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Communication

Catalytic hot gas filtration for tailoring vapor-phase chemistry of fast pyrolysis bio-oils

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Abstract: Carboxylic acids such as acetic acid and propionic acid have been investigated as representative components for fast pyrolysis (FP) bio-oil upgrading. Selective catalytic conversion of carboxylic acids can enhance bio-refinery processing economics through catalyst preservation and process intensification. Various metal-doped molybdenum carbide bead catalysts have been synthesized and developed in this work. Our aim is to enable selective conversion of carboxylic acids. In the case of acetic acid conversion, calcium doped Mo_2C beads offer the highest yield of acetone ~96% at 450 °C among undoped and Ca or Ni doped catalysts. By comparing hot gas filter with and without Ca-Mo_2C catalyst tested with real FP vapors, the former showed a 36.7% reduction of acetic acid, a 37.5% reduction of small ketones in aqueous phase, and a ~50% reduction of methoxies (methoxy phenols and methoxy aromatics) in organic phase. The conversion resulted in the formation of more long chain chemicals in the organic phase, which are more amendable for downstream upgrading.

Keywords: bio-oil; biomass conversion; carbide catalyst; ketonization; doped carbides.

1. Introduction

Hot Gas Filtration (HGF) can reduce alkali and alkaline earth metals and solid content from bio-oil, in order to improve vapor composition and protect downstream upgrading and hydrotreatment catalysts from fouling[1]. Packing the catalyst beads to the filter, which becomes Catalytic Hot Gas Filtration (CHGF), can further upgrade bio-oil vapor and provide chemical tailoring of the feed vapors before they enter the downstream upgrading. Among various bio-oil components, carboxylic acids, such as acetic acid and propionic acid, are commonly found in large amounts in bio-oils and contribute to the acidic and corrosive nature of bio-oil[2]. Furthermore, these acids are of low value and present challenges in downstream bio-oil upgrading processes. Small organic acids in liquid bio-oil can catalyze polymerization of reactive species such as sugars and aldehydes during hydroprocessing, cause catalyst fouling, and consume an excessive amount of H_2 producing low-value alkane hydrocarbon gases[3]. This study applied CHGF to address the issues related to carboxylic acids and small carbonyl compounds. The design of CHGF is shown in Figure 1.

Various reactions for carboxylic acids on metal or oxide catalysts have been well studied. For instance, hydrodeoxygenation (HDO) of acetic acid produces ethanol[4], decarboxylation (DCO) produces CO_2[5], dehydration yields ethenone[5], reduction produces acetaldehyde[6], and ketonization leads to the production of acetone[7]. The selectivities for these reactions depend strongly on the nature of the catalyst surface. In general, HDO is an attractive route to upgrade bio-oil considering that this process is well established in the petroleum industry; however, HDO of bio-oil usually requires precious metals, high temperatures, and high hydrogen pressures[8]. For example, Huber *et al.* used Ru/C and Pt/C catalysts to produce bi- and tri-cyclic products from phenol

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with 85% selectivity at 160 °C and 5 MPa hydrogen pressure. The amount of precious metals needed for the degradation of cellulose was relatively high, 4– 10 mg per gram of cellulose [10]. Also, precious metals have a greater tendency towards DCO over HDO, and tend to fully saturate double bonds via hydrogenation. Therefore, it is desirable to develop inexpensive catalysts that can perform carboxylic acid conversion under mild conditions. Interstitial carbides are robust materials which have catalytic properties similar to those of precious metals due to their electronic structure.[10] On the other hand, carbides, such as Mo_2C, have been shown to be more selective towards HDO than DCO as well as have superior stability under upgrading conditions[11–13]. By being less active towards C-C bond scission the hydrocarbons produced typically have greater molecular weight and value[11].

Most of the studies on Mo_2C focus on its direct hydrodeoxygenation properties. In this study, we explored the ketonization activity for acetic and propionic acid conversion by modifying Mo_2C with Ca and Ni in catalyst beads form. We found that we could tune the selectivity toward ketone production by doping Mo_2C with Ca. In-situ chemistry tailoring of hot pyrolysis vapors by CHGF platform serves as an alternative processing method to process vapors before they are condensed into bio-oil liquid for more facile subsequent upgrading to hydrocarbon fuels and chemicals. Besides the filtration removal of inorganic mineral (alkali/alkaline metals), catalyst beads-loaded hot gas filters are being developed to enable selective target conversions (such as conversion of carboxylic acids and small carbonyls). Therefore, transforming these carboxylic acids/carbonyls into larger more upgraded molecules before condensation would be beneficial with respect to H and C economy and hydroprocessing catalyst lifetime.

