the catalysts with Cu content higher than 40 %. This is because 189 of the hydrogenalysis is a structure sensitive reaction, alloying with Cu shall readily inhibits 190 the adsorption mode that leads to C-C cleavage.⁶³ 191

Dehydration of the hydrogenated product, 2-propanol was separately investigated over H- β catalyst at 448 K. Figure 6 shows that 2-propanol conversion increased with the contact time. Two products, propylene and diisopropyl ether are initially observed in parallel from an intra-molecular dehydration and inter-molecular dehydration, respectively. However, the ether drops gradually at higher contact time (1.5-4.7 g.h.mol⁻¹). This indicates that the ether can be converted to propylene and 2-propanol⁶⁴, as demonstrated by the reaction of diisopropyl ether over H- β (Table 4) and below.



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As also seen from Table 4, zeolite Y and β provide relatively higher activity, as compared to other zeolites. However, the cage structure of Y can retain both feed and products, which promotes the inter-molecular dehydration, as observed with high diisopropyl ether selectivity at low contact time (3 g.h.mol⁻¹). In addition to the structural effect, a closer site-proximity in HY (Si/Al ~8), as compared to that of H- β (Si/Al ~14) would enhance the bimolecular dehydration. This also leads to a more rapid deactivation, as seen from a relatively lower activity of HY after 6 h on stream, despite the acidity of HY is higher.

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208	At higher contact time (15 g.h.mol ⁻¹), it is clearly observed that the catalyst with three
209	dimensional pore opening (H- β) provides higher activity, as compared to those with two and
210	one dimensional pore opening (HZSM-5 and H-Mordenite), respectively. With a comparable
211	Si/Al, this suggests that diffusivity of the feed and products plays important role on
212	dehydration at relative low temperature (448 K). With poor mass transfer, re-hydration may
213	well take place at high contact time. Hence, mordenite gives even lower activity; as compared
214	to ZSM-5 despite the pore size is larger. In addition to the observed activity, ZSM-5 yields
215	only 2% di-isopropyl ether at 55 % conversion while β gives 10% di-isopropyl ether at
216	similar conversion. The result indicates that the medium pore size of ZSM-5 somewhat
217	constrains the size of intermediates and products while the large pores of β provides intrinsic
218	space for the bimolecular reaction. Moreover, the large one-dimensional pore system
219	particularly enhances the inter-molecular dehydration as the feed can be exceedingly retained
220	in the pore. In line with this view, thermogravimetric analysis shows that < 1 % hard coke is
221	detected on the used zeolite with medium pore while > 3 % is observed for the larger ones
222	(Table 3). The TGA under N_2 defines that most of deposits in HZSM-5 are the high
223	molecular weight compounds that cannot diffuse out of pore at the reaction temperature.
224	From Figure 7a, it can be seen that 2-propanol conversion is increased with the

temperature. Selectivity to propylene is also increased with the decrease in di-isopropyl

ether. This is simply because elimination of di-isopropyl ether to propylene is promoted at

high temperature. Again, the effect of pore size is revealed particularly at lower temperature.

228	When H- β was used (Figure 7b), similar pattern to H-ZSM-5 was observed. As discussed
229	earlier, β possesses higher activity, as compared to ZSM-5, but higher selectivity to di-
230	isopropyl ether at low temperature. No higher hydrocarbon was detected for both catalysts at
231	this temperature range, presumably due to the strong adsorption of the feed and ether over the
232	acid sites.

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234 **3.4 Ketones hydrodeoxygenation to olefins**

In this work, hydrogenation – dehydration approach was employed for ketone hydrodeoxygenation. To combine the two reactions with exothermic and endothermic nature into one process, temperature has to be primarily optimized. For nickel - zeolite system, hydrogenation with no hydrogenolysis takes place at 373 - 448 K (Figure 3). While dehydration rate increases significantly above 423 K (Figure 7). Accordingly, only small gap from 423 to 448 K is allowed for a consecutive hydrogenation-dehydration over Ni/SiO₂zeolite system, as illustrated below



For Cu/SiO₂ - zeolite system, no hydrogenolysis can be promoted up to 575 K (Figure 3). However, the reaction over acid site is limited at 473 K to avoid the drastic oligomerization.⁶⁵ Accordingly, the window for hydrodeoxygenation over Cu/SiO₂ - zeolite system is widely opened (423 - 473 K), as illustrated above.

