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Selectivity patterns in heterogeneously catalyzed hydrogenation of conjugated ene-yne and diene compounds

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ABSTRACT

Selectivity control in heterogeneously catalyzed hydrogenation of conjugated hydrocarbons (ene-yne and diene compounds) is a challenging task. Available studies on the topic mainly encircle 1,3-butadiene as the substrate and palladium as the catalyst, while more elaborated playground molecules and other metals remain largely unexplored. This study investigates the gas-phase hydrogenation of valylene (2-methyl-1-butene-3-yne) and isoprene (2-methyl-1,3-butadiene) over Pd, Pb-poisoned Pd, CO-modified Pd, Cu, Ni, and bimetallic Cu—Ni catalysts. Chemoselectivity, regioselectivity, full hydrogenation, and C—C bond formation/scission footprints of the catalytic systems at different inlet hydrogen-to-hydrocarbon ratios and conversion degrees have been rationalized. Complementary studies of 3-methylbutyne and 1-penten-4-yne hydrogenation were carried out in order to analyze (i) the impact of isomerization on the observed mono-olefin distribution in valylene/isoprene hydrogenation and (ii) the conjugation issue in partial ene-yne hydrogenation. Our results lead to an improved understanding of hydrogenation of polyunsaturated hydrocarbons and open doors to design more selective heterogeneous catalysts and related processes for this practically important class of reactions.

1. Introduction

The catalytic hydrogenation of targeted functional groups in hydrocarbons is frequently used in multiple industrial sectors, yielding a wide variety of intermediate and end-user products [1,2]. Therefore, chemo-, regio-, and/or stereoselectivity control upon hydrogenation of multi-functionalized substrates attracts much interest for fundamental and applied research in catalysis [3,4]. Specifically, the partial hydrogenation of highly unsaturated hydrocarbons, that is, mono-alkynes and dienes, is a crucial catalytic step for the purification of alkene streams and for fine chemical production [5,6]. Although this class of reactions runs industrially on Pd-based catalysts for several decades, the topic has recently gained substantial interest due to the wide margin to improve commercial systems. For instance, many modified Pd/Al_2O_3 catalysts used for alkyne hydrogenation in C_2—C_4 cuts of steam crackers display moderate alkene selectivities and insufficient lifetime due to fouling.

The application of modern experimental methods, controlled routes for catalyst preparation, and computer simulations led to an improved understanding of the factors governing selectivity in alkyne hydrogenation on bare and modified Pd catalysts [7–17], and also enabled the identification of alternative non-Pd catalysts [18–23]. Nevertheless, available works in the literature have mostly tackled mono-alkynes (e.g., ethyne, propyne, pentyne, and hexyne). The hydrogenation of polyunsaturated hydrocarbons, such as ene-yne and diene compounds, over a variety of heterogeneous catalysts is comparatively much less studied. An exception is 1,3-butadiene due to its practical relevance in C_4 hydrorefining [5,6,24–29]. Hydrogenation of this diene experiences regioselectivity (the first hydrogenation can follow 1,2- or 1,4-addition mechanisms to produce 1-butene or 2-butenes, respectively) and stereoselectivity (cis- versus trans-2-butene) issues. Another appealing substrate for hydrogenation studies is isoprene (2-methyl-1,3-butadiene). This compound is a common structure motif to a variety of other natural compounds, collectively named isoprenoids. The presence of the methyl group in isoprene suppresses the stereoselectivity issue intrinsic to 1,3-butadiene hydrogenation and produces an additional mono-olefin from the 1,2-addition. As it occurs with 1,3-butadiene and mono-alkynes, isoprene hydrogenation has been mainly studied on palladium-based catalysts [6,30–32].

Valylene (2-methyl-1-butene-3-yne) is the smallest branched hydrocarbon possessing conjugated double and triple bonds and could be a very interesting playground molecule to improve knowledge on catalyst design for the hydrogenation of conjugated systems (Fig. 1). In particular, the conversion of valylene to isoprene is of practical interest [33,34], since isoprene is used to produce cis-1,4-polyisoprene, a synthetic version of natural rubber.

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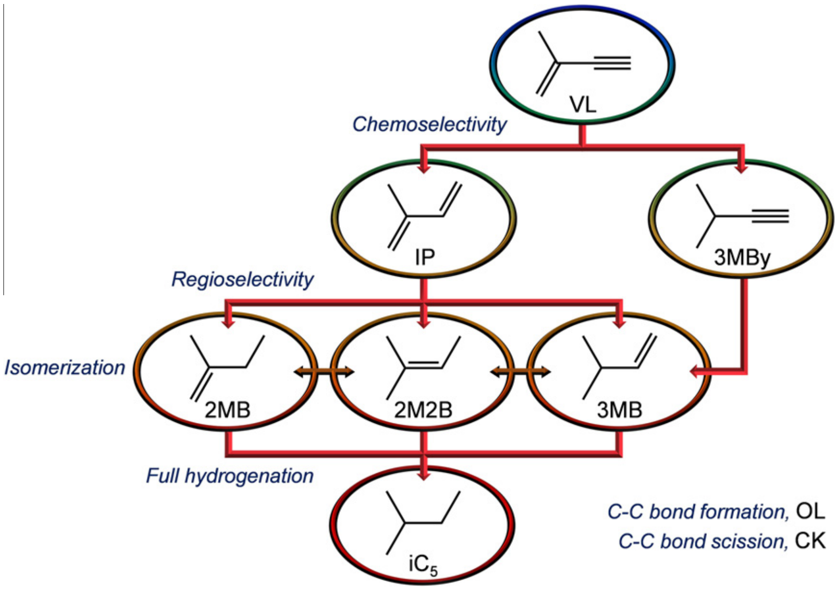

Fig. 1. Reaction scheme of valylene hydrogenation. Compound codes are VL = valylene, IP = isoprene, 3MBy = 3-methylbutyne, 2MB = 2-methylbutene, 2M2B = 2-methyl-2-butene, 3MB = 3-methylbutene, and iC_5 = isopentane. The sum of methylbutenes is denoted as MBs. Products coming from C—C bond formation (oligomers, OL) and scission (cracked products, CK) are not displayed for the sake of clarity.

Early work by Freidlin et al. [35,36] reported valylene hydrogenation over Zn, Pd black, and Raney-type cobalt catalysts. Aduriz et al. [32] studied the properties of supported palladium in the gas-phase valylene hydrogenation on alloying with a second metal. Isoprene was obtained with a maximal selectivity of 78% at 80% valylene conversion on Pd—Pb/α-Al_2O_3.

Herein, we have systematically investigated the gas-phase hydrogenation of valylene, isoprene, 3-methylbutyne, and 1-penten-4-yne over various catalytic systems, with the aim of rationalizing selectivity patterns associated with the type of metal and the presence of modifiers. Bare Pd, CO-modified Pd, Pb-poisoned Pd, Cu, Ni, and Cu—Ni catalysts have been studied in a continuous-flow reactor at ambient pressure covering a broad range of feed hydrogen-to-hydrocarbon ratios and conversion levels.

2. Experimental

Hydrogenation studies were conducted over six catalysts: commercial 1 wt.% Pd/γ-Al_2O_3 (Aldrich, ref: 20,570-2, $S_{BET} = 210\ m^2\ g^{-1}$), commercial Lindlar-type Pb-poisoned 5 wt.% Pd/$CaCO_3$ (Alfa Aesar, ref: 043172, $S_{BET} = 13\ m^2\ g^{-1}$), and self-made Cu_3Al (65 wt.% Cu and 8 wt.% Al, $S_{BET} = 71\ m^2\ g^{-1}$), Ni_3Al (58 wt.% Ni and 8 wt.% Al, $S_{BET} = 206\ m^2\ g^{-1}$), and $Cu_{2.75}Ni_{0.25}Fe$ (50 wt.% Cu, 5 wt.% Ni, and 18 wt.% Fe, $S_{BET} = 35\ m^2\ g^{-1}$). The catalysts are denoted along the manuscript by their respective active metal and modifiers, that is, Pd, Pd—CO (carbon monoxide was continuously added to the feed mixture), Pd—Pb, Cu, Ni, and Cu—Ni. The alumina-supported Pd catalyst was characterized and evaluated in the gas-phase hydrogenation of ethyne and propyne [13]. Details on preparation and characterization of the Cu, Ni, and Cu—Ni samples, as well as on their catalytic response in the gas-phase hydrogenation of propyne, can be found in recent publications [23,37–39]. The reader is addressed to these references for details on synthesis protocols and physico-chemical properties of the samples.

