Supporting information for:

Support effects for catalytic depolymerisation of lignin to alkylphenolics using phopshided NiMo catalyst

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Table S1. GC-MS identification of compounds in Kraft lignin oil with 20NiMoP/SiO_2 catalyst (initial hydrogen pressure of 100 bar at RT, 2 h @ 400 °C, 1200 RPM).

Pentane	2,3-dimethyl-phenol
Hexane	2,4-dimethyl-phenol
Cyclohexane	2,6-dimethyl-phenol
2-methyl-tetrahydrofuran	3,4-dimethyl-phenol
3-methyl-tetrahydrofuran	3,5-dimethyl-phenol
Cis-1,2-dimethyl-cyclopentane	2-ethyl-4-methyl-phenol
Cis-1,3-dimethyl-cyclopentane	2-ethyl-6-methyl-phenol
Isopropyl-cyclobutane	3-ethyl-5-methyl-phenol
Heptane	4-ethyl-3-methyl-phenol
Methyl-cyclohexane	2-(1-methylethyl)-phenol
Ethyl-cyclohexane	3-(1-methylethyl)-phenol
Propyl-cyclohexane	2,4,6-trimethylphenol
Butyl-cyclohexane	2,3,6-trimethylphenol
1,3,5-cycloheptatriene	2,5-diethyl-phenol
1,2-dimethyl-cyclohexane	3,5-diethyl-phenol
1,3-dimethyl-cyclohexane	2-(1-methylpropyl)-phenol
1,4-dimethyl-cyclohexane	4-(1-methylpropyl)-phenol
1-ethyl-2-methyl-cyclohexane	2-allyl-4-methylphenol
1-ethyl-3-methyl-cyclohexane	2-cyclopentyl-phenol
1-ethyl-4-methyl-cyclohexane	4-cyclopentyl-phenol
Ethylbenzene	Naphthalene
Propylbenzene	1-methylnaphthalene
p-xylene	2-methyl-naphthalene
o-xylene	1,4-dimethyl-naphthalene
1,3-dimethyl-benzene	2,3-dimethyl-naphthalene
1-ethyl-3-methyl-benzene	2,7-dimethyl-naphthalene
1-methyl-2-propyl-benzene	1,2,3,4-tetrahydro-naphthalene
1-methyl-4-propyl-benzene	1,2,3,4-tetrahydro-5-methyl-naphthalene
1-methyl-1-butenyl-benzene	1,2,3,4-tetrahydro-6-methyl-naphthalene
1-methyl-2-(1-methyl-2-propenyl)-benzene	Azulene
cis-octahydro-1H-indene	Cyclopentylcyclohexane
2,3-dihydro-1,6-dimethyl-1H-indene	6-methyl-4-indanol
Phenol	2,3-dihydro-1H-inden-5-ol
2-methyl-phenol	9-methylene-9h-fluorene
3-methyl-phenol	Anthracene
4-methyl-phenol	9-methyl-anthracene

2-ethyl-phenol	Phenanthrene
3-ethyl-phenol	1-methyl-7-(1-methylethyl)-phenanthracene
4-ethyl-phenol	2-isopropyl-10-methylphenanthrene
2-propyl-phenol	

