Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information for

Aromatization of ethylene over zeolite-based catalysts

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Abstract:

Light aromatic compounds (BTX: benzene, toluene and xylenes) represent an important class of building blocks in the chemical industry. Currently, light aromatics are obtained exclusively from fossil feedstock, whose utilization is associated with serious environmental concerns. Developing new routes for a more sustainable BTX production is, therefore, of high importance. In this work, aromatization of ethylene over well-defined metal-modified HZSM-5 zeolite catalysts is examined. The results show that modification of zeolite with gallium, zinc and silver leads to a significant increase in aromatics production. Metal species are responsible for catalysing dehydrogenation pathways with Ga being the most efficient for BTX production. Increasing temperature and ethylene partial pressure facilitate ethylene aromatization. Employing a combination of isotope labelling with a thorough characterization of zeolite-entrapped species by means of IR and MAS NMR spectroscopy provides evidence for the involvement of intra-zeolite aromatic hydrocarbon species in the catalytic cycle.

Table S1. *Catalyst preparation: the loadings of the parent zeolite and metal precursors for the incipient wetness impregnation.*

Ga/HZSM-5							
	Al, wt.%	Ga, wt.%	Si/Al, mol.	Ga/Al, mol.	HZSM-5, g	H_2O, ml[1]	Ga source[2], g
0.1Ga/HZSM-5	2.1	0.55	20	0.1	5	3	0.1766
0.25Ga/HZSM-5	2.1	1.4	20	0.25	5	3	0.4495
0.5Ga/HZSM-5	2.1	2.75	20	0.5	5	3	0.8830
Ag/HZSM-5							
	Al, wt.%	Ag, wt.%	Si/Al, mol.	Ag/Al, mol.	HZSM-5, g	H_2O, ml[1]	Ag source[3], g
0.25Ag/HZSM-5	2.1	2.15	20	0.25	5	3	0.1692
Zn/HZSM-5							
	Al, wt.%	Zn, wt.%	Si/Al, mol.	Zn/Al, mol.	HZSM-5, g	H_2O, ml[1]	Zn source[4], g
0.25Zn/HZSM-5	2.1	1.3	20	0.25	5	3	0.2957

[1] Zeolite water impregnation capacity was close to 0.6 ml/g.

