



Butadiene from acetylene–ethylene cross-metathesis†

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Acetylene to butadiene direct synthesis, via enyne cross-metathesis, is demonstrated with commercial ruthenium carbene catalysts. Using excess of ethylene, yields greater than 50% are obtained. High activity is observed in the first minute of the reaction (TOF > 800 h⁻¹ based on butadiene). Catalyst reusability and poisoning are discussed.

In recent years oil prices have fluctuated very strongly. Alternative routes to oil-derived commodities thus could become increasingly important in order to ensure that society's needs are still met throughout a transition period from an oil-based chemical industry to a situation with a higher feedstock diversity, including coal, gas, and renewables. Acetylene, which was at the heart of the chemical industry until roughly 50 years ago, could once again serve as a platform molecule for the synthesis of various bulk chemicals, considering that its main synthesis routes start from coal or natural gas, which are available in larger reserves than oil. This was already discussed in comprehensive reviews on this topic.^{1,2} The broad potential of this molecule is obvious, since it was used as a feedstock for various processes. After acetylene lost its central position in favor of oil-derived feedstocks, such as propylene and ethylene, significant advances have been made in catalysis and the understanding of catalytic processes. It thus seems worthwhile to investigate once more the possibilities that acetylene presents in the light of these developments.

Butadiene is mainly produced by steam cracking, which has been shifted to lighter feedstocks in recent years, thus leading to higher quantities of ethylene, but smaller quantities of the heavier products including butadiene. With butadiene being an important building block for synthetic polymers, pathways leading to this molecule which are not dependent on steam cracking seem to be desirable.³ In the past, particularly in Germany during the Second World War, synthesis routes to butadiene starting from acetylene

were applied also on an industrial scale. However, these were multi-step syntheses, for example, acetylene → butynediol → butandiol → butadiene.⁴ A one-step synthesis route from acetylene to butadiene, on the other hand, has not been reported yet. Coupling reactions of acetylene to introduce a diene functionality into a larger product are, however, known.^{5,6}

Enyne metathesis is an emerging organic synthesis technique which unites an alkyne moiety with an alkene moiety to form a conjugated diene.^{7–10} This reaction became widely used with the advent of ruthenium carbene type olefin metathesis catalysts,^{11–17} however, enyne metathesis is much less understood than olefin metathesis. Both the intramolecular (ring closing enyne metathesis or RCEYM)¹⁸ and the intermolecular versions (enyne cross metathesis or EYCM)¹⁹ of this reaction are known, but to the best of our knowledge no example of EYCM using unsubstituted acetylene has yet been reported. As the cross-metathesis of ethylene and acetylene should produce butadiene in a one-step reaction, we have undertaken an investigation into the possibilities of effecting this transformation. Furthermore, performing EYCM with ethylene and acetylene, the simplest molecules which can participate in this reaction, could offer additional mechanistic insight into EYCM.

The metathetic reaction pathways possible in an ethylene–acetylene atmosphere with a ruthenium carbene catalyst are depicted in Fig. 1. Assuming a typical enyne metathesis mechanism to be in operation,⁷ the key intermediates in this process are the ruthenium methylidene **1** and the ruthenium vinylcarbene **2**. As acetylene polymerization with ruthenium carbene catalysts is known to occur²⁰ and polymerization of alkynes has been reported even for RCEYM,²¹ it seems that an excess of ethylene would be required in order to stop the reaction at the butadiene formation stage and thus suppress the formation of larger oligomers. It is also worth mentioning that carrying out a RCEYM in an ethylene atmosphere (Mori conditions) has been reported to produce higher yields for certain substrates compared to an inert gas atmosphere,²² although this is not always the case.²¹ The ethylene atmosphere is generally required to suppress polymerization if sterically demanding alkynes are used as substrates.

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, catalyst screening, solvent screening, influence of catalyst loading, influence of using a butadiene containing feed. See DOI: 10.1039/c5cc00853k

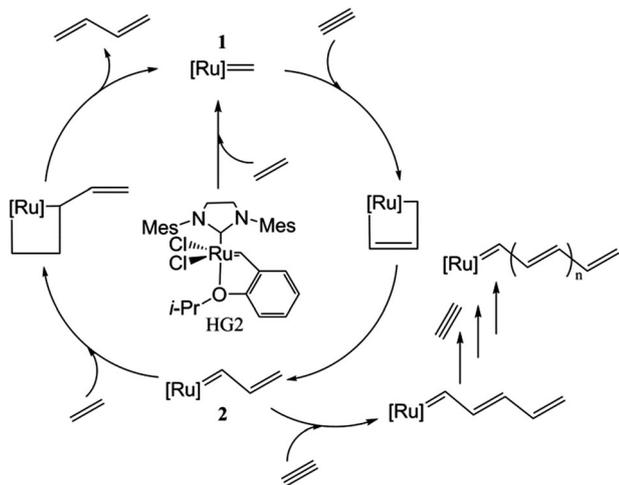


Fig. 1 Metathetical reaction pathways in an acetylene-ethylene atmosphere.

