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Research Note

Permanent alkene selectivity enhancement in copper-catalyzed propyne hydrogenation by temporary CO supply

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ABSTRACT

Temporary supply of CO during propyne hydrogenation over a copper-based catalyst derived from a Cu-Al hydrotalcite permanently increased the alkene selectivity from 60% to 92% at 100% alkyne conversion (473 K). The superior performance of the CO-modified copper catalyst (higher alkene selectivity and resistance against deactivation by fouling) was further confirmed at lower temperature (373 K). Our catalytic results suggested that carbon monoxide in the presence of propyne and hydrogen irreversibly restructures the catalyst surface leading to a smaller copper ensemble that minimizes C–C coupling. Consequently, the enhanced alkene production in the CO-modified catalyst was coupled to a decreased oligomer production and very little propane production. The pretreatment mixture, feed CO concentration, and type of alkyne are important aspects to attain a selective copper catalyst. The CO effect in alkyne hydrogenation over copper radically differs from that over palladium or nickel. On the latter two metals, the increased alkene selectivity in the presence of CO is mostly due to a reduction in the over-hydrogenation channel. In addition, the effect is fully reversible, that is, it vanishes on removing CO from the feed. The permanent modification of the copper ensemble by CO might be advantageous for (chemo) selective hydrogenations of high acetylenic substrates.

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1. Introduction

The importance of modifiers has been recognized since catalysts were first applied in industrial processes [1,2], and their use in commercial heterogeneous catalysts is common practice for a wide range of reactions [3]. A modifier can be generally defined as a component of the catalyst or an additional substance introduced in the chemical process that improves the activity, selectivity, or lifetime of the active substance without having any significant activity on its own [4]. The effect of modifiers on catalysts may be textural, structural, electronic, or a combination thereof, and in most cases, these promoting additives are identified in a purely empirical way [1]. A detailed understanding of the precise role(s) of modifiers in the catalytic reaction is often a very complex task.

Modifiers are widely applied in partial hydrogenation of acetylenic compounds. Their presence is mandatory to increase the selectivity and/or lifetime of palladium, which is the preferred active metal for this type of reactions [5,6]. For example, the Lindlar catalyst [7] is a classical for the three-phase selective hydrogenation of acetylenic compounds in the fine chemical industry. A typical Lindlar catalyst contains 5 wt.% Pd on CaCO₃ and requires

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being poisoned by lead and quinoline in order to minimize side paths reducing the alkene selectivity.

The partial hydrogenation of alkynes on palladium is widely applied in the petrochemical industry for the purification of olefin streams (ethylene, propylene, and butylenes) from steam crackers [8]. The standard catalyst contains 0.01-0.05 wt.% Pd on lowsurface-area alumina and is modified by a second metal (e.g. Ag and Au) in order to increase the alkene selectivity [4,5]. Continuous CO addition is a common way in practice to enhance the alkene selectivity in Pd-catalyzed front-end and tail-end alkyne hydrogenation [4,5,8,9]. The inlet CO concentration varies in the range of 150–5000 ppm depending on the hydrogen content in the stream. Both electronic and geometric effects account for the role of carbon monoxide as selectivity modulator in alkyne hydrogenation on Pd [10,11]. CO is a reversible modifier, that is, its positive effect on the alkene selectivity vanishes once removed from the feed [4,5]. Recently, Trimm et al. [12] observed increased propene selectivity on Ni/SiO₂ when CO was fed during propyne hydrogenation. Disadvantageously, CO addition led to increased oligomerization and decreased alkyne conversion due to the lowered concentration of surface hydrogen atoms. Similarly to palladium, the CO effect on nickel was found to be fully reversible.

Our recent studies in this field have accomplished an improved understanding of alkyne hydrogenation over different metals

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(namely Pd, Au, Ni, and Cu) in order to design more selective catalysts [10,11,13-18]. Copper-based catalysts have been investigated due to their intrinsic high alkene selectivity. However, their poor ability to split H₂ often leads to extensive oligomerization [16], unless being modified by nickel and iron [17]. To the best of our knowledge, the influence of CO on copper-catalyzed alkyne hydrogenation has not been assessed. In this study, a standard Cu-Al catalyst was namely tested in propyne hydrogenation in the absence and presence of CO. Temporary supply of carbon monoxide during C_3H_4 hydrogenation permanently increased the C_3H_6 selectivity from 60% in the unmodified catalyst [16] to >90% in the CO-modified counterpart (this work). CO irreversibly restructures the catalyst so that the oligomerization path is minimized. The pretreatment conditions and the type of alkyne are crucial aspects for attaining a selective copper catalyst. The function of CO as selectivity modulator on Cu is different compared to Pd and Ni and might open interesting opportunities in (chemo) selective hydrogenations of high acetylenic substrates.