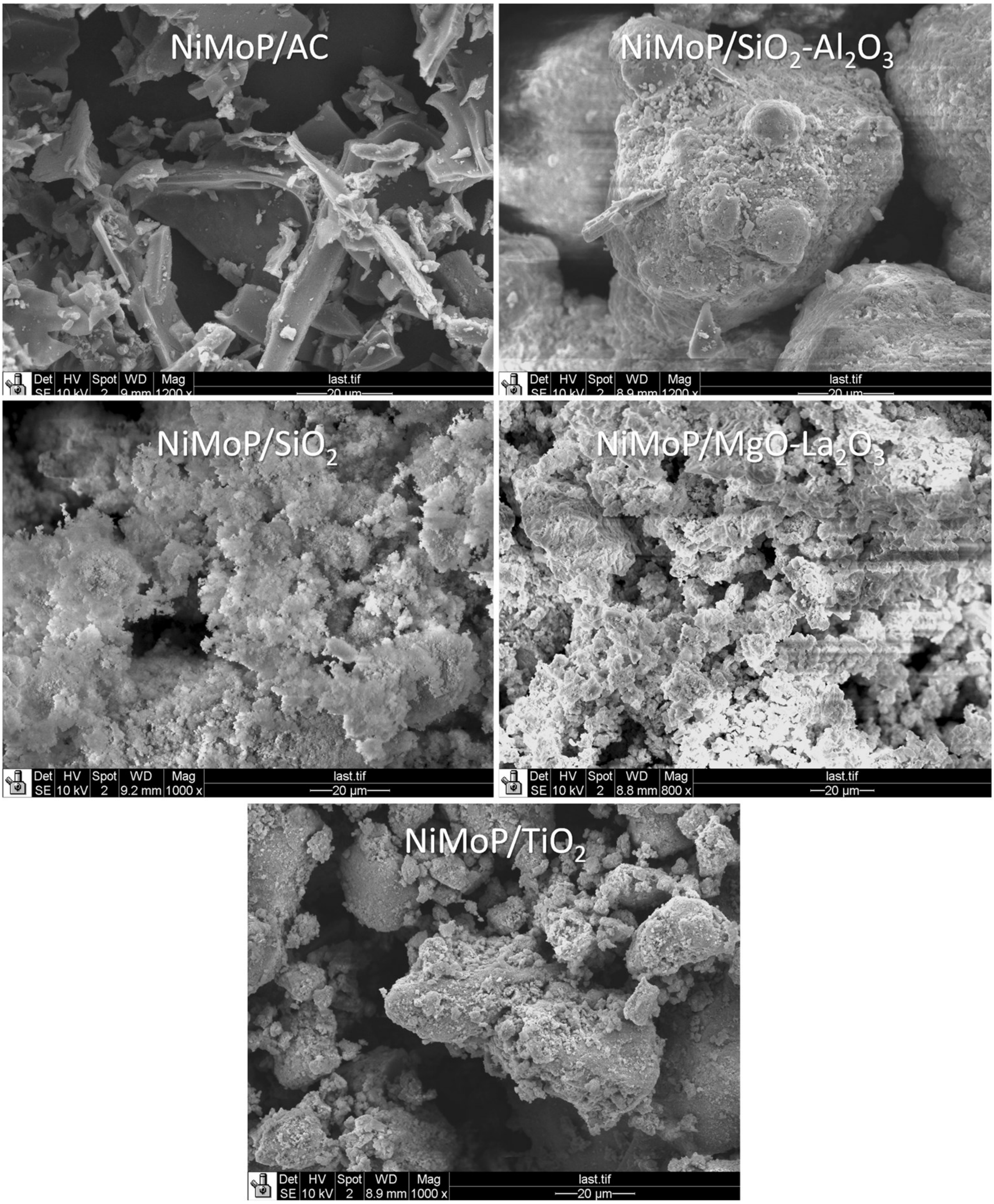
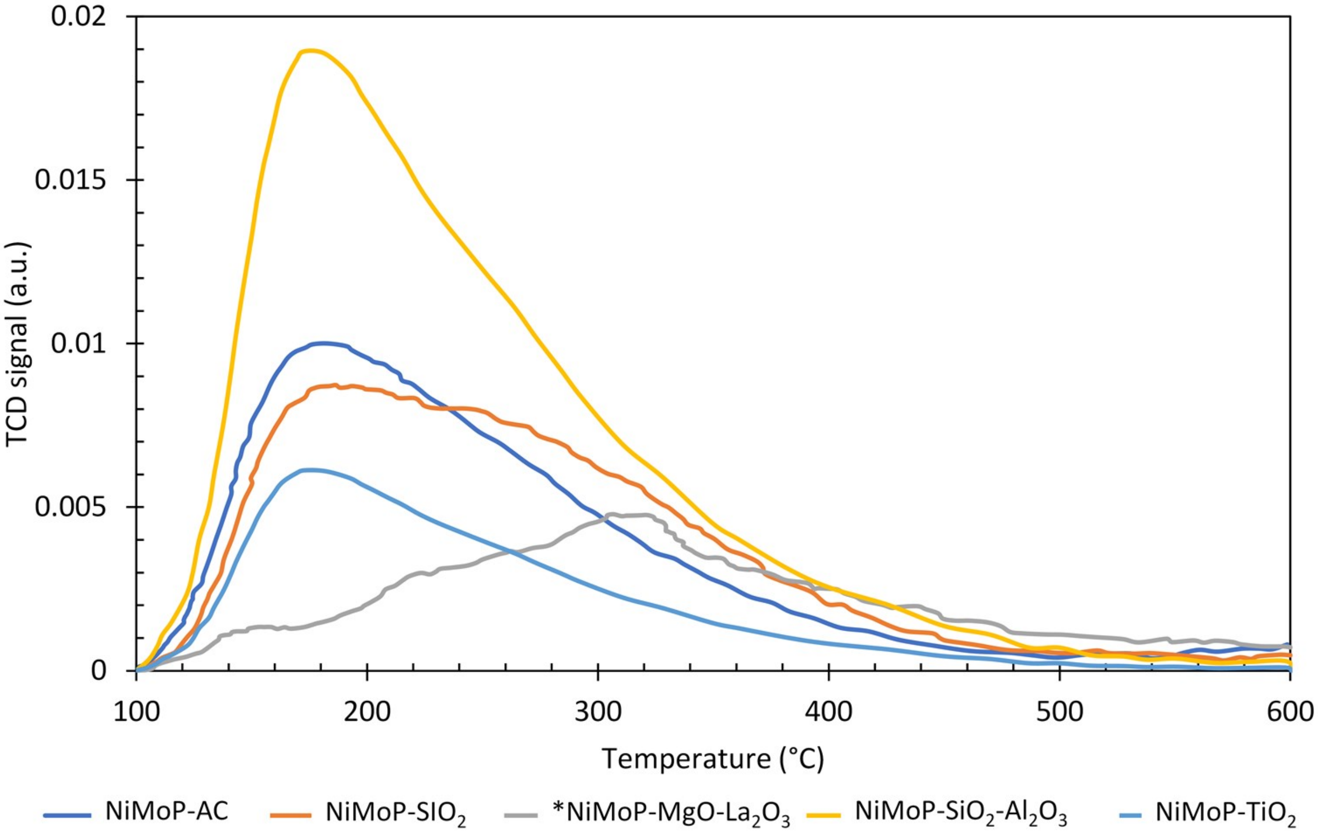


Figure S1. SEM images of the catalysts

Figure S2. Chemisorption data for the fresh catalysts using NH_3 (alle catalysts except NiMoP-MgO-La_2O_3) and CO_2 (NiMoP-MgO-La_2O_3) *