[2] $Ga(NO_3)_3*10.6H_2O$

[3] $AgNO_3$

[4] $Zn(NO_3)_2*6H_2O$

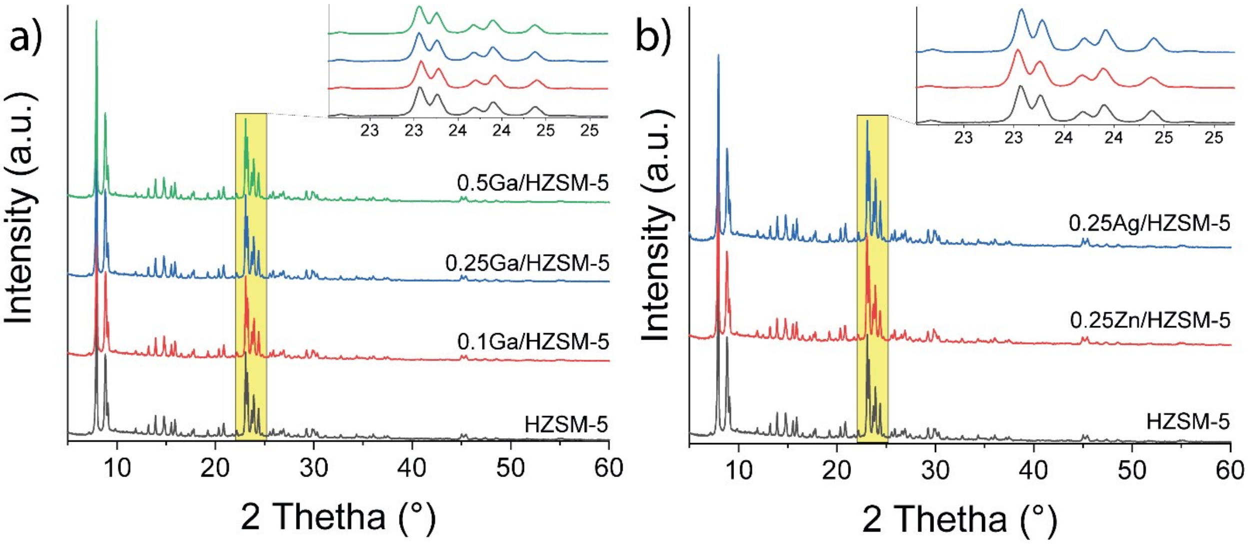

Figure S1. *XRD patterns of a) xGa/HZSM-5 and b) 0,25Zn/HZSM-5, 0,25Zn/HZSM-5 as compared to the pristine HZSM-5 zeolite. Enlarged is a region showing characteristic MFI reflections used to determine crystallinity (23.1° (051), 23.3° (501), 23.7° (511), 24.0° (033), and 24.4° (313)).*

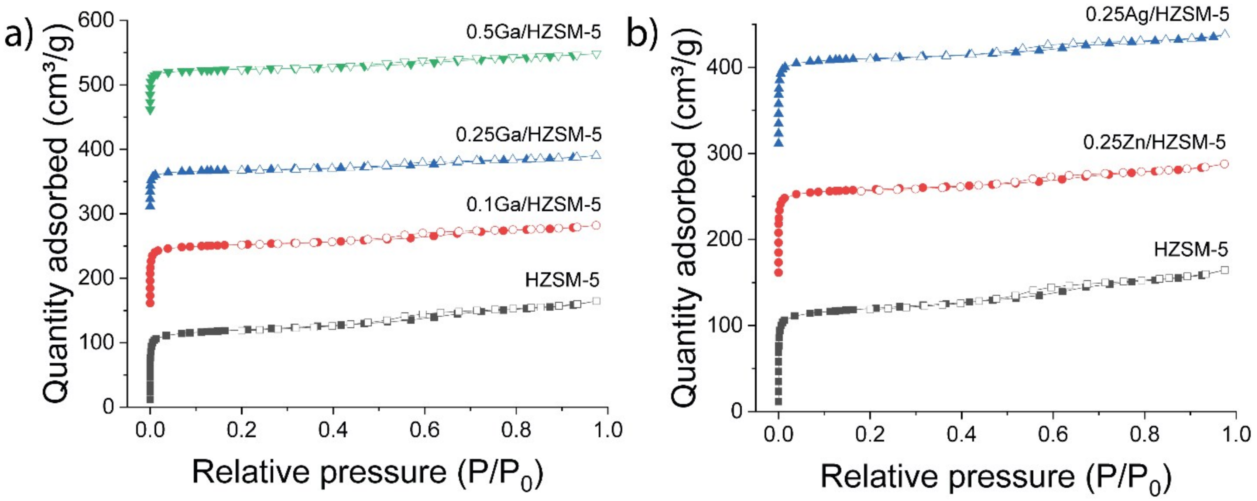

Figure S2. *Argon adsorption-desorption isotherms for a) xGa/HZSM-5; b) 0,25Zn/HZSM-5, 0,25Zn/HZSM-5 as compared to the pristine HZSM-5 zeolite.*

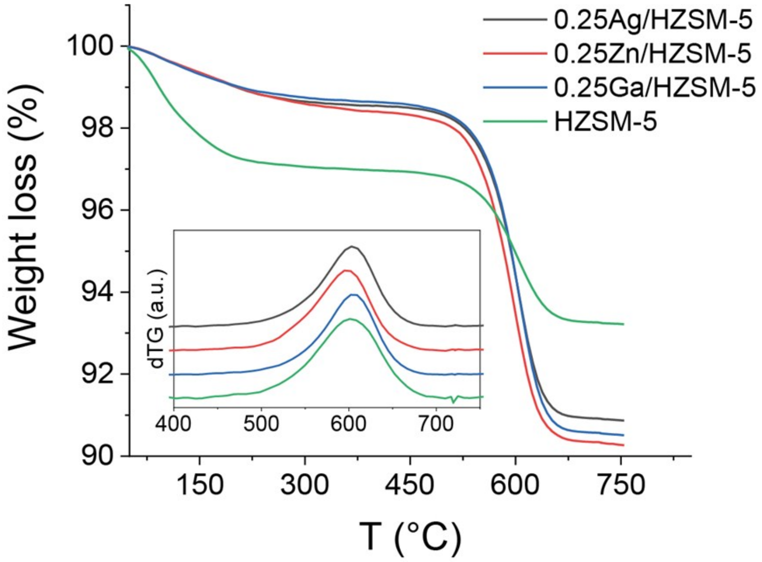

Figure S3. TGA and DTG profiles of as reacted catalyst samples.

