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Selective hydrodeoxygenation of bio-oil derived products: Acetic acid to propylene over hybrid CeO_2-Cu/zeolite catalysts

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Abstract

Conversion of acetic acid, the light oxygenate from biomass pyrolysis, to propylene can be achieved via keto-hydrodeoxygenation (KHDO) over hybrid CeO_2-Cu/zeolite catalysts at >573 K under atmospheric H_2. The catalyst containing CeO_2 and Cu/HY (25wt% of Cu/HY) was employed to obtain up to 85% conversion of acetic acid with 49% selectivity to propylene. Acetone, propylene and propane are obtained via ketonization-hydrogenation-dehydration over the three-component catalyst while ethanol, acetaldehyde, ethylene, ethane and ethyl acetate can also be produced from hydrogenation-dehydration over Cu/zeolites alone. The catalyst containing Cu/HY provides higher selectivity to olefin products, as compared to that containing Cu/HZSM-5. The reaction is suppressed by the presence of water. Nevertheless, high catalyst stability (>60 hours on stream) can be obtained. The KHDO can be applicable for the conversion of acetic acid, a biomass derived product, to hydrocarbons using a sequential bed system of the three-component catalyst and HZSM-5 catalyst.

1. Introduction

Today the world's highest demand for petrochemical feedstock is small olefins, especially propylene and ethylene.[1,2] As fossil reserves are running low, the biomass-derived products have become promising future sources. The strategy involves deoxygenation of small oxygenates to olefins with a minimal hydrogen consumption. Among those oxygenates derived from, acetic acid is a potential feedstock as it can be largely obtained from biomass pyrolysis[3,4] and fermentation of agricultural products and wastes.[5] However, the controlled deoxygenation of acetic acid to olefins is somewhat challenging. This is due to high oxygen content in the molecule, as compared to other feedstocks. Many works have focused on partially deoxygenation via ketonization over metal oxide catalysts (MgO, CdO, MnO_2, and Fe_2O_3) to acetone, CO_2 and water.[6-11] Alternatively, the dehydration of acetic acid to ethenone, which leads to rapid deactivation of catalyst, was also reported.[12,13] Meanwhile, the hydrodeoxygenation (HDO) of acetic acid have been investigated over Pt-Sn alloy, Cu and Co catalysts. In this case, ethanol, acetaldehyde and ethyl acetate are obtained.[14-16] The esterification facilitated by acidic support can increase the degree of oxygen removal but inhibit the further hydrogenation to hydrocarbons.[17] Many noble metals including Pt, Pd, Ni, and Rh were found to be effective catalysts for liquid and gas phase hydrogenation of acetic acid to hydrocarbons.[4,15,18,19] However, high H_2 pressure (> 4 MPa) or high temperature (typically > 698 K) is required to obtain appreciable activity over these metals.[4,20] In addition, the hydrocarbons obtained are mainly paraffins (ethane and methane), presumably due to successive hydrogenation, decarboxylation and hydrogenolysis over those metals.[15,18,21]

According to obstacles mentioned above, a novel approach for obtaining olefins from acetic acid is proposed in this work via keto-hydrodeoxygenation process. Previous work demonstrated that ketone could be hydrodeoxygenation to olefin via a controlled hydrogenation-dehydrogenation.[22] At the same time, acetic acid can be selectively ketonized over various metal oxides that are relatively inert for hydrogenation and dehydration.[23-25] Hence, it is possible to incorporate these metal oxides into the hydrodeoxygenation catalysts for a single stage conversion of acetic acid to olefins via ketonization-hydrogenation-dehydration. In this work, CeO_2 will be selected as ketonization catalyst due to high activity especially at low temperature.[9] Cu/HY and Cu/HZSM-5, showing high hydrodeoxygenation activity from the previous work,[22] will be incorporated for hydrogenation-dehydration of the ketone formed. Despite the difference in catalytic parameters for each step, formulation of the three-component catalyst (CeO_2/Cu/Zeolites) that works isothermally at relatively mild condition will be optimized. Their effects on the reaction and products are also highlighted, together with the role of water presents in acetic acid feed.

2. Experimental procedure

CeO_2 (99.9%) was purchased from Sigma-Aldrich®. HY and HZSM-5 were commercially obtained from Tohso and Zeochem®, respectively. The metal oxides and zeolite were calcined in air at 723 K for 5 h before use. 5 %wt Cu/zeolites were simply prepared by incipient wetness impregnation. Briefly, $Cu(NO_3)_2.3H_2O$ precursor (Ajax Fine Chem) was dissolved in deionized water (~0.01 M) and slowly droped onto zeolites until wet. The sample was dried at 333 K in an oven for 15 min, and then the loading was repeated until desired metal content was reached. The samples were kept to dry at 333 K overnight and calcined in air at 723 K for 5 h. The CeO_2 was physically mixed with Cu/zeolite to obtain hybrid CeO_2-Cu/zeolite catalyst (7-40 %wt Cu/zeolites) then pelletized to the size of 600–850 µm. The three-component catalyst is referred to as CeO_2-Cu/Zeolite(X), where X is %wt of Cu/Zeolite in the mixed catalyst.

Elemental composition of the catalysts 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/P_0. Reducible metal oxide species in the catalysts were analyzed by temperature programmed reduction (TPR). The catalysts were treated in air at 723 K for 5 hours prior to heating from 323-1173 K in 10% H_2/Ar. The hydrogen consumption was recorded with an on-line thermal conductivity detector (VICI).[26] Copper dispersion on zeolites support was also analyzed by surface-selective TPR technique. Briefly after typical TPR, the sample was *in situ* treated with N_2O

for selective oxidation of surface copper to copper (I) oxide at 333 K for 2 hours. Then, the surface-oxidized sample was subjected to a secondary TPR, in which the reduction took place only at the copper (I) oxide on the surface. The surface copper could be calculated directly from hydrogen consumption of Cu(I) → Cu(0) as described by Hoang *et al.*[27] The Cu dispersion is referred to mole ratio of Cu on the surface over the bulk. Detail of calculations for Cu dispersion using this procedure can be found as described in by Sagar *et al.*[28] Acidity of all zeolite samples was quantified by NH_3-TPD. 1% NH_3/He was pre-adsorbed at 323 K. TPD was carried out in He at 10 K.min^{-1} from 323–973 K.[29] The particle size of Cu on support was estimated by TEM with LaB_6 emitter (FEI Tecnai G^2 20, 200 kV).

The catalytic testing was conducted in a fixed bed flow reactor (6 mm i.d. Pyrex®) at atmospheric pressure. The CeO_2-Cu/Zeolites catalysts were primarily activated at 723 K (2 K.min^{-1}) under stream of air (30 ml.min^{-1}) for 5 h. Subsequently, the catalyst was flushed with N_2 and treated in H_2 at 723 K for another 2 h. The system was cooled down to the reaction temperature (573 K) and the reaction was carried out at atmospheric hydrogen pressure. The acetic acid was introduced by a syringe pump at the rate of 0.5-1.0 g/h. The products were analyzed by an on-line GC-FID. A Hayesep® P (1/8” X 8’) was used as separating column.

3. Results and discussions

3.1 Catalyst characterization

All copper/zeolite samples possess relatively high surface area (> 360 $m^2.g^{-1}$) with dispersion 54-65% as tabulated in Table 1. The copper loading is approximately 5%wt for both zeolites. The CeO_2 shows relatively low surface area, due to low porosity (< 11 $m^2.g^{-1}$). The increase in weak acidity of Cu/HY and Cu/HZSM-5, as compared to the parent zeolites (NH_3-TPD), is an evidence for exchangeable copper cation in zeolites.

The Cu/HY and Cu/HZSM-5 samples show two reduction peaks at 473 and 520 K (Figure 1), corresponding to copper oxide aggregates and highly dispersed copper oxide in the pore of zeolite[30,31], respectively. The Cu dispersion on HY is somewhat higher than that on HZSM-5 (peak at ~520 K), presumably due to a better diffusion of the Cu precursor in the larger pore of HY. This is consistent with the TEM images shown in Figure 2. The Cu/HY possesses relatively small Cu particles (Figure 2a) and some of them (dark spot) are well aligned in the pore of HY (light grey plane). While a relatively lower Cu dispersion on HZSM-5 can be evidenced by large semicircle Cu particles, deposited on the external surface of HZSM-5 crystals (Figure 2b).

3.2 Catalytic activity testing

Effect of reaction temperature

Figure 3 displays the effect of temperature on acetic acid conversion over the three-component catalyst containing 75%wt of CeO_2 and 25%wt of Cu/HY (CeO_2-Cu/HY(25)). The conversion increases gradually with the reaction temperature and reaches 100% at above 598 K (Figure 3a). The C_3 products including acetone, propylene, and propane and CO_2 are produced via ketonization of acetic acid and subsequent hydrodeoxygenation of the acetone formed, so called keto-hydrodeoxygenation (KHDO) process. The selectivity to acetone is relatively high at 548 K suggesting that ketonization activity can be readily promoted over the CeO_2 component while the hydrogenation-dehydration of the acetone produced is not facilitated at this temperature. This is probably due to competitive adsorption by acetic acid over the Cu/HY at low temperature. It is worth noting that, over Cu/zeolites, the hydrogenation-dehydration of acetone alone can be accomplished at > 473 K, as reported in previous work.[22] When the temperature was increased from 548-598 K, the selectivity to propylene increases with the decrease in acetone. This is not only because acetic acid is less competitive at this temperature, but also the hydrogenation-dehydration is increasingly promoted by the Cu/HY component. However, the propylene selectivity turns down with a sharp increase in propane at > 598 K despite that the Cu alone cannot promote propylene hydrogenation.[22,32] The observed propane yield in this case is presumably derived from H-transfer process. As propylene is formed, it would be protonated on the acid sites within a proximate vicinity of Cu. Hence, some of the protonated propylene can be hydrogenated by H-transfer from the proximate metal sites. This is particularly the case at high temperature since H-transfer can also be promoted from the hydrocarbon pools.[33-35]

As mentioned earlier that acetic acid competitively adsorbed on Cu/HY at low temperature, the C_2 products including acetaldehyde, ethanol, ethylene, and ethane are also observed, together with ethyl acetate (Figure 3b). The result from acetic acid conversion over Cu/zeolites alone (Table 2) reveals that these C_2 products are derived from a direct hydrodeoxygenation (HDO) of acetic acid. Over copper catalyst, the acetic acid can be hydrogenated to acetaldehyde and then ethanol. Acetaldehyde selectivity is decreased while ethanol, ethylene, and ethane are increased when the reaction temperature is raised from 548-598 K (Figure 3b). Since ethanol can be readily dehydrated to ethylene over the acid sites at high temperature, the acetaldehyde-ethanol equilibrium is not limited over Cu/HY as ethylene is formed. Accordingly, acetaldehyde is largely consumed by hydrogenation-dehydration process as the temperature is raised. In a manner similar to propane, ethane can also be produced by H-transfer to ethylene at relatively high temperature.