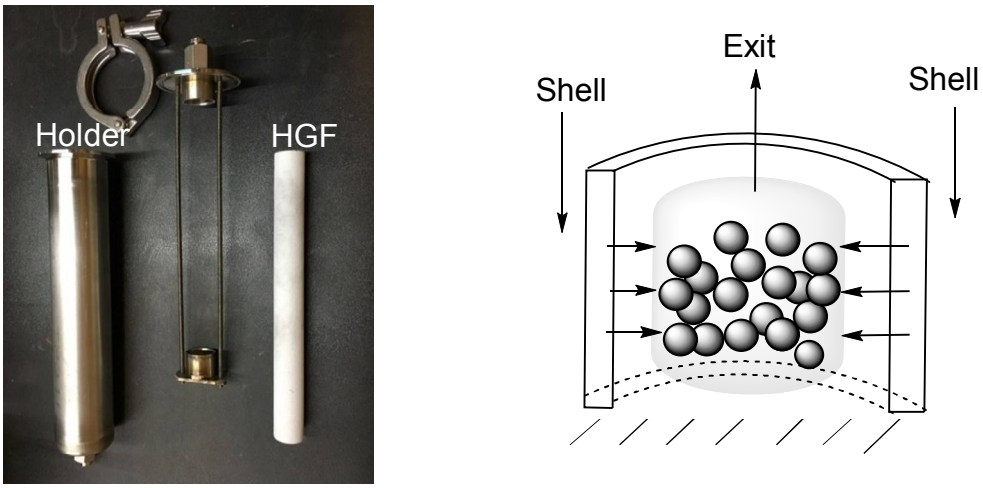

Figure 1. Schematic pictures of CHGF: Hot gas filtration holder and the filter (left); Packed bed of catalyst beads/pellets inside ceramic filter tube (right).

2. Results and Discussion

Propionic acid conversion and product selectivity was dependent upon reaction temperature for all three Mo_2C catalysts [Figures 2 (A, B and C)]. Un-doped Mo_2C [Figure 2 (A)] had three main products, C3 hydrocarbons (propane and propene), C2 hydrocarbons (ethane and ethylene), and propionaldehyde. At 250 °C, propionaldehyde was the major product (55% selectivity) indicating that hydrogenation was the dominant reaction pathway. The presence of C3 species were also significant at 35% selectivity. The propene could have come from dehydration of 1-propanol produced by propionaldehyde hydrogenation. It is known that Mo_2C surface can possess acidic sites due to the presence of surface oxygen[14]. 1-Propanol, however, was not detected throughout the experiment. This suggests that either 1-propanol dehydration was very fast (i.e., consumed as soon as it formed) or propene was produced by direct hydrogenolysis of the aldehyde carbonyl group[11]. C2 products, on the other hand, were negligible. This suggests that cracking or hydrogenolysis reactions were not predominant under these conditions. As the reaction temperature increased from 250 to 350 °C, the selectivity shifted away from propionaldehyde to C3 species. The olefin selectivity is the alkene selectivity over the sum of the alkane and alkene species. Propene was ~ 80% of the C3

products, indicating that the catalyst had moderate activity toward double bond hydrogenation under these conditions. A similar trend was observed with C2 species. Increasing the reaction temperature further to 450 °C drove the selectivity towards C2 species with ethylene being the major fraction. One possible explanation for this transition is that C-C bond cleavage of propene molecules became a dominant reaction pathway at high temperatures. However, considering the limited CH_4 formation, its reactivity towards C-C bond cleavage was still relatively modest compared to precious metal catalysts which would have produced predominantly CH_4 gas at this temperature. Reducing the temperature back down to 250 °C revealed that the catalyst's activity had significantly decreased over the experiment, evidenced by the low propionic acid conversion (~5%).

Nickel-doped Mo_2C [Figure 2 (B)] was subjected to a slightly different reaction temperature scheme which was as follows: 250 → 350 → 450 ℃. As in the case of Un-doped Mo_2C, propionaldehyde was the major product. However, selectivity patterns as a function of temperature presented some substantial differences. This catalyst exhibited a dramatic increase in 3-pentanone at 450 °C as compared with the un-doped catalysts (25 vs. 2.5% selectivity). Interestingly, the 3-pentanone selectivity was much higher at 350 °C at the end of the experiment than it was in the beginning (15 vs. 1.5%). On the other hand, the C3 selectivity decreased from 30 to 3% over the course of the experiment. The olefin selectivity appeared unchanged. This suggests that as the catalyst became less active towards propionic acid hydrogenation and dehydration (and/or deoxygenation), the ketonization activity improved. Further investigation into the catalyst acidity and the mode of deactivation is necessary to understand the phenomena behind this mechanistic shift.

