

Supplementary Material: Selective Hydrogenation of Acetylene over Pd-Mn/Al₂O₃ catalysts

Cymantrene Decomposition

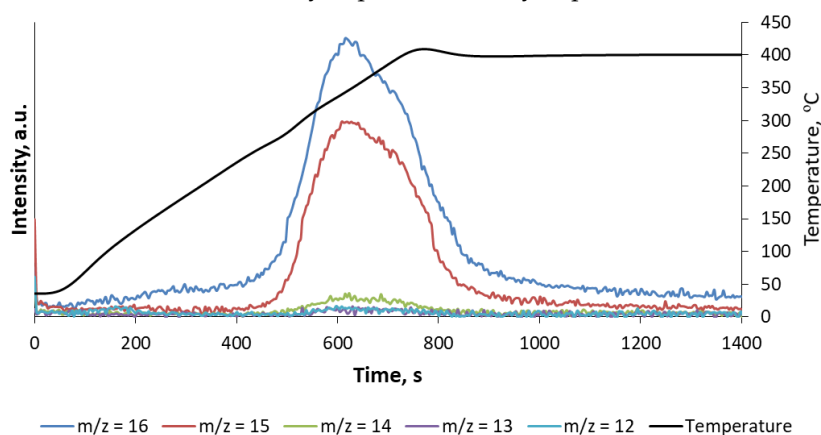
In decomposition of cymantrene (Cm) a number of m/z ions is formed. To identify compounds that correspond to them is a complicate problem. Taking into account the cymantrene formula, one can expect formation of the next products during Cm decomposition in H₂ flow at the temperature range of 40-400 °C, namely CO, methane, cyclopentane, cyclopentene, and cyclopentadiene. Figure S1 shows peaks of m/z ions, which could be related to: (a) methane; (b) cyclopentane; (c) cyclopentene; (d) cyclopentadiene [1].

The peaks, which can be related to methane, are found in the temperature range 270-400 °C in agreement with data on CO methanation over Pd [2].

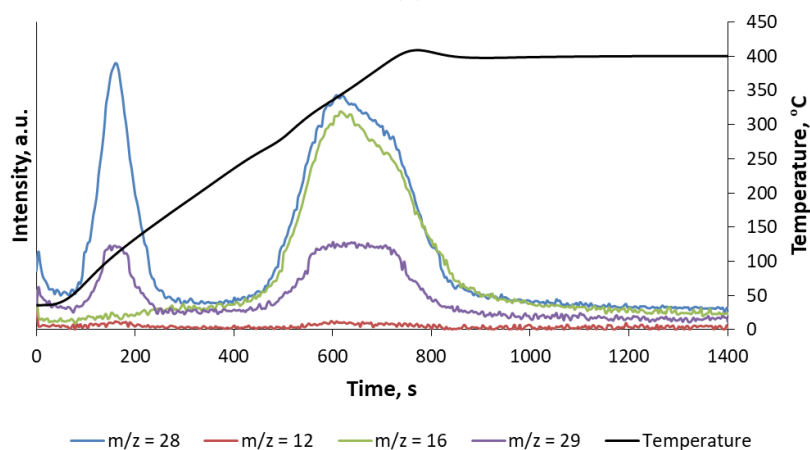
The peaks, which can be related to CO, are found in two temperature ranges: 80-150 °C and 270-400 °C. In the first temperature range, CO cannot be hydrogenated to methane over Pd, but at higher temperature range methanation is possible [2]. Taking into account methane peaks, one can conclude that CO is partially hydrogenated to methane.

The major m/z peaks for cyclopentane (42, 55) and cyclopentene (67, 68) are found only in the range 80-150 °C, so one may conclude that cyclopentadienyl ligands are hydrogenated to cyclopentane and cyclopentene in this range. Ions with m/z 39 and 41 are common both for cyclopentane and cyclopentene.

The major m/z peaks related to cyclopentadiene (66 and 65) are absent, so one may conclude that peaks m/z 39 and 40 could be related to cyclopentane and cyclopentene.



