

Reaction Kinetics of an Industrial Front-End Acetylene Hydrogenation Catalyst Using the Advanced TEMKIN Reactor

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In memory of Christoph Bäumlner who initiated this project within a long-term collaboration

The front-end process integration of the selective acetylene hydrogenation provides several advantages over the tail-end option. But extensive knowledge of the process and reaction kinetics are required. This work combines the ideal conditions of the advanced TEMKIN reactor in a laboratory plant for gradient-free kinetic analysis of eggshell catalyst under industrially relevant front-end conditions. With this system an industrial state of the art Pd-Ag/Al₂O₃ eggshell catalyst is investigated and the temperature dependent data under various feed compositions including information on the formation of C₄-species are reported.

Keywords: Acetylene hydrogenation, Catalysis, Front-end, Reaction engineering, TEMKIN reactor

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1 Introduction

Ethylene is the most widely used hydrocarbon base chemical in the chemical industry due to its many useful downstream products, most importantly polyethylene. It is produced mainly by steam cracking of hydrocarbon feedstock such as naphtha to light olefins, which yields a multitude of organic compounds, such as short chain olefins and paraffins, as well as hydrogen and carbon monoxide [1,2]. The components are fractionated by rectification. Complete purification of ethylene by these means proves difficult, as the low boiling point of ethylene and other short chain hydrocarbons require expensive cryogenic technology [3–5]. Other purification methods such as extractive distillation have disadvantages such as handling of toxic waste products and higher costs [6,7]. The by-product acetylene has a detrimental influence on both of the commonly used downstream polymerization processes, i.e., free radical polymerization (LDPE) due to rapid decomposition and reactor runaway [8] and catalytic polymerization (HDPE/LLDPE) due to catalyst deactivation [7]. For these reasons, selective hydrogenation of acetylene has become the favored method to reduce the acetylene content in the ethylene stream to below 1 ppm [9–11]. The current industrial standard is the tail-end process integration, in which the C₂-cut is separated from components such as methane, carbon monoxide and hydrogen before the selective acetylene hydrogenation step. Conditions typically range from temperatures between 40–120 °C and pressures of 15–35 bar to ensure quantitative acetylene conversion with stoichiomet-

rically dosed hydrogen [12,13]. The controllability and safety of this operating method were preferred in industry, so catalyst performance and long-time studies as well as kinetic models for these conditions are well established in literature [12–19]. However, the presence of hydrogen in excess amounts in the so-called front-end configuration is advantageous, if the process safety can be guaranteed. Advantages include a higher conversion of acetylene, suppression of the formation of oligo- and polymeric side products, that cover the catalyst surface and lead to catalyst deactivation, and therefore, longer catalyst life time [12,13]. Furthermore, using the hydrogen produced during steam cracking simplifies process integration, as the removal and subsequent adding of hydrogen becomes obsolete. The hydrogenation of unsaturated hydrocarbons is a highly exothermic reaction [20], which must be taken into consideration during reactor design. The amount of acetylene in typical steam cracking fractions at this stage is below 1 mol % and is therefore easily manageable [1,2]. However, large amounts of ethylene (up to 50 mol % [1]) are also present and can undergo hydrogenation, especially at high acetylene conversion when the selectivity of the catalyst drops [12,21]. This is a major safety concern especially in

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combination with the high hydrogen content in front-end operation. In addition, due to the sensitivity of the system, even small variation in process conditions such as feed stream composition and hotspot formation must be accounted for. Therefore, front-end conditions require extensive kinetic and operational investigations especially under industrial conditions.

