Unsupported CoMoS catalysts for isoeugenol hydrodeoxygenation: optimisation of synthesis parameters for catalyst performance

Supplemental information

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1 ICP results

Table A. ICP analysis results.

	Al (mg/g)	Co (mg/g)	Cr (mg/g)	Cu (mg/g)	Fe (mg/g)	Mn (mg/g)	Mo (mg/g)	Ni (mg/g)	S (mg/g)	Zn (mg/g)
Cat-001	2.8	200	0.1	0.5	1.3	0.07	358	0.3	293	0.2
Cat-101	3.2	141	0.1	0.9	0.3	0.01	377	0.1	212	0.3
Cat-011	2.7	135	0.1	0.5	0.3	0.02	385	0.1	428	0.2
Cat-111	4	130	0.1	0.5	0.1	0.01	406	0.1	453	0.2
Cat-000	5	6.2	2.8	0.4	6.3	0.03	517	2.8	239	0.3
Cat-100	4.4	98	0.1	0.3	2.5	0.01	456	2.9	202	0.3
Cat-110	3.4	125	0.1	0.2	0.2	0.01	391	0.1	413	0.2
Cat-010	4.1	31	0.1	0.2	1.2	0.01	406	2.3	494	0.2
CatCen 1	3.1	162	0.1	0.2	0.5	0.02	361	0.2	399	0.2
CatCen 2	3.1	150	0.1	0.3	0.7	0.02	357	0.2	381	0.2
CatCen 3	3.2	161	0.1	0.5	0.2	0.01	341	0.1	415	0.2

2 SEM images

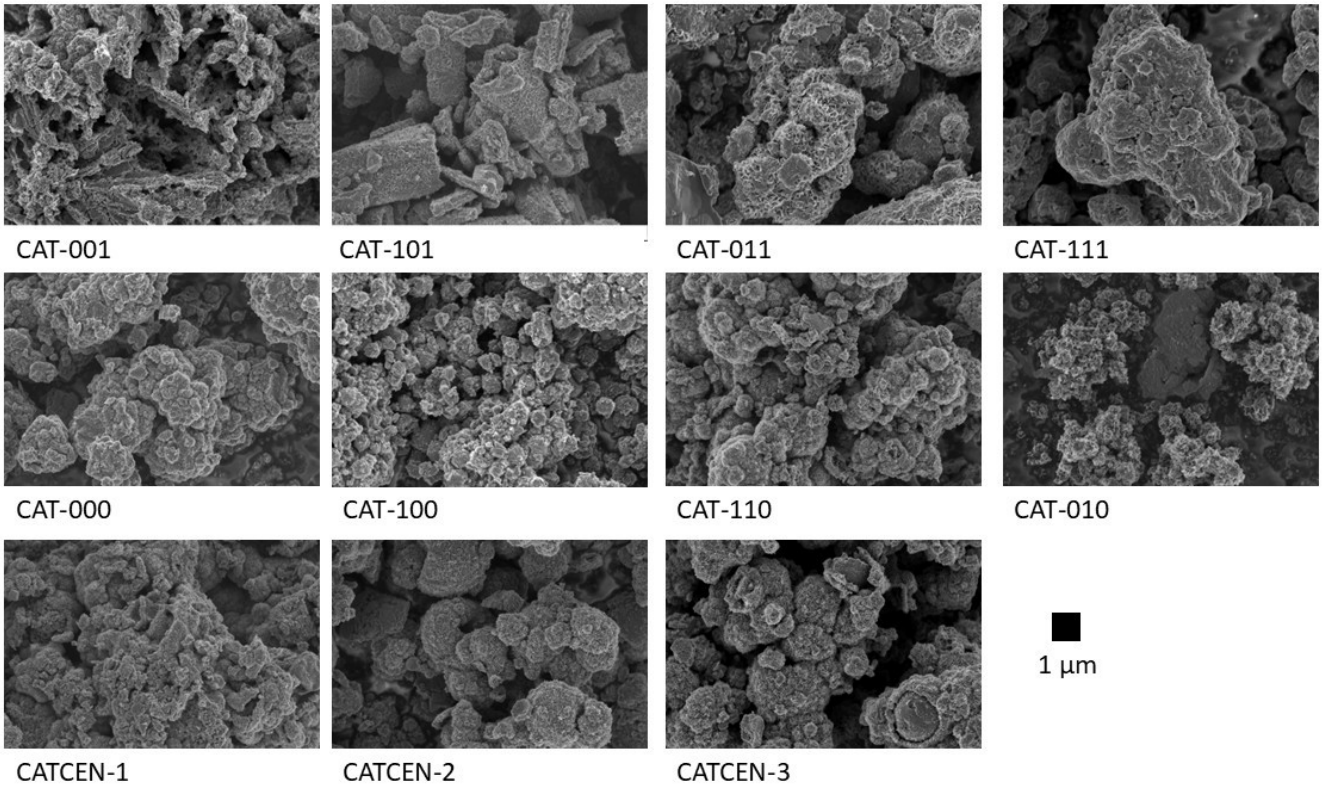

Figure A: SEM images of all studied catalysts, the square in lower corner for scale. Magnification power 10 000, acclereration voltage 2kV.

Comment [SR]: Lisää kiihdytysjännite ja suurennos, käännä sivu

Comment [SR]: @Viertiö Tyko Kahteen kertaan CAT-000!