2. Experimental

The preparation and characterization of the copper catalyst used in this study was detailed elsewhere [16]. Briefly, the precursor was a Cu-Al hydrotalcite with a nominal Cu/Al ratio = 3 prepared by continuous coprecipitation. The clay-like precursor was fully decomposed by calcination in static air at 873 K for 15 h using a heating rate of 5 K min⁻¹, leading to crystalline tenorite (CuO) and amorphous alumina. The gas-phase hydrogenation of propyne was studied at ambient pressure and 373-473 K in a MicroActivity Reference set-up (PID Eng&Tech). The calcined sample (150 mg, sieve fraction 200-400 µm) was loaded in the 12 mm i.d. guartz micro-reactor, heated in He up to 773 K and reduced in 5 vol.% H₂ in He at this temperature for 30 min to attain full copper reduction, and finally cooled down to the reaction temperature in He. The reduced catalyst presented a total surface area of 68 m² g⁻¹ (BET method, N₂ adsorption at 77 K), an average Cu crystallite size of 20 nm (Scherrer method, X-ray diffraction), and a copper surface area of 5.7 $m^2 g^{-1}$ (pulse N₂O chemisorption) [16]. The weight loss of the calcined sample during reduction was estimated at 16%, so that the amount of reduced catalyst prior to the alkyne hydrogenation tests was ca. 125 mg.

The standard catalyst testing protocol includes the following steps: (i) propyne hydrogenation using 2.5 vol.% C_3H_4 and 7.5 vol.% H_2 in He (denoted as mixture A) for 5 h, (ii) addition of

CO (0.5–5 vol.%) to mixture A (denoted as mixture B) for 5 h, and (iii) switch from mixture B to mixture A or vice versa. In addition, the reaction with mixture A was carried out over the catalyst pretreated at 473 K for 5 h in CO, H₂ + CO, C₃H₄ + CO, C₃H₆ + CO, C₃H₄ + H₂ + CO, and C₃H₆ + H₂ + CO (7.5 vol.% H₂, 2.5 vol.% C₃H₄ or C₃H₆, and 5 vol.% CO, He balance). The total flow in the various steps (reduction, pretreatment, and reaction) was kept at 42 cm³ STP min⁻¹ by balancing the feed mixture with helium. Fresh catalyst was loaded for each inlet CO concentration and pretreatment mixture. Ethyne hydrogenation was studied in the same reactor set-up at 523 K using a feed mixture of 2.5 vol.% C₂H₂ and 7.5 vol.% H₂ in He.

The concentrations of alkyne, alkene, and alkane at the reactor outlet were analyzed by a gas chromatograph (Agilent GC6890N) equipped with a GS-GasPro column and a thermal conductivity detector. The alkyne conversion was determined as the amount of reacted alkyne divided by the amount of alkyne introduced in the reactor. The selectivity to alkene (alkane) was determined as the amount of alkyne, and the selectivity to oligomers was obtained as S(oligomers) = 1 - S(alkene) - S(alkane).

Some of the catalysts used in propyne hydrogenation were characterized *ex situ* by X-ray diffraction (XRD) and temperatureprogrammed oxidation coupled to mass spectrometry (TPO-MS). XRD was measured in a Bruker AXS D8 Advance diffractometer equipped with a Cu tube, a Ge(1 1 1) incident beam monochromator ($\lambda = 0.1541$ nm), and a Vantec-1 PSD. Data were recorded in the range of 5–70° 2 θ with a step size of 0.02° and a counting time of 4 s per step. TPO in air was measured in a Thermo TPDRO 1100 unit coupled to a quadrupole mass spectrometer (Omnistar GSD 320 O1, Pfeiffer Vacuum). The sample (ca. 20 mg) was loaded in the quartz micro-reactor (11 mm i.d), and the temperature was ramped from 323 to 1173 K at 10 K min⁻¹ in 20 cm³ STP min⁻¹ of air. The atomic mass units m/z = 18 (H₂O) and m/z = 44 (CO₂) were monitored.