The kinetic data for advanced process design and operation must be obtained at conditions similar to the industrial reactor, which is challenging on the laboratory scale as gradient free conditions by exclusion of mass and heat transfer resistances can be difficult to maintain for packed bed tubular reactors. Depending on the size of the catalyst pellet, wall effects and axial dispersion can occur, which can only be neglected if the reactor has 10 times [22–24] the diameter and 30 times the length [22, 24, 25] of the catalyst pellet. Since the properties of the eggshell catalysts used in the industry are closely tied to the intact structure of the shell, these catalyst shaped bodies must stay intact for accurate catalytic testing. Therefore, testing of commercially available eggshell catalysts requires large reactor dimensions, which in turn requires large amounts of catalyst and feed stream per experiment. This expense can be reduced, by using a catalyst setup developed by TEMKIN and Kul'Kova in 1969 [26]. The goal of this reactor setup was to mimic the industrial process conditions while reducing the required amount of catalyst and volumetric flow rate. The reactor itself has a diameter only slightly larger than that of the pellets, which leads to a highly symmetric one-dimensional stacking of the catalyst pellet. To minimize axial dispersion, active and inert catalyst pellets are placed in alternating order. This also removes the danger of hot spot formation, as direct contact between active catalyst pellets is removed and each of the catalyst pellets can be seen as a distinct reaction volume. It was therefore postulated that the residence time distribution is analogous to that of a cascade of continuously stirred tank reactors (CSTRs), which transforms to that of a plug-flow reactor (PFR) with sufficiently high pellet count of 30 to 50 [22, 24, 26]. Since the catalyst pellets are only slightly smaller than the inner reactor diameter, the gas phase must flow through the small gap between pellet and reactor wall. This leads to defined, even and fast flow around the pellets and therefore faster external heat and mass transfer. The flow regime in the TEMKIN reactor was investigated by means of computational fluid dynamics in previous work [27]. It was found that, while temperature gradients were negligible in the TEMKIN reactor, concentration gradients behind the active catalyst pellets were existent and had to be considered. This led to the development of the advanced TEMKIN reactor design, which was first patented for spherical pellets in 2010 [28] and later published for cylindrical pellets [22, 24]. In this design, the catalyst pellets were

each suspended in cavities, which were connected via narrow channels. The channeling of the gas stream onto the frontside of the catalyst leads to an improved flow around the pellet [27]. Additionally, by narrowing behind the pellet, the contact between gas phase and backside of the pellet is improved. Therefore, dead zones behind and in front of the pellets are minimized which could be shown by CFD simulations [27]. Further insights were gained by calculating the product selectivity as a function of the shell thickness, where it was affirmed that the intactness of the shell is vital for the hydrogenation process [27]. This renders the advanced TEMKIN reactor ideal for catalytic testing of eggshell catalysts. The precision of the data allows for thorough kinetic investigation of complex systems such as the selective hydrogenation of acetylene.

In this paper, we present an advanced TEMKIN reactor for catalytic testing of eggshell catalysts based on previous work by Kuhn et al. [22, 24], which has been integrated into a sophisticated laboratory plant to obtain highly precise kinetic data under realistic feed compositions, high flow rates and withstand higher pressures to mimic industrial front-end conditions. With this design, not only main products but by-products in small quantities can be analyzed in detail across a large operating window and varying feed stream composition. Therefore, this setup is ideal to gain detailed insights into the front-end hydrogenation of acetylene.

2 Setup of the Advanced TEMKIN Reactor Miniplant

The advanced TEMKIN reactor developed by Kuhn et al. [22, 24] was the basis of this work and modified in two ways: With more precise CNC manufacturing methods the total volume of the cavities for the catalyst pellets was reduced in order to gain idealized gas flow behavior (Fig. 1). Also, the dimensions of the cavities were fitted to the size of the cylindrical catalyst pellets tested in this study with a

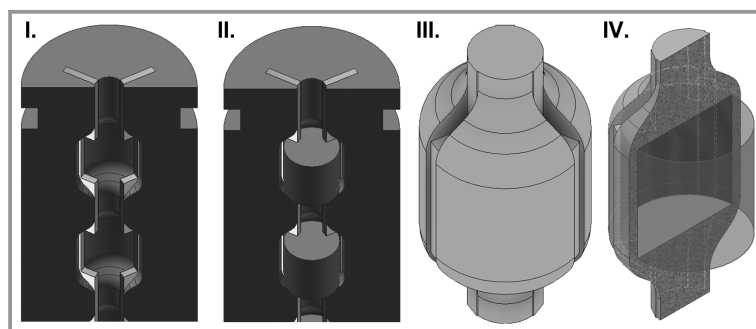


Figure 1. CAD cross section of the TEMKIN reactor module with two place-holders: I. without catalyst II. with cylindrical catalyst pellets in place. III. 3D display of the fluid volume of one cavity. IV. cross section of the fluid volume without the catalyst pellet in the center. The cylindrical catalyst pellet can be considered the scale bar with a diameter of 4 mm.

diameter of 4.0 mm resulting in a reduced cavity diameter of 4.5 mm. The corresponding annular gap between the reactor wall and the catalyst pellet of 0.25 mm, in combination with a well-controllable gas supply (see Fig. 3), enables the precise control of the linear velocity (LV) in a range of 0.5 to 20.0 Nm s⁻¹.