The reaction setup used for the catalytic tests is described in the ESI,[†] Fig. 1S. **Caution:** acetylene should be handled with great care, since it can explosively decompose and is highly explosive in mixtures with oxidizing compounds. After performing a screening of some commercially available catalysts (ESI,[†] Fig. 2S) and solvents (ESI,[†] Fig. 3S), we chose to study acetylene-ethylene EYCM in dichloromethane with the Hoveyda-Grubbs second generation catalyst (HG2). The influence of using different catalyst loadings was also tested in preliminary experiments (Fig. 4S, ESI[†]). While not fully conclusive, the results of these experiments suggest that butadiene production scales with the amount of catalyst present, while undesired side reactions are zero order in catalyst concentration. Therefore, in all following runs the highest catalyst loading of 10 mg (0.016 mmol), corresponding to a catalyst concentration of 800 μM , was used in order to maximize butadiene yield.

First the influence of the ethylene:acetylene ratio (E/A) and of reaction temperature on the conversion of acetylene and the selectivity towards butadiene were studied. The results depicted in Fig. 2 show that the conversion as well as selectivity toward the yield of butadiene, at identical reaction time, generally increase with E/A. While the increase in conversion can be explained by the presence of less acetylene in the gas mixture fed into the reactor, the increase in selectivity with E/A proves that excess ethylene is essential for this reaction.

It is worth noting that with careful choice of reaction conditions yields for butadiene higher than 50% were obtained in these experiments. Turnover numbers (TON) based on the amount of butadiene produced are only between 3 and 24. Increasing temperature seems to have a positive effect on butadiene productivity, which could be due to a higher fraction of the catalyst overcoming the initiation barrier at higher temperatures, as recent reports suggest that for this type of catalyst incomplete activation can occur.²³⁻²⁵ In addition, although care was taken to introduce the same amount of gas in all experiments, this becomes quite difficult at higher temperatures, due to the increase in vapor pressure of the solvent. This leads to the amount of gas mixture introduced at 40 °C being around 1.25 times higher than that

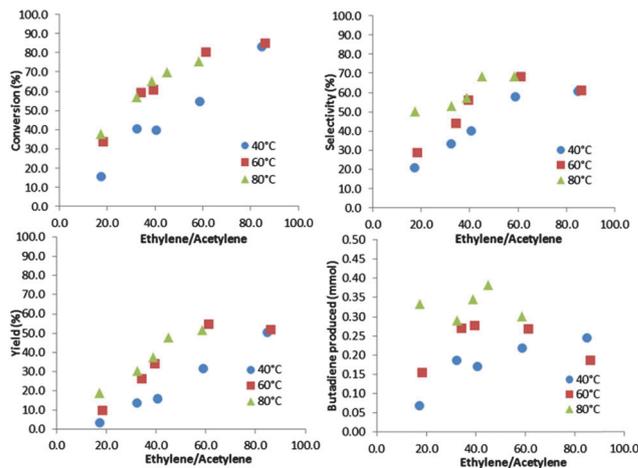


Fig. 2 Results of catalytic tests performed with 10 mg HG2 in 20 mL of CH_2Cl_2 at a reaction time of 15 minutes using 680–850 mL (STP) mixture of ethylene and acetylene, the total pressure of 11–14 bar. Conversion based on acetylene.

introduced at 80 °C. GC-FID analysis, of both the liquid phase and the gas phase, revealed that propylene, along with butenes, C5 dienes and C6 polyunsaturated compounds are also formed in these reactions, but they generally do not add up to more than 5% of the butadiene formed, which does not lead to a closed carbon balance for acetylene. This suggests that a significant part of the acetylene is converted to higher polyenes, which cannot be properly quantified, because they are formed in low amounts each and have low volatilities. Full analysis of the liquid phase is complicated by the formation of insoluble polyacetylenes, and was not performed for all experiments.