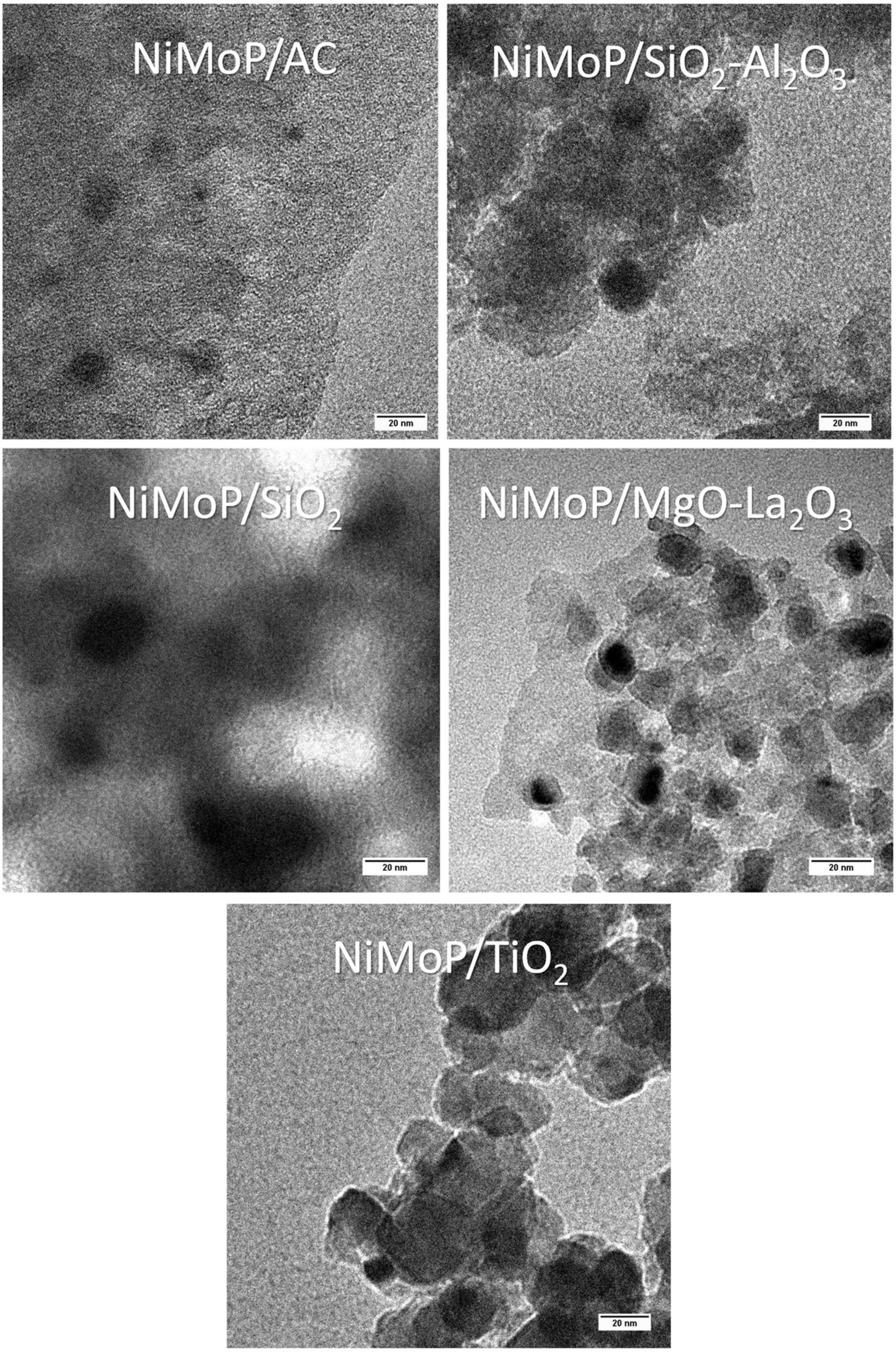


Figure S3. TEM images of fresh catalysts

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Table S2. Overview of experiments with Kraft lignin

Batch #	Catalyst support	Gasphase (%)	Mass balance (%)	Oil yield (%)	Solids (%)	Water (%)	Alkylphenolics (%)	Aromatics (%)	Total monomer (%)	Cyclic + Linear alkanes (%)
4	AC	8.3	81.5	52.0	2.3	18.8	24.9	3.9	37.4	4.3
5	TiO_2	7.8	83.0	56.5	1.1	17.7	24.0	4.1	38.1	5.3
6	TiO_2	16.3	96.9	61.1	2.2	17.3	26.6	4.7	43.0	6.6
7	AC	8.3	94.9	61.6	2.6	22.4	31.4	4.8	48.5	5.6
8	SiO_2-Al_2O_3	9.9	91.2	58.7	6.2	16.4	20.6	3.3	33.1	5.3
11	SiO_2	9.6	87.6	67.4	1.7	8.9	32.5	5.9	54.7	8.1
13	SiO_2-Al_2O_3	11.3	94.4	65.5	3.2	14.4	17.6	3.3	29.4	5.3
14	SiO_2	9.9	93.4	68.8	2.4	12.3	28.7	5.5	48.8	8.1
15	MgO-La_2O_3	10.0	93.7	57.5	13.9	12.4	21.7	4.1	36.1	5.7
16	MgO-La_2O_3	9.8	90.8	51.4	15.8	13.8	19.6	4.1	33.1	5.1

[a)] Reaction conditions: 15 g Kraft lignin, 1.5 g catalyst, initial hydrogen pressure of 100 bar at RT, 2 h @ 400 °C, 1200 RPM.