3. Results

Fig. 1 shows the selectivity to propene, propane, and oligomers of the copper catalyst in propyne hydrogenation at 473 K alternating mixtures A and B and other intermediate treatment steps. The reader is guided through this figure by the encircled codes 1–11. The propyne conversion in the whole set of experiments at this temperature was 100%. In the first 5 h (step 1), the catalyst was



Fig. 1. Selectivity to propene (circles), propane (diamonds), and oligomers (triangles) versus time in propyne hydrogenation at 473 K over the copper catalyst. The test involved the alternation of two different feed mixtures (A and B) and other intermediate steps. Mixture A ($C_3H_4/H_2/He = 2.5/7.5/90$) and mixture B ($C_3H_4/CO/H_2/He = 2.5/5/7.5/85$).

tested in mixture A ($C_3H_4/H_2/He = 2.5/7.5/90$), yielding the anticipated propene selectivity of 60% [16]. The selectivity to oligomers was 40%, and no over-hydrogenated product was observed. Continuous addition of carbon monoxide $(C_3H_4/CO/H_2/He = 2.5/5/7.5/85,$ mixture B) progressively increased the C₃H₆ selectivity up to 80%, coupled to a decreased oligomer production (step 2). Upon removal of CO from the feed (step 3), that is, restoring mixture A, the most striking result was observed. The selectivity to propene was boosted to 92%, the selectivity to oligomers dropped to 5%, and little but measurable propane production (3% selectivity) was observed. Together with the ternary Cu-Ni-Fe catalysts reported elsewhere [17], this is one the highest alkene selectivity values reported over a copper catalyst in gas-phase alkyne hydrogenation. After 5 h, CO was readmitted (step 4) and C_3H_6 selectivity went quickly back to 80% as in step 2 and oligomers comprised the only by-product. A new interruption of the CO feed (step 5) rapidly resumed the C_3H_6 selectivity at >90% as in step 3. The instantaneous decrease or increase in the propene selectivity when shifting from mixture A to B or vice versa after step 2 can be related to the fast CO adsorption/desorption equilibrium on the catalyst.

In order to demonstrate the permanent effect by CO addition on the alkene selectivity, the propyne hydrogenation in step 5 was sustained for 60 h, resulting in a very stable performance. These results strongly suggest that the presence of CO in the alkyne + hydrogen mixture during step 2 irreversibly changed the structure of the active sites, making them far more selective to the alkene. The state of the copper catalyst upon CO modification was very robust. The sample used in steps 1-5 was discharged from the quartz reactor and stored for 10 days in an open vial under ambient conditions (step 6). Afterwards, the sample was retested in mixture A (step 7). In the first minutes, the selectivity to propene was 85% and increased gradually to almost 90%, approaching the stable selectivity value of the long run in step 5. The irreversible modification by CO on the alkene selectivity in alkyne hydrogenation over copper radically differs from its reversible CO effect on Pd and Ni [4.5.12]. On the latter two metals, the selectivity modulation disappears when CO in the feed is cut off. This implies that, in practice, continuous CO feeding is required to sustain the higher alkene selectivity. Advantageously, the copper catalyst only requires a relatively short pretreatment in propyne, hydrogen, and carbon monoxide to attain an outstanding selectivity to the double bond.

Fig. 2 shows that the inlet CO concentration plays an important role in the alkene selectivity enhancement on copper. Carbon monoxide was fed at levels of 0.5, 1, and 5 vol.% to $C_3H_4 + H_2$ during 5 h, and then, it was discontinued from the feed mixture for another 5 h. Addition of 0.5 vol.% CO did not influence the selectivity of the catalyst with respect to the CO-free mixture (60% to propene and 40% to oligomers, open symbols). When CO was interrupted, the propene selectivity experienced a slight increase (67%). An increased inlet CO concentration led to a gradual increase in propene selectivity from 60% to 80% and the coupled decrease in oligomers selectivity from 40% to 20%. The attainment of the 80% alkene selectivity level was significantly faster in 5 vol.% CO (solid symbols) than in 1 vol.% CO (gray symbols). This indicates that the changes occurring in the catalyst are accelerated with the CO concentration. However, once the catalyst has been subjected to a sufficient amount of CO (or for sufficient time), the resulting system is equally selective once carbon monoxide is removed from the feed. This can be seen in Fig. 2 upon switching from $C_3H_4 + H_2 + CO$ to $C_3H_4 + H_2$. The C_3H_6 selectivity was stable at ca. 90% after modification by 1 or 5 vol.% CO during 5 h. The propane selectivity was not plotted in Fig. 2 for the sake of clarity. As shown in Fig. 1, the selectivity to propane over the modified catalyst (after CO removal) amounted to ca. 3%.