The TEMKIN reactor modules consist of two halve steel modules (Fig. 2): One half shell with a single placeholder for the catalyst and one with two placeholders as counterpart. Up to 11 catalyst pellets can be inserted in one reactor module set. The set is then sealed with two O-rings and placed in a reactor shell. These shells are inserted in an aluminum heating block, which can hold up to four reactors and thus, a total maximum of 44 catalyst pellets. The complete setup will be referred to in the following as reactor unit.

The TEMKIN reactor unit represents the centerpiece of an unprecedented laboratory plant for the investigation of the selective acetylene hydrogenation under front-end conditions (Fig. 3). A variable feed close to industrial conditions is achieved by the possibility to connect and use up to five gas bottles at the same time. With a mass flow controller for each of the gases/mixtures a highly variable feed in a combined range of 5 to 150 Lh⁻¹ is possible. The streams are combined and pass through an emergency shut-off valve

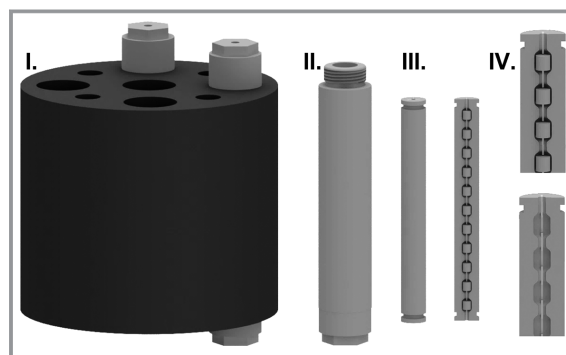


Figure 2. I. Heating block for four TEMKIN reactor modules, four heating rods and two thermocouples. II. Reactor shell for the TEMKIN module. III. TEMKIN modules attached together and cross section of a module with one placeholder and catalyst pellets. IV. Detailed view of the cross section with and without catalyst pellets (diameter of 4 mm).

controlled by a detection system for leaks of explosive and flammable gasses. A special feature of this plant is the piping of the reaction unit. By the use of three automated actuators, with two 3-way valves each, different flow paths and extraction points are possible. The first pathway is a direct bypass measurement of the feed composition, by

