Supporting Information

Butadiene from acetylene ethylene cross metathesis

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All solid and liquid chemicals and the butadiene used in this study were used as purchased from Sigma-Aldrich. All other gases were supplied by Air Liquide. A column filled with alumina and zeolite A was used to remove acetone from the acetylene stream. All other gases were used without further purification.

The experimental setup is depicted in figure 1S. Caution must be taken when handling acetylene as it can easily form explosive mixtures with oxidants and can also spontaneously decompose explosively[1]. The experiments were conducted in the following way: Gas cylinder 1 was filled to a set pressure with acetylene, and then ethylene was added to another set pressure. This allowed the preparation of gas mixtures of all needed compositions. Within the series of experiments the ratio of ethylene/acetylene (E/A) is kept constant while other parameters are varied, a standard deviation of E/A of 7% (on six experiments) is observed due to the difficulties involved in preparing mixtures of gases, especially at higher pressures. Gas cylinder 2 is heated to 60°C and filled with methane at atmospheric pressure, which is used as a standard for GC analysis. The variation of multiple GC injections from the same gas mixture in the second gas cylinder is within plus-minus 4%, thus mixing of the gases is considered to be achieved within an acceptable error. The smaller error due to mixing gases in the second cylinder with respect to the error mixing in the first cylinder can be explained by the much smaller pressures which are reached in the second cylinder.

In a typical experiment, first a calibration of the gas mixture is performed. The gas mixture of a defined composition is prepared in the first gas cylinder (pressure=30 bar), then with the autoclave empty, the gas mixture is released into the second gas container (already containing a defined amount of methane as a standard). The tubing, the first gas cylinder and the autoclave are flushed with nitrogen to make sure that all the ethylene and acetylene contained therein are sent to the second cylinder (final pressure around 2.5 bar in the second gas cylinder). After waiting for around 2 minutes to equilibrate the gas mixture in the second container a valve is opened to the GC and the mixture of ethylene, acetylene, methane and nitrogen (from flushing) is analyzed. In this way the amount and composition of the total gas mixture is determined.

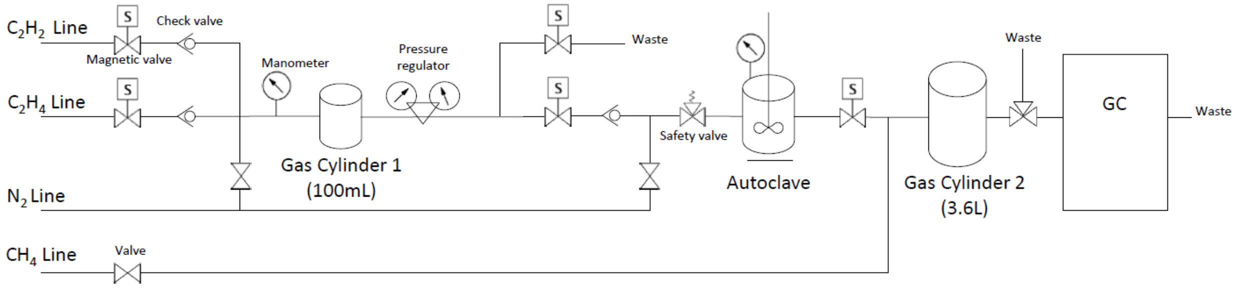

Figure 1S. Scheme of experimental setup for conducting ethylene-acetylene cross metathesis experiments.

After the calibration of the gas mixture the catalytic test is done. For this a gas mixture, with the same composition as for the calibration, is prepared by filling the first gas cylinder to the same pressures with acetylene and ethylene. The autoclave is charged with catalyst solution, and heated up to the desired temperature. When this temperature has been reached and stabilized, the autoclave is filled to a set pressure with the mixture of acetylene and ethylene via the pressure reducing valve (PRV) connecting gas cylinder 1 with the autoclave. The starting point of the reaction is set at the opening of the magnetic valve between the PRV and the autoclave. When the desired reaction time is reached, the magnetic valve between the PRV and the autoclave is closed and the gas phase from the autoclave is released into the second gas container. Nitrogen is then bubbled through the solvent for ten minutes via a cannula, introduced in the autoclave through a GC septum, to ensure that all the dissolved gases are released into the second gas container for analysis. This way the amount of all gaseous compounds in the autoclave, including the amount dissolved in the solvent, can be determined. The remaining gas in the first cylinder is then analyzed in the same manner as for the calibration of the gas mixture. The last step is necessary in order to determine how much acetylene and ethylene were introduced in the reactor, which is necessary for closing the mass balance.