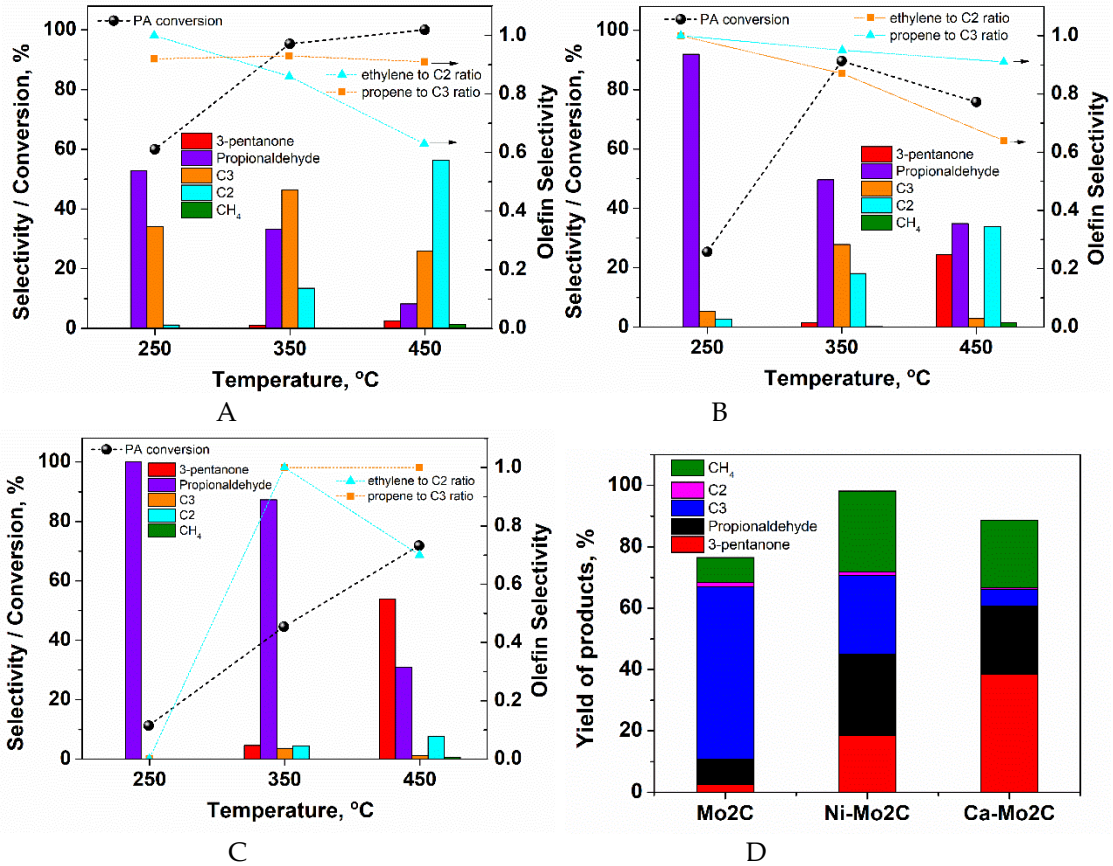

Figure 2. Product selectivity and of propionic acid conversion over three types of carbide pellet catalysts after pretreatment with 10% H_2 at 500 °C for 2 h: (**A**) Mo_2C, 4 h Time On Stream (TOS); (**B**) Ni-Mo_2C, 4 h TOS; (**C**) Ca-Mo_2C. 4 h TOS but *The final injection was taken after running the reaction for 12 h; (**D**) Yield of products at 450 °C over three types of carbide catalysts.

The Ca-doped Mo_2C was subjected to a temperature scheme: 250 → 350 → 450 °C [Figure 3 (C)]. The behavior of the calcium doped Mo_2C was remarkably different from the un-doped and the nickel doped catalysts. At 250 °C, the catalyst was less active (acid conversion ~ 10%). However, increasing

the reaction temperature improved acid conversion monotonously. At low temperatures, propionaldehyde was again highly favored but at elevated temperatures 3-pentanone was dominant. The C3 and C2 hydrocarbons remain minor byproducts over the entire temperature range. At 500 °C, 3-pentanone selectivity was 62% and propionic acid conversion was 96%. The reaction was continued at this temperature for 12 h at which point the 3-pentanone selectivity increased to 83% but the acid conversion had dropped to 45%. Therefore, the deactivation of Ca-Mo_2C was mainly accompanied by loss in its hydrogenation function while maintaining its ketonization selectivity.