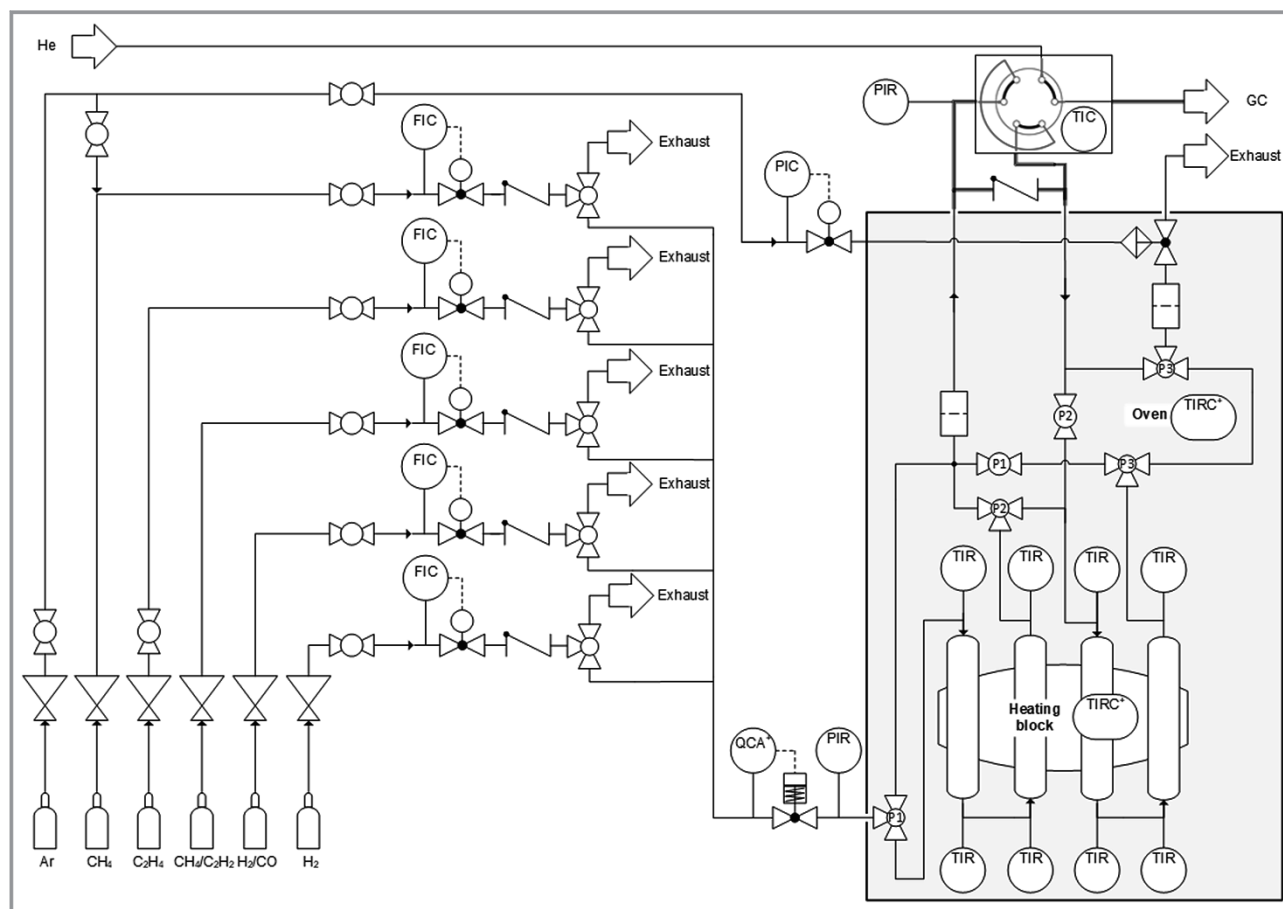


Figure 3. Piping and instrumentation flow diagram of the advanced TEMKIN reactor miniplant.

routing the flow directly into the analytic gas chromatograph (GC) without contact to the catalyst. The second pathway leads the volume flow through reactor 1 and 2, then into the GC and hereafter into reactor 3 and 4. With the third option, the reaction mixture flows through all of the four reactors and is then analyzed by GC. This setup enables automated bypass measurements and the possibility of analysis after reactor modules 2 and 4 and thus, after different amounts of catalyst pellets under stationary conditions in one experiment. An essential feature is that at all times during the reaction each reactor is constantly kept under flow conditions and no gas remains static inside the plant. Therefore, unwanted side reactions and catalyst deactivation can be avoided.

For the GC injection an actuated 6-way-valve is used, which operates under reaction pressure. The 6-way-valve and all pipes outside the oven, up to the GC are isolated and heated. The reactor unit can reach a maximum temperature of 100 °C and the oven 90 °C. The temperature is monitored by several thermo-indicators, which control the reactor unit, oven and GC. The usual operating pressure of the plant is between 20 and 25 bar and is controlled by a back pressure regulator (BPR). Four pressure indicators are installed: one before the oven, one before the GC, one before the BPR and one for the control of operating gas of the BPR.