The gas-phase hydrogenation of valylene (VL) (ABCR-Chemicals, purity 97%), isoprene (IP) (ABCR-Chemicals, purity 99%), 3-methylbutyne (3MBy) (Acros Organics, purity 96%), and 1-penten-4-yne (ABCR-Chemicals, purity 95%) was studied at 1 bar in a fully-automated set-up equipped with mass-flow controllers (Bronkhorst, EL-FLOW) to feed gases (H_2, CO, and He), a syringe pump (Chemyx, Fusion 100) to feed the liquid hydrocarbons, an electrically-heated oven with a 12 mm i.d. quartz micro-reactor, and a gas chromatograph. The catalysts (sieve fraction 200–400 μm) were loaded in the tubular reactor and heated in He at 573 K for 30 min. Pd and Pd—Pb were evaluated as such, while the other catalysts were subjected to an additional pre-treatment: Pd—CO (0.1 vol.% CO in He, 348 K, 10 min), Cu, Ni, and Cu—Ni (5 vol.% H_2 in He, 773 K, 30 min). The liquid hydrocarbon was evaporated at 353 K and mixed with the gas mixture prior to the reactor inlet. The hydrogenation reactions were carried out at 348 K (Pd, Pd—CO, Pd—Pb), and 523 K (Cu, Ni, Cu—Ni). Reaction temperatures and pre-treatment conditions were selected on the basis of previous tests over these specific catalysts in propyne hydrogenation [37]. The hydrogen-to-hydrocarbon ratio dependence and 3-methylbutyne and 1-penten-4-yne hydrogenation were carried out over 0.3 g of catalyst. The inlet hydrocarbon concentration was 2.5 vol.%, the inlet H_2 concentration varied in the range of 2.5–30 vol.%, and the total flow was kept at $84\ cm^3$ STP min^{-1} by balancing the feed mixtures with He. The influence of the degree of hydrocarbon conversion on the product distribution was studied using catalyst amounts in the range of 0.01–0.2 g. In the experiments with a weight of catalyst $\leqslant$0.1 g, the bed was diluted with SiC (sieve fraction 200–400 μm) to minimize by-passing. The inlet hydrocarbon concentration was 2.5 vol.%, the inlet H_2 concentration was 2.5 vol.% (Pd, Pd—Pb) and 5 vol.% (Pd—CO, Cu, Ni, Cu—Ni). The total flow was varied in the range of 20–270 cm^3 STP min^{-1}, yielding space velocities (*SV*) of 6000–1620,000 $cm^3\ g^{-1}\ h^{-1}$. High space velocities were necessary in order to attain a low degree of conversion on the palladium-based catalysts. Hydrogenation tests with Pd/γ-Al_2O_3 were also carried out in the presence of 0.1 vol.% CO. Fresh catalyst was loaded for each hydrocarbon substrate, while the hydrogen-to-hydrocarbon and conversion dependence were studied without changing the catalytic bed. The catalytic performance was measured in steady state, after equilibration for at least 1 h at each experimental condition. The catalysts were stable during time-on-stream which went up to 10 h and this was corroborated by running the same experimental condition in different stages. Additionally, tests with different particle sizes and different total volumetric flows (at constant space velocity) were conducted to discard internal and external mass-transport constraints. It was further emphasized by the fulfillment of the Weisz–Prater criterion. Products in the outlet stream were analyzed using an on-line gas chromatograph (Agilent GC7890A) equipped with a GS-GasPro column (and an additional HP-Plot Q for the separation of the 1-penten-4-yne hydrogenation products) and a flame ionization detector. The tubes from the syringe connection to the gas chromatograph were heated at 393 K to prevent reactants and products condensation. The conversion, *X*, was determined as the amount of converted hydrocarbon divided by the amount of hydrocarbon at the reactor inlet. The selectivity, *S*, was calculated as the amount of product formed divided by the amount of converted hydrocarbon. The selectivity to oligomers was obtained using the carbon balance as $S(\text{oligomers}) = 1 - \Sigma S(\text{all other products})$.

3. Results and discussion

3.1. Valylene and isoprene hydrogenation

3.1.1. Comparison of Pd and Cu—Ni

Fig. 2 shows the conversion and product selectivity of Pd and Cu—Ni catalysts in valylene and isoprene hydrogenation at different hydrogen-to-hydrocarbon ratios. These two representative samples were selected in order to describe in more detail the range of products formed during hydrogenation of the conjugated hydrocarbons and their dependence with the inlet H_2:HC ratio. At H_2:VL = 1 (stoichiometric ratio for partial hydrogenation to isoprene) and 348 K, valylene conversion over Pd was 80% but increased to 100% at higher ratios (Fig. 2a). The high activity of palladium is expected attending to its unique ability to dissociate H_2, providing atomic hydrogen species that are active for hydrogenation. In terms of product distribution, the isoprene selectivity of Pd decreased from 53% to 4% upon increasing the H_2:VL ratio from 1 to 2. The sharp drop in the selectivity to the partially hydrogenated product occurred at the expense of an increased selectivity to mono-olefins, from 23% to a maximum of 68% at H_2:VL = 2. Methylbutenes (MBs = 2MB + 2M2B + 3MB) result from the second hydrogenation of valylene (Fig. 1). Further increase in the H_2:VL ratio led to a progressive decrease in the selectivity to mono-olefins (down to zero) with the concomitant production of the fully hydrogenated alkane. Accordingly, the selectivity to isopentane exceeds 95% at H_2:VL $\geqslant$ 6. The observed selectivity pattern as a function of the inlet partial H_2 pressure is characteristic of a consecutive hydrogenation scheme. C—C coupling reactions also occurred during valylene hydrogenation on palladium. Oligomers were formed with a selectivity of ca. 25% at H_2:VL = 1 and steadily decreased at H_2-richer conditions. It can be noticed that the production of methylbutenes and oligomers ceased at the same H_2:VL ratio of 6. 3-Methylbutyne (3MBy) was not observed on palladium, suggesting that the first hydrogenation step is chemoselective, that is, it exclusively forms isoprene by partial hydrogenation of the triple bond in valylene. A full degree of IP conversion was measured in isoprene hydrogenation at all H_2:IP ratios studied (Fig. 2b). The highest selectivity to the partially hydrogenated methylbutenes (73%)

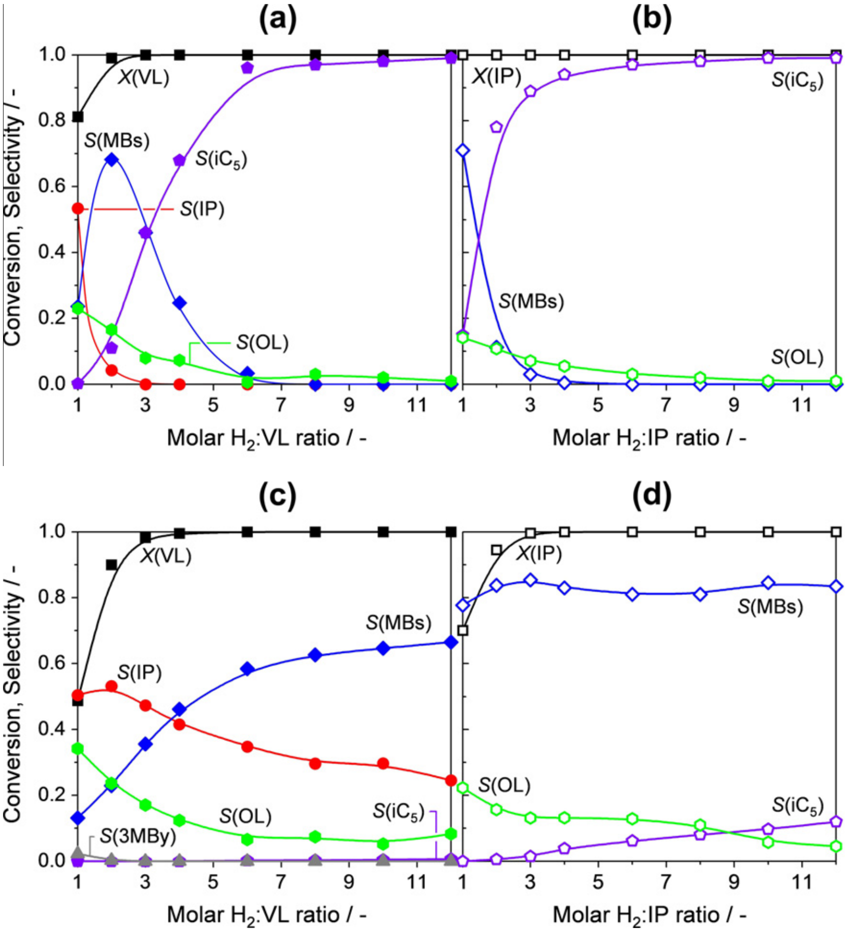

Fig. 2. Conversion and selectivity to products versus the feed hydrogen-to-hydrocarbon ratio in valylene (left graphs) and isoprene (right graphs) hydrogenation over (a, b) Pd at 348 K and (c, d) Cu—Ni at 523 K. Other conditions: HC = 2.5 vol.% and H_2:HC = 1–12, balance He, $SV = 16{,}800\ \text{cm}^3\ \text{g}^{-1}\ \text{h}^{-1}$, and $P = 1$ bar.

was obtained at H_2:IP = 1 and drastically decreased to zero at higher ratios at the expense of isopentane production. As expected, the selectivity to oligomers gradually decreased too.