In fact, the observed high selectivity of ethyl acetate (Figure 3a) at low temperature suggests that ethanol is readily formed, but captured by acetic acid via esterification. However, the selectivity to ester decreases when the temperature is increased due to the running low of acetic acid. It is noted that no esterification between acetic acid and *i*-propanol was found probably due to rapid dehydration of the *i*-propanol, as compared to the ethanol.

The selectivity to ethanol, ethylene and ethane turn down at > 598 K (Figure 3b) while C_3 hydrocarbons is largely observed. This is because the KHDO of acetic acid is more favorable at high temperature, as compared to the direct HDO. This is in consistence with observed increase in ketonization activity of CeO_2 at high temperature as shown in Figure S1. It is worth noting that, as the catalyst contains acidic zeolite (CeO_2-Cu/HY(25)), the ethylene and propylene produced can be further oligomerized to C_4-C_5 olefins, particularly at > 598 K. According to the products observed, the overall reaction scheme for keto-hydrodeoxygenation of acetic acid can be proposed in Figure 4.

Effect of the catalyst composition

The KHDO of acetic acid depends largely on the component of catalyst, as shown by the experiments with various %weight of the CeO_2 in the catalyst composition (Figure 5). It is clear that the acetic acid conversion increases when the CeO_2 is increased (Figure 5a). Since the ketonization of acetic acid is primarily promoted in KHDO, the catalyst with high CeO_2 content would be more active for overall acid conversion. In consistence with this result, the yields of KHDO products, including acetone (Figure 5a) and propylene (Figure 5b), are also increased, together with CO_2. However, the insufficient Cu/HY results in a drop of subsequent HDO activity, as seen by a decline in propylene yield when CeO_2 content is higher than 75%wt (CeO_2-Cu/HY(25), Figure 5b). The increase in CeO_2 plays no significant role for direct HDO of acetic acid initially. Yields of ethyl acetate and acetaldehyde remain similar from 60 to 75%wt CeO_2 (CeO_2-Cu/HY(40) to CeO_2-Cu/HY(25)). The observed increase in ethanol yield (Figure 5b) is resulted from a reduced concentration of acetic acid remained in the reaction stream when ketonization is boosted. In line with this view, dehydration to ethylene is also promoted initially. However, at CeO_2 content higher than 86%wt (CeO_2-Cu/HY(14)), the overall HDO activity is significantly suppressed. This is seen from drop of propylene, ethyl acetate, ethanol, acetaldehyde and ethylene. According to the results, it is clear that CeO_2 play significant role for initial activation of acetic acid to acetone while CuHY is essentially required for olefin production from both HDO of acetone produced and direct HDO of acetic acid. Hence, the combination of these catalysts would lead to a successful olefin production from acetic acid. With the reaction conditions used in this study, optimum yields of propylene and ethylene can be obtained over CeO_2-Cu/HY(25) with ~55% conversion.

Effect of the zeolite framework

It is clear from Figure 6a that CeO_2-Cu/HZSM-5(25) is more active for acetic acid conversion, as compared with CeO_2-Cu/HY(25). This is because a similar level of conversion is obtained from both catalysts, despite that Cu/HZSM-5 possesses lower acidity (by NH_3-TPD, Table 1). However, at the similar level of conversion, acetone yield from CeO_2-

Cu/HZSM-5(25), (~34%) is higher than that from CeO_2-Cu/HY(25) (~24%) while propylene yield from both catalysts is not so significantly different (3-5% differences) (Figure 6b). At steady state, one may expect that as higher acetone is left unconverted, yield of propylene should be accordingly lower. Nevertheless, the observed increased yield of acetone without proportional change in propylene yield can be attributed to the fact that ketonization of acetic acid to acetone can also be facilitated by HZSM-5 (250).[36,37] This is evidenced by a noticeable selectivity to acetone (11.3%) when acetic acid was fed over Cu/HZSM-5 alone (Table 2). Accordingly, the ketonization of acetic acid is additionally promoted as seen by higher yield to CO_2 over CeO_2-Cu/HZSM-5(25). However, the further hydrogenation-dehydration of the acetone produced to form propylene is somewhat limited over this catalyst. This is probably due to the competitive adsorption of acetic acid over the acetone in the zeolite and also the lower Cu dispersion as mentioned earlier (Figure 2).

Although CeO_2-Cu/HZSM-5(25), seems to be less effective for KHDO to produce propylene, this catalyst provides high selectivity for direct HDO of acetic acid to ethylene. It can be seen from Figure 6c that, higher yield to ethylene can be obtained from CeO_2-Cu/HZSM-5(25). In the opposite manner, CeO_2-Cu/HY(25) gives mainly ethyl acetate that is an ester of acetic acid and ethanol, derived from direct HDO of acetic acid (Figure 6a). In a support manner, the results in Table 2 provide the same conclusion as above. Over Cu/HY, high selectivity to ethyl acetate is obtained while ethylene selectivity is significantly enhanced over Cu/HZSM-5. This is presumably because esterification can be inhibited by the confinement of the medium pore zeolite; HZSM-5, which in turn, promotes mainly monomolecular dehydration of the ethanol formed to ethylene. It is worth emphasizing again that CeO_2-Cu/HZSM-5(25) provides much lower selectivity to ethyl acetate despite that the same level of conversion is obtained for both catalysts. This means that acetic acid must be converted to acetone from both CeO_2 and zeolite component in the CeO_2-Cu/HZSM-5(25). In a different manner, the ketonization is promoted solely by CeO_2 component in the CeO_2-Cu/HY(25) and the Cu/zeolite component of this catalyst facilitates mainly hydrogenation-dehydration and also the esterification.

Although several reaction networks take place over these three component catalysts, both CeO_2-Cu/HZSM-5(25) and CeO_2-Cu/HY(25) possess relatively high stability up to 60 and 30 hours on stream, respectively. However, a slightly drop in hydrogenation-dehydration over CeO_2-Cu/HZSM-5(25) can be noticed. This is presumably because ketonization of acetic acid to acetone also takes place over the Cu/HZSM-5 component, as discussed earlier. Hence, some of the acetone formed over the acid site may well undergo aldol condensation to higher MW products deposited in the pores.[38,39] On the opposite manner, no ketonization of acetic acid take places over Cu/HY, only hydrogenation-dehydration of acetone produced over CeO_2 component, is promoted over the Cu component in CeO_2-Cu/HY(25). Together with a high dispersion of Cu active site in this catalyst, acetone can be readily hydrogenated. Hence, the CeO_2-Cu/HY(25) provides a relatively higher stability for propylene production, as compared to the CeO_2-Cu/HZSM-5(25).

Physical mixed bed vs Sequential bed

To minimize direct HDO of acetic acid taking place over Cu/zeolite, two separated beds containing CeO_2 and Cu/HY catalyst was tested at the same total contact time (343+114 g.h.mol^{-1}) as the physical mixed bed (457 g.h.mol^{-1}). It can be seen from Table 3 that the sequential bed gives a relatively higher conversion, as compared to the physical mixed bed system. This is because, in the physical mixed bed, part of acetic acid is in contact with Cu/zeolite that possesses higher surface area, as compared to the CeO_2. Hence, a relatively less fraction of acetic acid is in contact with the CeO_2 and a lower activity can be expected over the physical mixed bed. This is because the ketonization is kinetically second order and highly sensitive to the partial pressure of acetic acid [25,40]. Accordingly, as the virtual pressure of acetic acid on the catalyst surface is reduced, the rate is markedly decreased. In a support manner, the reaction with the same contact time, but higher acetic acid partial pressure, provides a higher activity (Table 3). This emphasizes the role of acetic acid partial pressure on the ketonization activity, as discussed previously.

For the sequential bed, the acetic acid is solely in contact with CeO_2 in the first bed. Accordingly, a higher conversion of acetic acid to acetone can be expected, as also seen from an increase in CO_2 selectivity. The higher ketonization efficiency in the sequential bed also leads to the higher propylene selectivity after the second bed (Cu/HY). This is because the competitive adsorption by acetic acid over Cu/HY is reduced as more acetone is produced from the first bed and less acetic acid is remained in the reaction stream. Accordingly, hydrodeoxygenation of acetone can be readily promoted while the products from direct HDO of acetic acid are noticeably lower than those obtained from the mixed catalyst (i.e. ethyl acetate selectivity decreases from 29.6 to 4.3%). However, the paraffinic hydrocarbons (propane and ethane) were detected from the sequential bed system, probably due to higher H-transfer efficiency at high conversion.

Effect of water

Together with acetic acid, water is always present in gas stream from the pyrolysis biomass. Hence, the effect of water on the direct HDO is primarily studied as shown in Table 2. It can be seen that the conversion is significantly drop when 50%wt acetic acid (aq) is used as feed. This is due to (i) the effect of feed dilution as mentioned earlier and (ii) an interaction of water with the three component catalyst (CeO_2-Cu/HY(25)) . To verify the later, an experiment with alternate switching between acetic acid and aqueous acetic acid were tested as displayed in Figure 7. It can be seen that the acetic acid conversion drops markedly after the feed is replaced by aqueous acetic acid. Nevertheless, the activity can be fully recovered after water withdrawal. This is clearly due to the competitive adsorption between acetic acid and water on the catalyst (Figure 7a). The presence of water strongly affects the olefin yields including propylene and ethylene. This is not only because the conversion is decreased, but water would also interact preferentially with the zeolites. Hence, hydrogenation-dehydration of the acetone formed and direct HDO of acetic acid are somewhat inhibited. The observed similar yield of acetone after introducing water is attributed to a combination effect between (i) a reduced ketonization (to form acetone) over the CeO_2 component and (ii) a decrease in hydrodeoxygenation (to convert acetone) over the Cu/HY. The presence of water also decreases yield of ethyl acetate, as the esterification is a reversible process. Moreover, the intermediates carbonyl compound i.e. acetaldehyde is increased with a decrease in ethanol, as the hydrogenation activity is suppressed (Figure 7b). These results are in agreement with the direct HDO of acetic acid over Cu/HY as tabulated in Table 2. It is worth noting again that water does not permanently deactivate the catalyst. As seen in Figure 7, the activity and selectivity of all products was recovered after water was removed.