[b)] Percentages are in wt% on lignin intake.

Table S3 Overview of the gas phase composition of all batch reactions

Batch #	Catalyst support	Lignin type	CO_2 (mol%)	Ethylene (mol%)	Ethane (mol%)	Propylene (mol%)	Propane (mol%)	H_2 (mol%)	CH_4 (mol%)	CO (mol%)
4	AC	Kraft	7.6	0.0	1.9	0.0	1.0	58.2	31.1	0.1
5	TiO_2	Kraft	8.5	0.0	2.2	0.0	1.0	70.3	17.8	0.2
6	TiO_2	Kraft	15.0	0.0	4.1	0.0	2.2	29.4	48.9	0.4
7	AC	Kraft	7.5	0.0	1.9	0.0	1.1	56.7	32.8	0.1
8	SiO_2-Al_2O_3	Kraft	8.2	0.0	2.2	0.0	1.0	60.8	27.5	0.3
11	SiO_2	Kraft	8.3	0.0	2.5	0.0	1.1	50.4	37.7	0.1
13	SiO_2-Al_2O_3	Kraft	9.5	0.0	2.4	0.0	1.1	57.8	28.9	0.4
14	SiO_2	Kraft	8.1	0.0	2.0	0.0	1.0	54.8	33.9	0.1
15	MgO-La_2O_3	Kraft	8.1	0.0	2.6	0.0	1.2	61.7	26.2	0.3
16	MgO-La_2O_3	Kraft	7.4	0.0	2.6	0.0	1.2	62.7	25.8	0.3
17	SiO_2	Lignoboost	8.0	0.0	1.5	0.0	0.8	51.6	38.0	0.1
18	SiO_2	Lignoboost	9.4	0.0	2.0	0.0	1.0	63.1	24.3	0.2
20	SiO_2	Alcell	10.7	0.0	5.5	0.1	1.6	42.8	38.6	0.7
21	SiO_2	Alcell	10.8	0.1	4.8	0.1	1.6	44.1	38.0	0.6

a) As determined by GC-TCD.

b) Reaction conditions: 15 g lignin, 1.5 g catalyst, initial hydrogen pressure of 100 bar at RT, 2 h @ 400 °C, 1200 RPM.

Table S4. Elemental analysis for lignin oil for all batch reactions

Batch #	Catalyst support	Lignin	C (%)	H (%)	N (%)	S (%)
4	AC	Kraft	82.52	7.65	0.90	0.30
7	AC	Kraft	82.48	7.79	0.87	0.20
5	TiO_2	Kraft	83.89	7.74	0.85	0.30
6	TiO_2	Kraft	83.64	7.69	0.87	0.14
8	SiO_2-Al_2O_3	Kraft	81.96	7.22	0.89	0.22
13	SiO_2-Al_2O_3	Kraft	72.66	6.49	0.90	0.80
15	MgO-La_2O_3	Kraft	75.19	7.45	0.84	0.43
16	MgO-La_2O_3	Kraft	74.97	7.76	0.79	0.42
14	SiO_2	Kraft	83.54	7.58	0.95	0.25
11	SiO_2	Kraft	83.45	7.82	0.93	0.16
17	SiO_2	Lignoboost	83.20	7.70	0.00	0.12
18	SiO_2	Lignoboost	83.52	7.57	0.00	0.12
20	SiO_2	Alcell	75.35	7.32	0.09	0.05
21	SiO_2	Alcell	75.41	7.24	0.08	0.05

Table S5. Elemental analysis for solid residues for all batch reactions

Batch #	Catalyst support	Lignin	C	H	N	S
4	AC	Kraft	70.78	2.06	0.81	5.86
7	AC	Kraft	73.26	2.09	0.80	6.29
5	TiO_2	Kraft	6.39	0.66	0.27	5.98
6	TiO_2	Kraft	6.30	0.62	0.23	6.01
8	SiO_2-Al_2O_3	Kraft	25.48	1.82	0.81	4.67
13	SiO_2-Al_2O_3	Kraft	14.55	1.5	0.655	5.19
15	MgO-La_2O_3	Kraft	35.465	2.53	0.65	4.21
16	MgO-La_2O_3	Kraft	40.91	2.835	0.75	3.93
14	SiO_2	Kraft	5.625	0.835	0.36	6.06
11	SiO_2	Kraft	6.96	0.68	0.32	6.30
17	SiO_2	Lignoboost	4.455	0.885	0.065	7.08
18	SiO_2	Lignoboost	4.46	0.875	0.06	6.46
20	SiO_2	Alcell	13.265	1.385	0.17	0.44
21	SiO_2	Alcell	20.59	1.73	0.21	0.28