247	Therefore, the temperature at 448 K was selected for Ni/SiO ₂ - zeolite system to
248	obtain the maximum dehydration rate without hydrogenolysis. Since olefin hydrogenation
249	can also be promoted over Ni/SiO ₂ (Table 2), the hydrodeoxygenation is conducted in two-
250	bed system. The ketone is hydrogenated over Ni/SiO ₂ to an alcohol that becomes a feed for
251	the dehydration to olefin over the zeolite bed. On the other hand, hydrogenation of olefin
252	cannot be promoted over copper catalyst. Hence, single bi-functional bed system can be used
253	for hydrodeoxygenation over Cu/SiO ₂ - zeolite catalyst. A higher temperature (at 473 K) was
254	chosen to obtain highest hydrogenation rate without oligomerization of the olefin products.
255	However, an undesirable condensation of acetone may take place over the acid sites.
256	Moreover, the ketone hydrogenation activity is relatively low, as compared to that of the
257	alcohol dehydration, as observed from Figure 4 and Figure 6. Accordingly, the metal
258	component in the bi-functional bed system has to be greater than that of the zeolite.

259 Double bed system of Ni/SiO_2 – zeolite

For this system, HZSM-5 was used to minimize the ether formation (Figure 7). Table 5 shows that up to 60 % conversion can be obtained at 76+7 g.h.mol⁻¹. However, 2-propanol and di-isopropyl ether, which are intermediates, still remain in large amount. By increasing the zeolite bed (76+27 g.h.mol⁻¹), only 10 % 2-propanol is observed without ether. The propylene is produced selectively (90% mol). No aldol product derived from the condensation of acetone on zeolite is detected. This is probably because of strong adsorption of alcohol that prevents the ketone condensation. However, a slight deactivation can be

267 observed for the dehydration bed. This is concluded from a gradual decline in propylene 268 selectivity while the acetone conversion remains unchanged over 7 hours on stream (Figure 8). When a larger ketone, methyl ethyl ketone (MEK), is tested, a similar activity is obtained 269 $(\sim 60 \%)$. However, relative low selectivity to the alcohol (2-butanol) is observed due to the 270 higher reactivity of butanol, as compared to propanol. Again, no ether and aldol product are 271 272 detected for hydrodeoxygenation of MEK. This is presumably due to a larger steric constrain 273 of any C4 species in the zeolite pore which inhibits the bi-molecular reaction (either 274 etherification of the alcohol and aldol condensation of the ketone). Hence, the butanol 275 produced from MEK hydrogenation is selectively dehydrated to n-butene (1-butene + 2butene; 87%), and then isomerization to *i*-butene (13%). 276

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Physical Cu/SiO_2 – *zeolite* mixed bed

For a single mixed bed, 5% Cu/SiO₂ was physically mixed with the zeolites using 278 high metal/zeolite ratio at 473 K to prevent the condensation of ketone. From Table 6, it is 279 seen that 68 % conversion with excellent selectivity to propylene (96 %) is obtained over the 280 76+7 bed (For contact time, 76+7 refers to 76 g.h.mol-1 of Cu/SiO2 and 7 g.h.mol-1 of 281 282 HZSM-5; 83 g.h.mol-1 in total). A significant improvement in acetone conversion over the mixed bed, as compared to the equilibrium value (39% at 473 K, Figure 3) for acetone-283 284 alcohol, is presumably due to a simultaneous conversion of 2-propanol to propylene over the acid catalyst. This will noticeably reduce the rate of 2-propanol dehydrogenation to acetone, 285 and hence draw the conversion of the acetone beyond such equilibrium level. With this 286

catalyst composition and reaction conditions, no condensation products from acetone is
observed. In fact, small amount 2-propanol (3 %) is intentionally retained to inhibit the
condensation of the ketone.

However, when H- β (14) is primarily mixed (76+7 g.h.mol⁻¹), deactivation is severe. 290 291 The acetone conversion at 6 hours on stream drops drastically, as compared to ZSM-5. This 292 is because β possesses a larger pore size, as compared to ZSM-5. This facilitates a better diffusion and adsorption of acetone in the pore of β . Hence, relatively less fraction of the 293 294 acetone interact with the metal surface and hydrogenation is limited. In line with this view, the aldol products namely mesityl oxide, acetic acid and *i*-butene ($\sim 20\%$ in total) is instead 295 produced, as previously observed in literatures⁶⁶⁻⁶⁷. Since aldol condensation is largely 296 297 pronounced, high molecular weight deposits (Table 3) and a rapid deactivation can be expected. Accordingly, reducing the contact time of β to 2 g.h.mol⁻¹ can offer 92 % propylene 298 299 selectivity without the condensation products. However, the acetone conversion is still lower 300 than that over Cu/SiO₂/HZSM-5.