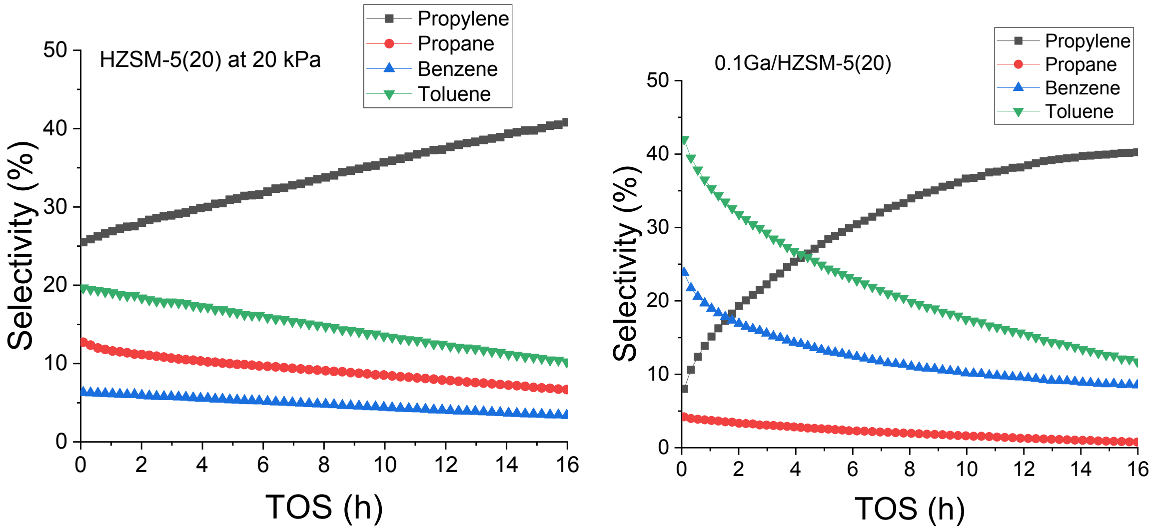

Figure S4. *Distribution of the main reaction products as function of time-on-stream during ethylene conversion over a) HZSM-5 and b) 0,25Ga/HZSM-5. Conditions: Conditions: atmospheric pressure; ethylene partial pressure 20 kPa; carrier flow 50 mL/min He, WHSV – 7.5 g/g*$_{cat}$.