Conversion is defined as:

$$C(\%) = \frac{[C_2H_2]_0 - [C_2H_2]}{[C_2H_2]_0} * 100$$

For the desired acetylene ethylene metathesis reaction:

$$C_2H_2 + C_2H_4 \rightarrow C_4H_6$$

The Selectivity is defined as:

$$S(\%) = \frac{[C_4H_6]}{[C_2H_2]_0 - [C_2H_2]} * 100$$

The Yield is defined as:

$$Y(\%) = \frac{[C_4H_6]}{[C_2H_2]_0} * 100$$

The following notations are used:

$[C_2H_2]_0$ – Amount of acetylene introduced in Autoclave (calculated as the difference between the total amount of acetylene in the first cylinder, determined from the calibration of the gas mixture, and the amount of acetylene left in the first cylinder after the catalytic test);

$[C_2H_2]$ – Amount of unreacted acetylene recovered from autoclave;

$[C_4H_6]$ – Amount of butadiene formed;

Ethylene conversions are too small related to the total amount of ethylene and cannot be determined given the experimental errors.

GC analysis is performed on two Agilent 6890 machines, connected in series, equipped with a sampling valve. The separations are carried out on a Rt®-Alumina BOND/Na_2SO_4 column, placed in the second GC, for C1-C4 hydrocarbons, and on a Rtx®-1 column, mounted in the first GC, for C5 and heavier hydrocarbons. The two columns are mounted in series so that the light hydrocarbons pass through the Rtx®-1 column within 2 minutes and then are sent to the alumina column and then to a FID. After 2 minutes a valve connecting the 2 columns is switched and the analytes exiting the Rtx®-1 column are no longer sent to the alumina column but to another FID.

Catalyst and solvent screening experiments, presented in figures 2S and 3S, were performed in a somewhat different manner, since the above described setup was at the time of these experiments not yet available. At first a solution containing 0.016 mmol of catalyst in 20 ml solvent was fed into a stainless steel autoclave, the autoclave was flushed with nitrogen and then the autoclave was cooled to -78°C in an acetone-dry ice bath. Using mass flow controllers, 50 mL of acetylene and 1500 ml of ethylene were fed into the autoclave. Due to the increased solubility of gases in liquids at lower temperatures, pressures never reached more than 3 bar during the filling step. Then the autoclave was heated up to 60°C and held at this temperature for 2 hours. Afterwards the gas phase was released into the second gas cylinder, the liquid phase was flushed with nitrogen, and the analysis was conducted in the same manner as for all other experiments. This different method of conducting the experiments has the drawback that it does not allow the determination of a clear starting point for the reaction, i.e. acetylene first comes in contact with the catalyst in the absence of ethylene, albeit at a very low temperature, and the method relies on the mass flow controllers to be accurately calibrated and to operate in a very stable, reproducible manner throughout the filling process. In this case it becomes clear that the results from these two figures are not expected to be identical with those from the other experiments, however for the purpose of choosing a catalyst and a solvent for the study of this reaction these experiments were considered acceptable despite their shortcomings.