When larger ketone (i.e. MEK) is tested over 5% Cu/SiO₂ - HZSM-5 mixed catalyst (Table 7), the conversion (56 %) is slightly lower than the acetone. This is probably due to steric hindrance of the adsorbed ketone on the metal surface. High selectivity to 1-butene and 2-butene (82 %) was observed with some isomerization products (*i*-butene; 14 %) and 2butanol (4 %). For larger cyclic ketone, cyclohexanone is more reactive than the aliphatic ketone. 96 % selectivity to cyclohexene is obtained with some methylcyclopentenes (4 %).

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307	This is presumably due to the stronger adsorption of cyclohexanone, as compared to those of
308	acetone and MEK. It is also worth noting that reducing the reaction temperature or contact
309	time affects the dehydration rate significantly.

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Bi-functional catalyst: Cu/zeolites

312 As high selectivity to olefin can be observed over Cu/SiO₂/HZSM-5 system, Cu 313 incorporated ZSM-5 is tested for acetone conversion. From Table 7, 100% acetone conversion can be obtained at 83 g.h.mol⁻¹, as compared to 67.5% from the physical mixed 314 bed at 76+7 g.h.mol⁻¹ (Table 6). It is worth noting that a zeolite with higher Si/Al is used for 315 316 the bi-functional catalyst in order to keep the number of acid sites and metal loadings the 317 same as in the physical mixed bed system. Despite of that, a remarkable increase in activity, 318 as compared to physical mixed catalyst, is probably due to the close proximity for the metal 319 and the acid site. The hydrogenated intermediate, 2-propanol, may well be removed 320 immediately by dehydration over a near-by acid sites, diminishing reversible dehydrogenation of the 2-propanol formed back to acetone. This successive dehydration of 2-321 322 propanol to propylene would significantly increase the rate of acetone conversion over the Cu 323 catalysts. In line with this view, the turnover frequency for hydrodeoxygenation (11.8×10^{-3}) sec⁻¹) is approximately four-fold higher than that of hydrogenation (2.6 x 10^{-3} sec⁻¹) at 473 K 324 325 (Table S2). However, propane is also produced over the bi-functional catalyst, probably via 326 the hydrogen transfer. It is likely that, at high contact time, propylene can be adsorbed onto 327 the acid site. The hydrogenation of the adsorbed propylene may well be promoted by metal-328 acid site interaction. In other words, the adsorbed hydrogen on the metal can be source of 329 hydrogen transfer to the adsorbed olefin on the proximate acid site. It should be noted that direct hydrogenation of propylene over copper metal surface is not the case, as evidenced and discussed previously. The propylene hydrogenation can be diminished by the decrease in contact time. This is because relatively small amount of propylene can be adsorbed on the acid site when large amount of alcohol is present in the reaction stream. For a comparison, 5%Cu/HY (100) shows a higher acetone conversion. This is because the HY (100) possesses a higher adsorption and dehydration activity, as compared to HZSM-5 (250) as discussed earlier

Over 5%Cu/HY (100), the activity is in the order of MEK < cyclohexanone <337 338 acetone, respectively. The observed low activity for MEK is due to a rapid deactivation as 339 seen by relatively higher carbon deposit shown in Table 3. As discussed previously, oligomerization is increasingly promoted for the larger ketone, particularly over the catalyst 340 with larger pore opening such as HY. Accordingly, as the catalyst is deactivating, the 341 observed activity of cyclohexanone conversion at 6th hours on stream become slightly lower 342 than that of acetone, despite cyclohexanone shows a higher conversion over the mixed 343 catalyst (Table 6). This is because the large pore size with the cage structure of Y enhances 344 345 the oligomerization of cyclohexanone, as compared to that over the medium channel of HZSM-5. The amount of coke deposit is in line with the observed activity (Table 3). 346