The Cu—Ni catalyst exhibited remarkable differences compared with Pd (Fig. 2c and d). The hydrogenation activity of Cu—Ni was much lower; full conversion was reached at H_2:HC > 4 and 523 K. Cu—Ni displayed a higher selectivity to partially hydrogenated products in both valylene and isoprene hydrogenation. The isoprene selectivity in valylene hydrogenation reached a maximum of 53% at H_2:VL = 2 and decreased to 25% at H_2:VL = 12 at the expense of mono-olefins, whose selectivity increased from 13% to 67% (Fig. 2c). Cu—Ni possesses a broader H_2:HC window for selective operation than Pd, that is, the drop in selectivity to partially hydrogenated products was much less pronounced on the former catalyst. Isopentane production was negligible at any ratio. Another distinctive feature of Cu—Ni compared to Pd in valylene hydrogenation was the detection of 3-methylbutyne (*S*(3MBy) = 3% at H_2:VL = 1). The selectivity to oligomers on Cu—Ni was slightly higher than on Pd in the whole range of inlet partial H_2 pressures. During isoprene hydrogenation (Fig. 2d), the product distribution over Cu—Ni was hardly affected by the H_2:IP ratio. The selectivity to MBs was practically constant at ca. 85%. The selectivity to oligomers decreased progressively with the hydrogen content in the feed at the expense of isopentane production. Still, the $S(iC_5)$ was as low as 12% at H_2:IP = 12 in comparison with the value of 90% on Pd. A final observation from Fig. 2 is that oligomer production over the two metals was somewhat higher on hydrogenation of the more unsaturated ene-yne compound than of the diene.

3.1.2. Influence of H_2:HC ratio

Fig. 3 presents the overall comparison of catalytic systems in valylene (solid symbols) and isoprene (open symbols) hydrogenation. The influence of Pd modification by continuous CO feeding or Pb addition as well as the influence of the metal (Pd, Cu, Ni, Cu—Ni) was analyzed as a function of the feed H_2:HC ratio. The lead-poisoned Pd catalyst displayed full hydrocarbon conversion under all conditions studied. The copper-containing catalysts showed a drastic increase in valylene conversion from 30% (Cu) and 49% (Cu—Ni) to ~100% by increasing the H_2:VL ratio from 1 to 3. The presence of nickel promotes a higher conversion at a lower partial H_2 pressure, as a consequence of the ability of Ni to dissociate H_2 in comparison with Cu [37,39]. Pd—CO and Ni are much less active catalysts, showing 100% VL conversion at inlet H_2:VL ratios of 8 and 10, respectively. The low activity of the CO-modified Pd catalyst is assigned to the ability of CO to form very dense layers even at a low partial pressure [13], which implies a reduction in the number of adsorption sites for hydrogen and valylene. The relatively low activity of Ni can be attributed to fouling (formation of carbonaceous deposits), attending to the high selectivity to oligomers (vide infra).

In previous studies of gas-phase hydrogenation of propyne over the same catalysts [13,23,38,39], the alkyne conversion was complete at lower hydrogen-to-hydrocarbon ratio compared to valylene hydrogenation. The higher hydrogen-to-hydrocarbon ratio required to achieve full conversion of the polyunsaturated compound agrees with Molnár et al. [3]. These authors stipulated that conjugated hydrocarbons are strongly adsorbed on the surface due to the contribution of the entire π-system and thus the adsorbed valylene strongly competes with hydrogen for the active sites, lowering its coverage. The conversion patterns in isoprene hydrogenation (open symbols in Fig. 3, left) are comparable to those in valylene hydrogenation, although higher activities are generally observed upon decreasing the degree of substrate unsaturation. For example, the H_2:HC ratio for 100% valylene conversion over Pd—CO (8) or Ni (10) is decreased in both cases to 2 for 100% isoprene conversion. This may be due to the fact that the adsorption of isoprene was not so strong (in contrast to that of valylene) to hinder hydrogen dissociation.

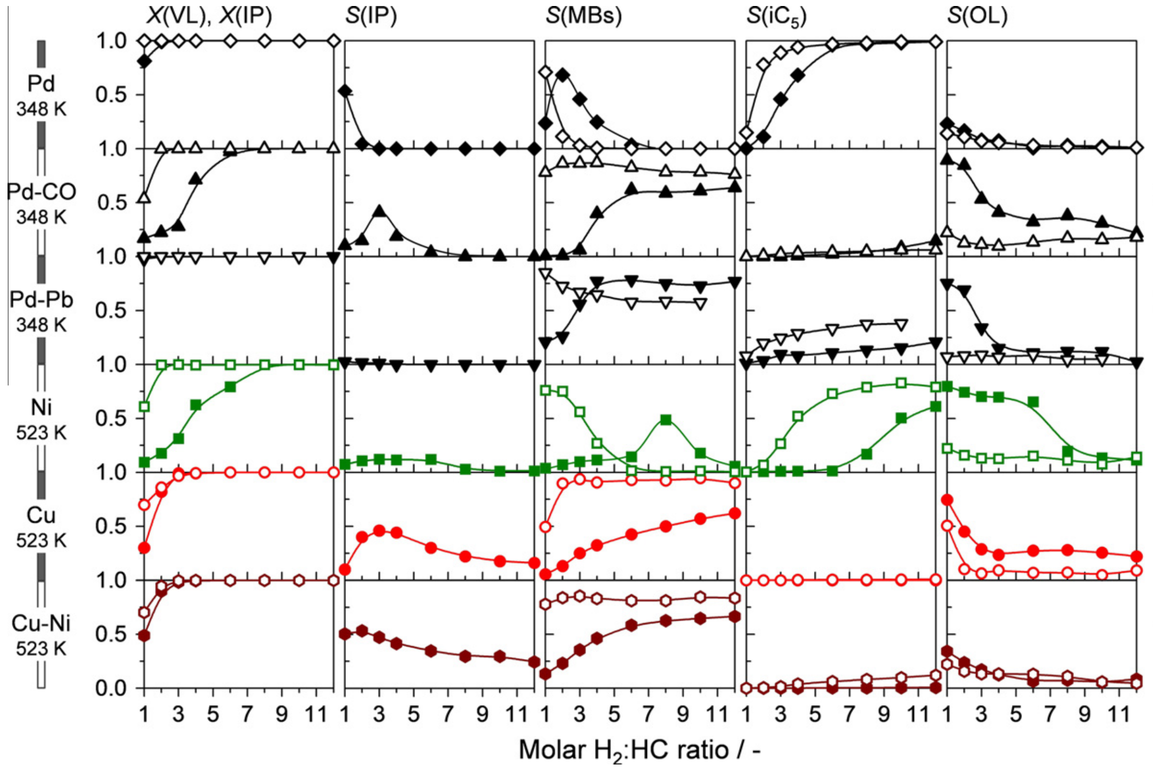

Fig. 3. Conversion and selectivity to products versus the feed hydrogen-to-hydrocarbon ratio in valylene (solid symbols) and isoprene (open symbols) hydrogenation. The side panels indicate catalyst and reaction temperature. Other conditions: HC = 2.5 vol.% and H_2:HC = 1–12, balance He, *SV* = 16,800 $cm^3\ g^{-1}\ h^{-1}$, and *P* = 1 bar.