Light distillated hydrocarbons from KHDO of acetic acid

In the practical point of view, a separate bed system would provide more advantage in controlling and tuning the catalyst performance. As olefins are obtained from KHDO of acetic acid, adding another sequential bed of HZSM-5 (Si/Al ~ 13) can lead to a production of higher hydrocarbon as shown in Figure 8. With excess of catalyst (the sequential beds of CeO_2-CuHY-HZSM-5), the hydrocarbon products including light olefins (ethylene, propylene, and butylene), LPG (C2-C4 paraffins), gasoline (C5-C10 olefins), and C7-C9 aromatics can be obtained from acetic acid. A slight increase of selectivity to intermediate acetone with the decrease of paraffins production indicates that the deactivation also takes place, presumably over the Cu/HY catalyst. While, the continuous increase in propylene selectivity with a decrease in C5-C10 olefins and C7-C9 aromatics selectivity are evidences for the HZSM-5 deactivation, which is typically observed for acid-catalyzed reaction. Nevertheless, this clearly demonstrates a potential catalyst system/process for conversion of acetic acid to hydrocarbon products.

4. Conclusion

The acetic acid can be successfully converted to propylene via keto-hydrodeoxygenation (KHDO) over the three component catalyst containing CeO_2 and Cu loaded acid zeolites (CeO_2-Cu/HZSM-5(25) or CeO_2-Cu/HY(25)) at relatively low temperature (573 K) and atmospheric pressure. Ketonization of acetic acid to acetone initially takes place and the acetone formed is subsequently hydrogenation-dehydration to propylene. Direct hydrodeoxygenation of acetic acid is also observed producing ethylene and other C_2-oxygenates. With higher Cu dispersion, CeO_2-Cu/HY(25) provides higher stability and more selective conversion of acetic acid to olefin products, as compared to that over CeO_2-Cu/HZSM-5(25). The presence of water suppresses the overall activity, particularly the hydrogenation-dehydration. With a sequential bed system composing of CeO_2, Cu/HY and HZSM-5, the KHDO can be applicable for the conversion of acetic acid, a biomass derived product, to olefins and higher hydrocarbons.

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Keyword: ketonization; hydrodeoxygenation; Cu/zeolites; acetic acid; olefins

Note

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1 *Market Study: Propylene*, Ceresana, 2014.

2 M. Eramo, *Global Ethylene Marketing Outlook [slide]*, IHS Chemical, 2015.

3 C. A. Mullen and A. A. Boateng, *Energy Fuels,* 2008**, 22**, 2104–2109.

4 J. J. Bravo-Suarez, V. Schwartz and M. K. Kidder, *Novel Materials for Catalysis and Fuels Processing,* American Chemical Society, USA, 2013.

5 A. Seidel, *Kirk-Othmer encyclopedia of chemical technology vol.1*, John Wiley and Sons, Inc., New York, 1998.

6 G. A. H. Mekhemer, S. A. Halawy, M. A. Mohamed and M. I. Zaki, *J. Catal.,* 2005, **230**, 109–122.

7 J. C. Kuriacose and R. Swaminathan, *J. Catal.,* 1969, **14**, 348-354.

8 R. Swaminathan and J. C. Kuriacose, *J. Catal.,* 1970, **16**, 357-362.

9 T. N. Pham, T. Sooknoi, S. P. Crossley and D. E. Resasco, *ACS Catal.,* 2013, **3**, 2456-2473.

10 R. Martinez, M. C. Huff and M. A. Barteau, *J. Catal.,* 2004, **222**, 404–409.

11 R. W. Snell and B. H. Shanks, *Appl. Catal., A*, 2013, **451**, 86– 93.

12 T. Waters, R. O'Hair and A. G. Wedd, *Int. J. Mass Spectrom.,* 2003, **228**, 599–611.

13 J. J. Vajo, Y. K. Sun and W. H. Weinberg, *J. Phys. Chem.,* 1987, **91***,* 1153-1158.

14 S. Zhang, X. Duan, L. Ye, H. Lin, Z. Xie and Y. Yuan, *Catal. Today,* 2013, **215**, 260–266.

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15 J. Cressely, D. Farkhani, A. Deluzarchi and A. Kiennemann, *Mater. Chem. Phys.,* 1984, **11**, 413-431.

16 V. J. Johnston, B. Kimmich, J. Potts, H. Weiner, J. H. Zink, J. T. Chapman, L. Chen and R. Jevtic, *U.S. patent,* 0263910 A1, 2011.

17 Y. Zhu and X. W. L. Shi, *Bull. Korean Chem. Soc.,* 2014, **35**, 141-146.

18 W. Rachmady and M. A. Vannice, *J. Catal.,* 2000, **192**, 322-334.

19 H. Wan, R. V. Chaudhari and B. Subramaniam, *Energy Fuels,* 2013, **27**, 487-493.

20 K. Zhang, F. Li, H. Zhang, H. Ma, W. Ying and D. Fang, *International Scholarly and Scientific Research & Innovation,* 2013**,** **7**, 488-492.

21 Y. K. Kharaica, W. W. Carothers and R. J. Rosenbauer, *Geochim. Cosmochim. Acta,* 1982, **47**, 397-402.

22 A. Witsuthammakul and T. Sooknoi, *Catal. Sci. Tech.,* 2015, **5**, 3639-3648.

23 C. Liu, A. M. Karim, V. M. Lebarbier, D. Mei and Y. Wang, *Top. Catal.,* 2013, **56**, 1782–1789

24 R. W. Snell and B. H. Shanks, *ACS Catal.,* 2014, **4**, 512−518.

25 T. N. Pham, D. Shi and D. E. Resasco, *Top. Catal.,* 2014, **57**, 706–714.

26 N. Peamaroon and T. Sooknoi, *Pet. Sci. Technol.*, 2012, **30**, 1647–1655.

27 D. L. Hoang, T. T. H. Dang, J. Engeldinger, M. Schneider, J. Radnik, M. Richter and A. Martin, *J. Solid State Chem.,* 2011, **184**, 1915–1923.

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28 G. V. Sagar, P. V. R. Rao, C. S. Srikanth and K. V. R. Chary, *J. Phys. Chem. B,* 2006, **110**, 13881-13888.

29 A. Ausavasukhi, S. Suwannaran, J. Limtrakul and T. Sooknoi, *Appl. Catal., A,* 2008, **345**, 89–96.

30 Z. Strassberger, A. H. Alberts, M. J. Louwerse, S. Tanase and G. Rothenberg, *Green Chem.,* 2013, **15**, 768-774.

31 C. Huo, J. Ouyang and H. Yang, *Sci. Rep.,* 2014, **4**, 1-9.

32 L. K. Frevel, M. J. Kressley and L. J. Kressley, *U.S. patent,* 3076858, 1963.

33 S. Ilias and A. Bhan, *ACS Catal.,* 2013, **3**, 18−31.

34 N. Ravasio and M. Gargano, *J. Org. Chem.,* 1993, **58**, 1259-1261.

35 G. Parravano, *J. Catal.,* 1970, **16**, 1-15.

36 A. Gumidyala, T. Sooknoi, and S. Crossley, *247th ACS National Meeting & Exposition,* 2014, 84.

37 A. Gumidyala, M. Godavarthy, T. Sooknoi and S. Crossley, *AIChE Annual Meeting,* 2014.

38 J. Novakova and L. Kubelkova, *J. Catal.,* 1990**, 126**, 689-692.

39 T. Tago, M. Sakamoto, K. Iwakai, H. Nishihara, S.R. Mukai, T. Tanaka and T. Masuda, *J. Chem. Eng. Jpn.,* 2009, **42** , s162-s167.

40 T. N. Pham, D. Shi and D. E. Resasco, *J. Catal.,* 2014, **314**, 149–158.

Selective hydrodeoxygenation of bio-oil derived products: Acetic acid to propylene over hybrid CeO_2-Cu/zeolite catalysts

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Figure 1 Temperature program reduction of 5%Cu/zeolites

Figure 2a TEM image of Cu/HY (i) at 440kX (ii) at 285kX (iii) insertion (1,580 kX) with background/contrast adjustmentat to display Cu particle well aligned in the HY pore

Figure 2b TEM image of Cu/HZSM-5 (i) at 440 kX (ii) at 97 kX

Figure 3 Effect of temperature to acetic acid KHDO over CeO_2-Cu/HY(25)* at 457 g.h.mol^{-1}, H_2 30 ml.min^{-1}

a)conversion, propylene, propane, acetone, ethyl acetate, carbon dioxide

b)ethylene, ethane, *n*-butane, C5 olefins, acetaldehyde, ethanol

**number in parenthesis represents %wt of Cu/Zeolite in the three-component catalyst*

Figure 4 The reaction network for acetic acid KHDO over CeO_2-Cu/zeolite

Figure 5 Effect of CeO_2-Cu/HY composition (from CeO_2-Cu/HY(40) to CeO_2-Cu/HY(7)) for acetic acid KHDO at 457 g.h.mol^{-1} and 573 K, H_2 30 ml.min^{-1}, 1st hour on stream

a)conversion, acetone, ethyl acetate, carbon dioxide

b)propylene, *i*-propanol, ethylene, acetaldehyde, ethanol

Figure 6 Comparison between CeO_2-Cu/HY(25) *(opened symbol)* and CeO_2-Cu/HZSM(25) *(closed symbol)* for acetic acid KHDO at 457 g.h.mol^{-1} and 573 K, H_2 30 ml.min^{-1}

a)conversion (circle), acetone (triangle), ethyl acetate (rectangular)

b)propylene (circle), acetaldehyde (triangle)

c)carbon dioxide (circle), ethylene (triangle)