Fig. 2. Selectivity to propene (circles) and oligomers (triangles) versus time in propyne hydrogenation at 473 K over the copper catalyst using different concentrations of CO in the feed. Black symbols: $C_3H_4/CO/H_2/He = 2.5/5/7.5/85$, gray symbols: $C_3H_4/CO/H_2/He = 2.5/1/7.5/89$. and open symbols: $C_3H_4/CO/H_2/He = 2.5/1/7.5/89$. 5. After the first 5 h, CO was removed from the feed and the inlet mixture contained $C_3H_4/H_2/He = 2.5/7.5/90$ (mixture A).

Fig. 3 compares the performance of unmodified (freshly reduced) and CO-modified (5 h in mixture B at 473 K) copper catalysts in propyne hydrogenation at 473 K and 373 K. At 473 K, full propyne conversion was attained over both catalysts with the



Fig. 3. Conversion of propyne (a) and selectivity to propene (b) and oligomers (c) versus time in propyne hydrogenation (mixture A) at 473 K and 373 K over unmodified and CO-modified (5 h in mixture B) copper catalysts.

indicated propene selective differences (60% and 92% for the unmodified and CO-modified samples, respectively). The alkyne conversion can be decreased by lowering the temperature and/or by shortening the contact time. It was decided to compare the unmodified and CO-modified catalysts at a lower temperature to demonstrate the superiority of the latter system in terms of higher selectivity and resistance toward deactivation by fouling as a consequence of the presence of smaller copper ensembles. Previous studies [16,19] have shown that copper catalysts strongly deactivate on propyne hydrogenation below 423 K due to extensive green oil formation. Accordingly, the propyne conversion on the unmodified catalyst at 373 K dropped to 3% and the oligomerization pathway is increased (selectivity \sim 87%). The propene selectivity decreased from 60% to 13%. On the contrary, the CO-modified catalyst showed stable behavior at a remarkably low temperature. The propyne conversion and propene selectivity decreased from 100% to 60% and from 92% to 67%, respectively. The turnover frequency, expressed as mol C₃H₆ produced per second and mol Cu exposed in the fresh catalyst, can be estimated at ca. 2 orders of magnitude higher in the CO-modified catalyst. The fact that the propyne conversion remains high at 373 K can point out to the fact that the rate-limiting step for hydrogenation on copper (H₂ splitting) is more favorable on the CO-modified catalyst. Thus, the proposed surface restructuring could account for this increased conversion.

Figs. 1 and 2 concluded that the pretreatment of the copper catalyst in mixtures containing C₃H₄, H₂, and CO raises its selective character toward the olefin in a substantial and permanent manner once carbon monoxide is cut off. We have tentatively suggested that this modification is caused by the CO-induced restructuring of the active copper sites. The gradual increase in the propene selectivity in step 2 is attributed to the progressive modification of the surface in the presence of CO, which irreversibly turned the copper catalyst more selective. In contrast, the propene selectivity from step 3 to step 4 immediately reached a stable value since the catalyst was already activated. This induction period is again required when the activated catalyst was calcined (steps 8 and 9). A key question to further understand the catalyst modification arises: does CO on its own alter the catalyst or does it require additional components in the mixture? Fig. 4 shows the steady-state selectivity of propene, propane, and oligomers of the



Fig. 4. Influence of pretreatment on the selectivity to propene, propane, and oligomers in propyne hydrogenation at 473 K over the copper catalyst. The plotted values were acquired after pretreatment for 5 h followed by reaction in $C_3H_4/H_2/$ He = 2.5/7.5/90 (mixture A) for another 5 h. The composition of the pretreatment mixtures is given in Section 2.