3 XPS results

Table B. XPS results by element

	Co	Mo	O	S
CAT-001	4%	25%	38%	30%
CAT-101	3%	28%	23%	43%
CAT-011	1%	30%	12%	49%
CAT-111	3%	28%	7%	58%
CAT-000	0%	29%	45%	19%
CAT-100	2%	28%	30%	38%
CAT-110	3%	27%	8%	53%
CAT-010	3%	23%	13%	60%
CATCEN1	1%	29%	13%	52%
CATCEN2	2%	28%	18%	47%
CATCEN3	1%	28%	13%	52%

Table C. XPS results by relative abundance of components.

	Cobalt		Molybdenum					Oxygen			Sulfur			
	CoO %	CoS2 %	Mo 2+	Mo (4-5+)	Mo 4+	Mo 5+	Mo 6+	O1 % (O2-)	O2 % (OH)	O3 % (organic)	S (161,0)	S (161,8)	S (162,4)	S (163,3)
CAT-001	43.8	56.2	0.9	19.7	26.9	24.9	27.7	15.8	76.0	8.2	9.5	53.2	30.1	7.2
CAT-101	24.2	75.8	4.8	10.3	67.3	8.4	9.3	60.2	33.0	6.8	8.7	72.7	15.2	3.4
CAT-011	37.4	62.6	0.0	14.5	64.3	16.9	4.3	32.4	55.9	11.7	14.3	65.0	11.8	8.9
CAT-111	17.8	82.2	3.9	35.7	53.9	5.7	0.9	41.1	43.0	15.8	7.3	83.1	6.2	3.4
CAT-000	71.2	28.8	0.0	16.3	20.4	32.5	30.8	70.3	27.3	2.4	22.6	46.6	12.6	9.9
CAT-100	24.2	75.8	0.1	60.7	8.8	22.8	7.6	59.4	32.6	8.0	7.2	67.7	8.9	16.2
CAT-110	24.0	76.0	0.6	32.6	54.7	10.4	1.7	24.4	61.5	14.2	14.6	77.0	4.7	3.7
CAT-010	38.5	61.5	9.1	55.0	34.1	1.6	0.2	23.0	67.2	9.8	1.2	41.8	16.4	40.5
CATCEN1	31.7	68.3	0.2	45.1	35.6	14.0	5.2	16.3	65.4	18.3	9.0	68.2	15.9	6.9
CATCEN2	30.6	69.4	0.0	41.0	36.6	13.5	8.8	22.1	62.9	15.0	10.9	62.6	19.4	7.1
CATCEN3	39.8	60.2	0.0	57.1	25.3	13.6	4.1	17.0	64.1	18.9	10.1	54.1	27.1	8.7

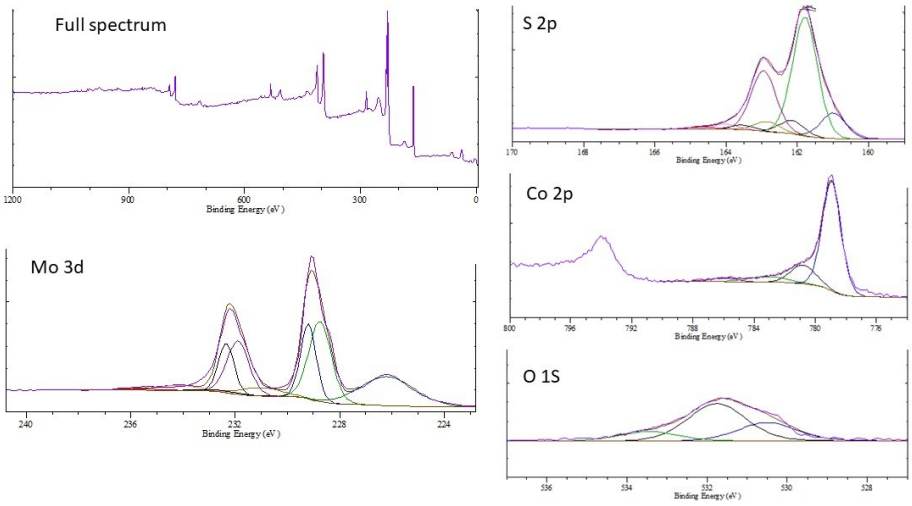

Figure B: An example of XPS spectra for catalyst CAT-110.