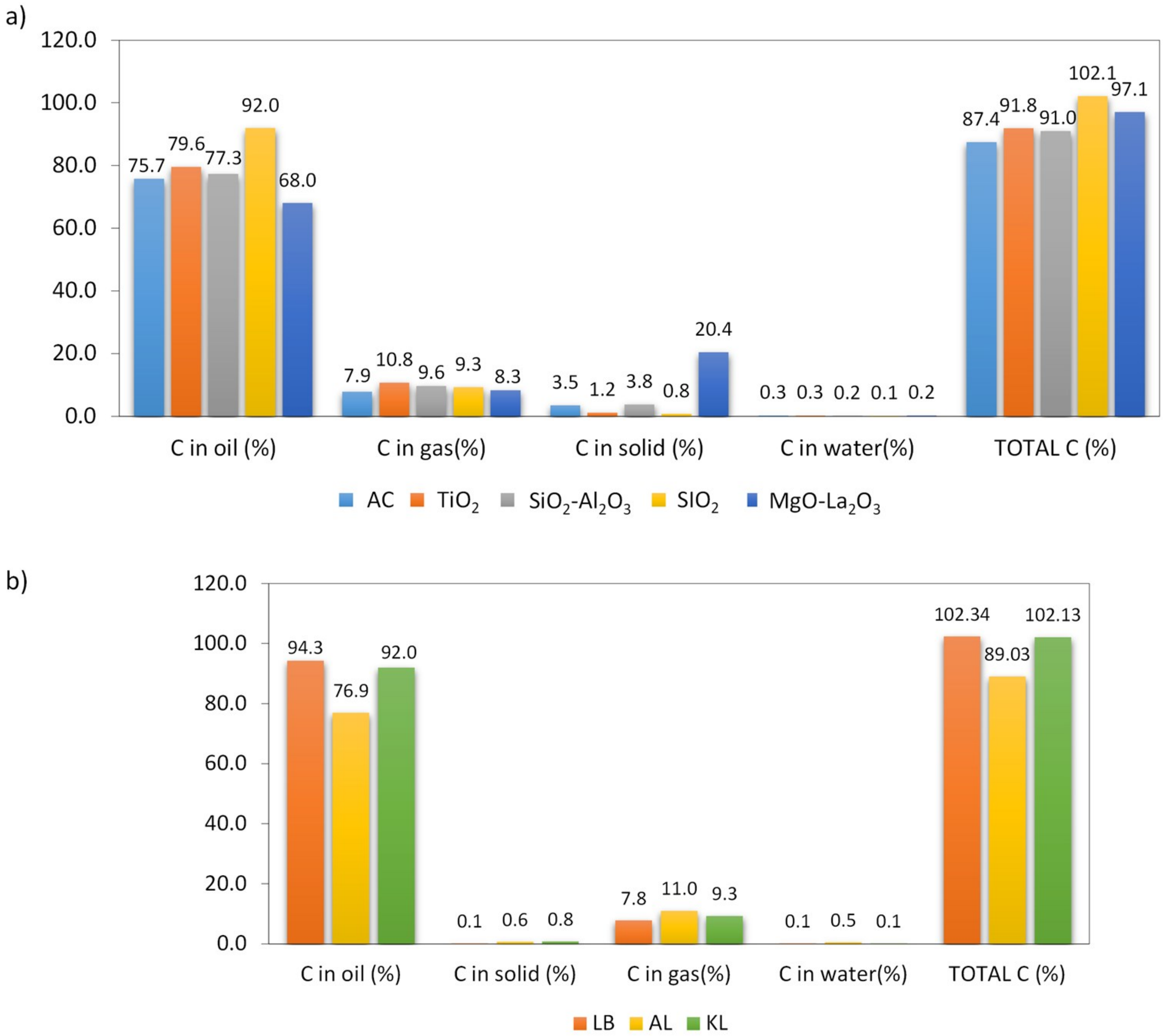

Figure S4. Carbon balance for a) hydrotreatment on different supports and b) hydrotreatment for some technical lignins

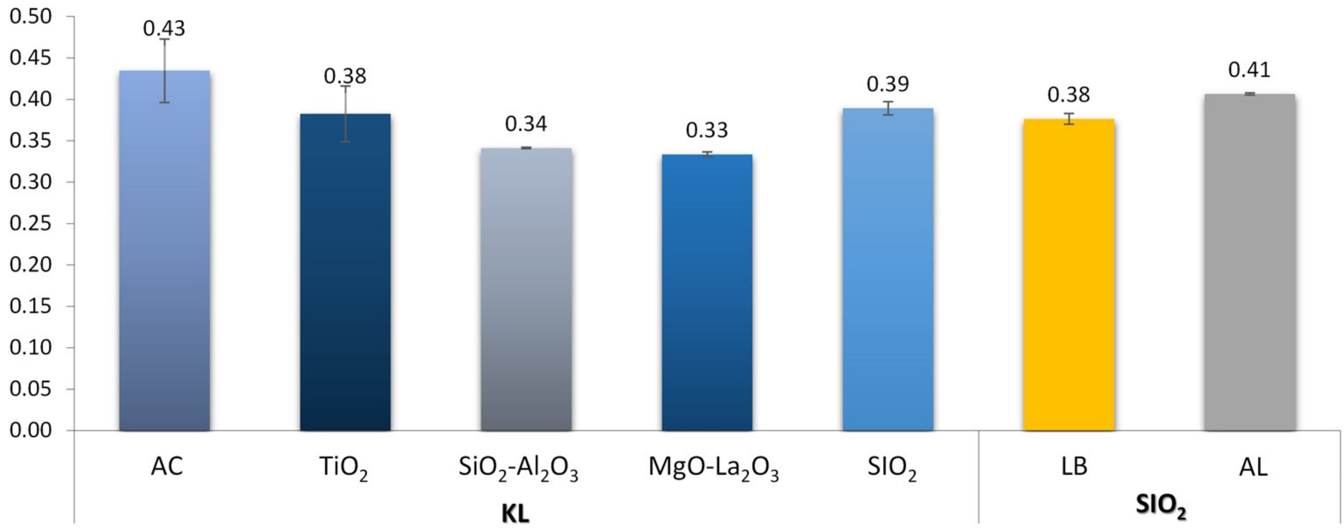

Figure S5. Hydrogen consumption in NL/g of lignin during hydrotreatment of Kraft lignin with NiMoP on various supports and different lignins on NiMoP/SiO_2