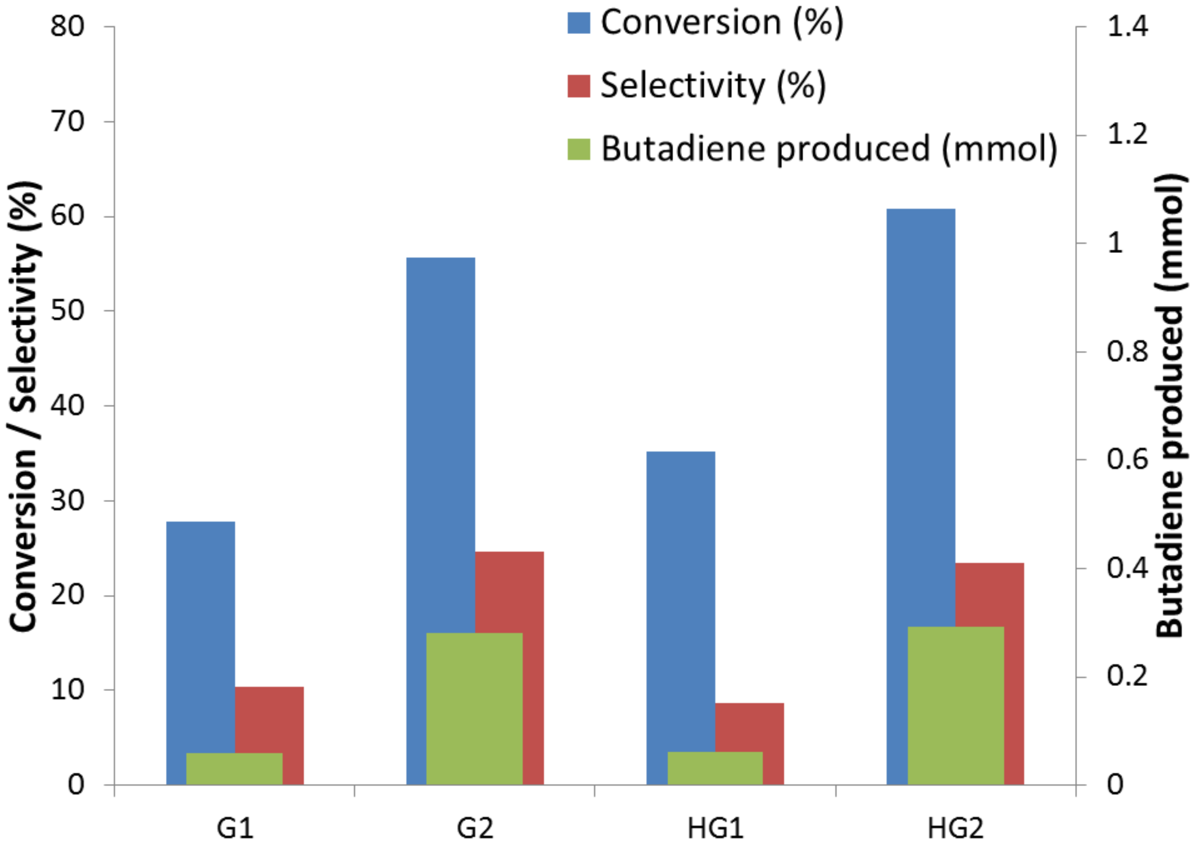

Figure 2S. Catalyst screening: Reaction performed as described above; E/A=30, 60°C, 2h in 20 mL dichloromethane, tested catalysts are Grubbs first generation catalyst (G1), Grubbs second generation catalyst (G2), Hoveyda-Grubbs first generation catalyst (HG1), Hoveyda-Grubbs second generation catalyst (HG2), all experiments done with 0.016 mmol of catalyst.

As it became apparent that the catalysts bearing NHC ligands perform better than those which only bear phosphine ligands, we chose HG2 for further study, since this produced the highest amount of butadiene. Interestingly, although HG2 often leads to higher TONs than G2 an effect which could be attributed to the release-return mechanism of the isopropoxy-styrene ligand, the presence of ethylene has been shown to hinder this mechanism[2]. This could explain the similar performances of these catalysts in this case. It must be kept in mind that, as this was a screening experiment, the two catalysts, although presenting similar conversions and selectivities after two hours, can still have significantly different activities, since no points between 0 and 2 h were investigated in the screening phase. It was later observed that with HG2 the reaction reaches 80% of the final conversion level within the first minute.

The solvent screening presented in figure 3S was performed to check whether dichloromethane, which was chosen for the catalyst screening, is indeed the best solvent for this reaction. From these results it would seem that a higher butadiene productivity is reached in acetone, however the catalyst was observed to have a lower stability in acetone (upon standing overnight at room temperature, an unused catalyst solution starts to turn from green to yellow), and reactions performed in acetone with the improved reaction setup (figure 1S) – probably due to the lower catalyst stability - produced less reproducible results. In consequence, all further studies were conducted in dichloromethane, the second best solvent in terms of butadiene productivity in this screening. It should be noted that only the E/A ratio fed in is known for all experiments. The E/A ratio in the liquid phase can be different from that in the gas phase, however, when using the same solvent, the trends based on varying E/A ratio should remain valid.

The E/A ratio in solution is very difficult to determine experimentally with accuracy and this was not attempted, nevertheless based on literature data for gas solubilities[3-5] it can be stated that this can vary substantially between solvents. Thus the data presented in figure 3S should be interpreted with caution since not only the coordinative properties of the solvents but also the relative solubilities of the gases involved vary significantly.