4 Mass balance

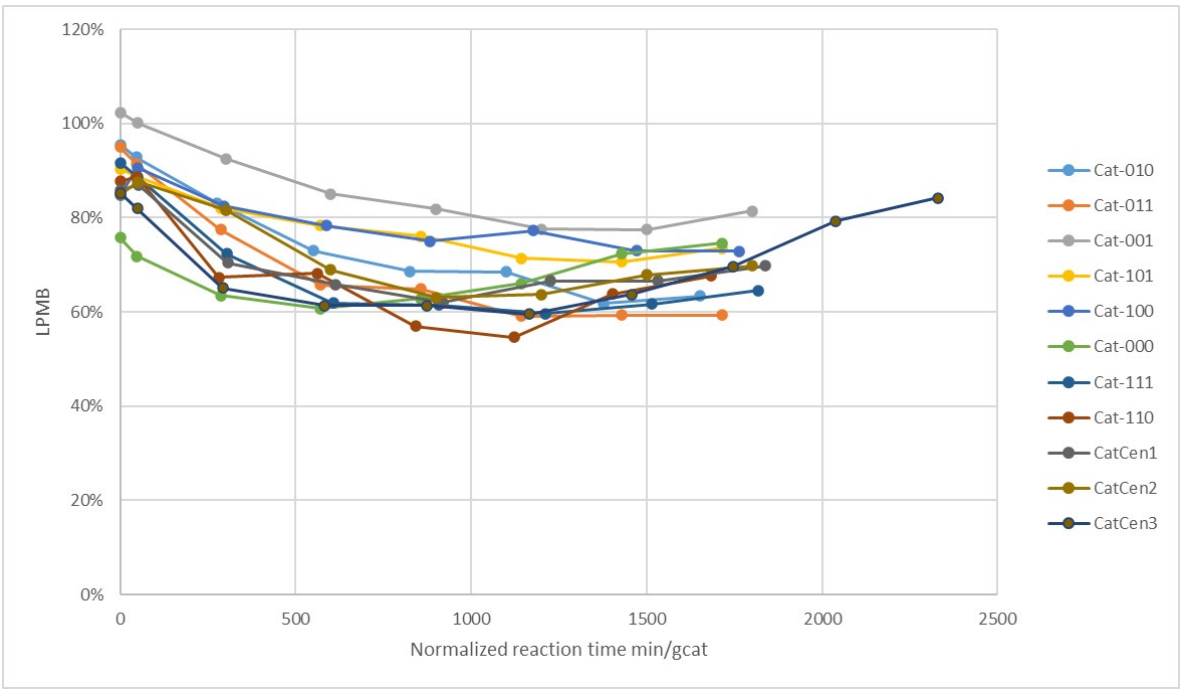

Figure C. Mass balances of the samples as function of reaction time.

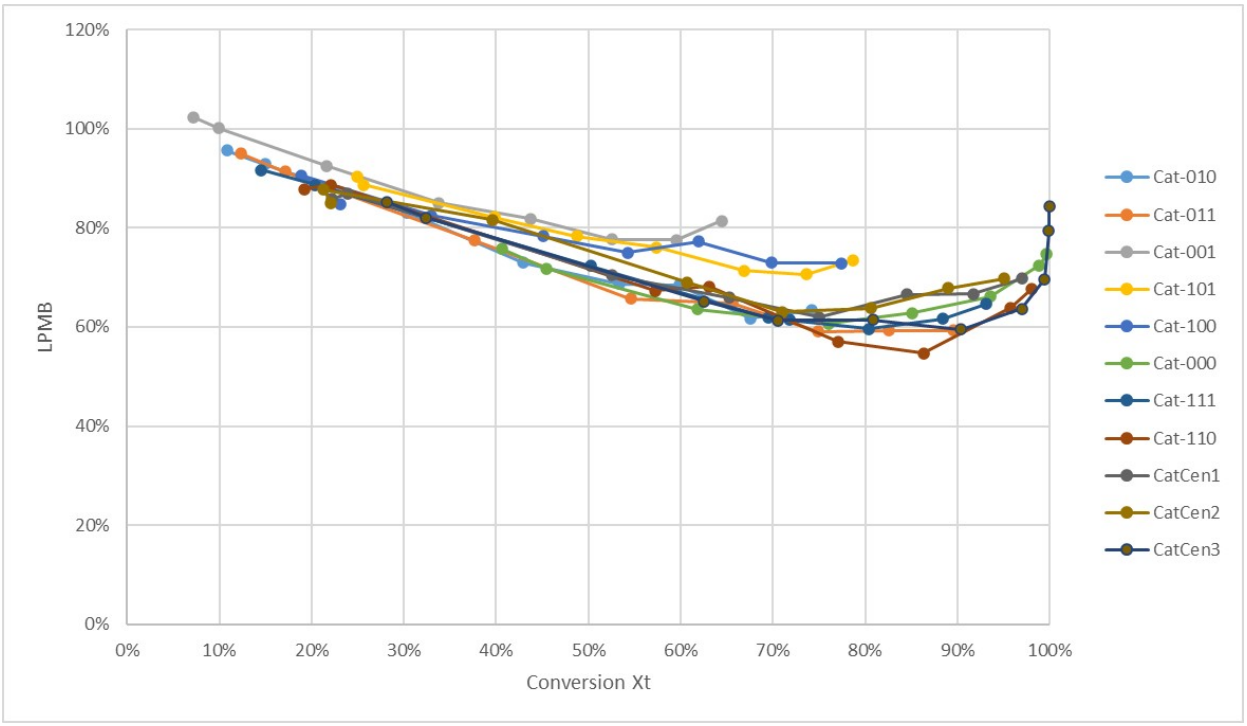

Figure D. Observed mass-balance as function of conversion.

5 Linearization and calculation of the rate constants

The 0th, 1st and 2nd order kinetics were tested for assaying the reaction rates over different catalysts. Data was evaluated based on RSQ of fitting to particular reaction rate.