Figure 7 Effect of water to acetic acid KHDO over CeO_2-Cu/HY(25) at 457 g.h.mol^{-1} and 573 K, H_2 30 ml.min^{-1}

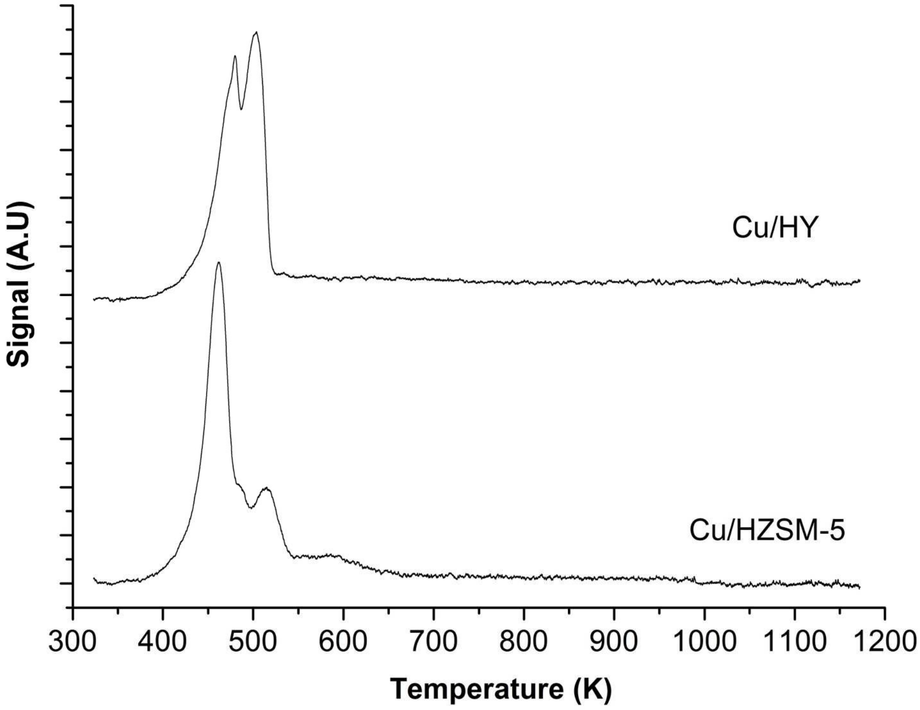
a)conversion, acetone, propylene, ethyl acetate

b)ethylene, ethanol, acetaldehyde, carbon dioxide

Figure 8 Light distillated hydrocarbons from acetic acid over sequential beds of CeO_2-Cu/HY - HZSM-5 at 343-114-80 g.h.mol^{-1} and 573 K, H_2 30 ml.min^{-1}

a)conversion, propylene, acetone, ethylene, carbon dioxide

b)butenes, paraffins C2-C4, olefins C5-C10, aromatics C7-C9



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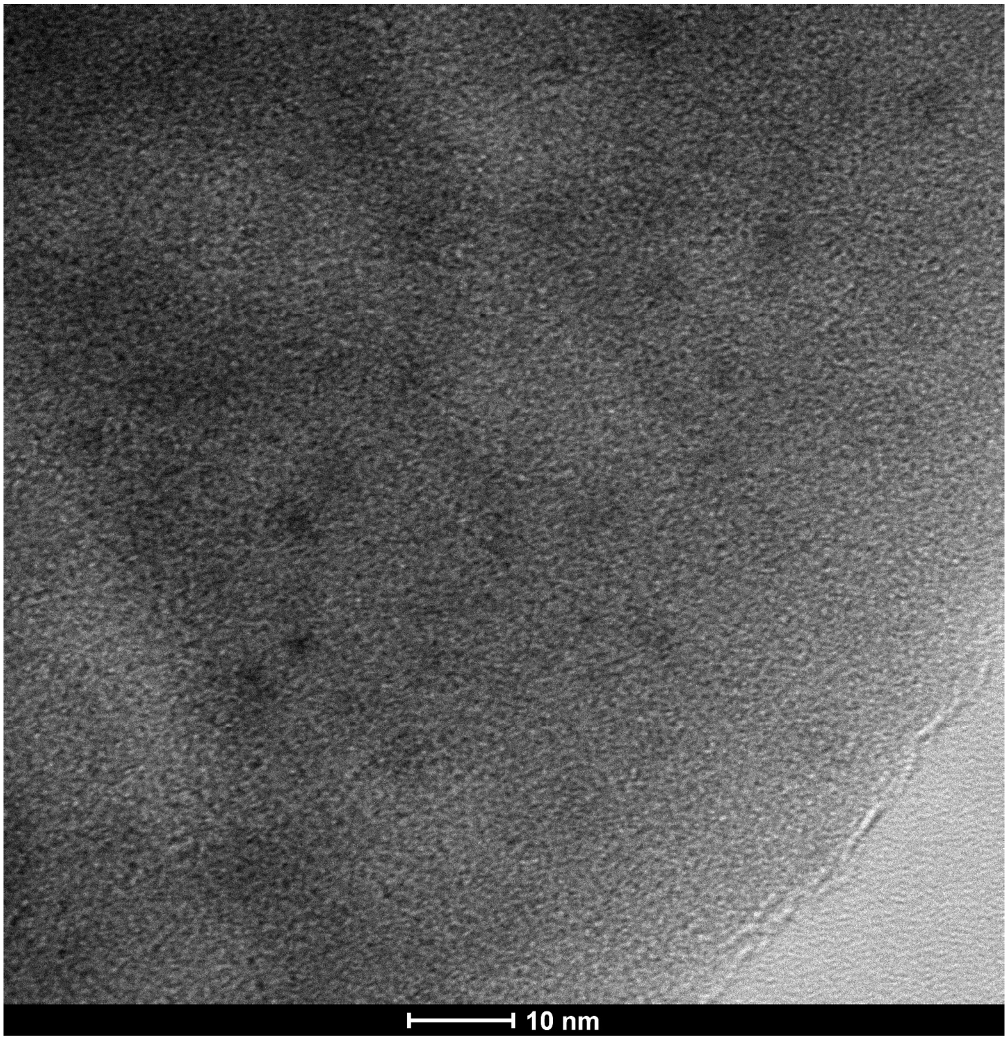
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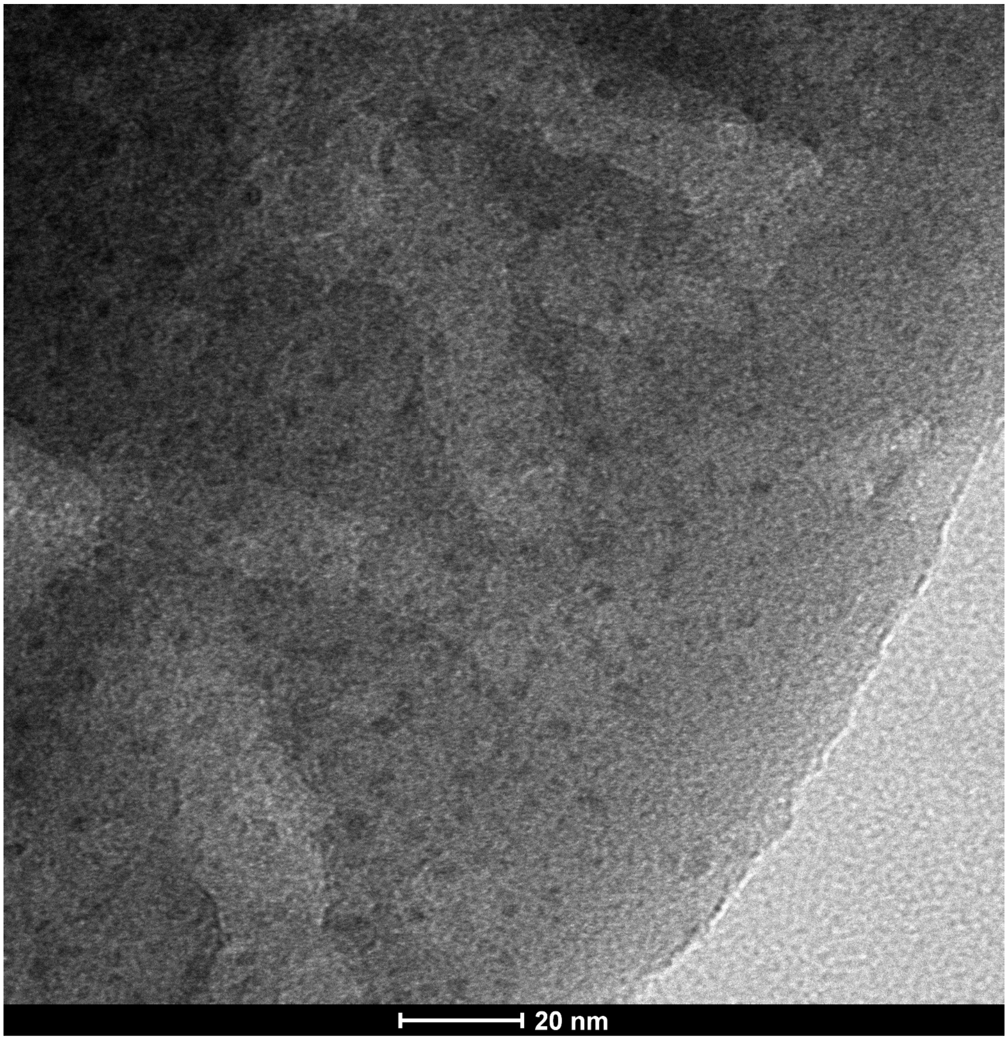
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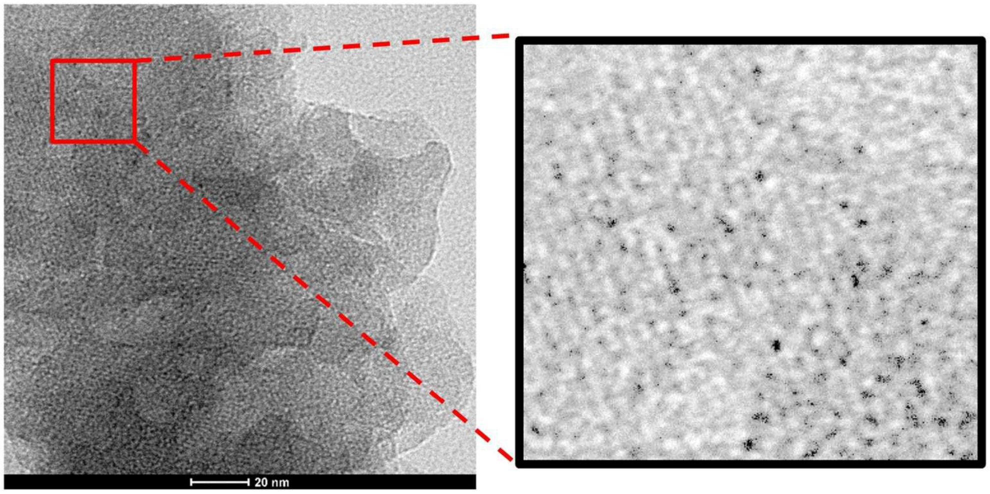