The most exciting differences between the catalysts is related to their diverse selectivity patterns. Lead, a common selective poison of palladium-based hydrogenation catalysts [3,6,12,24,40,41], is a major and essential component of the widely applied Lindlar catalyst [42]. Recent Density Functional Theory simulations [15] have shown that by means of both electronic and geometric modifications, Pb (i) decreases the hydrogen coverage on Pd, (ii) hinders the formation of sub-surface hydride and carbide species (that lead to selective or unselective hydrogenation in mono-alkynes [8,13]), and (iii) enhances the thermodynamic control of the reaction by lowering the adsorption energies of surface moieties compared to pure Pd. Nevertheless, at this particular condition, Pd—Pb was an extremely poor catalyst for valylene hydrogenation to isoprene, with practically zero selectivity. Additionally, the C—C bond formation channel leading to oligomers is enhanced (*S*(OL) = 75%) compared to bare Pd that favors the production of isoprene under the same condition. No methylbutyne was produced either. On the other hand, the presence of lead in the palladium catalyst eased the desorption of mono-olefins (*S*(MBs) = 78% at H_2:VL = 10) and minimized the formation of isopentane (*S*(iC_5) < 20%) compared to bare Pd.

Continuous addition of carbon monoxide is industrially applied to enhance the selectivity of Pd catalysts in partial hydrogenation of alkynes in C_2—C_4 cuts of steam crackers [3,5,6]. Similarly to Pb, CO improves the thermodynamic factor, decreases the hydrogen coverage, and prevents the formation of sub-surface hydrides and carbides [13]. Our results indicated that, for the particular catalysts evaluated here, CO has a stronger impact than Pb on decreasing the hydrogen coverage. This is already clear from the much higher H_2:VL ratio required for full valylene conversion on Pd—CO (10) compared with Pd—Pb (1). Besides, Pd—CO showed a significant selectivity to isoprene (41% at H_2:VL = 3) in contrast to the zero IP production over the lead-poisoned Pd sample. Minor amounts of 3-methylbutene (*S*(3MBy) ~ 1.5%) were observed (not shown in Fig. 3). The production of IP and 3MBy highlights the impact of CO on the so-called thermodynamic factor. Carbon monoxide enhances the differential energy of adsorption between valylene and the products of the first hydrogenation. Upon increasing the inlet partial H_2 pressure, the selectivity to methylbutenes on Pd—CO increased up to ca. 65% at H_2:VL = 6, remaining constant at higher ratios. Oligomers were produced to a larger extent over Pd—CO than over Pd—Pb in the whole range of H_2:VL ratios (*S*(OL) ~ 90% at H_2:VL = 1 and still 22% at H_2:VL = 12). Oppositely, the CO-modified Pd catalyst experienced minor over-hydrogenation; there is practically no iC_5 production at H_2:VL < 10. In isoprene hydrogenation, the modification of bare Pd catalyst by Pb addition or by continuous CO feeding remarkably increased the production of mono-olefins, being the main product at any H_2:IP ratios. Pd—CO was more selective for partial hydrogenation (*S*(MBs) = 75% versus 57% on Pd—Pb at H_2:IP = 10). Concomitantly, Pd—Pb was more prone to over-hydrogenation (*S*(iC_5) = 38% versus <10% on Pd—CO at H_2:IP = 10), while Pd—CO favored oligomerization (*S*(OL) = 22% versus <5% on Pd—Pb at H_2:IP = 10). The modification of Pd using 0.1 vol.% CO was chosen based on our previous study in ethyne and propyne hydrogenation [13]. It cannot be ruled out that an optimized CO addition upon increasing the substrate complexity leads to a reduced C—C formation at the expense of partially hydrogenated products. Nevertheless, the effect of CO concentration in valylene and isoprene hydrogenation is beyond the scope of this study.

The product distribution of valylene hydrogenation over Ni markedly differed from the Pd catalysts (Fig. 3, squares). The selectivity to isoprene was very low (ca. 10%) and methylbutyne was produced with a selectivity not higher than 1%. The selectivity to MBs presented a volcano shape with a maximum of 49% at H_2:VL = 8. Below this ratio, oligomers were the main product (*S*(OL) ~ 75%). At H_2:VL > 6, the selectivity to iC_5 increased with the inlet partial H_2 pressure with the concomitant decrease in oligomerization. The product distribution of VL hydrogenation is highly sensitive to the hydrogen coverage. A similar conclusion derived from isoprene hydrogenation. At H_2:IP = 1, the selectivity to mono-olefins was 76% but dropped to 26% at H_2:IP = 4, at the expense of iC_5. Contrarily to valylene, isoprene hydrogenation on nickel led to little oligomerization, *S*(OL) ~ 10%.

The ability of nickel to crack hydrocarbons during the reaction was quantified. Previous experiments and DFT calculations have shown that step-edges of Ni(1 1 1) dissociate C—C bonds leading to carbon-containing fragments on the surface [43]. Fig. 4 shows the selectivity to oligomers, methylbutenes, and cracked hydrocarbons (C_1—C_4) analyzed by gas chromatography during valylene hydrogenation as a function of the H_2:VL ratio. As expected, at low hydrogen content, C—C formation was favored, while C—C scission was enhanced at high H_2 pressure leaving a very narrow window for selective hydrogenation. This feature largely restricts the use of Ni in partial hydrogenation of unsaturated hydrocarbons. As often done for palladium, nickel would require additional modifiers, e.g., pre-sulfidation, to moderate its ability to hydrogenate unsaturated substrates in a wider range of operating conditions.

Cu and Cu—Ni (circles and hexagons in Fig. 3, respectively) showed comparable selectivity patterns in VL hydrogenation. The promotion by nickel in Cu—Ni originally identified in propyne hydrogenation [23] also applies to valylene hydrogenation. At H_2:VL = 1, oligomers comprised the major product over Cu (*S*(OL) = 75%) and the selectivity to isoprene was limited to 10%. Under the same experimental condition, and due to a higher hydrogen coverage induced by the presence of small amounts of nickel [23], isoprene became the main reaction product (*S*(IP) = 50%) and the selectivity to oligomers decreased to 35%. The selectivity to 3-methylbutyne decreased from 10% on Cu to 3% on Cu—Ni. At a higher H_2:VL ratio, the selectivity to 3MBy over both Cu and Cu—Ni dropped to zero and the selectivity to oligomers decreased to 22% (Cu) and 8% (Cu—Ni). The IP selectivity over Cu displayed a maximum of 46% at H_2:VL = 3, while the MBs selectivity steadily increased from 6% to 62% with the H_2:VL ratio. The selectivity patterns of IP and MBs over Cu—Ni and Cu very much resemble at H_2:VL $\geqslant$ 3.

Contrarily to palladium, in which the sub-surface chemistry of carbide/hydride species plays an important role [8,13], the hydro-

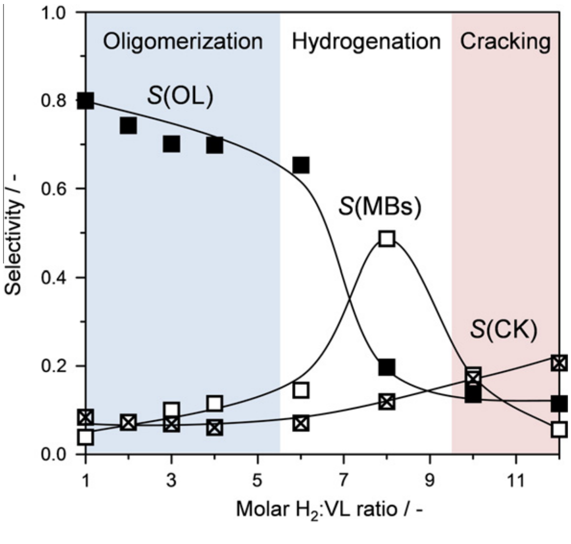

Fig. 4. Selectivity to oligomers, methylbutenes, and cracked products versus the feed hydrogen-to-valylene ratio over Ni at 523 K. Other conditions: VL = 2.5 vol.% and H_2:VL = 1–12, balance He, *SV* = 16,800 $cm^3\ g^{-1}\ h^{-1}$, and *P* = 1 bar.

genation over Cu-based catalysts is governed exclusively by surface species [37]. Therefore, the thermodynamic factor largely controls the product distribution. At low inlet partial H_2 pressure, the difference in binding energy between VL and IP (or 3MBy) was sufficient to induce high selectivity to the product of the first hydrogenation. However, at high H_2 content, the reaction was kinetically favored toward MBs. Nickel in the bimetallic Cu—Ni catalyst increased the hydrogen coverage to enhance the IP selectivity at a lower H_2:VL ratio, although this did not lead to isopentane production. The higher 3MBy selectivity in the absence of Ni suggests the low hydrogen coverage as the key factor to enhance the production of 3-methylbutyne on copper. During IP hydrogenation, Cu and Cu—Ni exhibited their intrinsically high and H_2-independent selectivity to mono-olefins (93% and 82%, respectively) at H_2:IP $\geqslant$ 2. Oligomers comprised the only side reaction over Cu, while the presence of Ni favored further hydrogenation of MBs to iC_5 (selectivity of 12% at H_2:IP = 12). Furthermore, it is important to note that the small addition of Ni in the Cu-based catalyst was not sufficient to enhance the cracking ability of the catalyst. This is in line with our previous study [44], where we reported by means of surface-sensitive in situ X-ray photoelectron and X-ray absorption spectroscopies that Ni would most probably not form large surface ensembles required to split C—C bonds.