5.1 0th order

Equation for 0th order

$$n_{IE_t} + n_{DHE_t} = n_{IE_0} - kt_r$$

Linearization for reaction rate constant calculation

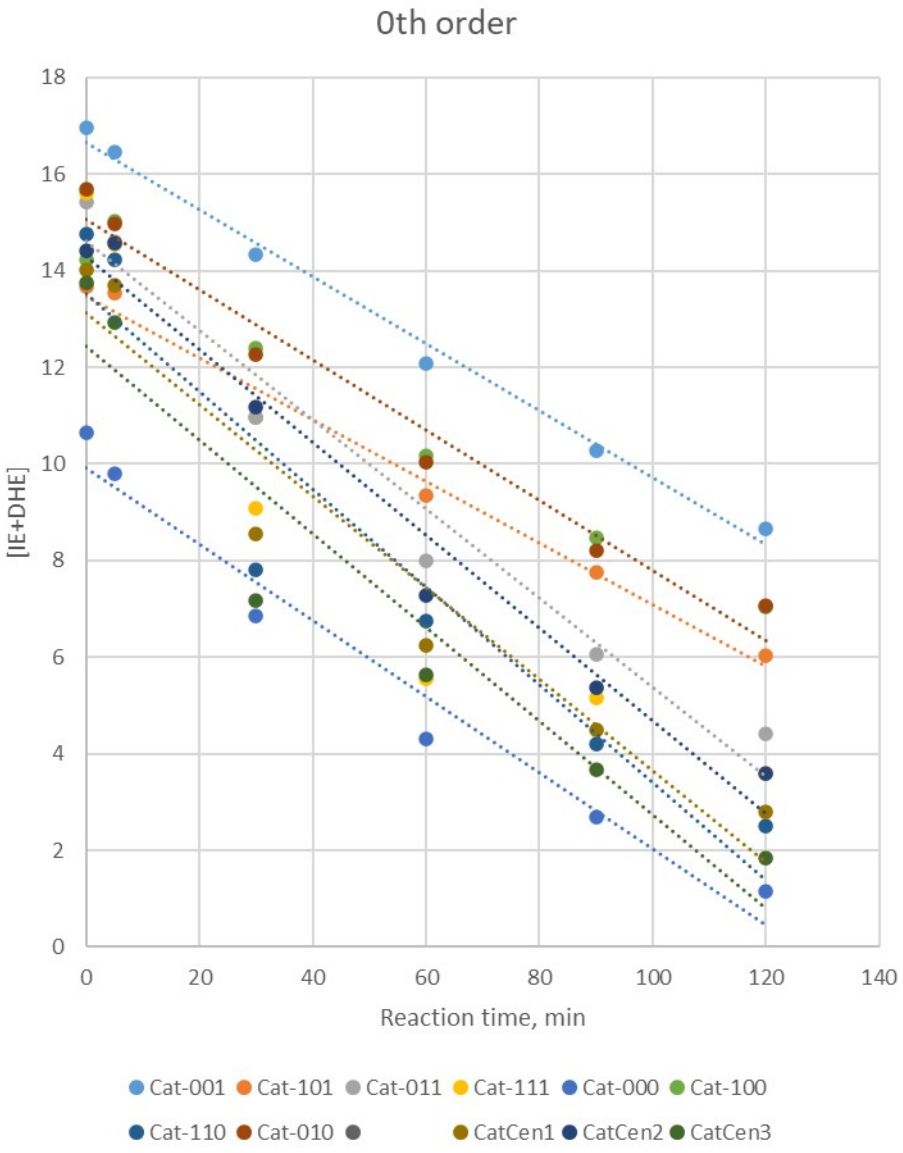

Figure E. Normalization of 0th order.