copper catalyst at 473 K after 5 h pretreatment in several mixtures (x-axis) followed by propyne hydrogenation (mixture A) for 5 h. The propyne conversion in these tests was 100%. Pretreatments in CO, H_2 + CO, C_3H_6 + CO, and C_3H_6 + H_2 + CO did not lead to any measurable change, that is, the propene selectivity was the same as on the non-pretreated catalyst (60%). Only mixtures containing carbon monoxide and propyne (and additionally hydrogen) were able to induce modification of the catalyst surface. The attainment of a highly selective catalyst strongly depends on the nature of the hydrocarbon, that is, the mixture of carbon monoxide, propene, and hydrogen caused no effect on the selectivity. According to Fig. 4, pretreatments in $C_3H_4 + CO$ and $C_3H_4 + H_2 + CO$ led to very similar steady-state C_3H_6 selectivity after 5 h on stream (~90%). However, the achievement of this selectivity during reaction was instantaneous when H₂ was included in the pretreatment mixture and took longer (1-2h) in its absence. We put forward that specific partially hydrogenated moieties derived from propyne and carbon monoxide are responsible for the selectivity enhancement on the copper catalyst.

The X-ray diffraction patterns of the catalyst after reaction in mixture A (without CO) for 5 h or to mixture B (with CO) for 20 h were nearly identical (Fig. S1). No shift or broadening of the reflections of metallic copper was observed, indicating no change in the bulk structure of the catalyst after alkyne hydrogenation in the absence or in the presence of CO.

We believe that the carbonaceous deposit generated during alkyne hydrogenation in the presence of CO might lead to a reduced size of the copper ensemble. This would explain the attenuated oligomerization since C–C coupling reactions require a larger copper ensemble than the hydrogenation to propene or propane [16]. Such deposit should have the distinctive feature of incorporating CO, since the deposit generated during propyne hydrogenation in the absence of CO did not improve the selective character of the catalyst. It is known that carbon monoxide can be incorporated in the oligomers formed during alkyne hydrogenation on palladium catalysts, leading to carboxylic acids or aldehydes [20].

Taking this into account, the CO-modified copper catalyst (after step 7 in Fig. 1) was calcined to eliminate the carbonaceous adlayer, which in principle should resume the original performance, that is, setting the alkene selectivity back to 60%. The calcination conditions in step 8 (773 K, 30 h) secured the full combustion of the deposit. This was confirmed by temperatureprogrammed oxidation of a CO-modified copper catalyst (Fig. S2). The hydrogenation performance of the calcined sample was reevaluated in mixture A (step 9). After a 2-h period, in which the reoxidized catalyst gets reduced in the reaction mixture, the propene selectivity reached the steady-state value of ca. 80%. Our original hypothesis was not validated since this value is significantly higher than the 60% propene selectivity for the fresh catalyst that never 'saw' CO. The removal of the carbonaceous deposit formed in the presence of CO did not fully resume the original selectivity values. Consequently, the deposit is not the only responsible for the outstanding selectivity enhancement of copper by CO. We cannot discard an irreversible restructuring of the catalyst surface induced by the mixture of propyne, hydrogen, and carbon monoxide. Exposure of the catalyst to CO for 5 h (step 10) maintained the C₃H₆ selectivity at 80% (like in steps 2 and 4), and subsequent discontinuation of CO in the feed (step 11) fully restored the situation in steps 3, 5, and 7 with the CO-modified catalyst, that is, $S(C_3H_6) =$ 92%, S(oligomers) = 5%, and $S(C_3H_8) = 3\%$.

The gas-phase hydrogenation of ethyne was studied over the Cu catalyst to check whether the remarkable selectivity enhancement observed with propyne applies to other practically relevant alkynes. Ethyne hydrogenation was studied at 523 K since operation at 473 K (used for propyne) led to catalyst deactivation due to extensive oligomerization. In $C_2H_2/H_2/He = 2.5/7.5/90$, the selectivity to



Fig. 5. Selectivity to ethene, ethane, and oligomers versus time in ethyne hydrogenation at 523 K over the copper catalyst. Feed mixture: $C_2H_2/H_2/He = 2.5/7.5/90$. Treatment C: $C_2H_2/CO/H_2/He = 2.5/5/7.5/85$, 523 K, 5 h. Treatment B: $C_3H_4/CO/H_2/He = 2.5/5/7.5/85$, 473 K, 5 h.