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348 4. Conclusion

349	The optimization of reaction conditions and catalyst system for both hydrogenation
350	and dehydration leads to a potential approach for ketone deoxygenation to olefins. Nickel
351	catalyst is more reactive than the copper, but it is also capable to promote hydrogenation of
352	the olefin produced. Accordingly, a double bed system containing Ni/SiO_2 and zeolites is
353	ideal for ketone hydrodeoxygenation to olefins. In contrast, the mixed Cu/SiO2-zeolites and
354	Cu/zeolites can be used for single bed system. For the latter case, copper can hydrogenate
355	ketone to alcohol without hydrogenolysis and it is somewhat inert for olefin hydrogenation.
356	While zeolite can promote dehydration of the alcohol formed at the same temperature range
357	(\leq 473 K). A close-proximity found in Cu/zeolites synergistically promotes the activity
358	towards olefin formation as the alcohol formed is subsequently removed over the neighboring
359	acid sites. The simultaneous conversion of alcohol to alkene, observed in both single bed
360	systems, boost the ketone conversion to exceed the ketone-alcohol equilibrium level.

361

362

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Selective Hydrodeoxygenation of Bio-Oil Derived Products: Ketones to Olefins

Ayut Witsuthammakul and Tawan Sooknoi*

Graphical Abstract



Hydrogenation of a ketone primarily takes place on the metal surface resulting in a corresponding alcohol that can be dehydrated to olefin over the acid function. A rapid dehydration synergistically prevent reversible dehydrogenation of alcohol while excessive olefin hydrogenation can be limited over selected metal.

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Table & Figure

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Table 1 Copper surface area, copper dispersion, and acidity of Cu catalysts

Catalyst	Cu area	% Cu dispersion	Acidity (µmol/g)	
	(m^{2}/g_{Cu})		Weak	Strong
2%Cu/SiO ₂	257	n/a	-	-
5%Cu/SiO ₂	646	95	-	-
10%Cu/SiO ₂	437	66	-	-
15%Cu/SiO ₂	220	24	-	-
5%Cu/HY (100) ^a	499	65	158	62
HY (100) ^a	-	-	54	65
5%Cu/HZSM-5 (250) ^a	414	54	-	-

^aNumber in the parenthesis represents Si/Al of the sample

 Table 2 Initial activated temperature for hydrogenation and hydrogenolysis over metal catalysts

from 373 – 623 K

Catalyst		Initial activated temperatu	ire ^a
	Acetone hydrogenation to i-propanol	Acetone hydrogenolysis to paraffins	Propylene hydrogenation to propane
2%Cr/SiO ₂	inactive	inactive	-
10%Cr/SiO ₂	inactive	inactive	-
2%Fe/SiO ₂	inactive	inactive	-
10%Fe/SiO ₂	473K	inactive	523K
2%Co/SiO ₂	523K	523K	498K
2%Ni/SiO ₂	< 373K	473K	< 398K
2%Cu/SiO ₂	< 373K	Inactive	Inactive
2%NiCu/SiO ₂ [50:50]	< 373K	573K	< 473K
2%Pd/SiO ₂	423K	573K	Active [58-59]

^aTemperature at which >3% conversion is obtained over the catalyst at W/F of 30 g.h.mol⁻¹,

 H_2 as carrier 30 m/min

Catalyst	Feed	Temp	Contact time	V	Veight loss (%)	
		K	(g.h.mol ⁻¹)	473-573 K	>573 K	Total
5%Ni/SiO ₂	Acetone	448	15	-	-	-
5%Cu/SiO ₂	Acetone	473	15	-	-	-
HY(7.5)	Acetone	448	3	-	2.6	2.6
Η-β(14)	Acetone	448	3	-	5.5	5.5
H-Mordenite(15)	Acetone	448	15	2.1	5.4	7.5
HZSM-5(13)	Acetone	448	15	6.1	0.88	7.0
HZSM-5 (13); TGA in N ₂	Acetone	448	15	5.9	0.00	5.9
5%Cu/SiO ₂ +HZSM-5(13)	Acetone	473	76+7	1.9	2.2	4.1
	MEK	473	76+7	2.1	2.4	4.5
	Cyclohexanone	473	76+7	2.0	2.0	4.0
5% Cu/SiO ₂ +H- β (14)	Acetone	473	76+7	1.3	1.9	3.2
	Acetone	473	76+2	1.6	1.0	2.6
5%Cu/HY(100)	Acetone	473	19	1.9	1.3	3.2
	MEK	473	19	4.3	2.1	6.4
	Cyclohexanone	473	19	2.8	1.6	4.4