5.2 1st order

$$\ln\left(\frac{n_{IE_t} + n_{DHE_t}}{n_{IE_0}}\right) = -kt_r$$

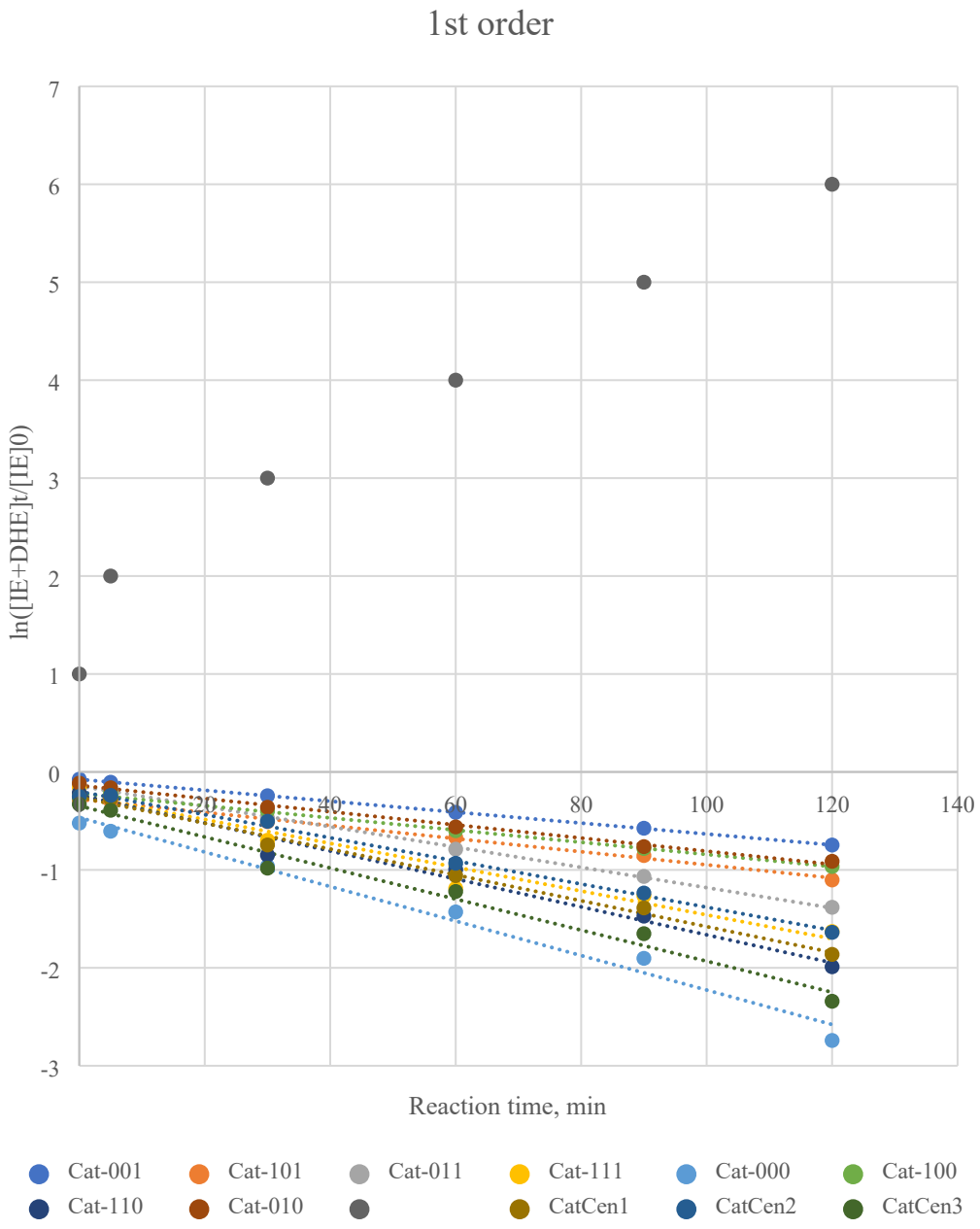

Figure F. Normalization of 1st order

5.3 2nd order

$$\frac{1}{n_{IEt}+n_{DHEt}} = -kt_r$$

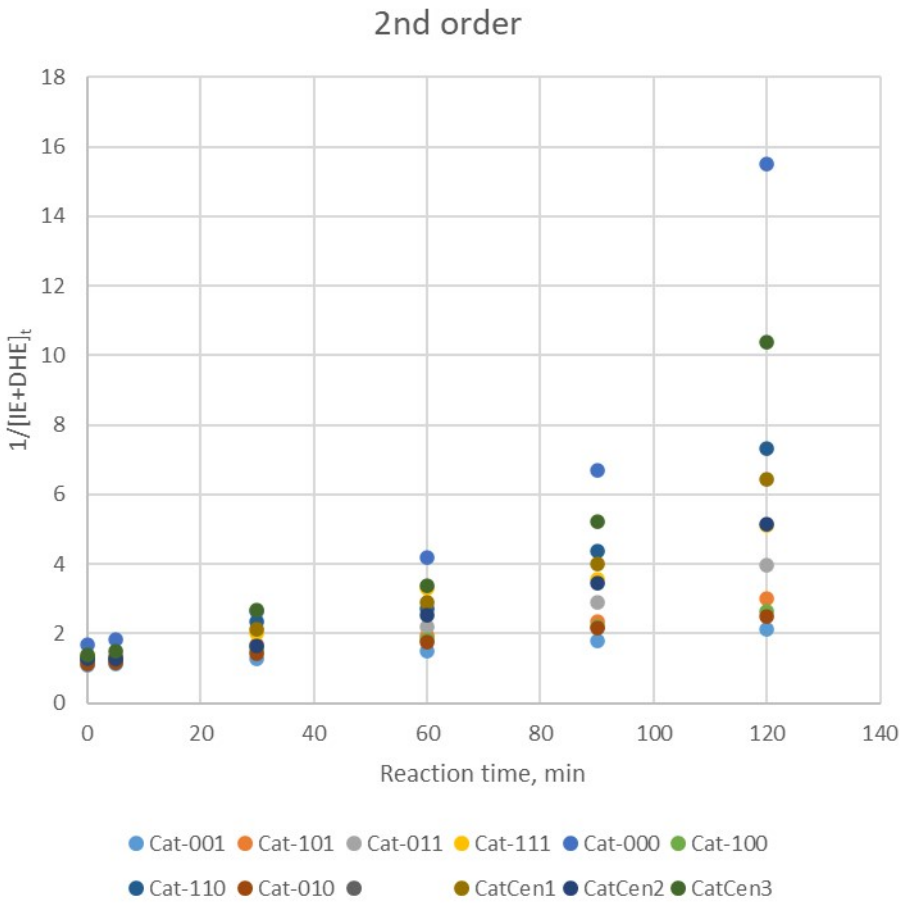

Figure G Normalization of 2nd order

Table D. Comparison of reaction orders via RSQ of fitting

	Cat-001	Cat-101	Cat-011	Cat-111	Cat-000	Cat-100	Cat-110	Cat-010		CatCen1	CatCen2	CatCen3
0th	0.991798	0.985607	0.964476	0.879058	0.967601	0.977602	0.90816	0.969637		0.933065	0.973081	0.913171
1st	0.999945	0.995242	0.999031	0.956104	0.982484	0.991763	0.978555	0.994481		0.992674	0.995608	0.980867
2nd	0.991351	0.956266	0.859884	0.838377	0.5514	0.93254	0.68305	0.969501		0.66305	0.731923	0.510329