3.1.3. Product distribution at variable conversion

The conversion and selectivity dependence on the feed hydrogen-to-hydrocarbon ratio in VL and IP hydrogenation enables a clear distinction between the catalytic systems. Nevertheless, the full degree of conversion at low hydrogen-to-hydrocarbon ratio over Pd, Pd—Pb, Cu and Cu—Ni implies that all reactants are consumed at a certain point within the catalytic bed and further reactions (hydrogenation, isomerization, and oligomerization) of the products might occur on the remaining catalyst. Fig. 5 shows the selectivity to products as a function of the degree of conversion during valylene hydrogenation over the catalysts. The feed H_2:VL ratio was established based on Fig. 3 and the degree of conversion was varied by changing the space velocity. As expected [32,40,45,46], an increase in space velocity over all catalysts decreased valylene conversion and enhanced selectivity toward partially hydrogenated products.

During hydrogenation over Pd, IP selectivity slightly decreased from 52% to 44% at the expense of MBs from X(VL) = 28–90%, respectively. A further increase to full conversion led to a drastic decrease in isoprene selectivity, an increased in mono-olefin selectivity, and to iC_5 production (14%). 3MBy was not formed, but oligomers were produced at all conversions and reached a minimum of 19% at X(VL) = 90%. The amount of oligomers progressively increased on decreasing the conversion, probably due to slow deactivation of Pd by fouling. On the other hand, the higher oligomerization at full degree of conversion is attributed to the low space velocity used. If full conversion is achieved at a certain depth within the catalytic bed, the low hydrogen coverage present in the remaining part enhances the formation of partially hydrogenated intermediates inducing C—C bond formation. This phenomenon was not observed upon varying the H_2:HC ratio (Fig. 3), since above the stoichiometric ratio (needed to reach full conversion), there was enough hydrogen in the feed to favor overhydrogenation.

Pd—Pb showed similar trends with important distinctive features that further highlight the effect of lead poisoning. As mentioned above, the presence of lead favors the mono-olefin desorption (S(MBs) = 75%) and suppresses the formation of iC_5 compared to bare Pd at full degree of valylene conversion. Nevertheless, the most striking difference is the increase in IP selectivity that reached ca. 70% at X(VL) = 82% and remained constant upon increasing the space velocity. This in agreement with Aduriz et al. [32] that reported an enhanced selectivity of the Pb-poisoned Pd catalyst at different degrees of conversion. The poor IP selectivity and the high C—C bond formation compared to Pd observed in Fig. 3 (H_2:VL = 1 and 2) is the proof of a sub-optimal space velocity which enhanced oligomer production. Nevertheless, the high mono-olefin selectivity at H_2:VL = 12 emphasized Pb as an efficient selective poison that enables the production of the MBs under extreme conditions (large catalyst amount and high H_2:HC ratio).

Cu and Cu—Ni exhibit remarkable differences compared to Pd as the decrease in conversion at a constant H_2:VL ratio (Fig. 5) did not strongly affect the product distribution. Selectivity to products at low degree of conversion over the Cu-based catalysts were stable up to X(VL) = 80% with an expected higher selectivity over Cu—Ni, S(IP) = 28% ant 60% for Cu and Cu—Ni, respectively. Nevertheless, upon further increase in conversion, the product distribution was barely changed over Cu, while the IP selectivity decreased from 60% to 44% over Cu—Ni. 3MBy was only observable over Cu (S(3MBy) = 8%).

3.2. Hydrogenation of 3-methylbutyne

The hydrogenation of 3-methylbutyne was carried out in order to analyze the interplay between isomerization and intrinsic regioselectivity in the obtained mono-olefin distribution during valyl-

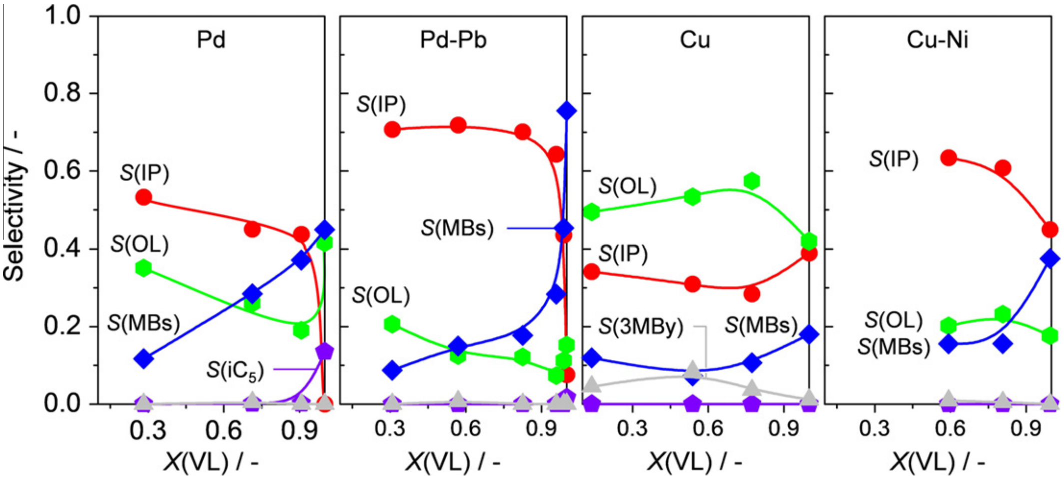

Fig. 5. Selectivity to products versus the degree of valylene conversion over Pd, Pd—Pb, Cu, and Cu—Ni. Conditions: VL = 2.5 vol.% and H_2:VL = 1 (Pd, Pd—Pb) and 2 (Cu, Cu—Ni), T = 348 K (Pd, Pd—Pb) and 523 K (Cu, Cu—Ni). Other conditions are detailed in the Experimental section.

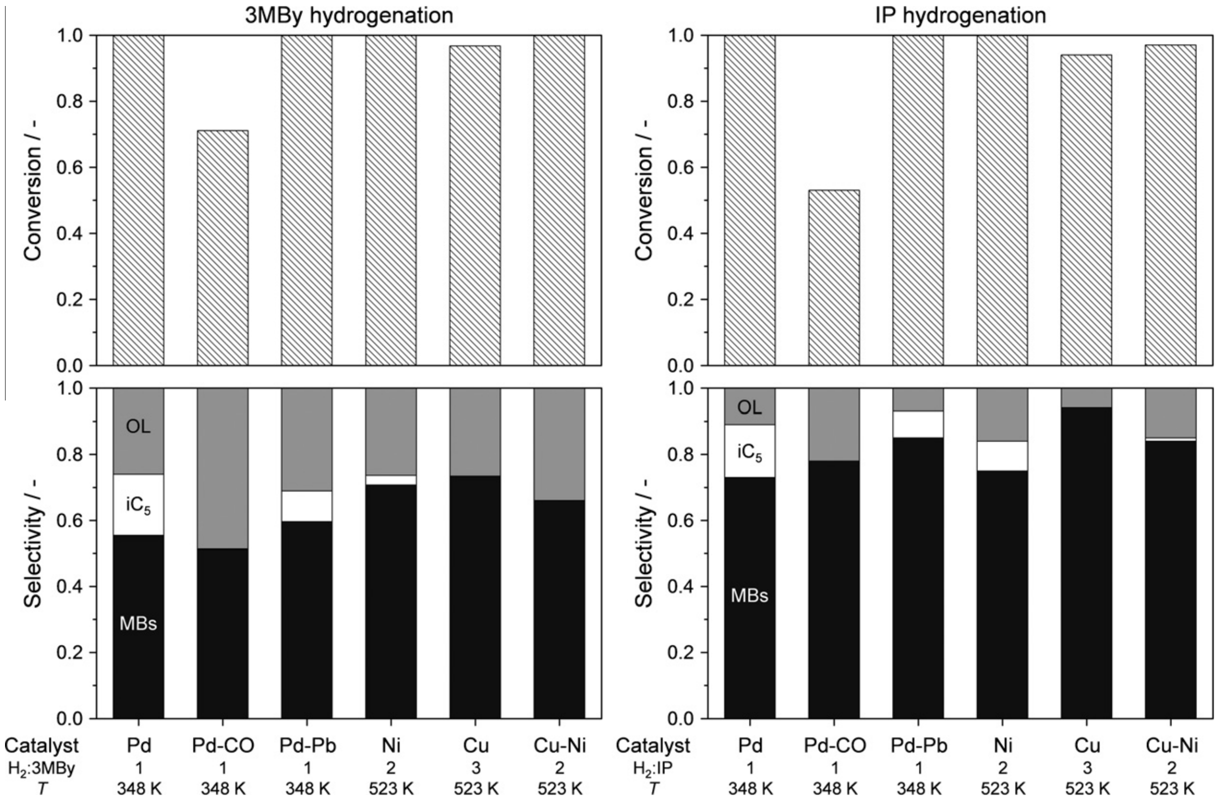

Fig. 6. Conversion (striped bar) and selectivity to MBs (solid bar), iC_5 (open bar), and OL (gray bar) in hydrogenation of 3-methylbutyne (left) and isoprene (right) over the catalysts. Reaction temperature and feed H_2:HC ratio for each catalyst are indicated. Other conditions: $SV = 16{,}800\ cm^3\ g^{-1}\ h^{-1}$ and $P = 1$ bar.