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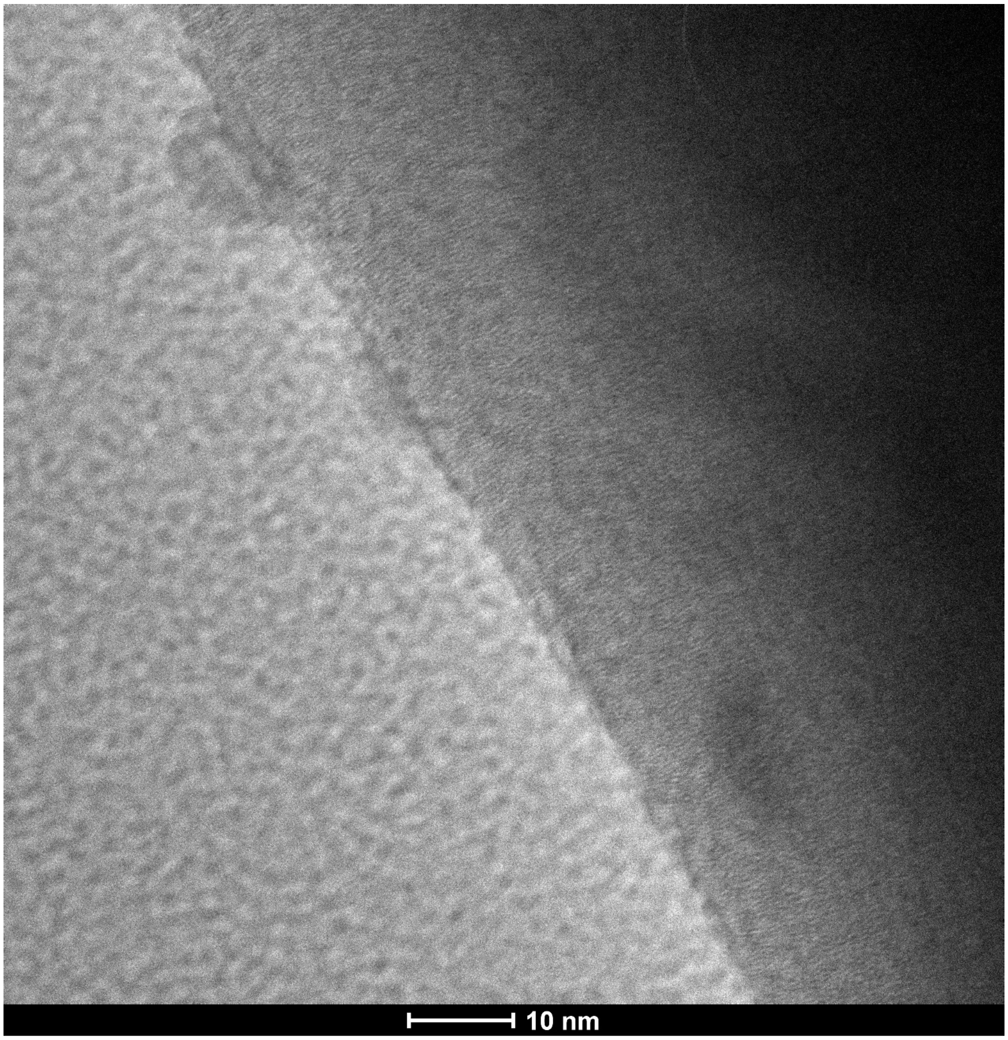
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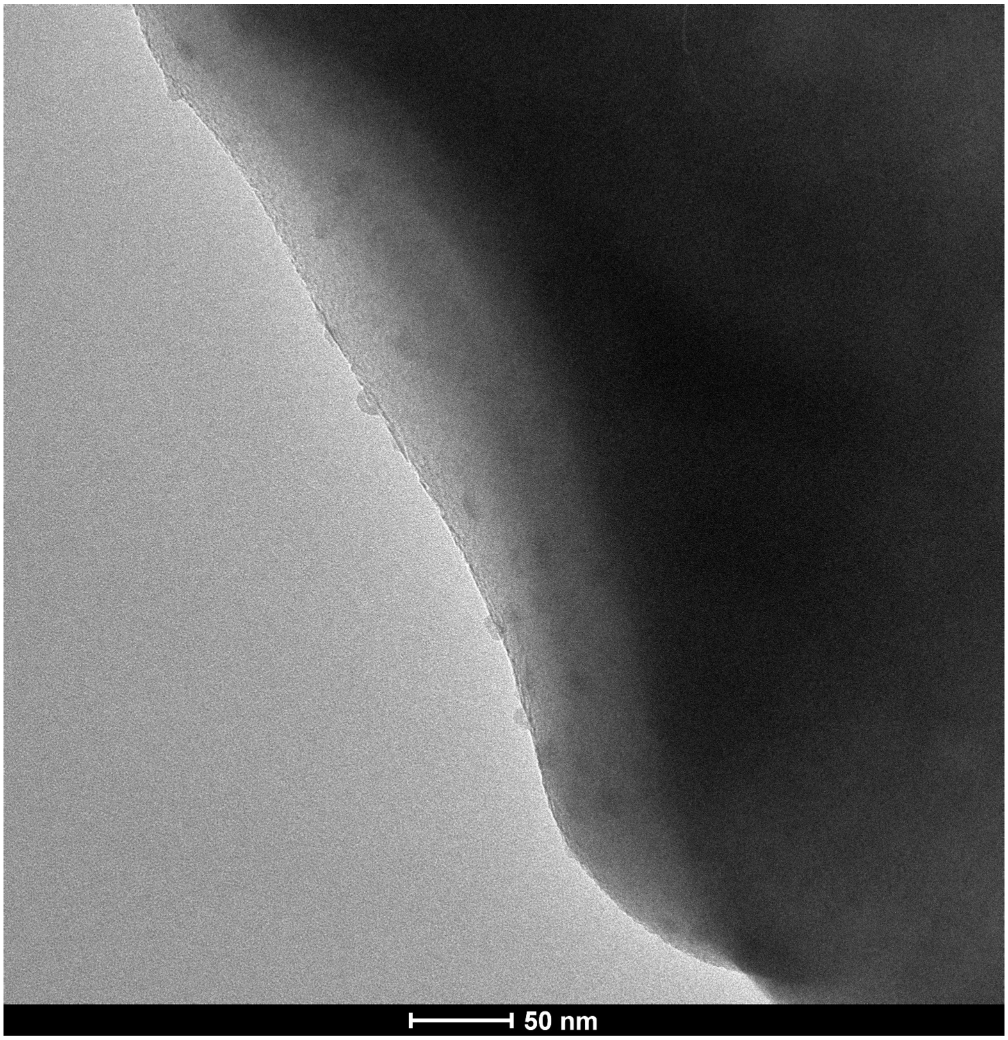
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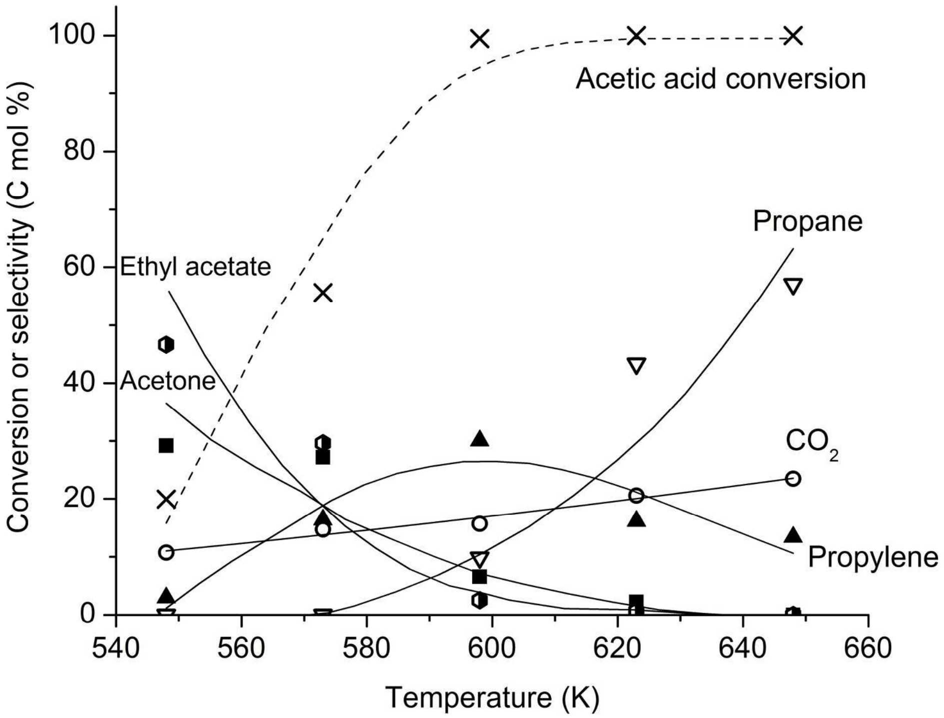