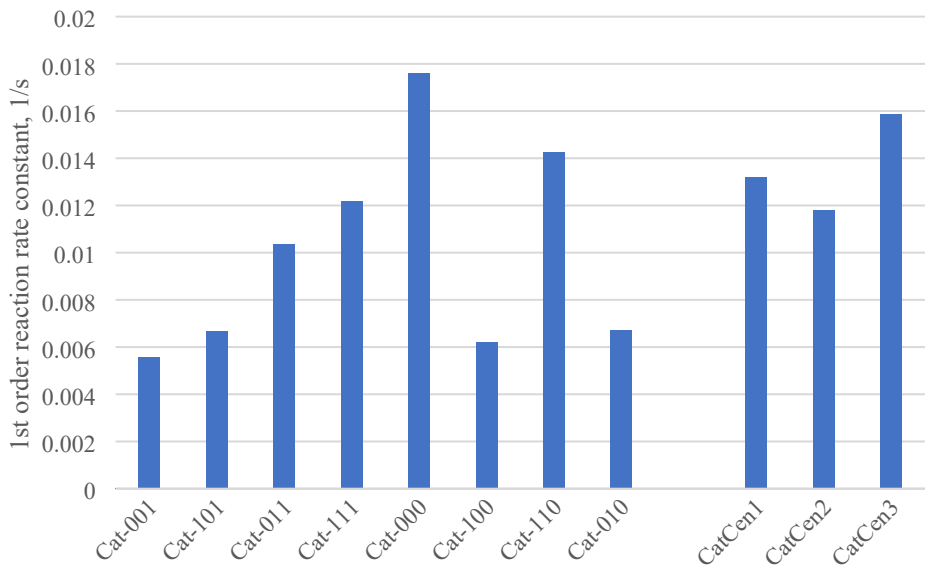

Figure H: Calculated 1st order reaction rate constants.

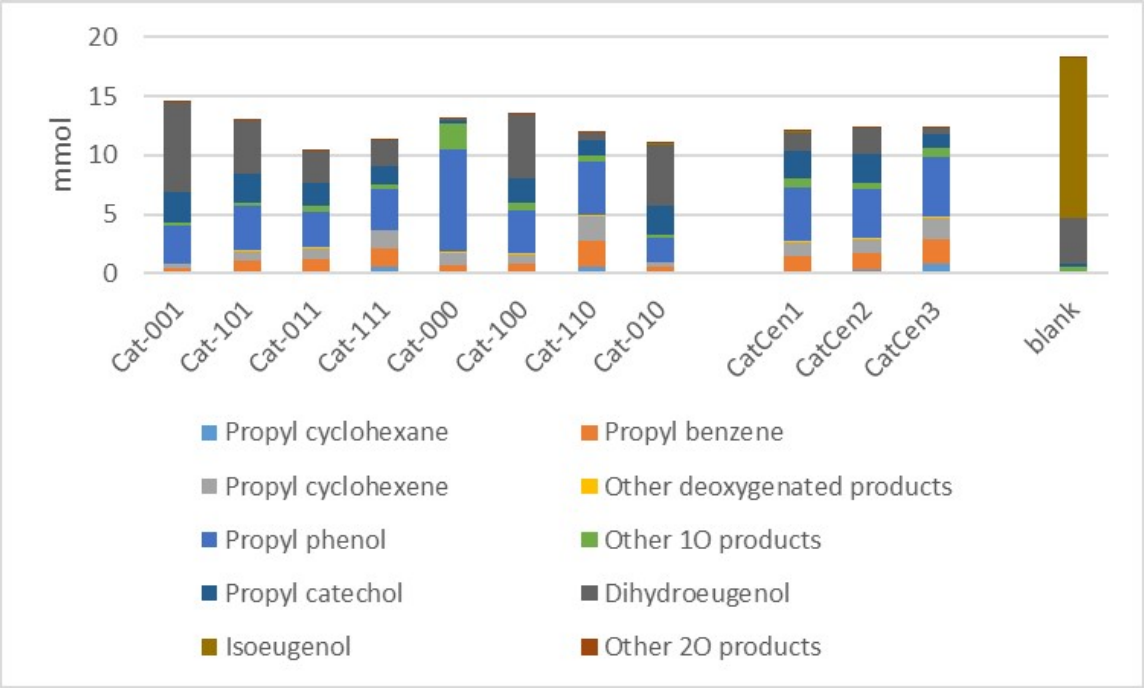

Figure I. Detected products after the reaction time of 1500 min $gcat^{-1}$.

5.3.1 Gas phase results

The gas sampling was performed after the experiment and represent the status of the gas phase after reaction cooldown, and therefore could not be used for mass balance purposes more than on indicative approach. The gas phase results of the compounds are presented in Figures J, K and L. As seen in Figure J, methane was the most important carbon-containing compound in the gas phase, corresponding 92-98 mol-% of the gas phase carbon. Only small amounts of other compounds, most importantly cracking products ethane, propane and propylene, as well as deoxygenation product benzene, were detected in gas phase.

Gas phase results are aligned with the observed results of the liquid phase, as the calculated abundance of methane as moles was clearly dependent on the conversion of methoxy group containing liquid-phase reactants isoeugenol and dihydroeugenol, as seen in Figure L.

Additional source for methane is the sulfiding agent DMDS, as 4.8mmol of methane was expected to be originating from the 0.23g of DMDS added. It is noteworthy when plotting methane amount as function of rate constant, intercept referring to methane amount at conversion 0% was 5.3 mmol, same order of magnitude with calculated amount of methane from DMDS.