In view of our results of propionic acid hydrodeoxygenation over metal carbides, we reasoned that acetic acid could go through ketonization to form acetone over metal carbides as well. Hydrogenation of acetone can lead to 2-propanol which can subsequently be dehydrated to propene. Hydrodeoxygenation of acetic acid was carried out over un-doped, Ni-, and Ca-Mo_2C. Product selectivity and acid conversion as a function of reaction temperature are summarized in Figures 3 (A, B and C). Each reaction in this series was subjected to the same temperature sequence which was as follows: 250 → 350 → 450 °C. The only exception to this was Ca-Mo_2C's final temperature was 350°C because sampling at 250 °C would not have yielded useful data due to low conversion.

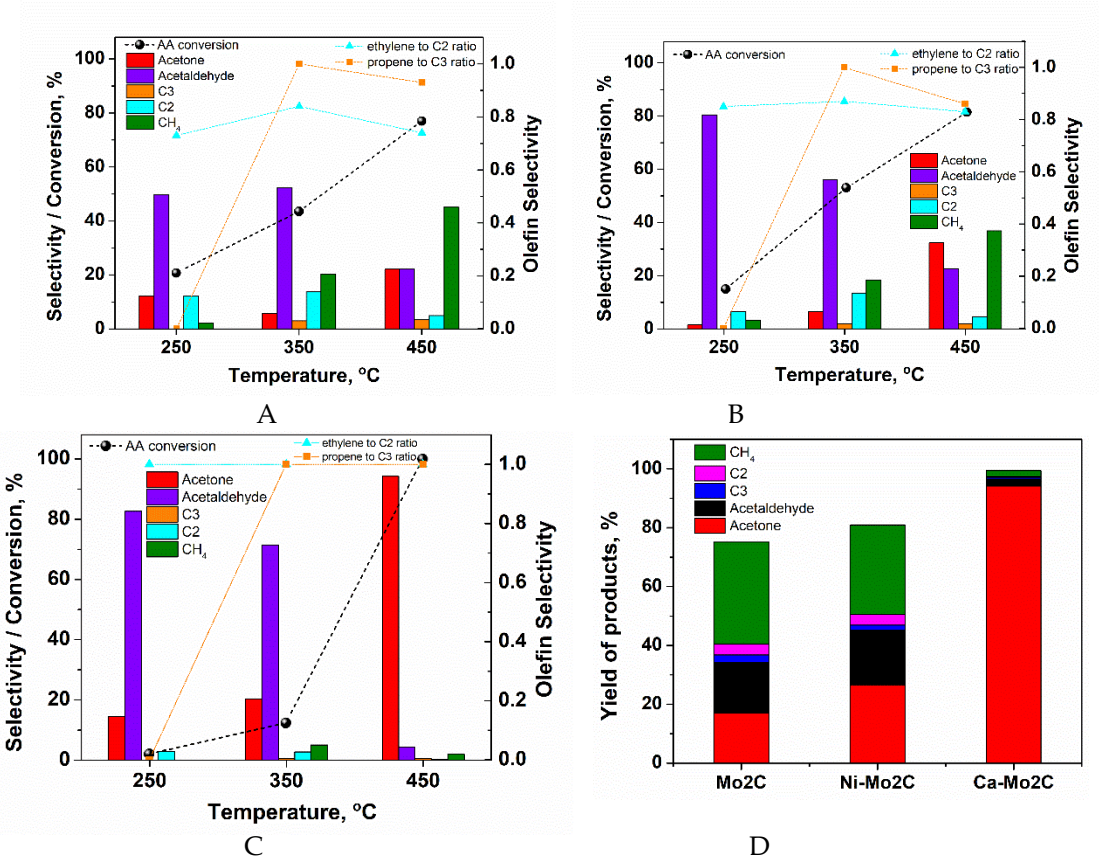

Figure 3. Product selectivity and of acetic acid conversion over three types of carbide pellet catalysts after pretreatment with 10% H_2 at 500 °C for 2 h: (**A**) Mo_2C, 4 h TOS; (**B**) Ni-Mo_2C, 4 h TOS; (**C**) Ca-Mo_2C, 4h TOS. (**D**) Yield of products at 450 °C over three types of carbide catalysts.