3 Experimental

For the kinetic investigations of the industrial Pd-Ag/Al₂O₃ catalyst (cylindrical pellets, supplied by Clariant Produkte (Deutschland) GmbH) the four TEMKIN reactor modules are filled with a total of 22 catalyst pellets and 22 inert aluminum pellets in alternating order. One reactor can take up to 11 pellets, resulting in 5 catalyst and 6 inert pellets for reactor 1 & 3 and 6 catalyst and 5 inert pellets for reactor 2 & 4. The modules 1 & 2 and 3 & 4 are directly connected in series. After reactor module 2 the total reaction flow can either be led directly into reactor 3 or to the online GC for analysis and then into reactor 3. Therefore, measurements

after half and after all of the inserted catalyst pellets are possible. For an experiment the feed and reaction conditions listed in Tab. 1 are adjusted, respectively. Before each experiment, bypass measurements are carried out to determine the exact concentrations of the reactants. The samples are taken via a 6-way-valve with a 5 µl sample loop under reaction pressure and are carried out with a Shimadzu GC 2010 Plus with RT-Alumina BOND/MAPD column (30 m; ID 0.53 mm; Film Thickness 10 µm; carrier gas Helium) using a FID analyzer. For each experiment a temperature ramp with an increment of 10 °C, starting at 30 °C and ending at 90 °C, is investigated. The resulting 7 temperatures are held for a total of 180 min: 90 min while measuring the reactants after reactor 4 (22 pellets) and 90 min while measuring after reactor 2 (11 pellets). Then the reaction system is heated to the next temperature. The time at each temperature was determined experimentally and is sufficient to obtain at minimum 5 GC measurements for all of the tested variations with a standard deviation below 0.5 % conversion as steady state conditions.

The GC data is converted to mol % using specific GC factors, which were calibrated for each reactant. The conversion of acetylene is calculated from the experimental data based on the calibration and the internal standard propane to compensate experimental fluctuations with Eq. (1). \dot{n}_0 refers to the average amount of substance of the bypass measurements before the start of the experiment. For the correction with the internal standard the measured $\dot{n}_{\text{acetylene}}$ is multiplied with the average amount of propane in the feed $\dot{n}_{0,\text{propane}}$ and divided by the measured value \dot{n}_{propane} . As propane and acetylene are fed, dosed and measured from the same gas bottle, potential fluctuations can be avoided this way. The selectivity towards ethane, 1-butene, t-butene, c-butene or -butadiene (C₄) is calculated by Eq. (2), which is based on the acetylene conversion. Under certain reaction conditions also ethylene is hydrogenated to ethane and therefore the ethane selectivity can appear to be greater than 100 %. For the calculation of the reaction rate (Eq. (3)) the total catalyst pellet weight and not the weight of the active component is used.

Table 1. Feed composition and reaction parameters for the studied experiments.

	#1	#2	#3	#4	#5
Volume flow [L h ⁻¹]	62.7	62.7	62.7	62.7	62.7
Total pressure [bar]	22.5	22.5	22.5	22.5	22.5
C ₂ H ₄ [mol %]	37.00	45.00	40.00	56.00	51.00
H ₂ [mol %]	35.56	35.56	36.00	24.44	28.00
CH ₄ [mol %]	26.86	19.04	23.58	19.37	20.62
C ₂ H ₂ [mol %]	0.30	0.20	0.20	0.10	0.20
Propane [mol %]	0.25	0.17	0.17	0.08	0.17
CO [ppm]	350	350	500	50	100

$$X_{\text{acetylene}} = \frac{\dot{n}_{0,\text{acetylene}} - \dot{n}_{\text{acetylene}}}{\dot{n}_{0,\text{acetylene}}} \frac{\dot{n}_{0,\text{propane}}}{\dot{n}_{\text{propane}}} \quad (1)$$

$$S_i = \frac{\dot{n}_i - \dot{n}_{i,0}}{\dot{n}_{0,\text{acetylene}} - \dot{n}_{\text{acetylene}}} \frac{\dot{n}_{0,\text{propane}}}{\dot{n}_{\text{propane}}} \frac{\nu_{\text{acetylene}}}{\nu_i} \quad (2)$$

$$r_{\text{acetylene}} = \frac{\dot{n}_{0,\text{acetylene}} - \dot{n}_{\text{acetylene}}}{m_{\text{catalyst pellets}}} \frac{\dot{n}_{0,\text{propane}}}{\dot{n}_{\text{propane}}} \quad (3)$$