(a)



(b)

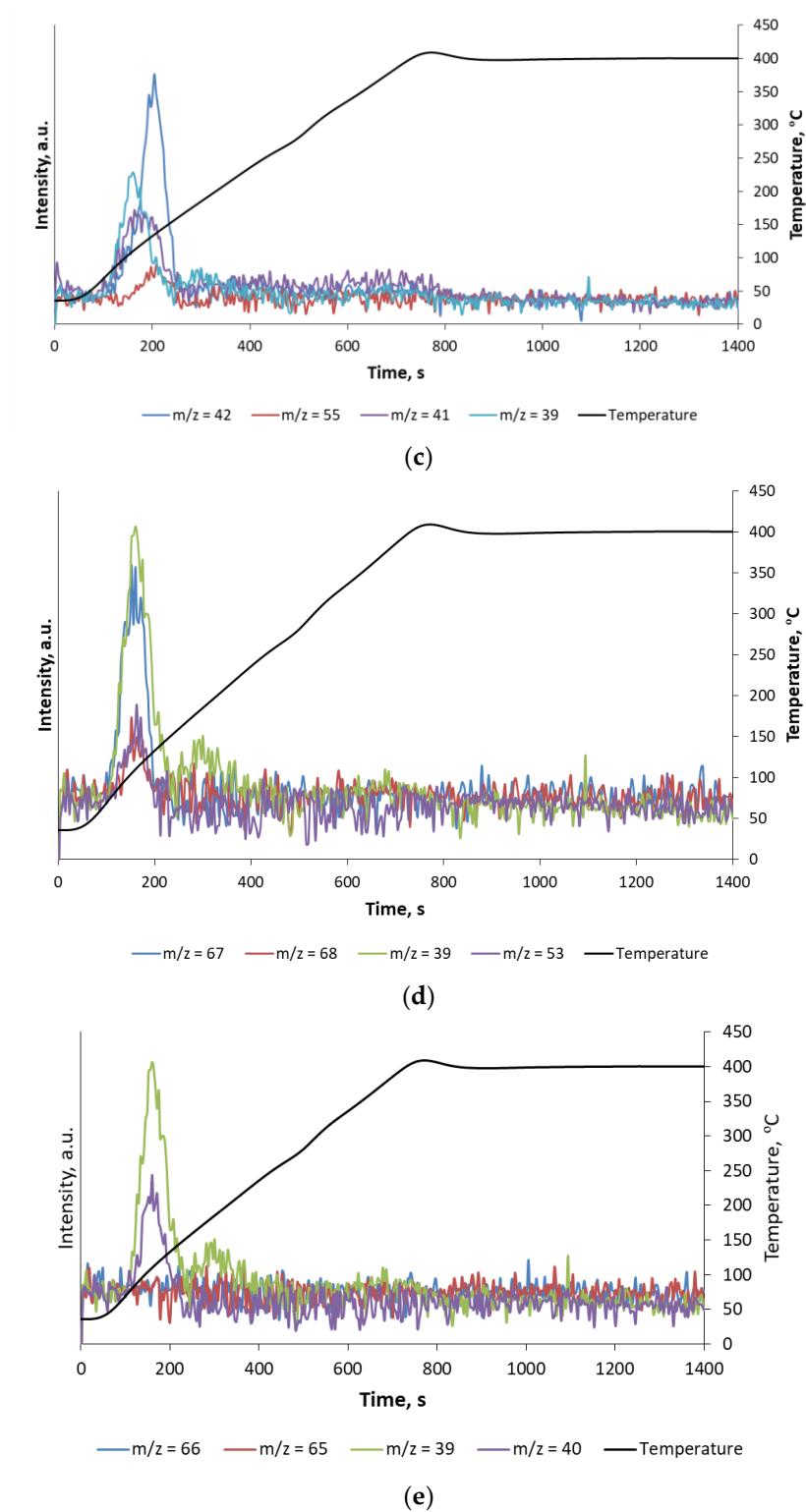


Figure S1. Peaks of m/z in decomposition of cymantrene in H_2 , which could be related to: (a) methane; (b) CO; (c) cyclopentane; (d) cyclopentene; (e) cyclopentadiene.