As many of the experiments presented in Fig. 2 did not reach full conversion after 15 minutes, a time dependent study of the reaction was performed. Fig. 3 presents a conversion vs. time plot for EYCM at 80 °C with E/A = 32.5, showing also the yield, selectivity and amount of butadiene produced. Interestingly, more than 80% of the butadiene produced after 30 minutes is actually formed in the first minute of the reaction. This suggests that the catalyst has a reasonably high initial activity. If the reactor was scaled up to accommodate 1 L of solution and if the conditions of the first minute were sustained over one hour, the butadiene productivity would be around 35 g per hour and liter. While one might argue that a 32.5 to 1 ethylene-acetylene mixture (around 3% acetylene) seems impractical for large scale application, it should be considered that ethylene produced from steam crackers can contain up to 2% acetylene, which needs to be removed because it acts as a poison for ethylene polymerization catalysts. This is typically done *via* selective hydrogenation over palladium based catalysts.²⁶ It might be profitable, if instead of hydrogenating the acetylene to ethylene, one could convert it to butadiene. While this would require a further separation step to recover the newly produced butadiene from the ethylene, depending on the prices of the different products this could possibly be an attractive option considering that a C4 separation unit is anyway present in the downstream processing of a steam cracker.²⁶ However, in order

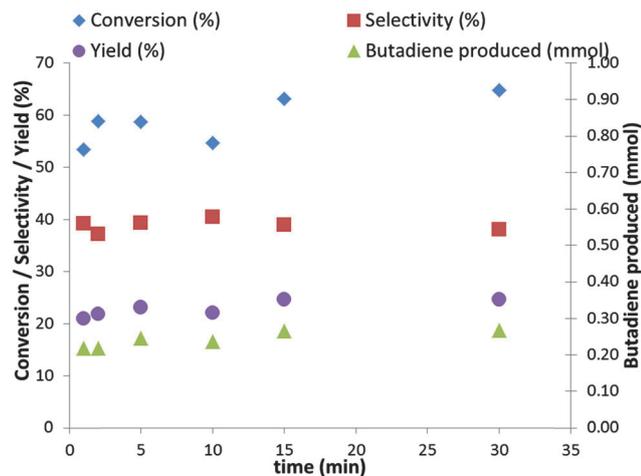


Fig. 3 Conversion time plot at 80 °C with 10 mg HG2 in 20 mL of CH₂Cl₂ using 680–730 mL (STP) E/A = 32.5 mix at a total pressure of 14 bar.

for this process to be useful, the catalyst needs to be either very cheap, or very stable in that it can easily be applied to a continuous process. In addition, basically full conversion of the acetylene is required because the unconverted acetylene would still act as a poison in the downstream olefin polymerization reaction.

In order to assess the reusability of the catalyst an experiment was designed where the reaction was performed at 40 °C for 2 minutes in 20 mL of dichloromethane with 0.016 mmol of HG2 at 11 bar with a mixture of E/A = 32.5. After 2 minutes the gas phase was removed and the solvent was flushed with nitrogen for 10 minutes to remove the dissolved ethylene, acetylene and butadiene which were determined by GC analysis. Then the solvent volume was adjusted to 20 mL by adding fresh dichloromethane and the reaction was performed once again for 2 minutes, then the process was repeated for a second reuse. The results are shown in Fig. 4. The amount of butadiene produced in the second run is around 26% of that produced in the first run, and the amount of butadiene produced in the third run is around 32% of that produced in the second run.

The loss in butadiene productivity and acetylene conversion could be due to the accumulation of polyunsaturated compounds of low volatility in the solvent which would lead to an increase in the number of possible nonproductive reaction pathways.²⁷ Additionally, ruthenium methylidenes **1** are known to be quite unstable,^{28,29} and the ruthenacyclobutane intermediate in the nonproductive reaction of ethylene with the ruthenium methylidene was shown to decompose, producing propylene,³⁰ which we also observed in trace amounts (*vide infra*). Decomposition of the catalyst could thus be an extra factor responsible for the observed decrease of activity when reusing the catalyst solution.

The detrimental effect of ethylene on catalyst stability has been previously reported for olefin metathesis.^{31–33} However, direct comparison is not possible since the experimental setup as well as the conditions and the actual reaction being studied are significantly different. It was thus investigated to which extent ethylene, acetylene and butadiene contribute to the observed loss in productivity. For these experiments, the catalyst solution was first