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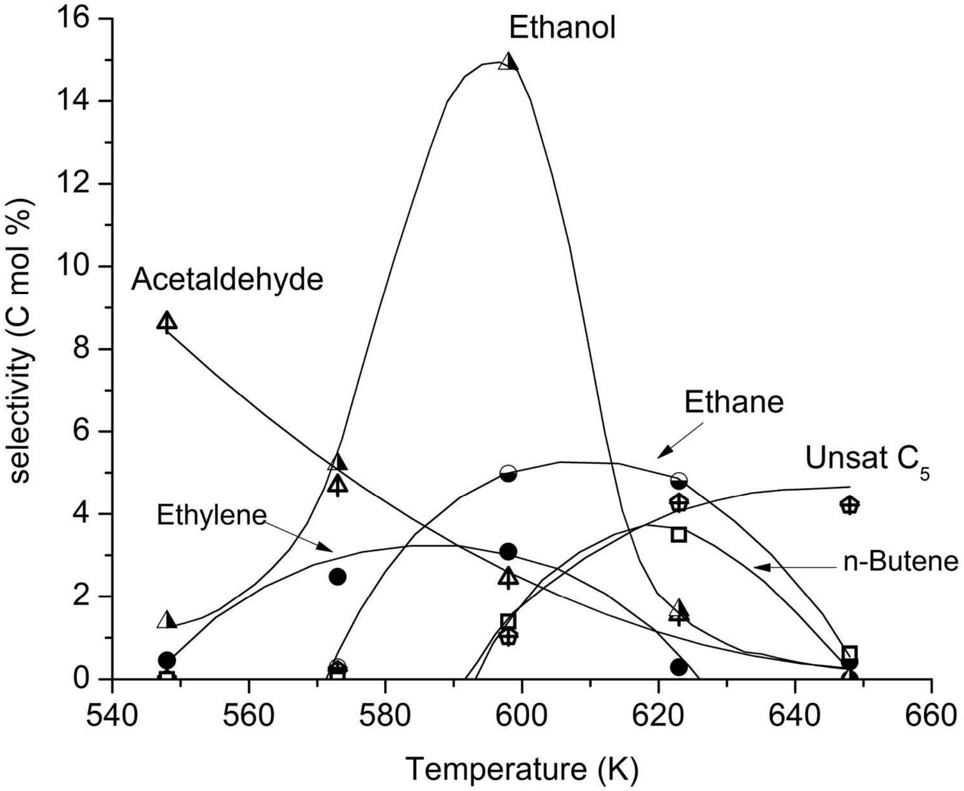

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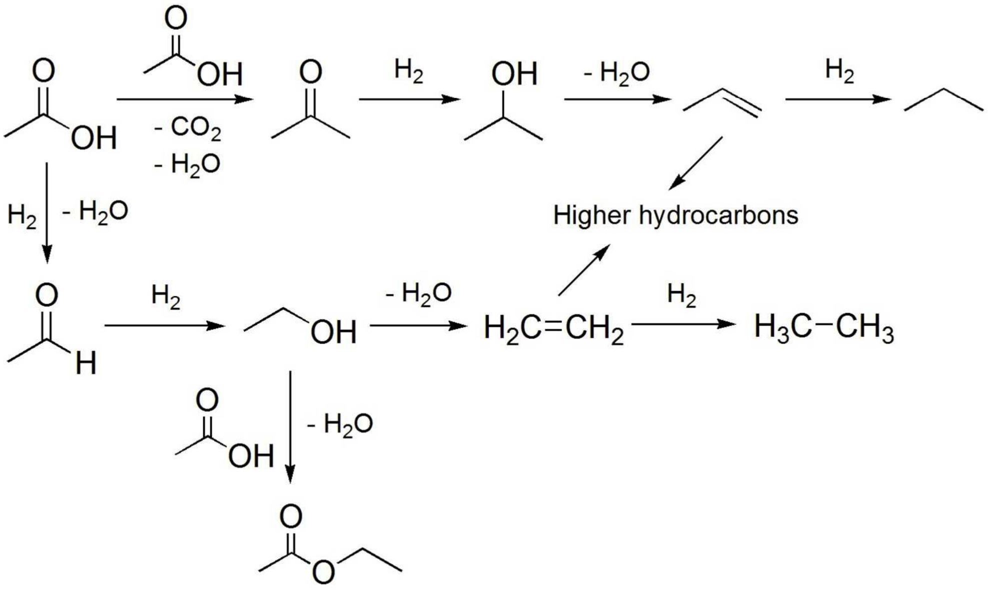

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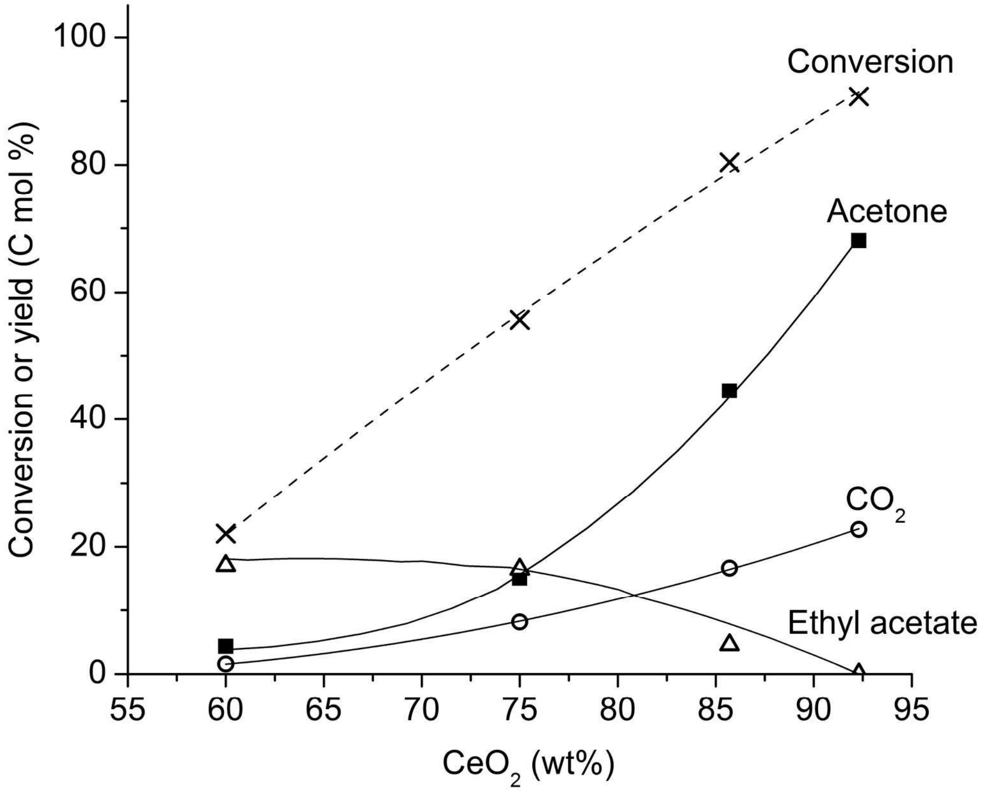

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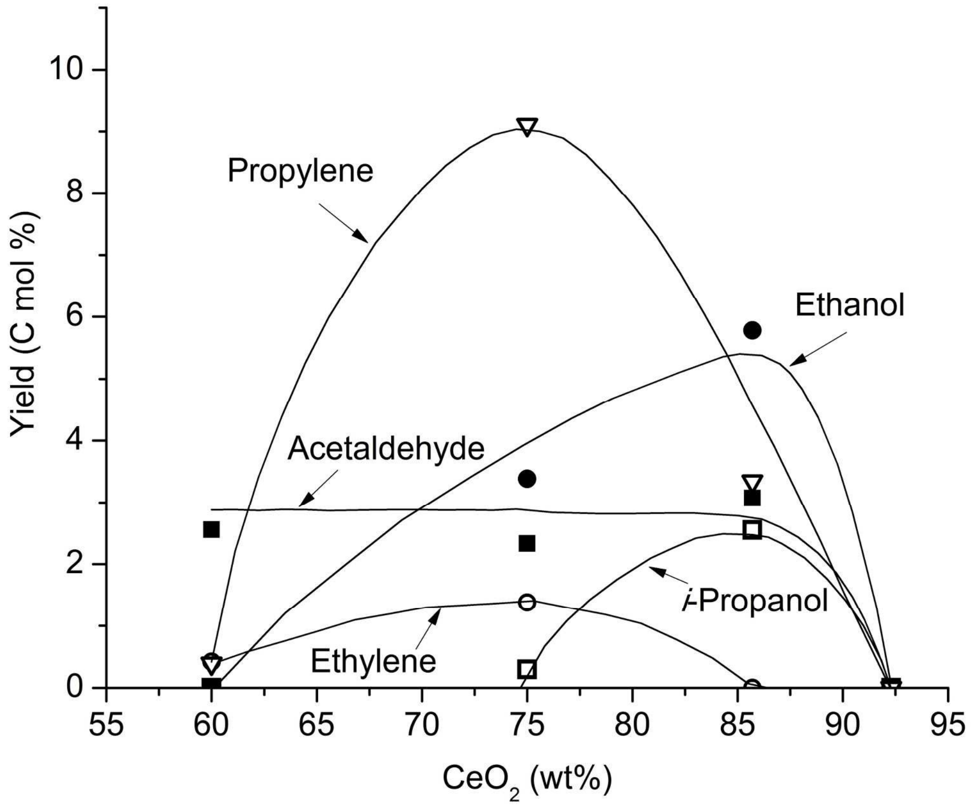