ene and isoprene hydrogenation (see Fig. 1). Fig. 6 compares conversion and selectivity in hydrogenation of 3MBy (left) and IP (right) over the six catalytic systems included in this study. These tests were done at a fixed H_2:HC ratio, which was selected to maximize the production of methylbutenes. Marked differences in 3MBy conversion and selectivity to MBs, iC_5, and OL were observed. The conversion over Pd, Pd—Pb, Cu, Ni, and Cu—Ni was ca. 100%, and 71% over Pd—CO. At the conditions applied, Cu proved to be the most selective catalyst to mono-olefins (65–70%), closely followed by nickel- and palladium-based catalysts (50–60%). Pd, Pd—Pb and Ni produced iC_5. Similarly to the valylene and isoprene tests, CO feeding suppressed over-hydrogenation at the expense of a lower activity.

Through the comparison of conversion and product distribution in 3MBy and IP hydrogenation at the same temperature and feed H_2:HC ratio (Fig. 6), the intrinsic selectivity of the diene and mono-alkyne to mono-olefins over the catalysts can be figured out. The conversion of 3MBy was slightly higher as well as the selectivity to oligomers. This is tentatively attributed to the stronger adsorption of the alkyne with respect to the diene [47]. IP hydrogenation led to an enhanced selectivity to MBs, while the iC_5 production from both substrates was comparable. Therefore, it can be concluded that 3MBy is slightly more reactive than IP and the alkyne functionality increases the oligomerization ability of 3MBy, while mono-olefin production is favored during IP hydrogenation. This is in line with Fig. 3, where more oligomers were produced in VL hydrogenation than in IP hydrogenation.

3.3. Selectivity patterns

In the case of valylene, chemoselectivity is regarded as the competitive hydrogenation of $C{=}C$ versus $C{\equiv}C$, leading to 3-methylbutyne or isoprene, respectively. The catalysts evaluated in this study

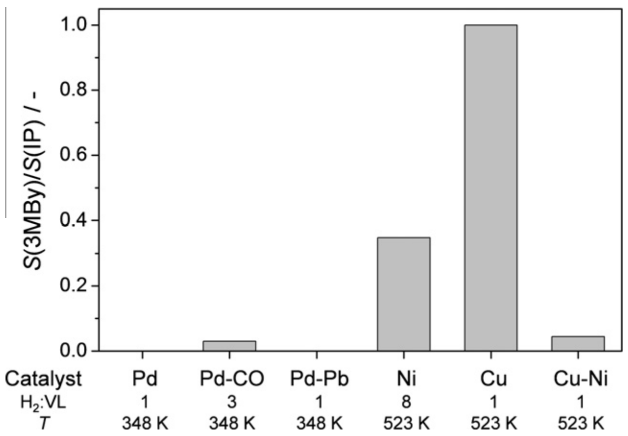

Fig. 7. Ratio of selectivities to 3-methylbutyne and isoprene in valylene hydrogenation over the catalysts. Reaction temperature and feed H_2:VL ratio for each catalyst are indicated. Other conditions: $SV = 16{,}800\ cm^3\ g^{-1}\ h^{-1}$ and $P = 1$ bar.

were generally highly chemoselective to isoprene, that is, the triple bond is predominantly hydrogenated. Fig. 7 shows the selectivity ratio of 3-methylbutyne and isoprene during valylene hydrogenation over the catalysts. In this comparison, the feed H_2:VL ratio for each catalyst was selected to maximize the production of 3MBy. Only Pd and Pd—Pb were purely chemo specific, that is, 3-methylbutyne was not detected at the reactor outlet. In the other extreme, Cu produced equivalent amounts of IP and 3MBy at H_2:VL = 1. Pd—CO and Cu—Ni produced very low though measurable amounts of 3-methylbutyne ($S(3MBy) \sim 1$–2%). Due to its extensive oligomerization, the chemoselectivity pattern of Ni could not be clearly established. The higher 3MBy production over

Pd—CO with respect to Pd and the lower 3MBy production of Cu—Ni with respect to Cu highlight the H coverage as an important factor governing chemoselectivity.

Isoprene hydrogenation raises an interesting feature during the first and second hydrogen addition as it reveals the regioselectivity patterns of each catalytic system. A regioselective reaction is one in which a specific direction of bond making or breaking occurs preferentially over all other possible directions. In the case of isoprene, it is a favored reduction of one C=C bond over the other by 1,2-addition of hydrogen (forming 2MB or 3MB) or by 1,4-addition (forming 2M2B) (Fig. 1). Nevertheless, it is very complicated to unravel the true regioselectivity patterns of each catalyst based on the mono-olefin distribution at the reactor outlet during valylene/isoprene hydrogenation, since isomerization that lead to C=C shift within the products may play an important role. Nevertheless, the isomerization ability of the catalyst can be derived from the mono-olefin distribution during partial hydrogenation of 3MBy. In addition of being a probe molecule that belongs to the valylene hydrogenation pathway, 3-methylbutyne possesses a terminal alkyne that should lead exclusively to 3MB upon H_2 addition.

Fig. 8 compiles the MBs distribution during VL, IP, and 3MBy hydrogenation under the same condition that maximized the methylbutene production. Pd was very prone to isomerize and produced 66% and 12% of 2M2B and 2MB, respectively during 3MBy hydrogenation. The use of modifiers decreased (Pd—Pb) or even suppressed (Pd—CO) the ability of palladium for mono-olefin isomerization. Anderson et al. [12] reported that Pd modification by Pb is more efficient in suppressing cis–trans isomerization than the double-bond shift in the liquid-phase 2-hexyne and 1-hexyne hydrogenation, respectively. Nevertheless, in gas-phase valylene hydrogenation, Pb-poisoned Pd significantly reduced isomerization compared to bare Pd. On the other hand, Silvestre-Albero et al. [45] concluded that CO is inefficient in suppressing isomerization during 1,3-butadiene hydrogenation using a feed H_2:1,3-butadiene = 2. Nevertheless, under our condition (H_2:3MBy = 1), negligible isomerization of 3MB occurred, which further highlights the influence of the H coverage on isomerization during the overall hydrogenation process. Contrarily to Pd, Cu did not isomerize and produced exclusively 3MB during 3MBy hydrogenation. This result is in agreement with Koeppel et al. [47] that reported only 1-butene production during 1-butyne hydrogenation over Cu/SiO_2. The bimetallic Cu—Ni catalyst was inactive for isomerization, too. This result could have been anticipated as nickel itself showed minor isomerization, with only 2% and 1% of 2M2B and 2MB, respectively.