ethane was 40% and the remaining 60% comprised oligomers (Fig. 5). The degree of ethyne conversion was 100%. The lower alkene selectivity achieved with ethyne (40%) compared to propyne (60%) is a general characteristic of partial hydrogenation catalysts [5,11,15]. Higher alkynes are less prone to oligomerize due to steric hindrance in the C-C bond-forming step. After 5 h in C₂H₂ + H₂, the catalyst was exposed to $C_2H_2/CO/H_2/He = 2.5/5/7.5/85$ for additional 5 h (treatment C in Fig. 5), followed by the removal of CO from the feed. The selectivity to ethene stayed at 40%, that is, CO does not influence the selectivity of the catalyst in ethyne hydrogenation. However, if the catalyst is treated in $C_3H_4/CO/H_2/He = 2.5/5/7.5/85$ (treatment B in Fig. 5) and switched back to $C_2H_2 + H_2$, the ethene selectivity markedly increased to 73%, the oligomer selectivity decreased to 24%, and, similarly to propyne hydrogenation, little ethane (\sim 3% selectivity) was produced. In contrast to the case of propene, the enhanced ethene selectivity was not stable: it decreases with time-on-stream due to increased oligomerization. This result further emphasizes the importance of the pretreatment mixture to attain a selective state of the surface.

4. Discussion

The increased alkene selectivity in alkyne hydrogenation by continuous CO feeding over Pd catalysts is widely practiced in industry for olefin purification in steam cracker cuts [8,9]. This gas-phase modifier induces electronic and geometric effects [5,10,11,18]. The binding energies of H₂, alkyne, and alkene on CO-covered palladium are slightly lowered than that on clean palladium, thus leading to a lower H coverage and a better thermodynamic control in partial alkyne hydrogenation. The geometric effect of CO derives from its preferential adsorption on Pd, reducing the amount of active sites on the catalyst surface and blocking the formation of unselective hydride and carbide phases. The effect of CO in partial alkyne hydrogenation over nickel apparently shares many features with palladium [12]. Both metals dissociate H₂ easily [18]. CO lowers the hydrogen coverage and blocks the appearance of the hydride phase, which is strongly linked to the over-hydrogenation path. The nature of the CO modification on copper is different. H_2 dissociation on Cu(1 1 1) is marginally endothermic (0.16 eV) and hindered by a sizeable barrier (0.83 eV). Due to the low H coverage on copper, extensive oligomerization and no over-hydrogenation occurs (step 1 in Fig. 1). The increased propene selectivity upon CO feeding on Cu (from 60% to 80%, step 2 in Fig. 1) cannot be attributed to a lowered H coverage as one would reason for Pd and Ni. Accordingly, the electronic effect of carbon monoxide on copper is regarded as minor. Rather, the alkene selectivity increase upon CO addition should mainly derive from a geometric (ensemble) effect.

NMR analysis of oligomers on palladium formed in the presence of carbon monoxide indicated that CO was incorporated in the hydrocarbon chain, and carboxylic acids or aldehydes were produced [20]. Borodziński [21] pointed out the role of carbonaceous deposits on the selective character of Pd. It was hypothesized that the deposits diminish the abundance of large palladium ensembles and increase alkene selectivity. Similar incorporation of CO in the oligomers on Cu may generate a stable state of the surface rendering higher propene selectivity after the addition of CO and mainly after its removal. Our catalytic data strongly suggest that carbon monoxide in the presence of propyne and hydrogen leads to smaller copper ensembles. The ensemble needed for polymerization is larger than for hydrogenation, which substantiates the increased propene selectivity on increasing the copper dispersion in the catalysts [16,22]. One can anticipate that a small copper cluster would be highly selective toward the alkene due to minimized oligomerization. The difficulty is to prepare such clusters and, more importantly, to stabilize them under reaction conditions. We think that the use of carbon monoxide enables to synthesize stable catalysts with an extremely high degree of copper isolation.