The un-doped catalyst produced mainly acetaldehyde at 250 °C and the conversion was low (~20%) [Figure 3 (A)]. As the reaction temperature increased to 350 and 450 °C the conversion improved. However, selectivity towards methane became dominant (45% at 450 °C) indicating increased contribution from the DCO pathway. Acetone, the ketonization product, was being produced over the un-doped carbide; however, the yield was only ~15% at 450 °C [Figure 3 (D)].

Ni-doped Mo_2C had highest selectivity towards aldehyde product at at 250 °C [Figure 3 (B)]. This was consistent with the results seen from propionic acid hydrodeoxygenation. At higher temperatures methane and acetone became major products and the acetaldehyde selectivity was diminished similarly to the un-doped Mo_2C. Returning to the lower temperature again revealed that

catalyst deactivation had occurred to this catalyst also. Acetone selectivity was yet again enhanced in the catalyst's less active state. As described in the Catalyst Characterization section, the surface area and porosity of this catalyst did not experience any significant changes. Hydrogen activation property of carbides is known to suffer with surface oxygen accumulation, while oxygen-modified carbide surfaces present acid properties[15]. The observed deactivation could therefore be related to surface oxygen accumulation with TOS and temperature[14].

Ca-doped Mo_2C provided the highest acetone selectivity [Figure 3 (C)]. At 450 °C quantitative conversion was achieved with 94% selectivity towards the ketone. At lower temperatures acetaldehyde selectivity was dominant. Little selectivity towards light gases including methane was observed. Furthermore, the C2 and C3 products detected were purely alkene as shown in the olefin selectivity. This suggests that Ca-Mo_2C was less active in reactions involving H_2 activation such as acid hydrogenation, alkene hydrogenation, and hydrogenolysis. This property may arise from its "basic" nature. In one study looking at the decomposition of 2-propanol over Mo_2C, acetone selectivity was greatly enhanced by NH_3 poisoning[16,17]. This suggests that the basicity of the catalyst surface controls selectivity[16,17]. It has also been shown that both acid and basic sites exist on Mo_2C and modification of these sites can have a profound effect on reactivity.[18]

For better understanding the dopant effect on the acetic acid reactions, the total number of basic sites on three types of carbide catalysts were determined by temperature-programmed desorption of carbon dioxide (CO_2-TPD). The temperature for CO_2 desorption is usually an indication of the base site strength[18]. The amounts of CO_2 that desorbed from the carbide catalysts (Table 1) showed that Ca doped Mo_2C has the highest densities of basic sites (~1.77 micromoles/m^2), which is more than double the amount for Mo_2C and Ni-Mo_2C. Our reaction data - Ca-Mo_2C showed the highest ketonization selectivity – suggests that basic sites were responsible for ketonization[19][20]. Previous work has shown that the doped Mo_2C synthesis method can have a dramatic effect on the physical and chemical properties of the catalyst[21]. The surface properties of the carbide catalysts both before and after reaction are also summarized in Table 1. Metal doping (which was done before carburization) had a significant effect on the surface area of the resulting catalyst. The fresh catalysts, the un-doped, Ni-doped and Ca-doped had BET surface areas of 23.5, 18.3, and 9.55 m^2/g, respectively. The addition of calcium had the greatest impact on surface area. It is believed that calcium slows the carburization process which leads to greater sintering, thus lowering the surface area[22]. The total pore volume followed a similar trend. The surface areas, post acetic acid hydrogenation, remained relatively unchanged, especially for Ca-Mo_2C. This suggests that the catalyst morphology was not greatly altered under our reaction conditions.

Table 1. Surface properties of three types of carbide catalysts.

Catalyst	CO_2 desorbed during TPD up to 550°C, micromoles/m^2	Surface Area, m^2/g	Surface Area after reaction*, m^2/g	Total Pore Volume, cm^3/g	Total Pore Volume after reaction*, cm^3/g	Average Pore Size, Å	Average Pore Size after reaction*, Å
Mo_2C	0.86	23.5	23.7	0.0925	0.0869	77.2	73.5
Ni-Mo_2C	0.79	18.3	17.2	0.0779	0.0701	85.2	81.4
Ca-Mo_2C	1.77	9.55	7.14	0.0375	0.0346	78.5	97.0

*Post reaction with Acetic Acid.