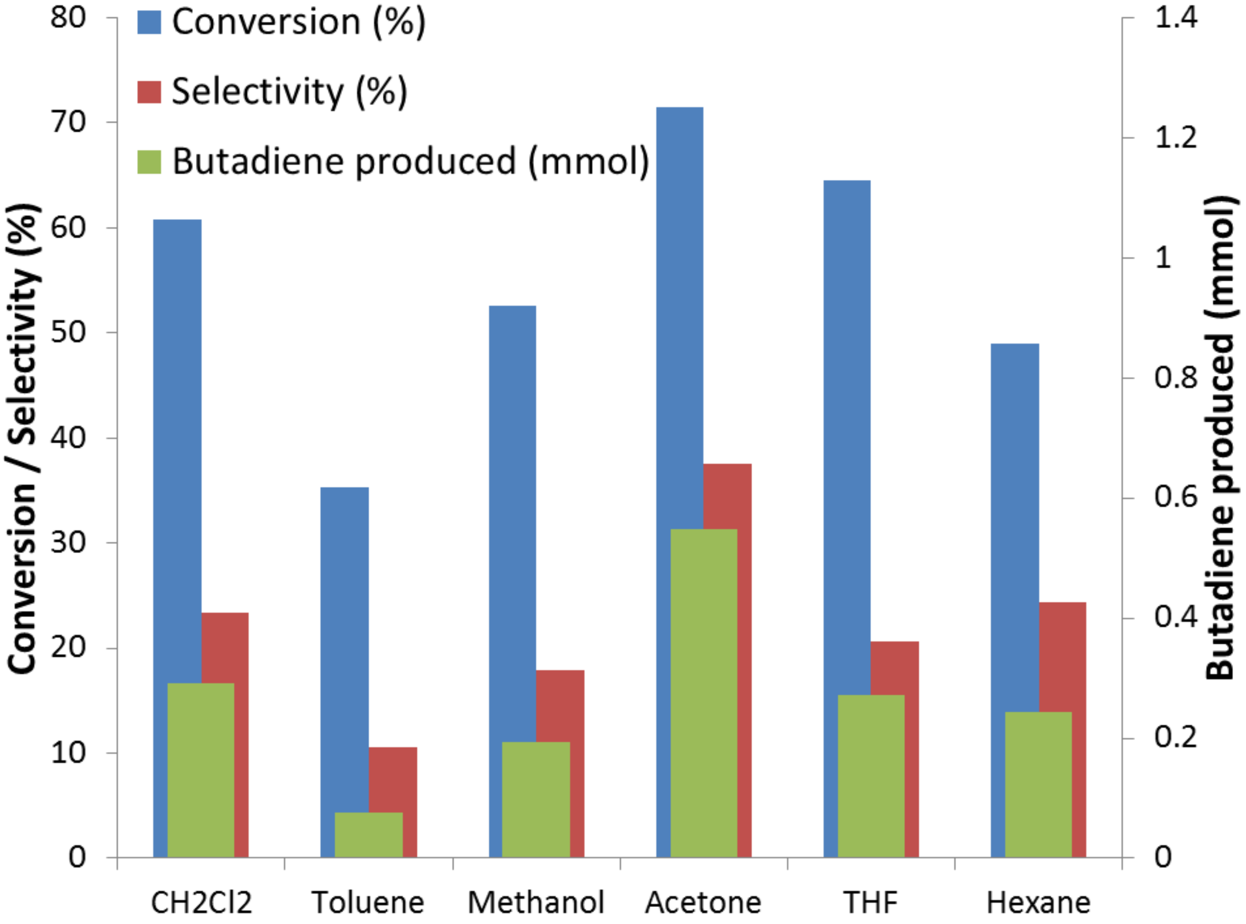

Figure 3S. Solvent screening, reaction performed as described above, E/A=30, 60°C, 2h in 20 mL of solvent, 0.016 mmol HG2 (10 mg).

The use of different catalyst loadings was also investigated (fig. 4S) and it was found that with increasing catalyst loadings turnover numbers seem to decrease while butadiene production and selectivity increase. The increase in butadiene production was found to be almost linear. This could suggest that a butadiene production is a first order reaction with respect to catalyst concentration, while the further oligomerization of acetylene to form compounds which are not quantified does not depend on catalyst concentration. One should bear in mind, though, that the experimental errors, especially at low conversions, are quite high (from repeated runs, the error in conversion was estimated at plus-minus 8 percent points). One should also consider that most of the conversion occurs in the first minutes. Since the products were analyzed after 15 minutes of reaction, the reaction kinetics severely overlap with the deactivation. The results should therefore be interpreted with caution.