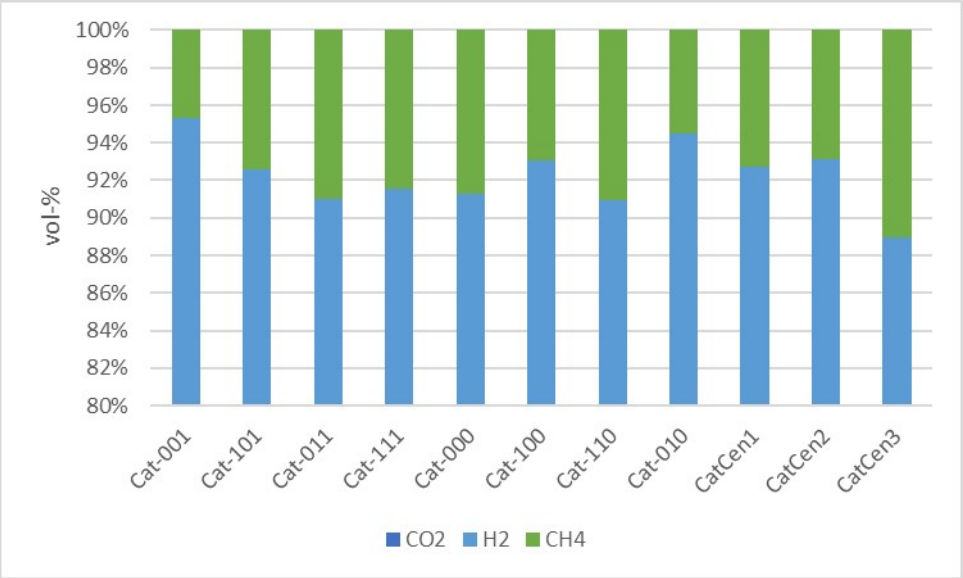

Figure J. Gas composition, note cut y-axis.

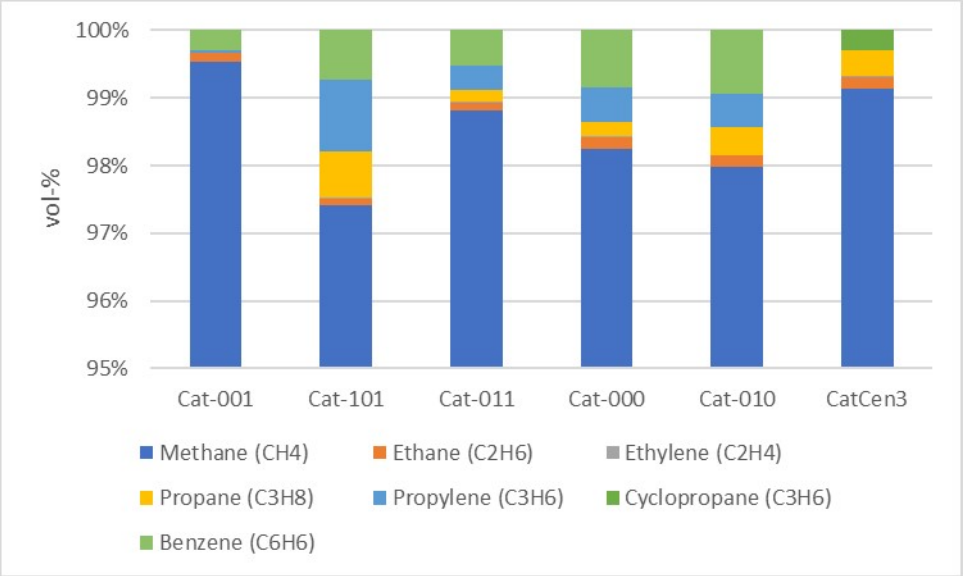

Figure K. Gas-phase composition, compounds other than hydrogen, note cut y-axis

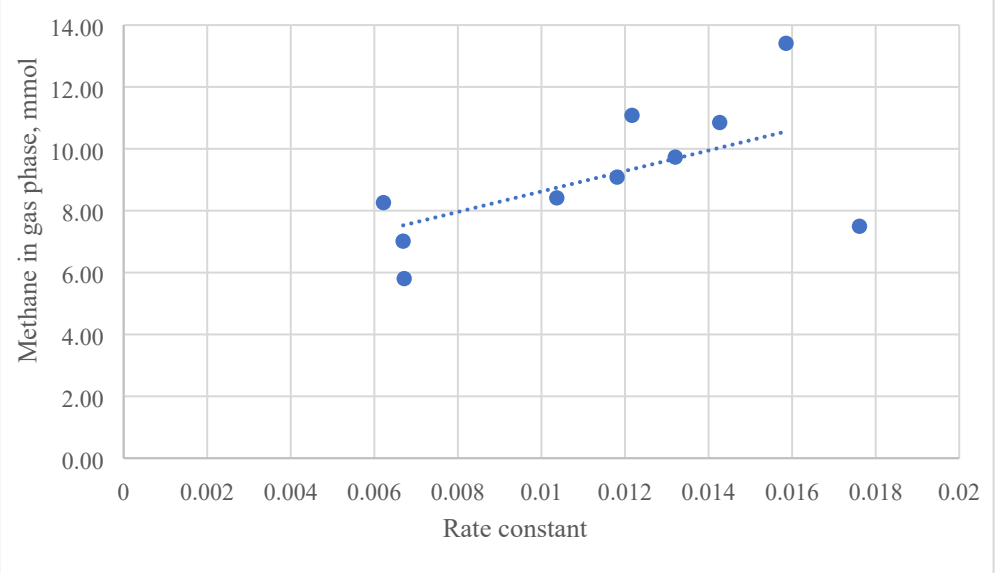

Figure L. Methane amount in gas phase as function of reaction rate.