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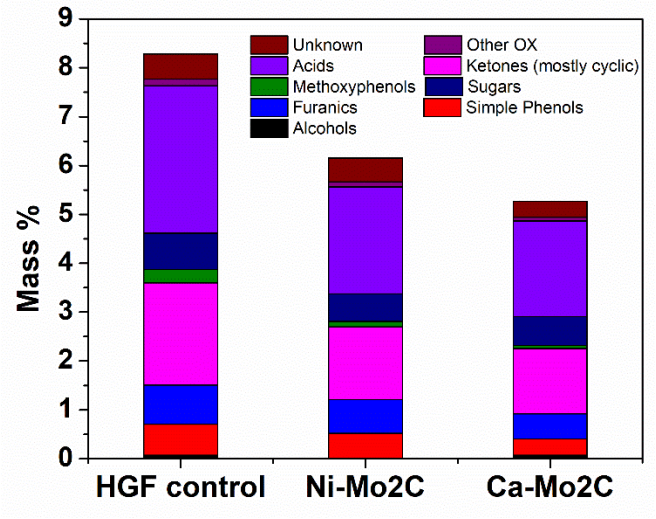

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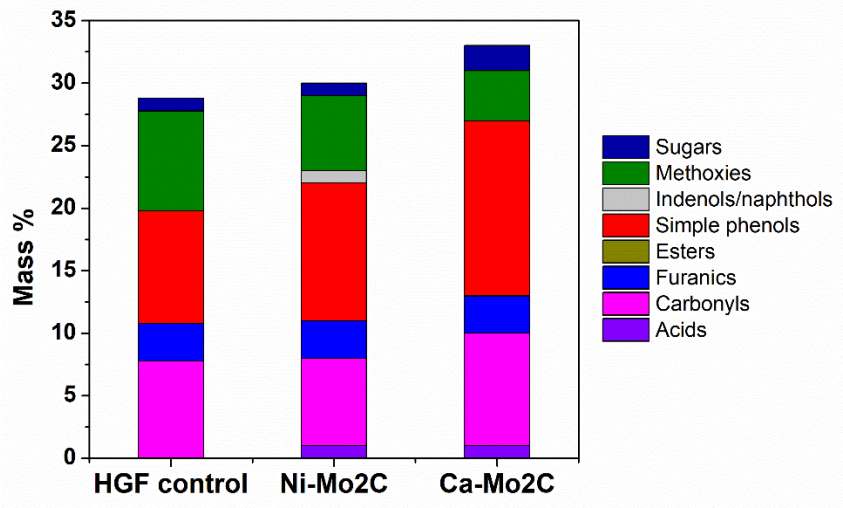

B

Figure 4. Oxygenates products of real FP vapor over Ni and Ca doped carbide catalysts (CHGFs) compared with blank HGF sample in aqueous phase (A) and in organic phase (B).

The real FP vapor testing has been performed as shown in Figure 4. The goal of CHGF is to convert small carbonyl and carboxylic acid to more upgraded long chain chemicals. The products condensed into aqueous and organic phases, the aqueous products were analyzed by GC-FID and GC-MS, and organic phase products were analyzed by MBMS. In aqueous phase (Figure 4A), Ca-Mo_2C showed the greatest reduction in water soluble furanics, ketones, and most notably, acid content. From this analysis >99% of the acid content was acetic acid. Therefore, acetic acid decreased from 3% on HGF control sample to 1.9% on Ca-Mo_2C which is 36.7% reduction of acetic acid; and 2.19% on Ni-Mo_2C, which is 27% reduction of acetic acid. Also, the water-soluble ketone decreased from 2.09% on HGF control sample to 1.34% on Ca-Mo_2C, which is 37.5% reduction. Thus, we suppose these acetic acid and carbonyl compounds have been upgraded to chemicals with longer chains and went into the organic phase. These conclusions are further supported by the performance of the Ni-Mo_2C and Ca-Mo_2C CHGF catalysts for the organic phase results and compared with HGF control sample, shown in Figure 4B. Figure 4B summarizes oxygenates products in the organic phase (not soluble in water) which include long chain acids, carbonyls, furanics, esters, simple phenols, indenols/naphthols, methoxies, and sugars. Specifically, Simple Phenols are phenol, alkylphenols,

and catechols; methoxies are methoxy phenols and methoxy aromatics, furanics are furans/benzofurans.