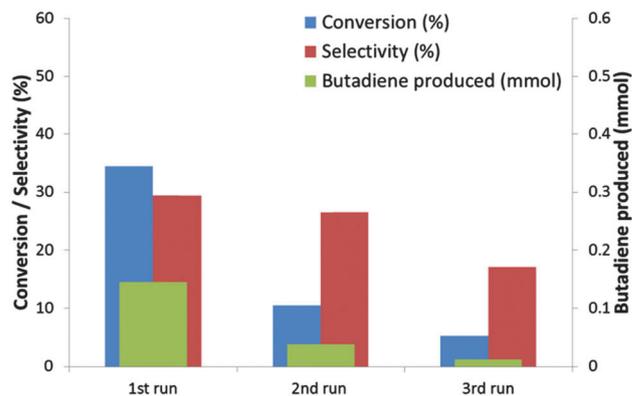


Fig. 4 Reusability of the catalyst at 40 °C with 10 mg HG2 in 20 mL of CH₂Cl₂ using 800–850 mL (STP) E/A = 32.5 mix at a total pressure of 11 bar.

exposed to each of the three compounds alone for 2 minutes at 40 °C, in quantities comparable to those which are present during a typical catalytic test, then the solvent was purged with nitrogen for 10 minutes to remove the dissolved gas, the solvent volume was adjusted to 20 mL by adding fresh dichloromethane and the pretreated catalyst was tested in EYCM with ethylene and acetylene. As blank, a nitrogen pretreatment followed by nitrogen flushing and the addition of fresh solvent was also performed to exclude the possibility of other influences. As can be observed from Fig. 5, the nitrogen pretreatment provides the same result as the catalytic reaction within the experimental error without any pretreatment.

However, when the catalyst is pretreated with ethylene, acetylene or butadiene the amount of butadiene produced drops to around 60% of that which is obtained in the absence of pretreatment. The differences in conversion and selectivity are quite close to the experimental error (plus–minus eight percent points, see ESI†), however, the loss of butadiene productivity is significant, and it shows that in fact all three key compounds in the reaction have a negative effect on butadiene production. For butadiene, this is corroborated by the fact that the addition of butadiene to the feed during reaction results in lower butadiene productivity (Fig. 5S, ESI†). Another interesting aspect is that during pretreatment with acetylene or ethylene no butadiene was observed, thus proving that the butadiene obtained in the reaction indeed comes from a reaction of acetylene and ethylene, not from an unknown side-reaction involving either of the two reactants alone. Also noteworthy is that during the ethylene pretreatment an amount of propylene equal to around 30% of the catalyst amount was formed. Considering that after ethylene pretreatment the amount of butadiene formed is around 60% of the amount formed in the absence of pretreatment, this fits together with the findings of van Rensburg³⁰ that propylene is formed upon ethylene treatment, leading to a complex which is inactive for metathesis. Propylene formation was not observed upon acetylene or butadiene pretreatment.

We have shown for the first time EYCM reaction using acetylene and the first directed one-step synthesis of butadiene from acetylene. For this reaction it is essential to use a high E/A

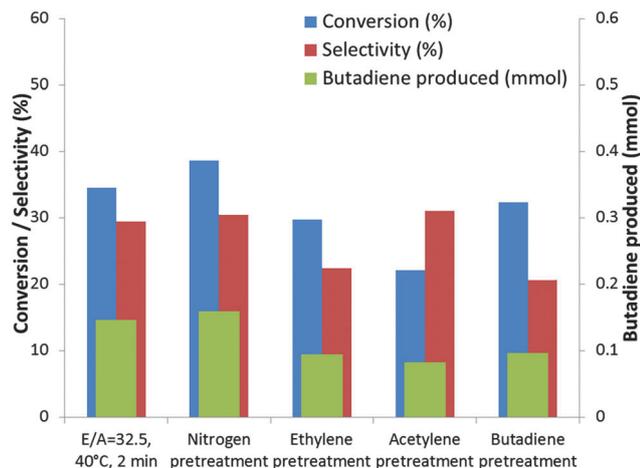


Fig. 5 Influence of catalyst pretreatment at 40 °C with 10 mg HG2 in 20 mL of CH₂Cl₂ using 800–850 mL (STP) E/A = 32.5 mix at a total pressure of 11 bar.

ratio in order to suppress unwanted acetylene polymerization; significant quantities of butadiene are only observed if E/A is greater than 20. However, catalyst stability and/or selectivity pose some problems for this synthesis, since pretreatments with any of the three components of the reaction, *i.e.* acetylene, ethylene and butadiene, have been shown to decrease butadiene production.

This study only provides proof of concept that direct butadiene formation is possible following this pathway. For a practical application, however, a catalyst needs to be developed which has higher stability towards ethylene, lower acetylene polymerization activity, and a preference for reacting only with the smallest molecules (ethylene and acetylene), in order to avoid loss of selectivity due to further reactions of butadiene and loss of activity due to nonproductive metathesis events.

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