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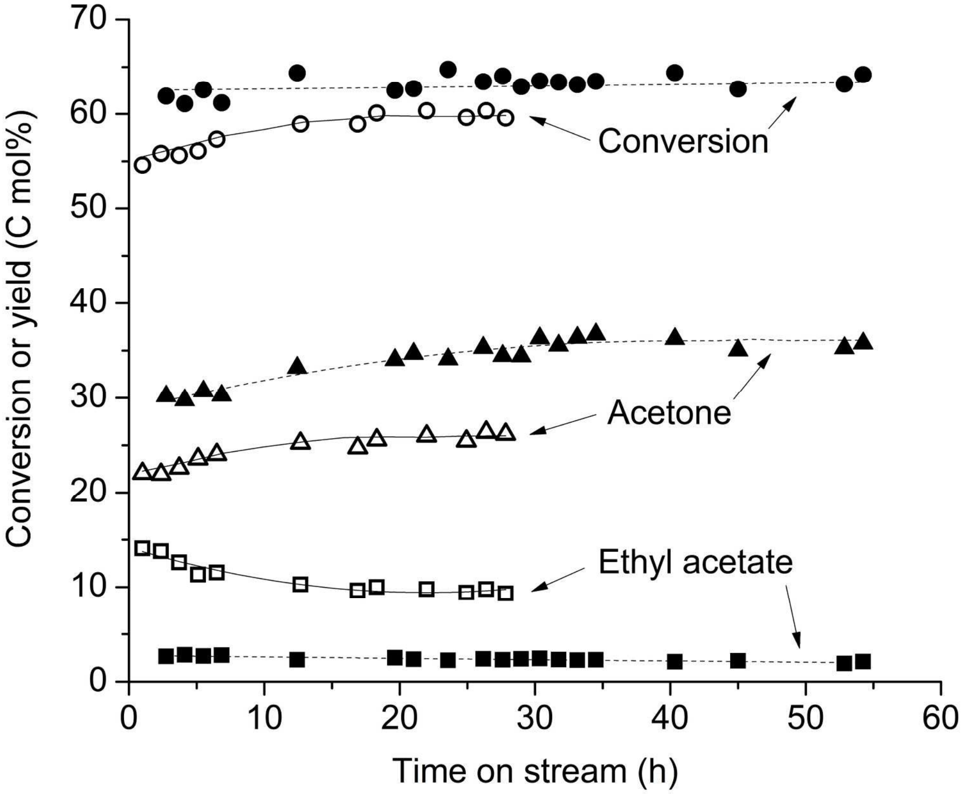

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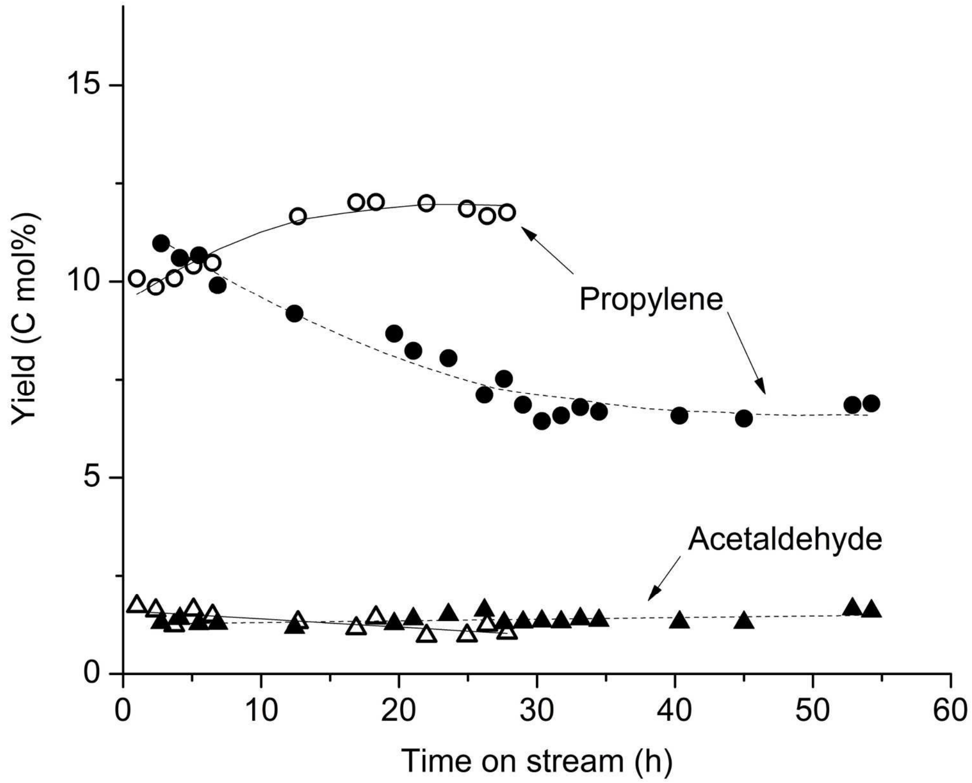

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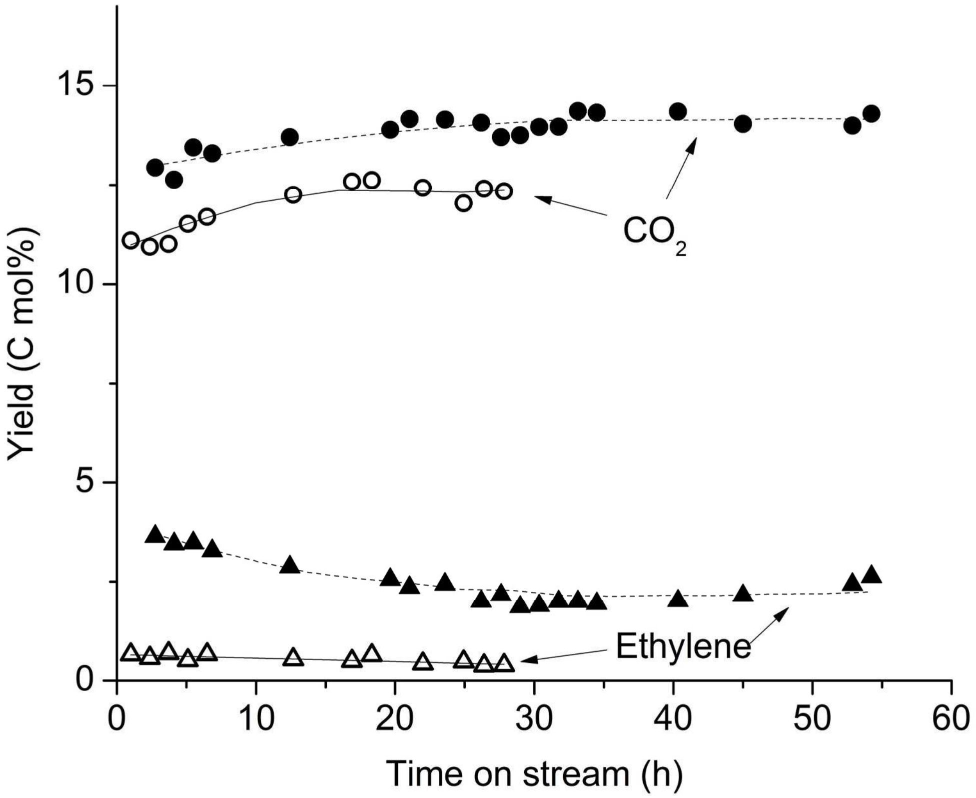

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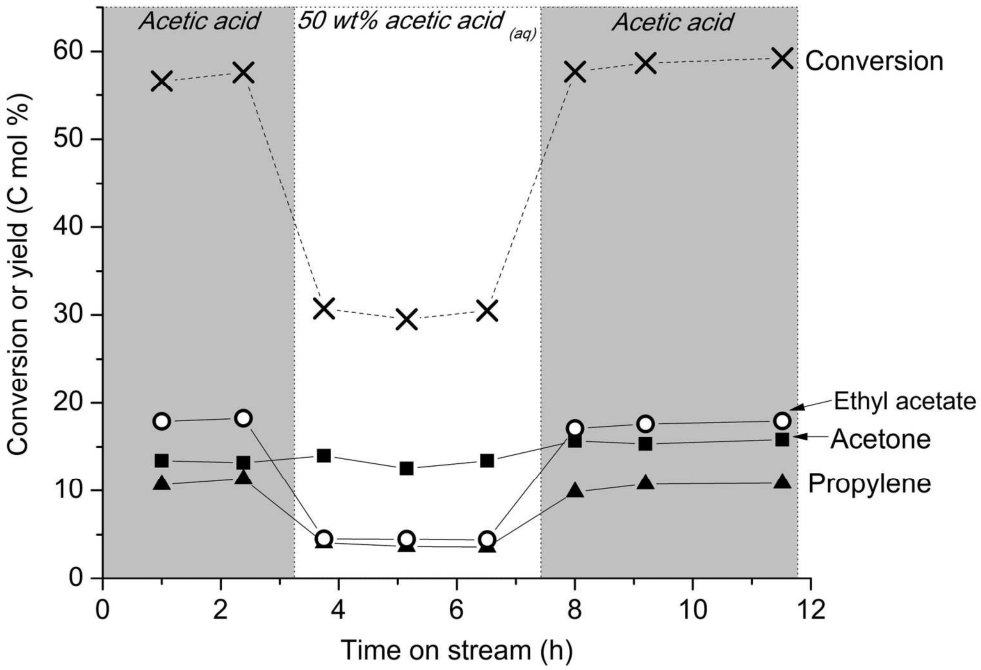

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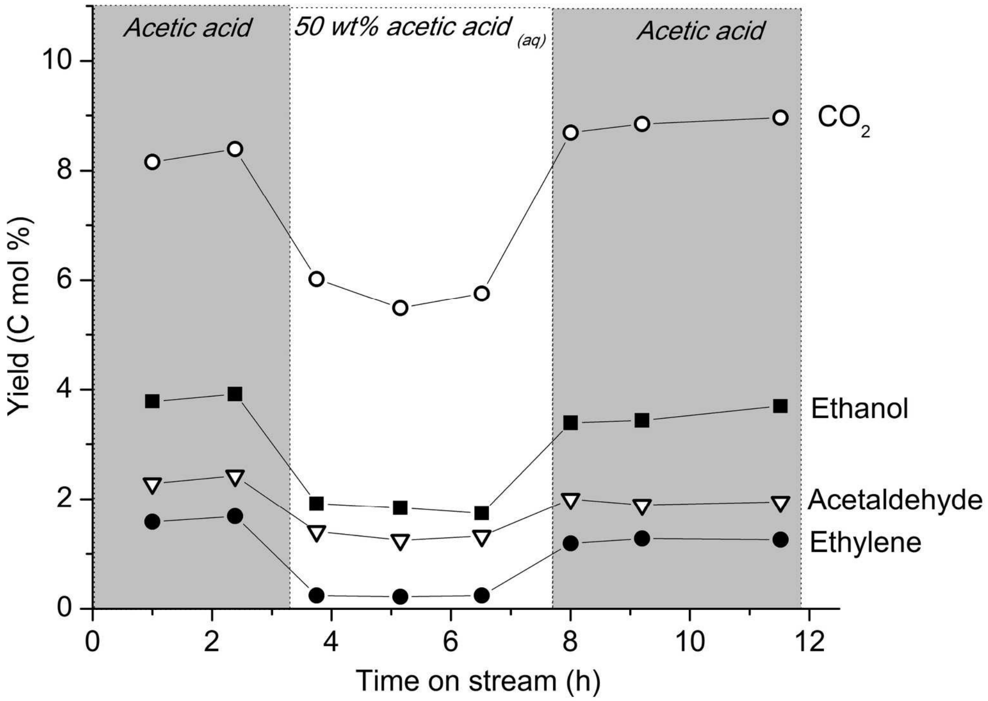