Regarding the total mass percent shown in y axis, this is a measure of GC analyzable content of the organic non-water-soluble samples. The larger oxygenates that were either polymeric or have more complicated functional groups did not make it through the column to the detector. By this reasoning, a more upgraded product would have a greater mass% reported by the GC than a less upgraded, or raw, pyrolysis product. Thus, the organic phase of real FP vapor over Ca-Mo_2C showed the highest mass% (more GC analyzable compounds), indicating that the FP vapor was more upgraded. For CHGF, the goal is to convert compounds that are less amenable to deoxygenation reactions before they reach the primary upgrading reactor. The most problematic compound is methoxy phenol, due to the high bond dissociation energy of the hydroxyl group, compared to cresol. Ideally, a CHGF catalyst would convert these directly to product compounds like benzene, toluene and xylene. Note that the methoxy phenols decreased from control HGF sample (8%) to CHGF samples over Ni-Mo_2C (2.5%) and Ca-Mo_2C (4%). Meanwhile, simple phenols increased from control HGF (9%) to CHGF samples over Ni-Mo_2C (10%) and Ca-Mo_2C (14%). Fortunately, these changes were due to increased catechol production in Ni-Mo_2C (6%) and Ca-Mo_2C (4%) and increased alkylphenols in Ni-Mo_2C (6%) and Ca-Mo_2C (8%) and not due to changes in phenol content, which remained constant across treatments. Further, the carbonyl content of the control HGF sample was similar to the Ni-Mo_2C (8%) while increasing under Ca-Mo_2C (10%) treatment. With respect to aromatic content, the yields in the control HGF sample were low (0.3%), but the Ni- Mo_2C showed a small decrease (0.2%) while the Ca-Mo_2C slightly increased (0.4%). Therefore Ca-Mo_2C loaded CHGF showed the best upgrading performance by reducing 50% of less upgraded compounds into more upgraded long chain phenols, carbonyls and aromatics.

3. Materials and Methods

Materials: The propionic acid (≥ 99.5%), acetic acid (> 99%), $CaCl_2$ and $NiCl_2$ were purchased from Sigma-Aldrich and used as received. CH_4 (99.99%) and H_2 (99.999%) were purchased from AirGas; MoO_3 and ammonium heptamolybdate powders were purchased from Alfa Aesar.

Catalyst Synthesis and Characterization

Carbide catalysts beads synthesis

The bulk Mo_2C catalysts used in this chapter were synthesized via a temperature-programmed carburization (TPC) described previously[23]. The undoped Mo2C was prepared using pressure-pelletized heptamolybdate. To study the effects of metal doping on molybdenum carbide properties, metal doped MoO_3 precursors were prepared before carburization. The precursors were prepared via a gelation method[24]. In brief, MoO_3 powder was suspended in an aqueous solution of sodium alginate. The oxide slurry was dropped into an aqueous solution of a metal chloride ($CaCl_2$ or $NiCl_2$). The Na^+ ions in the alginate binder exchanged with the divalent metal ions (e.g., one Ca^{2+} ion for two Na^+ ions) causing the alginate polymer molecules to cross-link. This process created a rigid MoO_3 bead.

The precipitated oxide beads were separated from solution, rinsed, dried, and heat-treated to 600 °C for 2 h in air. Alginate was removed by calcining the particle leaving behind the doped MoO_3 beads. Carburization was accomplished via the TPC method in a tubular quartz reactor of ~2.5 cm internal diameter. During carburization, the oxygen was removed from molybdenum in the form of water and carbon monoxide leaving behind Mo_2C. The carburizing gas consisted of 15% CH_4 and 85% H_2 (flow rate: 104 sccm per gram of precursor), the sample temperature was raised from room

temperature to 700 °C at 1 °C/min and held for 1 h. After cooling to room temperature, the synthesized carbides were passivated in a 1% O_2/N_2 flow for 12 h.[25]

Specific Surface Area and pore size analysis (BET)

The morphology of carbides was analyzed via N_2 sorption using a Quantachrome Autosorb-1. The samples were outgassed for 24 h at 400 °C prior to analysis. The total pore volume was measured at (p/p_0=0.99) using Barrett-Joyner-Halenda (BJH) method. The pore size distribution was found using 19 point adsorption and 19 point desorption isotherms. The surface area was calculated from adsorption points with $p/p_0 < 0.35$ per Brunauer-Emmett-Teller (BET) method.