The genesis of small ensemble size from CO addition in the feed is supported in Fig. 3 as the pathway to oligomers is largely hampered at low temperature on the CO-modified catalyst compared to its unmodified counterpart that deactivated totally. Nonetheless, the higher propene selectivity after removal of the carbonaceous deposit by calcination (step 9 in Fig. 1) highlights that the latter are not the only responsible for the outstanding selectivity enhancement of copper. The catalyst might have also experienced surface restructuring. The production of propane in the active catalyst (steps 3 and 5 in Fig. 1), which is rarely observed for copperbased systems, also suggests an irreversible change in nature of the active sites.

Fig. 4 reveals that CO individually was not the responsible for the distinctive modification of the Cu catalyst. The different behavior in the presence of a double or a triple bond unravels the deep interaction between the nature of beneficial carbonaceous deposit and the presence of highly unsaturated moieties. Our previous work [16] highlighted that Cu, in opposition to Ni, produces highly unsaturated oligomers that contain conjugated double and triple bonds. The latter carbonaceous moieties were detected only at 423 K and correlated with the fast deactivation of copper at low temperature [16]. The presence of such highly unsaturated oligomers at 473 K is unlikely but as it was mentioned above, in the presence of adsorbed CO, H_2 dissociation is hindered and unsaturated oligomers causing the copper modification are produced. Therefore, it is not surprising that this phenomenon appears only upon Cu-catalyzed hydrogenation as the specific partially hydrogenated moieties needed to build up the modified surface result from its poor ability in H_2 splitting.

Besides the degree of insaturation of the hydrocarbon, Fig. 5 shows that the nature of the alkyne is also a decisive factor in the modification. No increase in alkene selectivity was observed upon addition and removal of 5 vol.% CO during 5 h in ethyne hydrogenation. Nevertheless, a Cu-based catalyst which was modified 5 h in mixture B at 473 K and used in ethyne hydrogenation showed a markedly increased selectivity to ethene. The same explanation of the enhanced alkene selectivity in propyne hydrogenation upon short CO supply (reduction in the ensemble leading to minimized oligomerization) applies to ethyne hydrogenation. However, the decreased ethene selectivity during time-on-stream is attributed to the proneness of ethyne toward oligomerization that overwhelmed the beneficial effect of the $C_3H_4 + H_2 + CO$ activation. The ensemble required for oligomerization in ethyne hydrogenation is smaller due to the smaller size of the alkyne substrate, and the barrier of C-C coupling is in general lower for C2 than C3 [11].

At this final point, it must be emphasized that the above interpretations are based on observations derived from detailed catalytic evaluation and some of the conclusions require further support by characterization studies. Our attempts to identify, through standard (ex situ) XPS and FTIR techniques, conclusive differences between the catalysts used in propyne hydrogenation with or without CO were futile. A rigorous understanding of the complex mechanism of CO modification on copper in propyne and ethyne hydrogenation requires dedicated operando studies. These are beyond the scope of the manuscript and should be tackled in future work using infrared spectroscopy coupled to online analysis of reaction products.

5. Conclusions

We have discovered that temporary addition of CO during propyne hydrogenation over a conventional copper-based catalyst permanently increases the alkene selectivity from 60% to 92% at 100% alkyne conversion (473 K). The superior performance of the CO-modified copper catalyst was also evidenced at lower temperature (373 K), where the unmodified sample completely deactivated due to extensive oligomerization and fouling. Pretreatment in C₃H₄ + H₂ + CO mixtures is essential to attain a selective copper catalyst. Our catalytic results suggest that CO in reaction mixture alters the structure of the catalyst surface, effectively reducing the ensemble size responsible for undesired C–C bond formation reactions. This effect is mainly attributed to the formation of beneficial carbonaceous deposits, although surface restructuring can also contribute to the result. The irreversible effect of CO on copper-catalyzed alkyne hydrogenation differs from the typically recognized reversible character of this selectivity moderator on palladium and nickel catalysts. The remarkable alkene selectivity increase in propyne hydrogenation over the CO-modified copper catalysts was not fully attainable in ethyne hydrogenation due to the marked oligomerization ability of the C2 alkyne. These novel catalytic results are of significant interest in the hydrogenation field, although assessing the industrial potential requires catalyst scale-up and pilot studies. We put forward that the permanent modification of the copper ensemble by CO might be advantageous in (chemo) selective hydrogenations of high acetylenic substrates.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.11.024.

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