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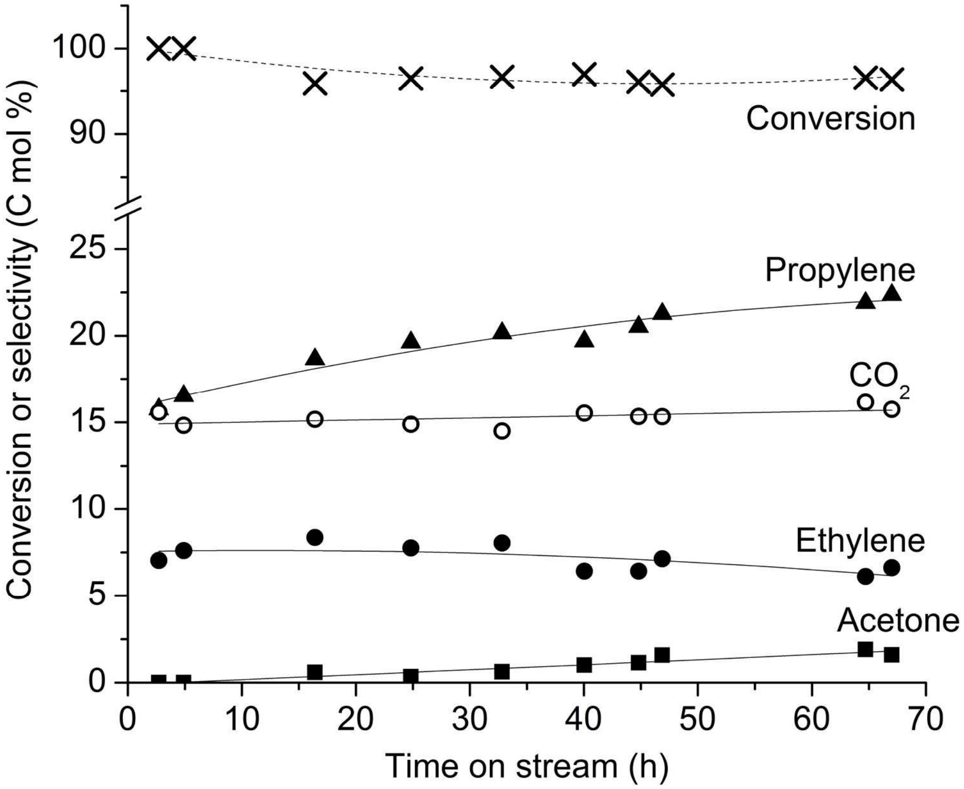

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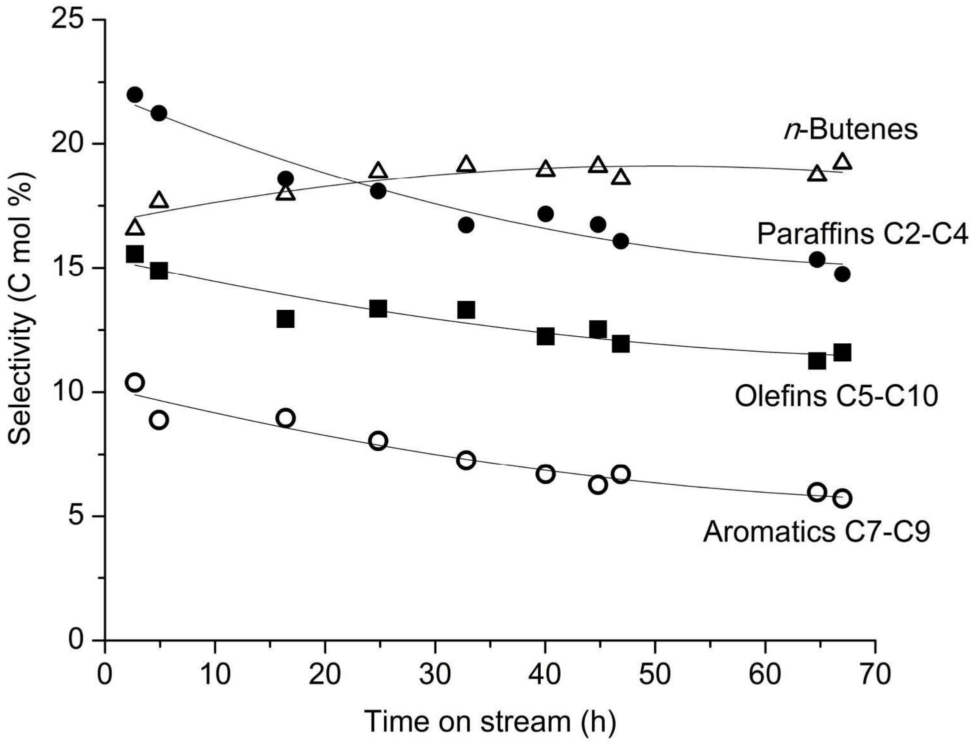

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Selectivehydrodeoxygenationof bio-oil derived products:keto-hydrodeoxygenationofAceticacid topropyleneoverhybrid CeO_2-Cu/zeolite catalysts

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Tables

Table 1% Dispersion, copper area, surface area, and acidity of copper catalysts and supports

Catalyst	**Si/Al**	**%Cu loading**	**% Dispersion**	**Cuarea**	**BET surfacearea**	**Acidity**(μmol /g)	
		wt%		(m^2/g_{Cu})	(m^2/g)	Weak	Strong
CeO_2	-	-	-	-	11	-	-
HY	153	-	-	-	713	54	65
HZSM-5	152	-	-	-	376	56	65
Cu/HY	166	5.1	65	499	568	158	62
Cu/HZSM-5	173	5.2	54	414	361	92	20
CeO_2-Cu/HY*	166	1.3	-	-	150	43	15
CeO_2-Cu/HZSM-5*	173	1.3	-	-	98	26	5

*values estimated from those of the parent catalysts

Table 2 Direct HDO of acetic acid over 5%Cu/zeolites

	Cu/HY	**Cu/HZSM-5**	
Feed	Acetic acid	50wt% aq. acetic acid	Acetic acid
Conversion(Cmol%)	24.2	2.9	13.9
Selectivity(Cmol%)			
Acetaldehyde	11.7	16.4	24.2
Ethanol	2.8	-	-
Ethyl acetate	81.6	83.6	42.1
Ethylene	3.9	-	15.1
Acetone	-	-	11.3
Propylene	-	-	1.8
CO_2	-	-	4.3

48 g.h.mol^{-1}and 573 K, $H_2$30 ml.min^{-1}, 1st hour on stream

Table 3KHDO of acetic acid overCeO$_2$-Cu/HY(25)by different systems and acetic acid concentrations

	Mixed catalyst (457g.h.mol^{-1})	**Sequentialbed** (343+114g.h.mol^{-1})	
Acetic acid in H$_2$(mol%)	1.2	2.3	1.2
Conversion(Cmol%)	55.6	85.4	88.9
Selectivity(Cmol%)			
Acetone	27.2	8.8	1.7
Propylene	16.4	45.9	49.4
Propane	-	2.6	7.8
Acetaldehyde	3.4	2.6	2.4
Ethanol	5.2	5.2	5.9
Ethyl acetate	29.6	7.7	4.3
Ethylene	2.5	3.6	4.1
Ethane	-	1.4	4.4
CO$_2$	14.7	19.2	19.6

573 K,H$_2$30 ml.min^{-1}, 1sthour on stream

Selective hydrodeoxygenation of bio-oil derived products: Acetic acid to propylene over hybrid CeO_2-Cu/zeolite catalysts

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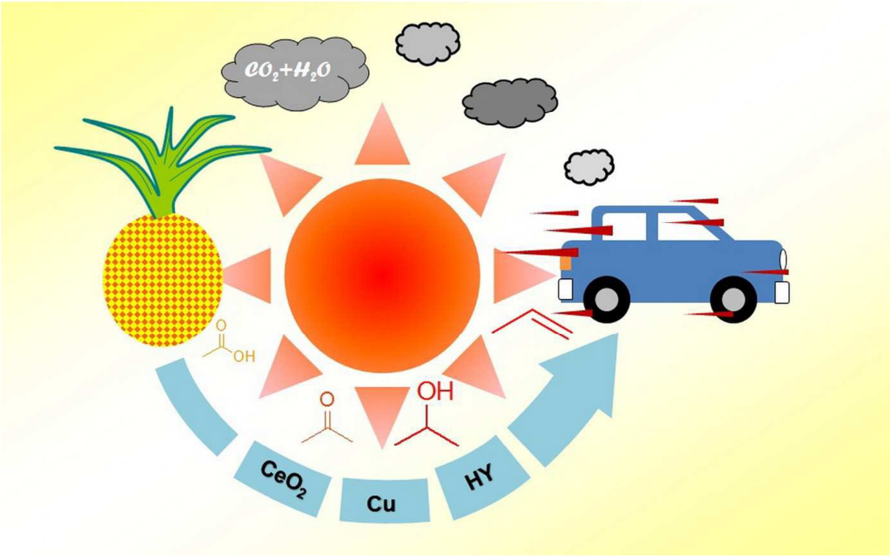

Propylene and light distillates can be directly obtained from keto-hydrodeoxygenation of acetic acid over a single bed of CeO_2-Cu/zeolite catalyst.