Temperature programmed desorption of carbon dioxide (CO_2-TPD)

An Altamira AMI-200 characterization instrument was used for the measurements. The samples were pretreated under 50 mL/min of 4% H_2/Ar for 3 h at approximately 500 °C, and then flushed in 50 mL/min of Ar for 30 min at the same temperature. After, the sample was cooled down to 30 °C under 50 mL/min of argon. Once at 30 °C, 45 mL/min of 2% CO_2/Ar were flowed through the sample for 1 h. The gas flowing through the sample was switched to 45 mL/min of argon and 1 h was allowed for weakly bound CO_2 species to desorb before the temperature programmed desorption (TPD) experiment was started. For the TPD experiment, 45mL/min of argon were used as the carrier gas. The temperature was ramped from 30 °C to 1000 °C at a rate of 10 °C/min, and then held at 1000°C for 1 h. The CO_2 desorbed was analyzed using a mass spectrometer.

Catalysts Testing

Acid hydrodeoxygenation experiments were conducted using a bench-top flow through reactor system. The product selectivity and reactant conversion were measured as a function of temperature and time on stream (TOS). These experiments were run under atmospheric pressure. In a typical test, 400 mg of catalyst was packed in a 1 cm I.D. quartz tube. After loading the catalyst, the bed was heated to 500 °C at a rate of 5 °C/min under 45 sccm helium. At 500 °C, 5 sccm H_2 was added to the helium stream. The pretreatment was continued for 2 hours before cooling the reactor to a desired reaction temperature (e.g, 250 or 350 °C) at a rate of ~10°C/min. The carboxylic acid was introduced into the reactor by redirecting H_2-He gas through a bubbler/saturator with an average flow of 0.15 ml/h affording an effective space velocity of 0.37 h^{-1} WHSV (acid basis). The exit vapor was analyzed by directly injecting to either the GC-FID for product quantification or GC-MS for product identification. After the 1st injection, the reactor temperature was increased and allowed to equilibrate for an hour. This was again repeated and after the third injection the reactor was cooled to the initial temperature. Another sample was taken after an hour of equilibration. The fourth injection was meant to assess the stability of the material over the 4 hours of operation.

FP real vapor testing

Catalytic hot gas filtration of pine pyrolysis vapors was carried out on a 40 g/hr slipstream from the NREL Vapor Phase Upgrading unit. The filter units were a scaled down version of the Pall Diaschumalith filter elements with a gas filtration grade of 0.3 μm. The filter support is constructed from SiC with an outer alumina (mullite) membrane. The filter ends were kaolin-sealed to prevent vapor bypassing and mounted in a 316SS filter housing with flow passing from the outside of the membrane into the interior of the filter. Empty filters were used for the control and 1g catalyst beads or pellets were packed into the interior of the filter with quartz wool at either end, to give a WHSV of 23 hr^{-1} of pine pyrolysis vapor. Inert SiC chips were employed to fill the additional filter volume. The output of the CHGF filter was further analyzed by MBMS and then condensed to liquid product and the remaining volumetric flow of product gas was measured by means of a dry test meter and the carbon content analyzed by an HP5890 GC with an Activated Research PolyArc

and FID. The CHGF filters were weighed on a high-precision Mettler-Toledo balance before and after the experiment to quantify the mass of coke deposited on the filter and the catalyst bed.

4. Conclusions

We have shown that un-doped Mo_2C is active towards both acetic and propionic acid hydrodeoxygenation under atmospheric pressure. Additionally, we found that doping the MoO_3 with Ni or Ca prior to carburization can have dramatic effects on the physical characteristics as well as the reactivity of the resulting carbides. Ni-Mo_2C was found to be more active towards hydrogenation than the other catalysts. Ca-Mo_2C was found to exhibit superior selectivity (94%) for the acetone production especially at high temperatures relevant to pyrolysis vapor upgrading, e.g., 450 ℃. Overall, the reactivity trends observed on a given catalyst type was consistent between acetic and propionic acids. Carbide catalysts particularly Ca-doped one were shown to effectively upgrade the real FP vapor as well. Thus, carbide catalysts appear promising for deoxygenation of bio-derived compounds with possibility of tailoring product selectivity via metal doping. Further catalyst characterization would be useful to understand the deactivation pathways, which could provide insight into the nature of the various active sites. This information would aid in designing the physical and chemical properties of these materials to achieve greater conversions, enhanced selectivity and extended durability.

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Author Contributions: M.L. A.L., J.-S.C. and M.Z.H conceived and designed the experiments; M.L. and A.L performed the experiments; M.L., A.L and M.J. analyzed the data; Z.L., K.M., B.P., Z.W and F.P contributed during experiments and discussion; M.L. and A.L wrote the paper with contribution from the other co-authors."

Conflicts of Interest: The authors declare no conflict of interest.

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