4 Results

Fig. 4 shows typical reaction profiles depending on the temperature profile measured under reaction parameter set #1 (Tab. 1) and compares the product stream composition after 11 and 22 pellets by intermediate sampling, respectively. For

increasing acetylene conversion, the data shows an increasing selectivity towards ethane. The combined C₄ selectivity (“green oil formation”) is very similar after 22 and 11 catalyst pellets and decreases with increasing temperature. The data of the individual C₄ selectivities (Fig. 4b)) indicates that at lower temperatures with higher acetylene concentrations mainly 1,3-butadiene is formed. With advancing acetylene conversion and higher temperatures, the 1,3-butadiene concentration declines and more 1-butene, t(trans)-butene and c(cis)-butene are detected, apparently in a constant ratio. The comparison between 11 and 22 pellets indicates that the amount of available acetylene is a stronger driving force for the formation of 1,3-butadiene than the reaction temperature.

For a comparison of the impact of the feed composition, a temperature of 70 °C is chosen, because at this temperature for any condition acetylene is close to but below full conversion and this also represents a common and relevant temperature for industrial reactors [13]. In Fig. 5 the con-

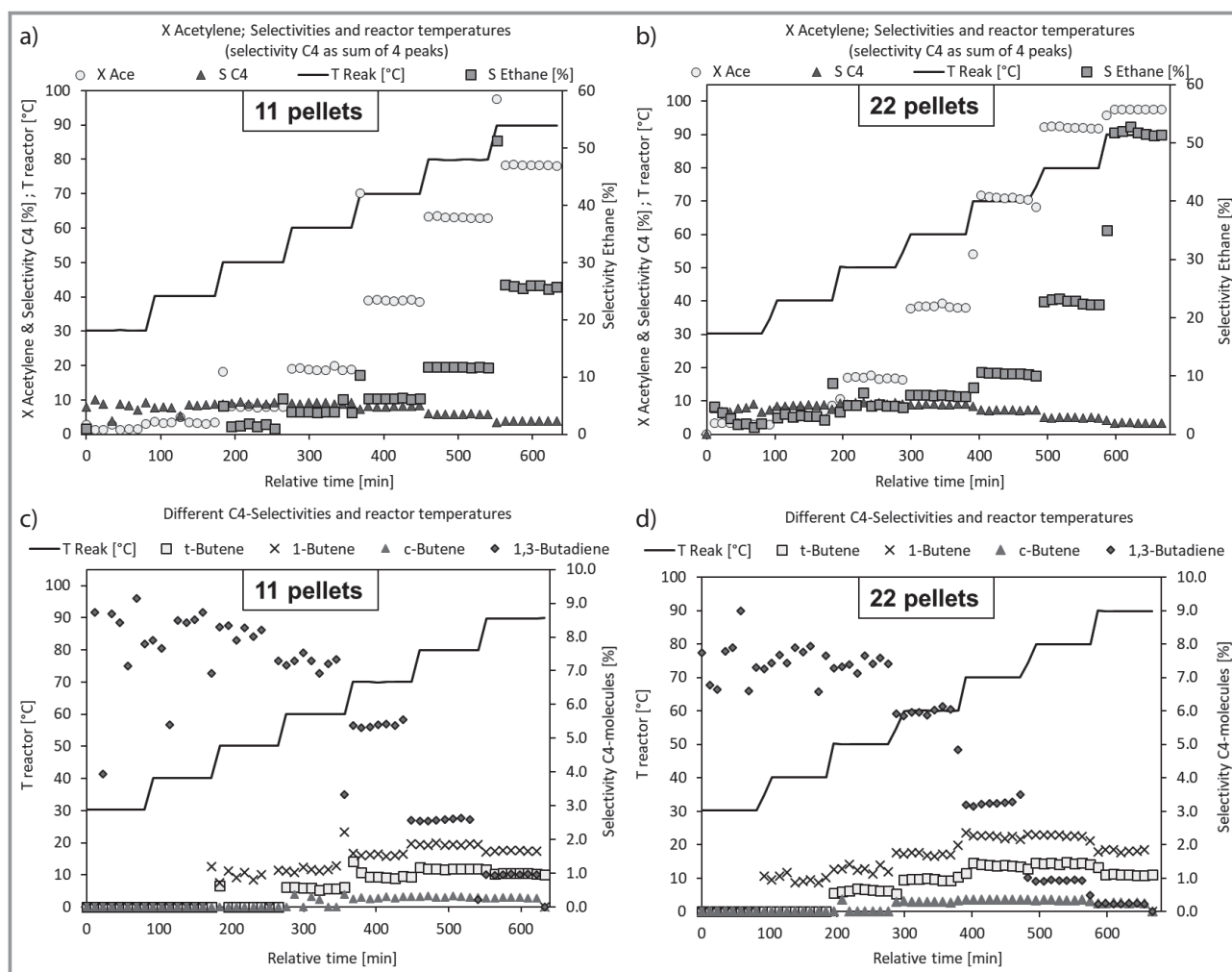


Figure 4. Experimental data of a temperature ramp from 30 to 90 °C under the feed condition/reaction parameter set #1 (Tab. 1). Conversion of acetylene, selectivity to ethane and combined C₄ selectivity depending on the reaction temperature for 11 (a) and 22 pellets (b). Selectivity of 1-butene, t-butene, c-butene and 1,3-butadiene with regard to the reaction temperature for 11 (c) and 22 pellets (d).

version of acetylene, the selectivity to ethane and the combined C_4 selectivity of the five different experiments at 70°C is compared and shows the major influence of carbon monoxide for this reaction in terms of activity and selectivity control. For example, between #2 and #3 the CO content is increased by 43 % from 350 ppm to 500 ppm at the same acetylene concentration of 0.2 mol %. This reduces the conversion from 81.5 % to 62.6 % at 70°C . For #4 with the lowest CO concentration with 50 ppm and only 0.1 mol % acetylene, the reaction is already near full conversion at 