air-zero, 10K/min

cript

Catalysis

Zeolite (Si/Al)	Feed	Contact time	Conversion	Selectivity (C mol%)			
		(g.h.mol ⁻¹)	(C mol%)	Propylene	Di-isopropyl ether	<i>i</i> -propanol	C6 olefir
IY (8)*	<i>i</i> -propanol	3	18.0	51.4	48.6	-	-
Ι- β (14)	<i>i</i> -propanol	3	58.8	90.3	9.69	-	-
IY (8)	<i>i</i> -propanol	15	89.5	99.6	0.37	-	-
I- β (14)	<i>i</i> -propanol	15	99.5	100	0.00	-	-
I-Mordenite (15)	<i>i</i> -propanol	15	27.9	80.0	20.0	-	-
IZSM-5 (13)	<i>i</i> -propanol	15	54.6	98.0	1.96	-	-
I-β (14)	Di-isopropyl ether	15	83.5	69.4	0.00	28.7	1.93

1. 1 11 1 1

Results at 6th hour on stream, 448K, H₂ as carrier 30 m/min

*numbers in parenthesis represent Si/Al

Table 5 Ketones hydrodeoxygenation on 5%Ni/SiO₂ - HZSM-5 (13) double-bed system

Feed	Contact time (g.h/mol)	Conversion				
	1^{st} bed + 2^{nd} bed	(C mol%)	Alcohols	Ethers	n-Alkenes	i-Alkenes
Acetone	76+7	61.9	52.2	0.45	47.4	0.00
	76+29	59.9	15.8	0.00	84.2	0.00
MEK	76+7	61.8	39.4	0.00	51.6	9.00
	76+29	58.7	0.00	0.00	87.1	12.9

Result at 6th hour on stream, 448 K, (1st bed+2nd bed), H₂ as carrier 30 ml/min

Feed	Catalyst	Temp.	Contact time (g.h/mol)	Conversion		Select	tivity (C mol%)		
		(K)	Metal+Zeo lite	(C mol%)	Alcohols	n-Alkenes/ cycloalkenes	i-Alkenes/ methyl cycloalkenes	Acetic acid	Mesi ⁺ y oxid;;
Acetone	5%Cu/SiO ₂ +HZSM-5 (13)	473	76+7	67.5	3.24	95.6	0.00	0.00	0.00
	5%Cu/SiO ₂ +H-β (14)	473	76+7	21.1	0.00	75.1	1.12	2.34	16.6
		473	76+2	40.9	5.57	92.1	0.00	0.00	0.00
MEK	5%Cu/SiO ₂ +HZSM-5 (13)	473	76+7	56.2	4.36	82.1	13.6	0.00	0.00
Cyclohexanone	5%Cu/SiO ₂ +HZSM-5 (13)	473	76+7	100	0.00	95.8	4.21	0.00	0.00
		473	27+3	45.5	43.0	57.0	0.00	0.00	0.00
		423	76+7	57.6	64.3	35.7	0.00	0.00	0.00

Result at 6^{th} hour on stream, H₂ as carrier 30 ml/min

Table 7 Ketones hydrodeoxygenation on 5%Cu/zeolites

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ownloaded b	Table 7	Ketones hydroc	leoxygenation	n on 5%Cu/	zeolites			
2015. D	Feed	Catalyst	Contact time	Conversion		Selectiv	vity (C mol%)	
on 27 April			(g.h/mol)	(C mol%)	Alcohols	n-Alkenes / cycloalkene	<i>i</i> -Alkenes / methyl cycloalkenes	Alkanes
Published	Acetone	5%Cu/HZSM-5 (250)	83	100	0.00	68.9	0.00	31.1
		5%Cu/HZSM-5 (250)	19	51.6	15.9	81.1	0.00	2.01
		5%Cu/HY (100)	19	90.5	6.3	88.3	0.00	5.40
	MEK	5%Cu/HY (100)	19	24.7	0.00	87.3	12.7	0.00
	Cyclohexanone	5%Cu/HY (100)	19	85.4	18.2	81.8	0.00	0.00

Result at 6th hour on stream, H₂ as carrier 30 ml/min, 473 K,



499x353mm (300 x 300 DPI)







499x378mm (300 x 300 DPI)







500x396mm (300 x 300 DPI)







508x386mm (300 x 300 DPI)



461x351mm (300 x 300 DPI)



479x346mm (300 x 300 DPI)



472x346mm (300 x 300 DPI)