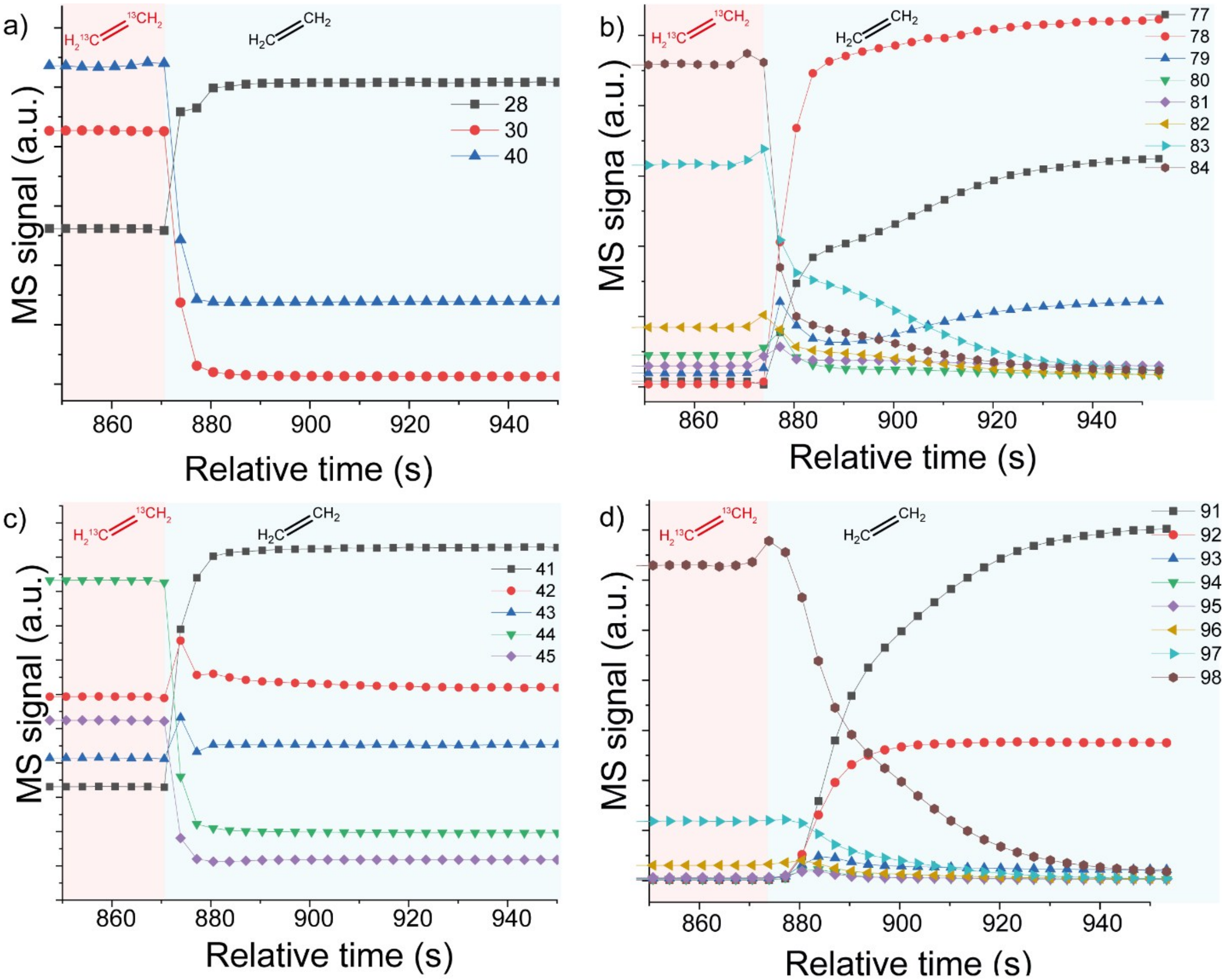

Figure S5. *MS data collected during ethylene reaction following switches between* ^{13}*C-ethylene and* ^{12}*C-ethylene: signals of a) ethylene and argon; b) benzene; c) propylene; d) toluene. Conditions: atmospheric pressure; ethylene partial pressure 10 kPa; carrier flow 50 mL/min He.*

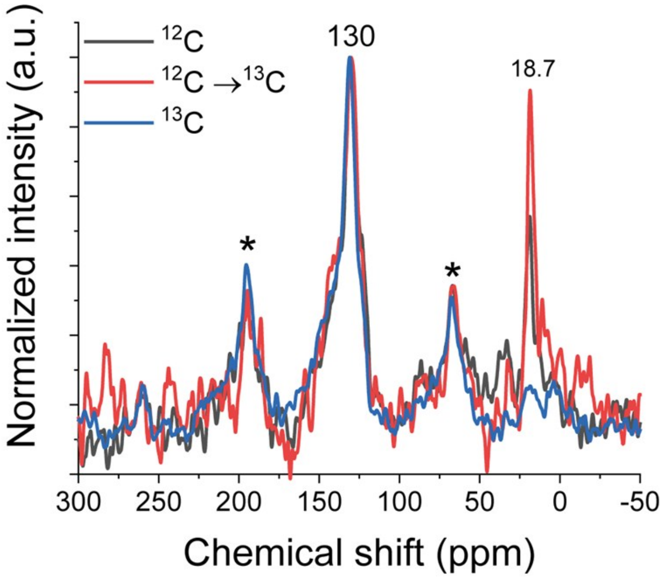

Figure S6. *$^{13}C\{^1H\}$ cross-polarization (CP) MAS NMR spectra of HZSM-5 subjected to ethylene aromatization reaction for 30 minutes with a) switch from ^{13}C ethylene feed to ^{12}C ethylene feed after 15 minutes of reaction; b) switch from ^{12}C ethylene feed to ^{13}C ethylene feed after 15 minutes of reaction. Conditions: T = 500 °C; atmospheric pressure; carrier flow 50 mL/min He.*