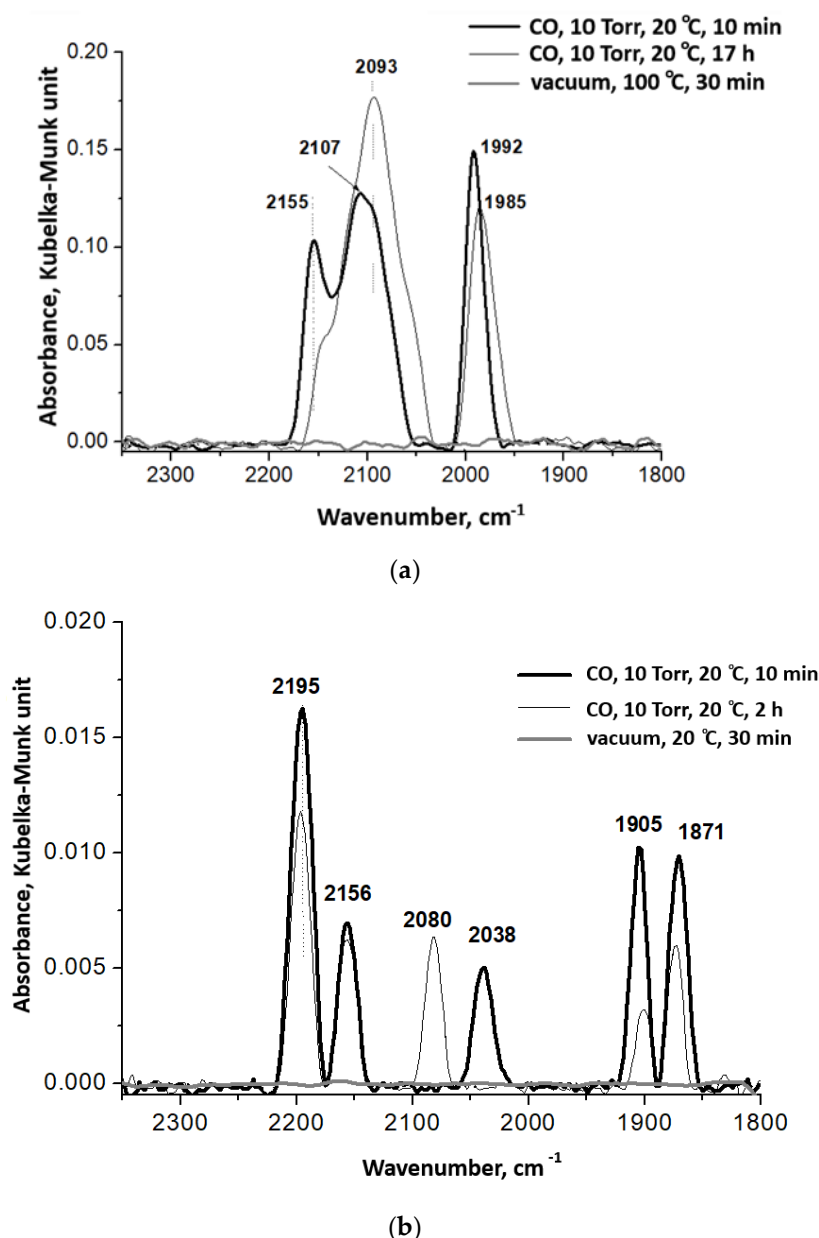


Figure S2. DRIFT spectra of CO after adsorption and vacuum treatment: (a) on Pd/Al₂O₃; (b) on Pd-Mn/Al₂O₃.

Figure S2,a shows DRIFT spectra of CO adsorbed on Pd/Al₂O₃. After CO adsorption, three bands appear: 2155, 2107, and 1992 cm^{-1} . Increasing treatment time decreases intensity of the band 2155 cm^{-1} , a shoulder at 2116 cm^{-1} appears, the band 2107 cm^{-1} is moved to lower wavenumbers (2093 cm^{-1}) and the intensity increases; the band 1992 cm^{-1} is moved to 1985 cm^{-1} and the intensity increases. Probably, the band 2155 cm^{-1} corresponds to the linear form of CO adsorption on Pd⁺, bands 2107–2093 cm^{-1} – on metallic Pd. Bands 1992–1975 cm^{-1} relates to bridge forms of CO on metallic Pd [3–5]. Vacuum treatment at 100 °C for 30 min completely desorbs CO. As compared with CO spectra on Pd-Mn, however, the intensity of bands is ten times larger. We may conclude, therefore, that addition of Mn to Pd in equal amount completely suppresses CO adsorption.

Figure S2,b shows spectra of Pd-Mn/Al₂O₃ after treatment with CO where five weak bands appear with maxima at 2195, 2156, 2039, 1905, and 1871 cm^{-1} . In the course of time of treatment with CO, intensity of adsorption maxima decreases, a new band at 2080 cm^{-1} appears, and the band 2038 cm^{-1} disappears. After vacuum treatment at room temperature, all peaks in the range of 2195–1871 cm^{-1} disappear. So, one may conclude the absence of strong CO chemisorption on the Pd-Mn catalyst that is weak and negligible (at most 0.015 units Kubelka-Munk).

The band 2195 cm^{-1} may be related to CO complexes with low coordinated Al^{3+} , the band 2156 cm^{-1} – to the linear adsorption of CO on Pd^+ , and the bands 2080 and 2038 cm^{-1} – on metallic Pd, respectively. The bands 1905 and 1871 cm^{-1} may be related to bridge forms of CO adsorption on metallic Pd.