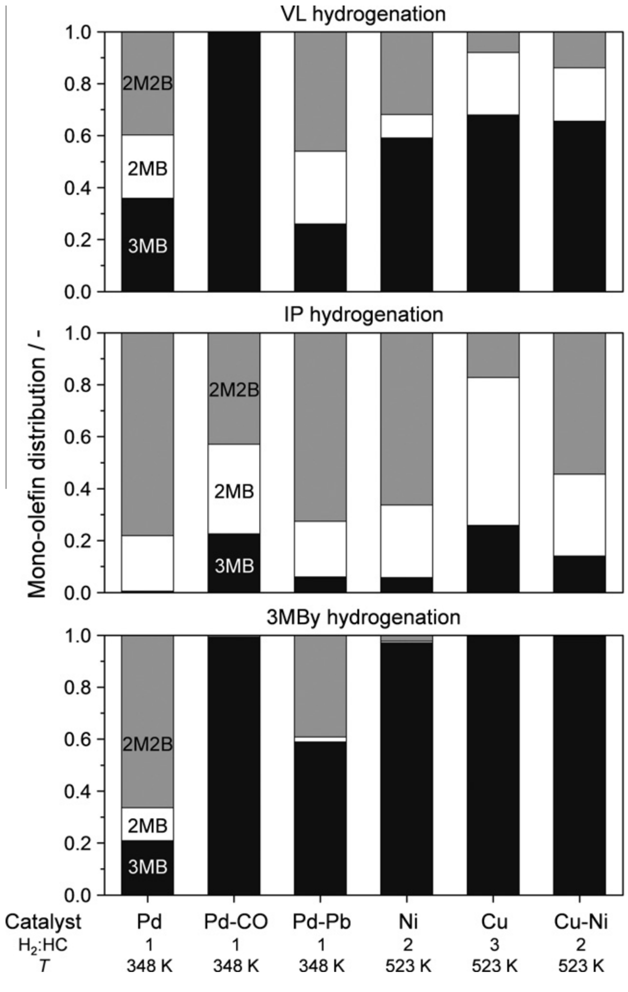

Fig. 8. Mono-olefin distribution in hydrogenation of valylene, isoprene, and 3-methylbutyne over the catalysts. Reaction temperature and feed H_2:HC ratio for each catalyst are indicated. Other conditions: $SV = 16{,}800\ cm^3\ g^{-1}\ h^{-1}$ and $P = 1$ bar.

No definitive conclusion can be derived on the intrinsic regioselectivity of the catalysts that showed isomerization for system in which it was not possible to quantify the C = C shift. As mentioned above, inappropriate space velocity promotes consecutive (over-hydrogenation) and/or side reaction (isomerization and oligomerization) that may lead to inconclusive interpretations of the mono-olefin distribution. Fig. 9 shows the mono-olefin distribution according to the degree of conversion during isoprene hydrogenation over the catalysts. The H_2:IP feed ratio was established according to Fig. 3 and the degree of conversion was varied by changing the space velocity. As expected from the 3MBy hydrogenation, Cu was the only catalyst that did not show any variation in its mono-olefin distribution upon decreasing conversion. The most drastic changes were observed over Pd. At 100% conversion, 2M2B was the predominant MBs (88% of the mono-olefins). Upon increasing the space velocity up to X(IP) = 65%, the relative 2M2B production drastically decreased to 53% at the expense of both terminal alkenes. Nevertheless from X(IP) = 65% to 28%, little variation in the mono-olefin distribution was observed. Similar selectivity patterns were derived during IP hydrogenation over Pd—Pb and Pd—CO. 2M2B production concomitantly decreased with the conversion degree at the expense of 2MB and 3MB. The only difference was that below X(IP) = 85% and 80% for Pd—Pb and Pd—CO, respectively, the mono-olefin distribution during IP hydrogenation became conversion independent. Goetz et al. [40] reported that two mechanisms are involved in isomerization. The Horiuti–Polanyi type mechanism that is favored at high H coverage, and the intra-molecular hydrogen shift mechanism that does not require the participation of adsorbed hydrogen. Both mechanisms are clearly identified over Pd. At low conversion (X(IP) < 65%), the H coverage is sufficiently high to favor the former mechanism. Upon increasing conversion, the lack of H on the surface enhances the intra-molecular mechanism and therefore, the drastic variation of mono-olefin at high degree of conversion is attributed to the co-existing isomerization mechanisms. Contrarily, over Pd—Pb and Pd—CO, the variation on the mono-olefin distribution only occurs at high degree of conversion. This is attributed to the intra-molecular isomerization mechanism (favored at low H coverage). In agreement with 3MBy hydrogenation, both Pb and CO modifiers reduce the degree of isomerization over Pd. The suppression of the Horiuti–Polanyi isomerization mechanism at low conversion enables the identification of regioselectivity. During IP hydrogenation, 40% of H additions over Pd—Pb occurred through 1,4-addition and 60% through 1,2-addition leading to equal amounts of 2MB and 3MB. Pd—CO showed a different regioselectivity exhibiting 62% of 1,4-addition products.

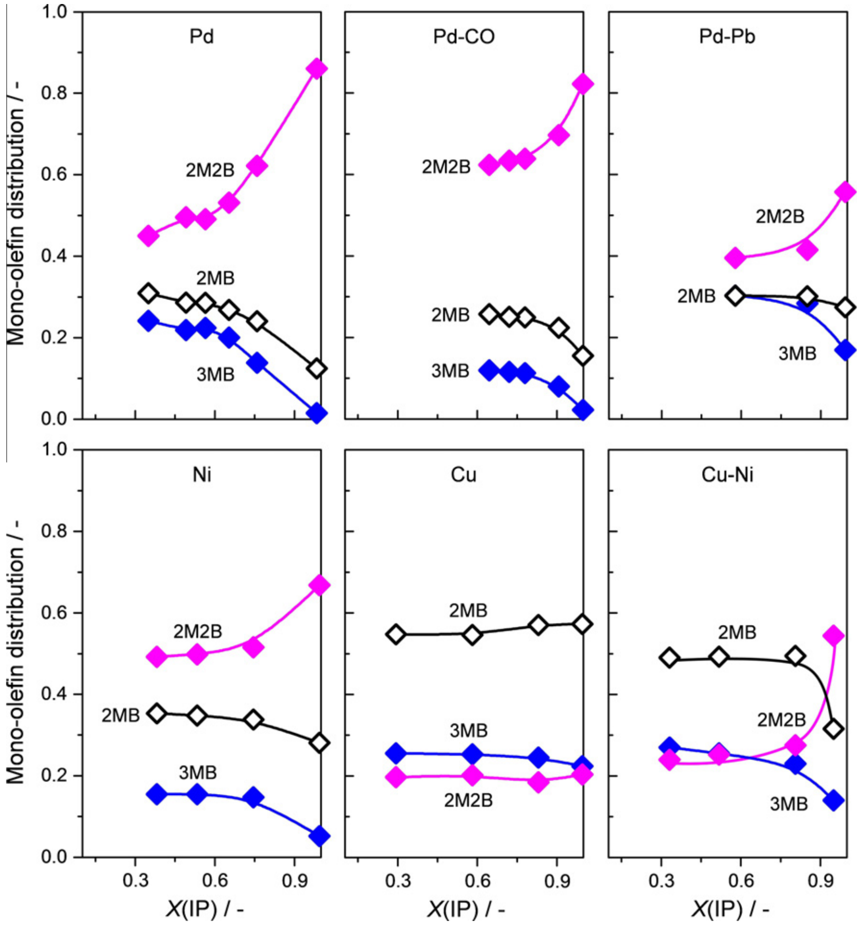

Fig. 9. Mono-olefin distribution versus the degree of conversion in isoprene hydrogenation over the catalysts. Conditions: IP = 2.5 vol.% and H_2:IP = 1 (Pd, Pd—Pb) and 2 (Pd—CO, Cu, Ni, Cu—Ni), T = 348 K (Pd, Pd—CO, Pd—Pb) and 523 K (Cu, Ni, Cu—Ni). Other conditions are detailed in the Experimental section.

Likewise, the mono-olefin distribution over Ni was conversion independent from X(IP) = 38% to 75%, with 50%, 35%, and 15% of 2M2B, 2MB, and 3MB, respectively. At high conversion, the increase in 1,4-addition products reveals the presence of intra-molecular isomerization. This is in close agreement with the results of 3MBy hydrogenation in which little isomerization was observed at 100% conversion.

The mono-olefin distribution during IP hydrogenation over Cu—Ni is independent of the degree of conversion up to 80% and shows an intrinsic regioselectivity resembling that of Cu (Fig. 9). The 1,2-addition is favored toward 2MB production (50%). Nevertheless, a clear increase in 2M2B at the expense of 2MB at higher conversions evidenced intra-molecular isomerization. This result is not in disagreement with Fig. 8 as most of the 2M2B was produced from 2MB isomerization that was not produced during 3MBy hydrogenation. We assume that isomerization by intermolecular hydrogen over Cu—Ni is favored over the branched carbon from 2MB to 2M2B than from 3MB to 2M2B.