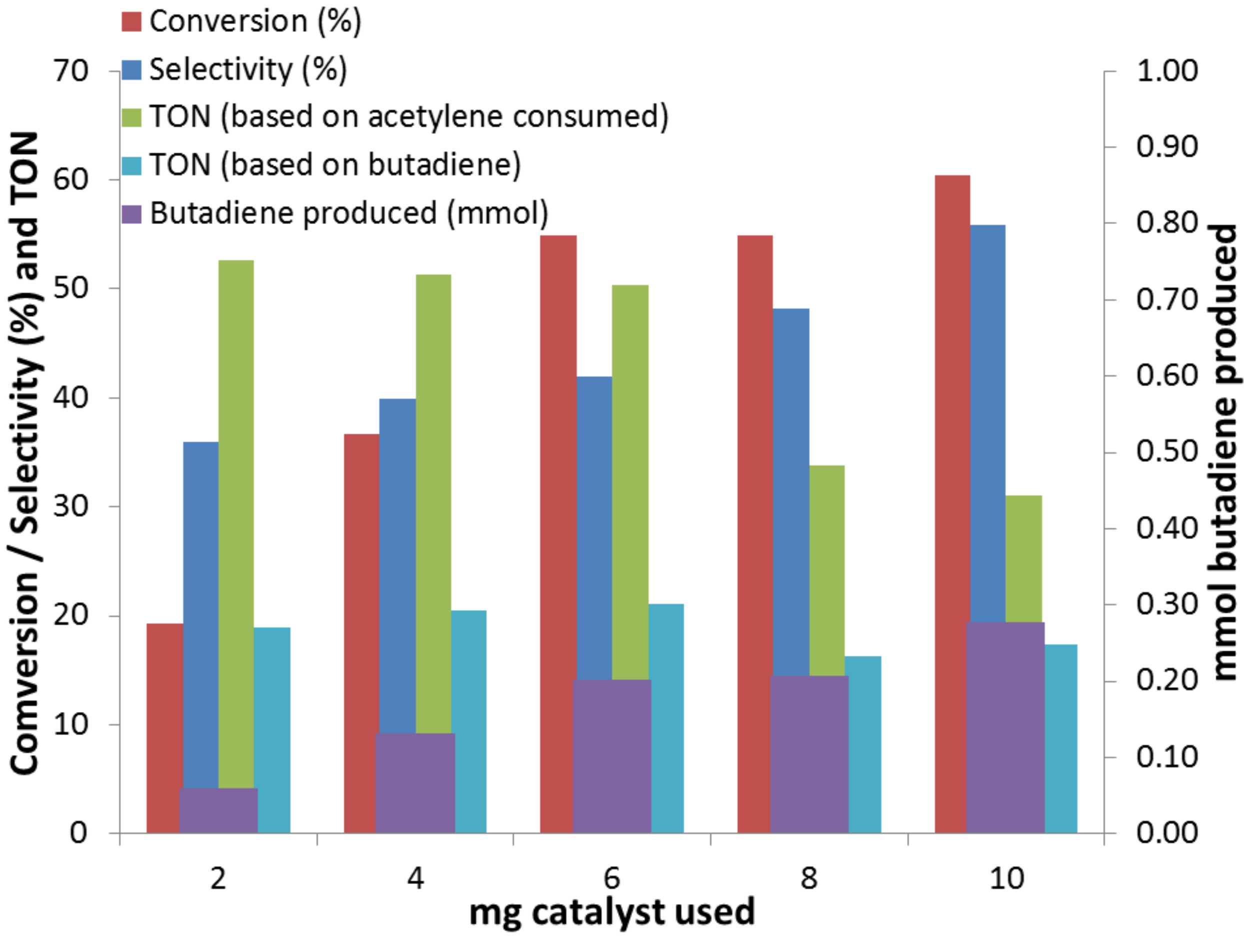

Figure 4S. Influence of catalyst loading, reaction performed using the method described below figure 1S, 680-730 mL (stp) of E/A=40, 80°C, 15 min, different amounts of HG2 in 20 mL of dichloromethane.