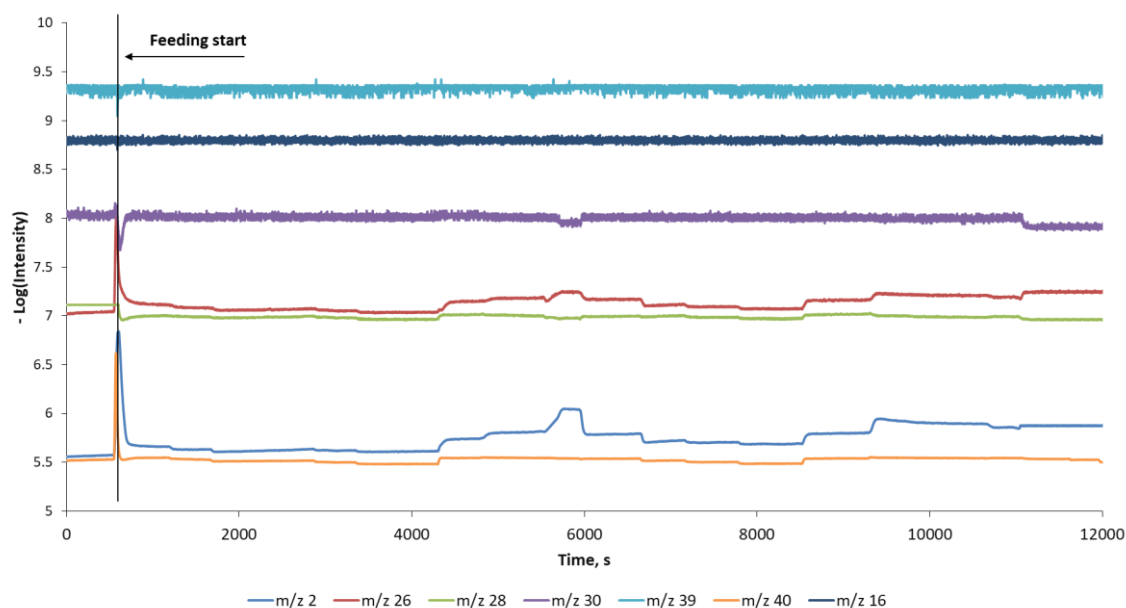


Figure S3. Mass spectra of the effluent gas during testing Pd-Mn/ Al_2O_3 catalyst for 3.5 h at 40°C .

Figure S3 illustrates the effluent gas composition during one day test of the Pd-Mn/ Al_2O_3 catalyst. A peak with m/z 39 is chosen because it is the main ion in 1,3-butadiene MS spectrum [45]. As figure S3 shows, the intensity of m/z 39 maintains at a noise level.

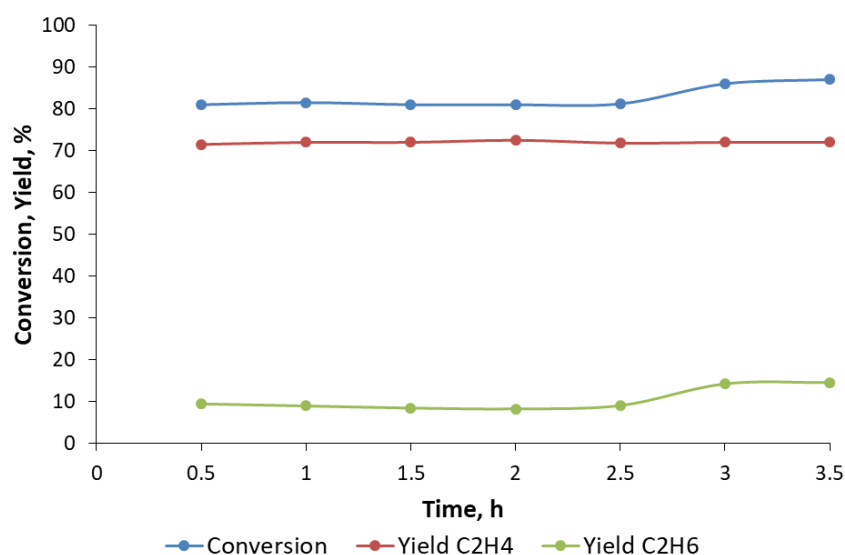


Figure S4. Conversion of acetylene and yield of ethylene and ethane vs. time on stream at 40°C and various contact times on Pd-Mn/ Al_2O_3 .

Figure S4 shows the yield of ethylene as a function of time on stream at few contact times. It is obviously that the yields of ethylene and ethane are stable during the experiment.

References

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