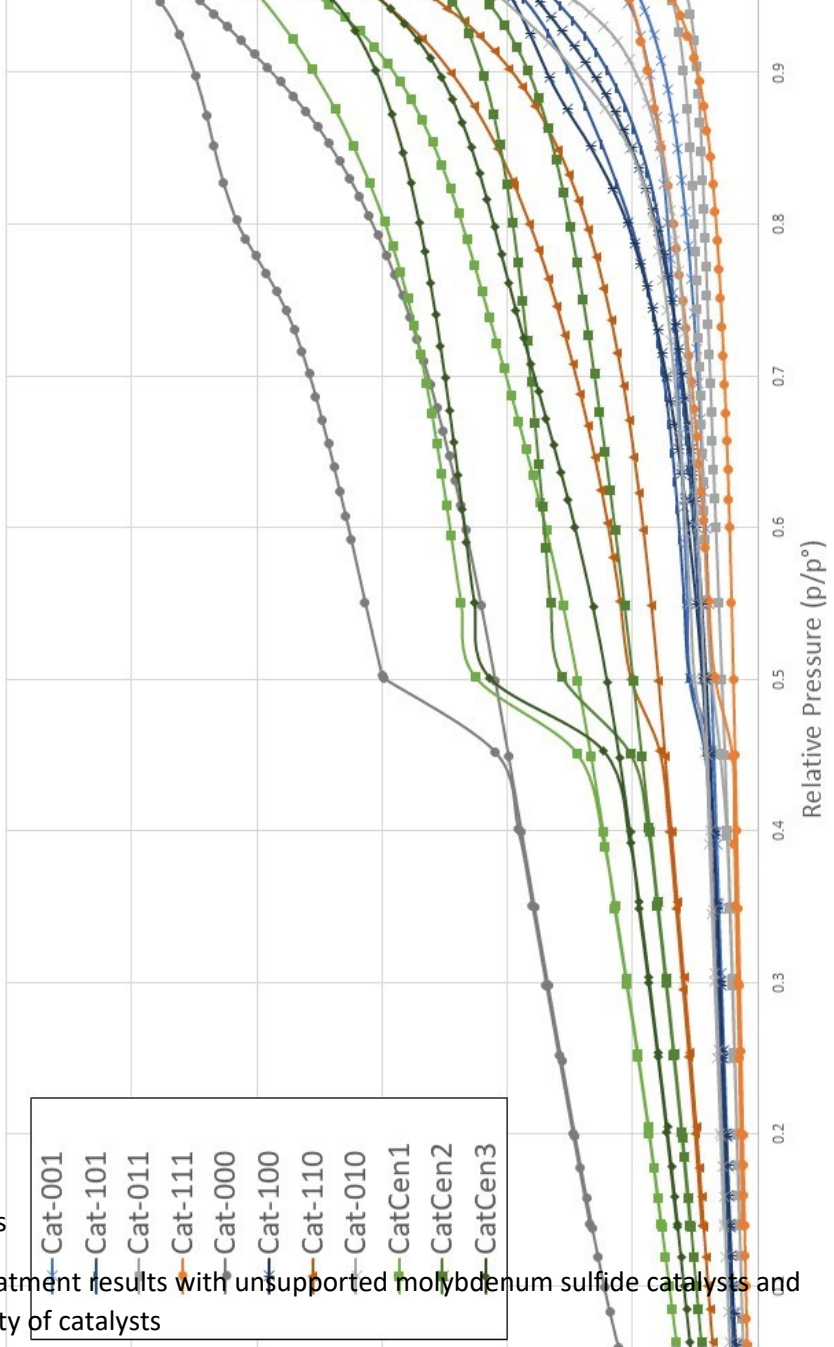

Figure M. N_2 physisorption isotherms

Table D. Literature data on hydrotreatment results with unsupported molybdenum sulfide catalysts and similar model compounds with variety of catalysts

Catalyst	Reactant	T	P (bar)	Reaction time (h)	Catalyst loading (g)	Reactant loading (g)	Reactant / catalyst	Conversion	Reference
1-oxygen containing model compounds									
MoS_2	p-cresol	300	40	4	0.6	13.5	22.5	100	[1]
CoMoS2	phenol	350	28	1	0.075	0.3	4.0	98	[2]
CoS2/MoS2	p-cresol	250	40	1	0.03	4.8	160.0	98	[3]
CoS2/MoS2	4-ethylphenol	250	40	5	0.06	10.8	180.0	96	[4]
MoS2+surfactant	4-Methylphenol	300	40	3	0.6	13.5	22.5	99	[5]
single-layer MoS2	4-Methylphenol	300	30	5	0.02	0.28	14.0	99	[6]
single-layer Co-doped MoS2	4-Methylphenol	300	30	1	0.02	0.28	14.0	83	[6]
2-oxygen containing model compounds									
Thermally annealed MoS2	4-propyl guaiacol	300	50	2	0.066	1	15.2	85	[7]
2.3% Pt 12.7% Re/C	isoeugenol	250	30	2	0.05	0.1	2.0	80	[8]
3%Ni15%Mo/Al2O3	guaiacol	275	10	3	0.8	3.7	4.6	71	[9]

3%Ni15%Mo/Al2O3	propylguaiacol	275	10	3	0.8	3.7	4.6	70	[9]
Cat-110	isoeugenol	300	50	2.5	0.1	3	30.0	93	This investigation

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