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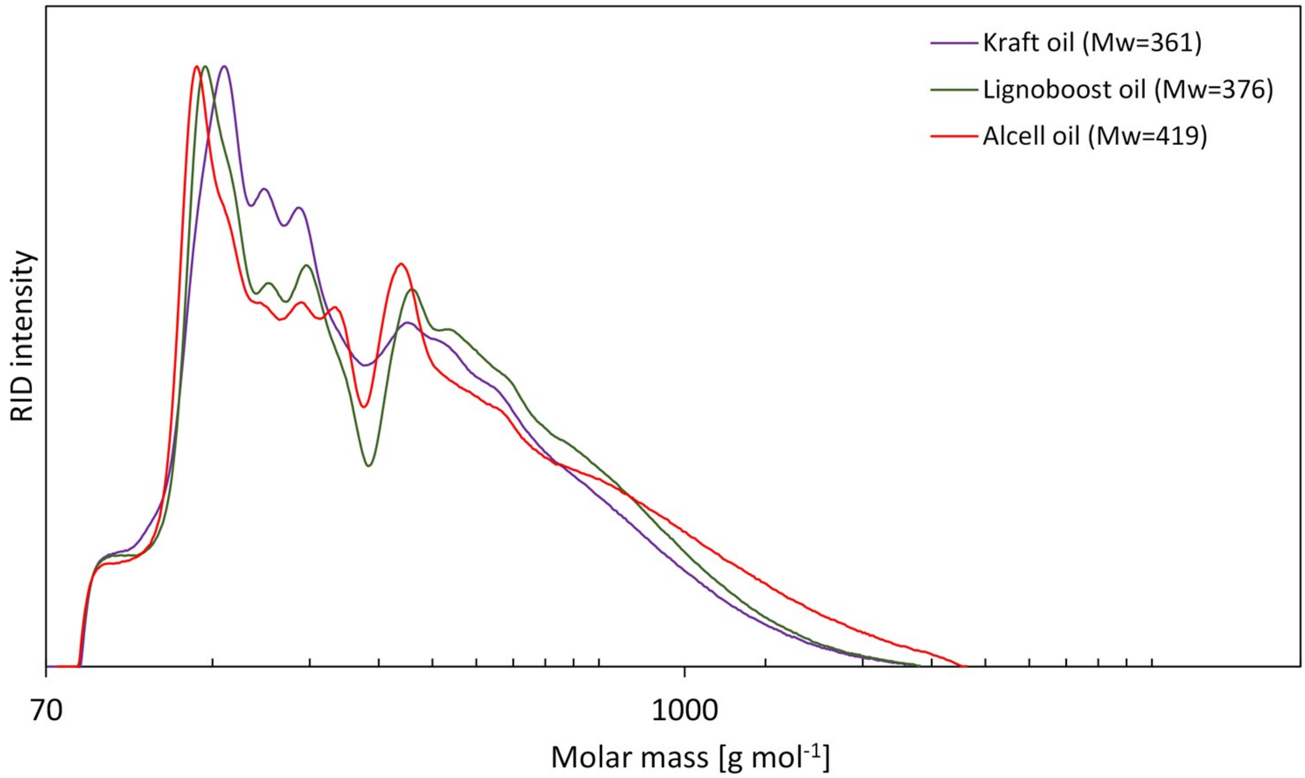
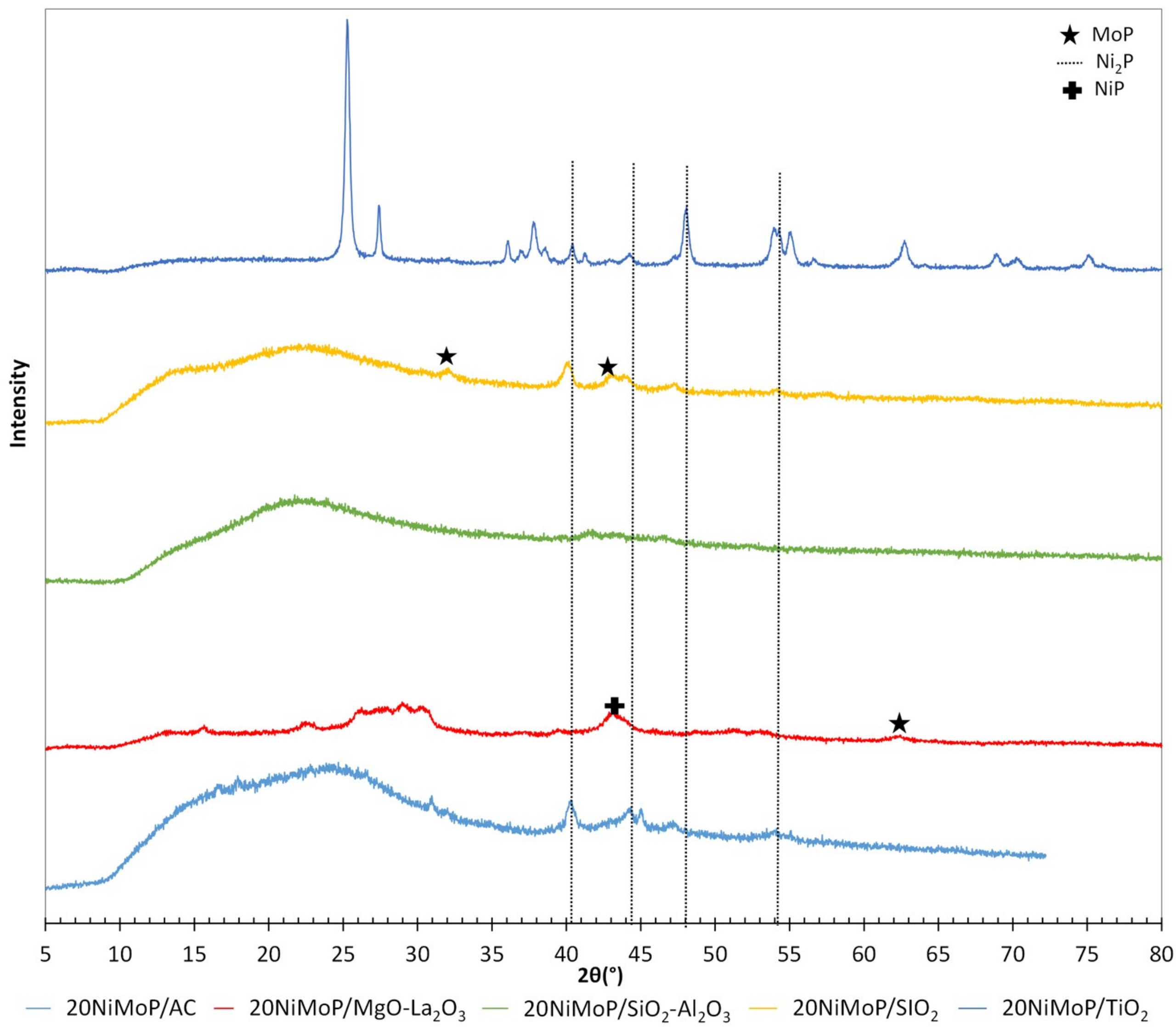