70°C . More importantly, here the ethane selectivity of 149.6 % indicates that not only all of the acetylene is fully hydrogenated to ethane but also the catalyst is starting to hydrogenate ethylene to ethane. This is an early indicator of a possible runaway condition in the case acetylene is fully converted and then preferentially the excess amount of ethylene is hydrogenated in a highly exothermic reaction with a self-accelerating temperature increase.

For a comprehensive evaluation of the performance of a research catalyst and direct performance comparison especially with state-of-the-art industrial catalysts a reliable determination of the reaction rate is essential. Therefore, Fig. 6 shows the reaction rate of the investigated industrial catalyst as determined from experimental data acquired after 22 and after 11 catalyst pellets. The reaction rate is normalized to the total catalyst pellet weight. This leads to a reaction rate roughly three orders of magnitude lower compared to a rate that is exclusively based on the active component in general, a fact that is crucial to be taken into account when comparing catalyst performances.

The results of Fig. 6 underline the dependence of carbon monoxide as a moderator and inhibitor of the acetylene hydrogenation. In addition, the reaction rate is strongly dependent on the overall acetylene concentration. For all experiments, the data after 11 pellets shows a higher reaction rate than after 22 pellets. This difference strongly increases with progressing conversion and thus, lower acet-

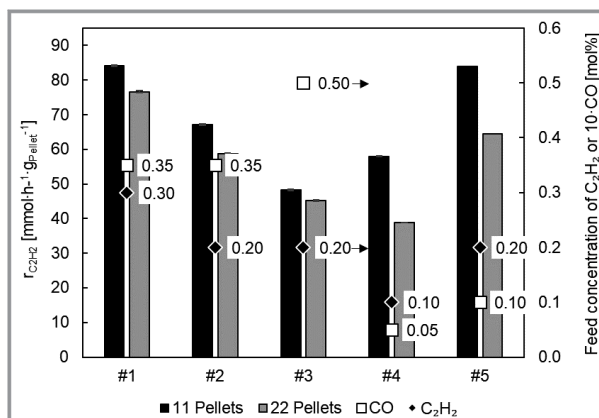


Figure 6. Comparison of the reaction rates under different feed conditions at 70°C for 22 and 11 catalyst pellets. The feed concentration of acetylene and concentration of carbon monoxide multiplied by the factor 10 is displayed on the second y-axis.

ylene concentrations. For example, at 81.5 % conversion in experiment #2–22 pellets, the reaction rate of 11 pellets (at 48.9 % conversion) is 14 % higher and for experiment #5–22 pellets at 89.3 % conversion the reaction rate for 11 pellets (at 58.2 % conversion) is 30 % larger. This clearly shows that the specific conversion rate of acetylene strongly depends on the acetylene concentration, which is expected to decrease with increasing conversion as expected for a positive reaction order.