Before investigating the effect of the pretreatment with butadiene (figure 5) we have investigated the effect of using a butadiene containing feed, with butadiene amounts comparable to those obtained during a catalytic reaction, in order to study a possible poisoning of the catalyst by butadiene. The results are presented in figure 5S and they are in agreement with the observation that the presence of butadiene has a detrimental effect on the productivity towards butadiene, since less additional butadiene is produced in the experiments where butadiene is already present in the reactant feed. However, these results alone could not be used to determine whether butadiene has a poisoning effect, or if it just gets used up in a side reaction. For this reason the influence of the butadiene pretreatment was also investigated. Since in the butadiene pretreatment experiment around 0.19 mmol of butadiene were fed into the autoclave, and around 0.09 mmol of butadiene were not recovered from the autoclave, it can be concluded that butadiene is consumed under reaction conditions, and also leads to a decrease in butadiene productivity, possibly by forming other polyenes with terminal double bonds which keep the catalyst busy with nonproductive reactions. The formation of ruthenium species which are not active for metathesis, such as η3-vinylcarbene species could also be possible, although these have only been reported for electron rich vinyl carbenes thus far[6].

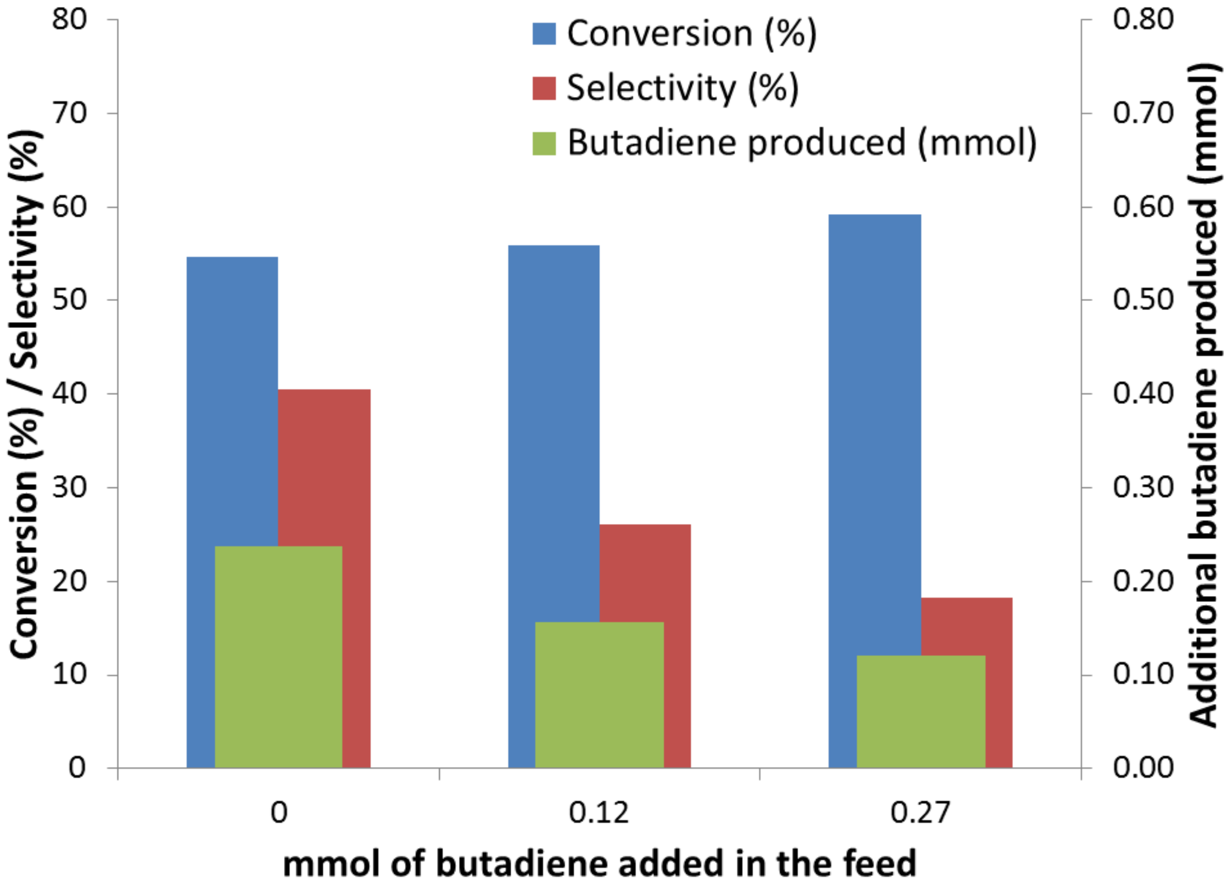

Figure 5S. Influence of adding butadiene to the gas feed, reaction performed using the method described below figure 1S, 680-730 mL (stp) of E/A=32.5, 80°C, 15 min in 20 mL of Dichloromethane

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