Figure S6. GPC chromatogram of the three lignin oils obtained from the hydrotreatment of them using NiMoP/SiO_2 (Measured in THF, see Table 1)

Figure S7. X-ray diffractograms of the supported NiMoP catalysts.



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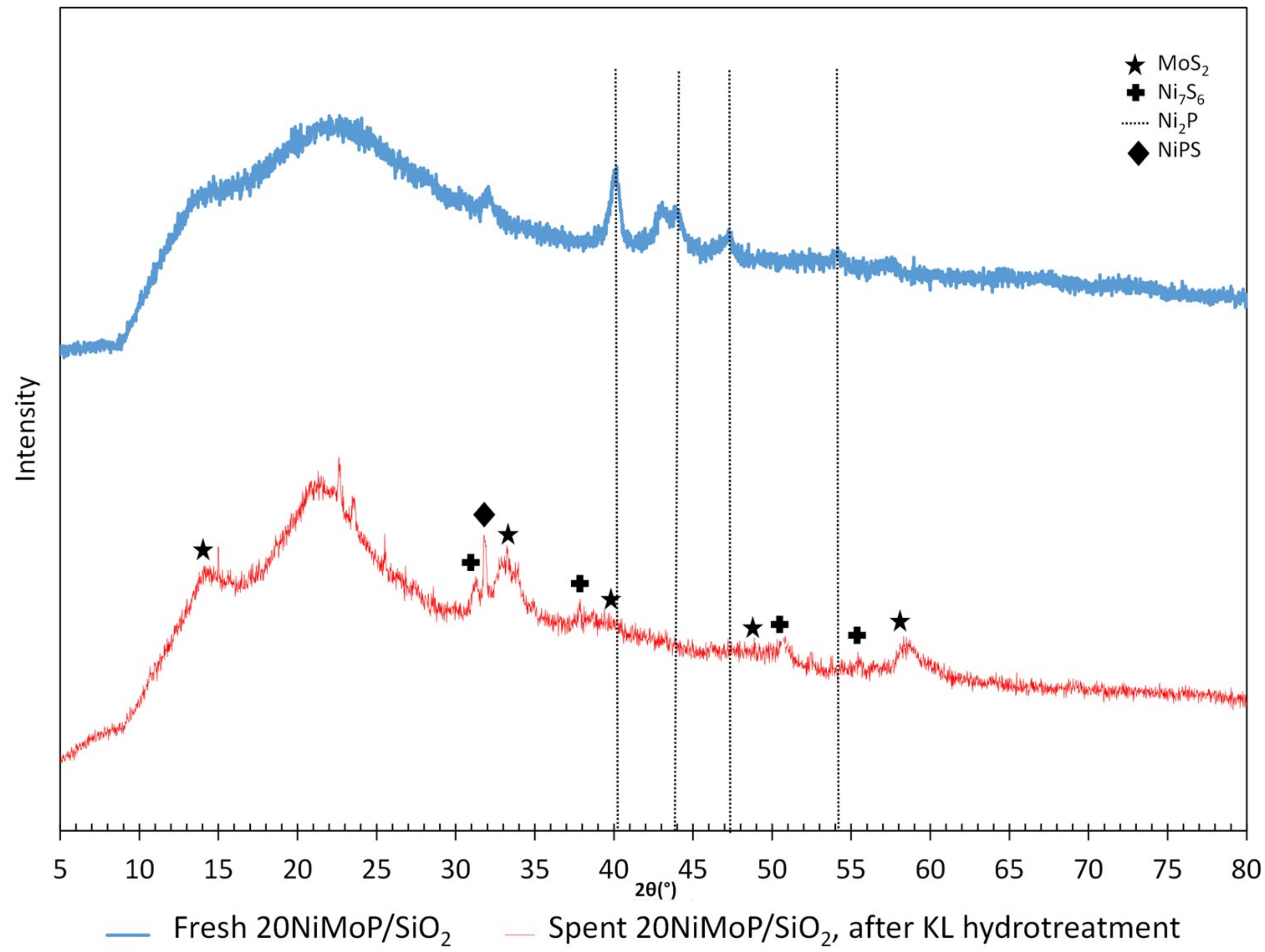