Finally, the comparison of the MBs distribution in VL and IP hydrogenation (Fig. 8) gives further insights into the chemoselectivity of the catalytic systems. The higher 3MB production during VL hydrogenation is the proof of the hydrogenation pathway with 3MBy as intermediate. Therefore, Pd and Pd—Pb, which were described as the only chemo specific catalysts, should be revised and restricted to the only catalysts that did not produce 3MBy. This is in agreement with the higher reactivity of the alkyne that once produced on Pd and Pd—Pb surface does not desorb and gets further hydrogenated. It has to be mentioned that the excessively high relative production of 3MB compared to 2MB and 2M2B during VL hydrogenation over Pd—CO should be taken with care due to the very low conversion under this condition. Cu was the only catalyst that allowed a clear interpretation of chemo- and regioselectivity according to the relative mono-olefin distribution. Taking into account that 2MB and 2M2B are produced exclusively from isoprene hydrogenation, and the composition of MBs is 3MB:2MB:2M2B = 1.5:3:1 and 8.5:3:1 during IP and VL hydrogenation, respectively, we can conclude that 56% of VL was hydrogenated through a 3MBy intermediate on Cu. This result is in agreement with the equivalent IP and 3MBy selectivity during valylene hydrogenation at H_2:VL = 1.

3.4. Ene-yne versus simpler alkynes

Fig. 10 shows the selectivity toward the products of the first hydrogenation of valylene, isoprene, and propyne, that is, isoprene + 3-methylbutyne, methylbutenes, and propene, respectively. These selectivities are compared under the same conditions that lead to the highest IP + 3MBy selectivity during VL hydrogenation (see Fig. 3). At first glance, the selectivity to the first hydrogenated product is lower in valylene hydrogenation than in isoprene or propyne hydrogenation. These results can be easily understood by the nature of the product from the first H_2 addition on VL (IP + 3MBy) that are still highly unsaturated products and their strong adsorptions compete with VL, which drastically enhance further hydrogenation. On the other hand, the products from the first hydrogenation of isoprene and propyne possess only one unsaturation and hardly compete with the reactant. In addition to chemoselectivity, regioselectivity, and

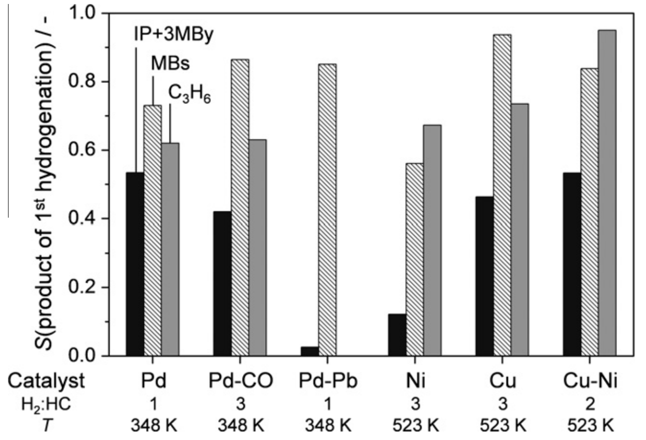

Fig. 10. Selectivity to the product of the first H_2 addition on valylene (solid bar), isoprene (striped bar), and propyne (gray bar). Reaction temperature and feed H_2:HC ratio for each catalyst are indicated. Other conditions: SV = 16,800 $cm^3\ g^{-1}\ h^{-1}$ and P = 1 bar.

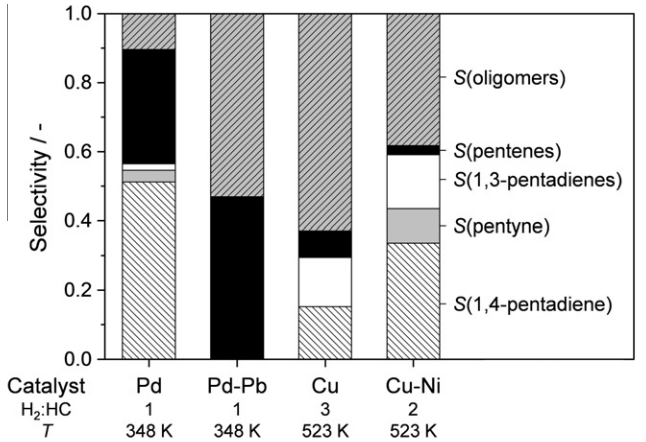

Fig. 11. Selectivity to products in 1-penten-4-yne hydrogenation over Pd, Pd—Pb, Cu, and Cu—Ni. Reaction temperature and feed H_2:1-penten-4-yne ratio for each catalyst are indicated. Other conditions: SV = 16,800 $cm^3\ g^{-1}\ h^{-1}$, and P = 1 bar.

isomerization issues intrinsic to valylene, the selectivity control in terms of consecutive hydrogenation remains a challenging task compared to propyne or even isoprene hydrogenation. Upon comparison between *S*(MBs) and *S*(propene) during isoprene and propyne hydrogenation, respectively, an interesting feature appeared. Due to the stronger adsorption of the alkyne with respect to the diene, one could expect a higher relative selectivity to the first hydrogenated product during propyne hydrogenation compared to IP hydrogenation. Nevertheless, the minor steric hindrance of propyne coupled with the ability of the alkyne to form oligomers decrease propene selectivity in propyne hydrogenation compared to MBs selectivity in IP hydrogenation.

Complementarily to valylene hydrogenation, 1-penten-4-yne, the smallest branched hydrocarbon possessing non-conjugated ene-yne, was used to investigate the impact of conjugation in heterogeneously catalyzed hydrogenation. Fig. 11 shows the selectivity to products during 1-penten-4-yne hydrogenation over Pd, Pd—Pb, Cu, and Cu—Ni. These catalysts were chosen since they are the most appropriate for ene-yne compounds hydrogenation according to Fig. 3. The reactions were undertaken at a fixed H_2:HC ratio, which was selected to maximize the partially hydrogenated production. A full degree of conversion was achieved over all catalysts. However, marked differences in product distribution were observed. The selectivity trends derived from valylene hydrogenation were ascertained. Under the conditions applied, no overhydrogenation leading to pentane was evidenced in any case. Pd was the most selective catalyst toward the non-conjugated diene (*S*(1,4-pentadiene) = 51%). No 1,4-pentadiene was formed over Pd—Pb which produced only pentenes and oligomers. The most important point arises with the production of the conjugated 1,3-pentadienes over Pd (2%), Cu (14%), and Cu—Ni (16%). The presence of the conjugated dienes is attributed to the isomerization of diolefin. This restores the conjugation, enhancing the stability of the molecule. Although operating at full conversion may bias the interpretation, the comparison from valylene and 1-penten-4-yne highlights that a single carbon atom between the ene and the yne functionalities is insufficient to overcome the "selectivity challenge" of partial hydrogenation of conjugated ene-yne compounds. More separation between the double and triple bonds in the hydrocarbon is required to minimize conjugation effects in partially hydrogenated intermediates, which makes selectivity control extremely difficult.

4. Conclusions

The gas-phase hydrogenation of valylene and isoprene has been systematically studied in a broad range of hydrogen-to-hydrocarbon ratios and degrees of conversion over heterogeneous catalysts, including Pd, Pb-poisoned Pd, CO-modified Pd, Ni, Cu, and Cu—Ni. Favorable reaction paths, leading to chemoselectivity, regioselectivity, isomerization, full hydrogenation, oligomerization, and C—C bond scission footprints, are determined by the nature of the metal and the modifier. Bare Pd and lead-poisoned Pd catalysts were highly chemo specific and continuous CO feeding is a particular effective strategy to decrease Pd activity and widen the window for selective hydrogenation. Cu produced equivalent amounts of isoprene and 3-methylbutene at a hydrogen-to-valylene ratio of 1. Ni-promoted Cu catalyst enhances isoprene selectivity and decreases oligomerization, while Ni-based catalyst was the less suitable catalyst for ene-yne and diene hydrogenation due to extensive oligomerization and cracking. The distribution of mono-olefins from isoprene and 3-methylbutyne hydrogenation was compared in order to understand the interplay between regioselectivity and isomerization on the catalysts. Cu, Cu—Ni, Ni, and Pd—CO showed negligible isomerization during 3-methylbutyne hydrogenation compared to Pd and Pb—Pd. Nevertheless, the mono-olefin distribution dependence on the degree of isoprene conversion highlighted that most catalysts promoted intra-molecular isomerization and favored the 1,4-addition product at full conversion. Cu was the only catalyst for which isomerization was not observed, resulting in an enhanced selectivity to 1,2-addition olefins. Low conversion levels enabled the study of catalytic performance in the absence of isomerization. Consequently, the intrinsic regioselectivity of Pd—Pb, Pd—CO, Ni, and Cu—Ni was derived. Comparison with simpler alkynes such as propyne or even isoprene emphasized the challenges in selectivity control during hydrogenation of conjugated (valylene) or non-conjugated (1-penten-4-yne) ene-yne compounds. Our results derived from the selectivity dependence on hydrogen-to-hydrocarbon ratio and the degree of conversion highlight the importance of catalyst and reactor design in ene-yne hydrogenation.

Acknowledgment

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