5 Conclusion

The advanced TEMKIN reactor provides an ideal setup to analyze eggshell catalysts under industrial conditions. Complex feed compositions can be applied, and the defined ring gap of the reactors enables realistic linear velocities for microkinetic analysis under demanding industrial condi-

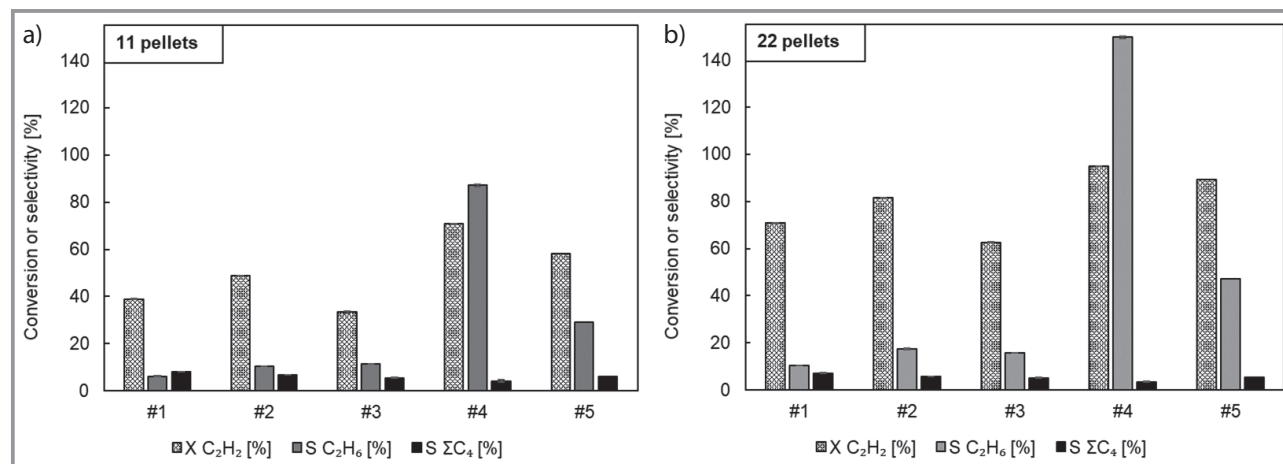


Figure 5. Comparison of the catalyst performance under different feed conditions (Tab. 1) at 70°C . with 11 (a) and 22 (b) catalyst pellets. The selectivity of ethane can exceed 100 % as it is calculated based on the conversion of acetylene while it can also be formed from the excess amount of ethylene in the feed.

tions. The ability to assess kinetic data at two different positions of the catalyst bed provide even more advanced insights into reaction kinetics. With the advanced online gas chromatography quantitative trends in the formation of C₄-species were identified with overall short analysis times. Applied to a state-of-the-art industrial catalyst the temperature dependent kinetic data alongside the influence of the feed composition, especially the moderation of the catalytic performance by the CO content and the effects of the catalyst amount were reported in this work and demonstrates on the one hand the need for such thorough and comprehensive kinetic testing and on the other hand the high experimental effort to gain fundamental insights into the catalytic performance of complex realistic catalytic systems.

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Symbols used

m	[g]	catalyst pellet mass
\dot{n}	[mol h ⁻¹]	molar flow of substance
\dot{n}_0	[mol h ⁻¹]	molar flow of substance in the feed
r	[mmol h ⁻¹ g _{Pellets} ⁻¹]	reaction rate
S	[%]	selectivity
X	[%]	conversion

Greek symbols

σ	[-]	standard deviation
ν	[-]	stoichiometric factor

Sub- and superscripts

0	before the reaction
C ₄	1-butene, t-butene, c-buten, -butadiene
i	individual reactant

Abbreviations

BPR	back pressure regulator
FID	flame ionisation detector
GC	gas chromatographie
HDPE	high density polyethylen
LDPE	low density polyethylen
LLDPE	linear low-density polyethylene
LV	linear velocity
MFC	mass flow controller

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