Figure S8. X-ray diffractograms of fresh and spent $NiMoP/SiO_2$ catalyst for the hydrotreatment of Kraft lignin.

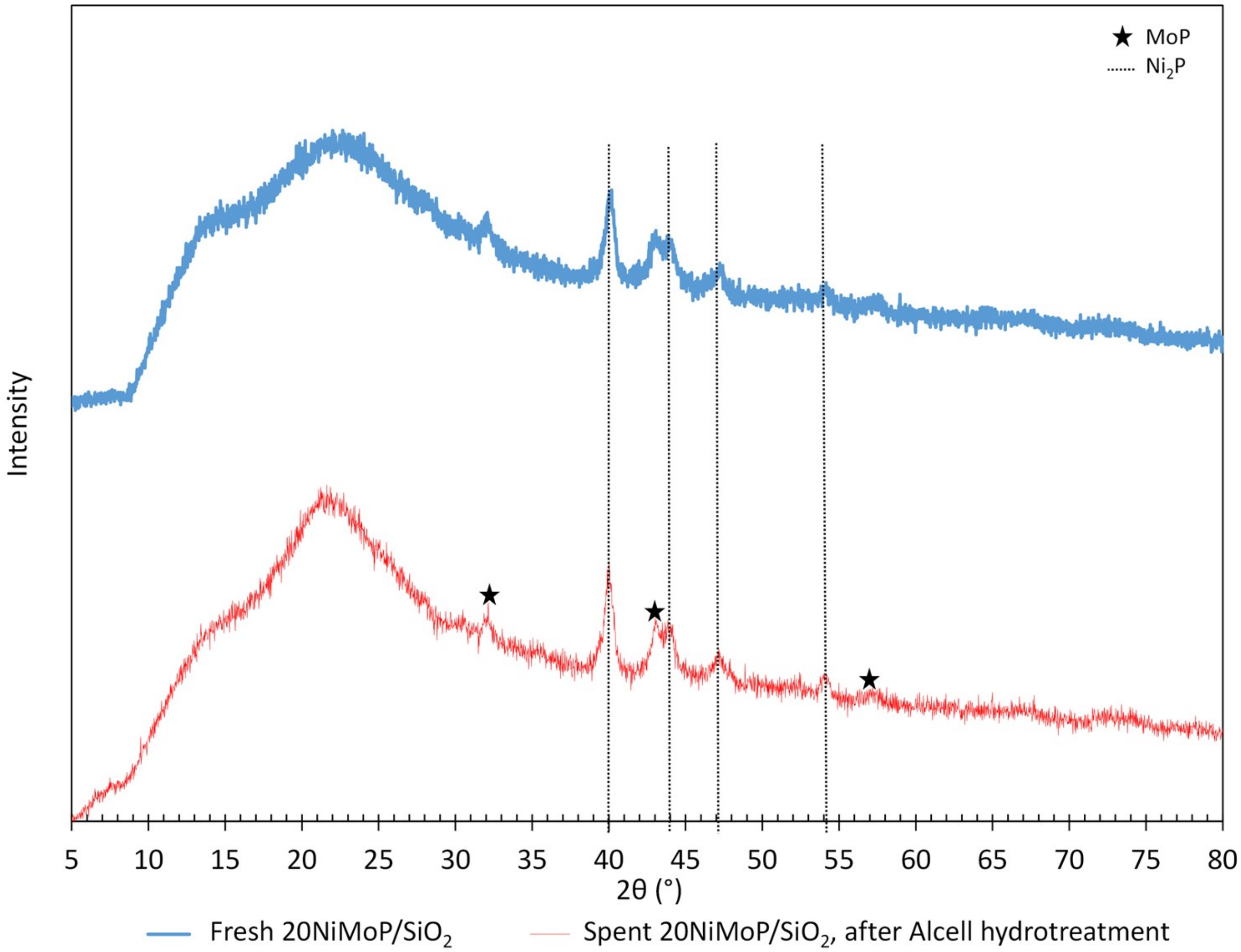

Figure S9. X-ray diffractograms of fresh and spent NiMoP/SiO_2 catalyst for the hydrotreatment of Alcell lignin

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Figure S10. Literature comparison of relevant data for the hydrotreatment of Kraft lignin.