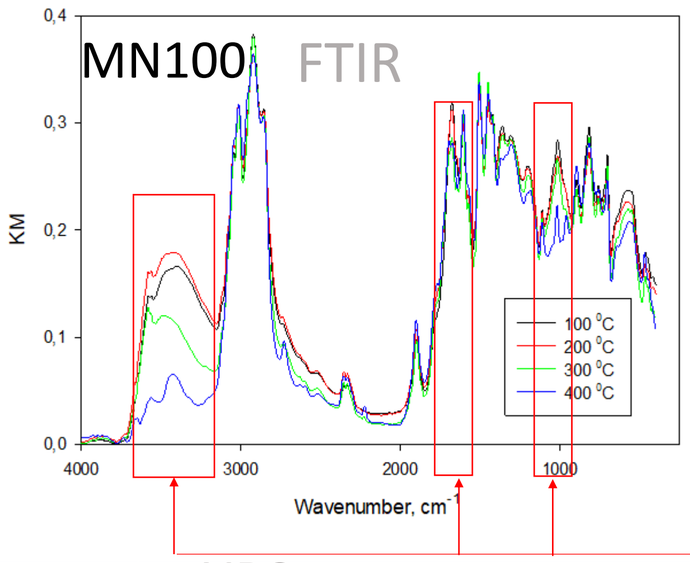
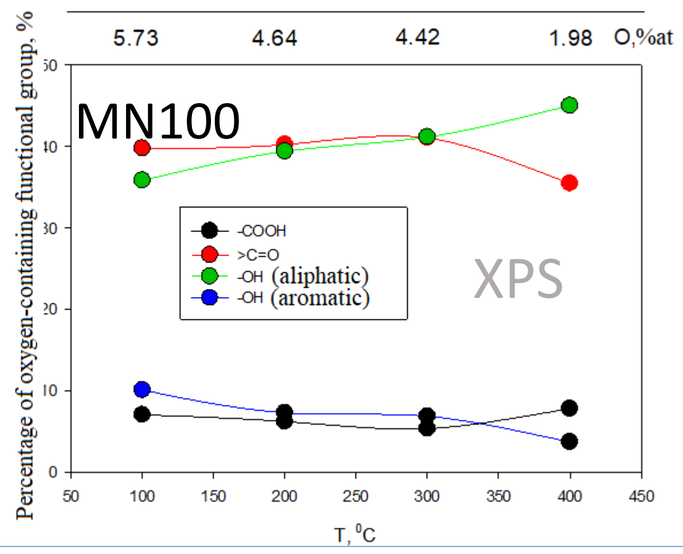
NOBLE METAL-CONTAINING NANOPARTICLES STABILIZED IN HYPERCROSSLINKED POLYSTYRENE AS EFFECTIVE CATALYSTS OF AROMATIC RING HYDROGENATION

Alexey Bykov, Galina Demidenko, Linda Nikoshvili, Elena Bakhvalova, Anastasiya Dobryanskaya, Valentina Matveeva, Antonina Stepacheva, Mikhail Sulman



Temperature, °C	Surface concentration, %at			
	C 1s	N 1s	O 1s	Cl 2p
100	92.18	1.77	5.73	0.33
200	93.58	1.52	4.64	0.27
300	94.04	1.34	4.42	0.2
400	97.27	0.71	1.98	0.04

XPS



XPS Pd/MN100

Time of reduction, h	Surface concentration, %at				
	C 1s	O 1s	N 1s	Cl 2p	Pd 3d
0	90.06	7.17	1.98	0.27	0.52
3	91.85	5.93	1.72	0.15	0.35
12	91.36	6.45	1.67	0.18	0.35
24	91.75	6.38	1.41	0.12	0.34

Reduction time	Pdi/ΣPdi, %			
h	Pd(0)	Pdn	PdO	PdAc2
0	10.5	0.0	55.7	33.8
3	28.7	40.8	30.5	0.0
12	23.7	24.9	51.0	0.0
24	20.5	28.1	51.3	0.0

XPS Pt/MN100

Reduction time, h	Surface concentration, %at				
	C 1s	N 1s	O 1s	Cl 2p	Pt 4f
0	80,72	3,23	11,11	1,27	3,68
3	87,27	1,4	7,81	0,73	2,79
12	87,19	1,49	7,78	0,84	2,71
24	87,29	1,5	7,7	0,82	2,69

Reduction time	Pti/ΣPti, %			
h	Pt(0)	$Pt(OH)_2$	PtO_2	$[PtCl_6]^{2-}$
0	4.1	78.1	15.0	2.8
3	19.4	61.9	18.7	0.0
12	36.1	52.0	11.2	0.7
24	36.0	51.4	12.6	0.0

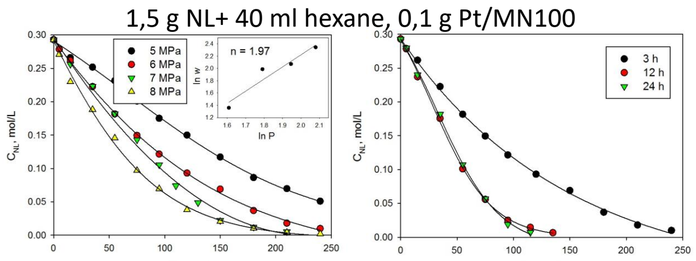
XPS Ru/MN100

Reduction time, h	Surface concentration, %at				
	C 1s	O 1s	N 1s	Cl 2p	Ru $3p_{3/2}$
0	82,9	12,5	2,8	0,3	1,5
3	83,7	10,4	2,3	0,8	2,8
12	88,8	8,5	0,9	0,5	1,3
24	89,2	8,2	1,0	0,4	1,2

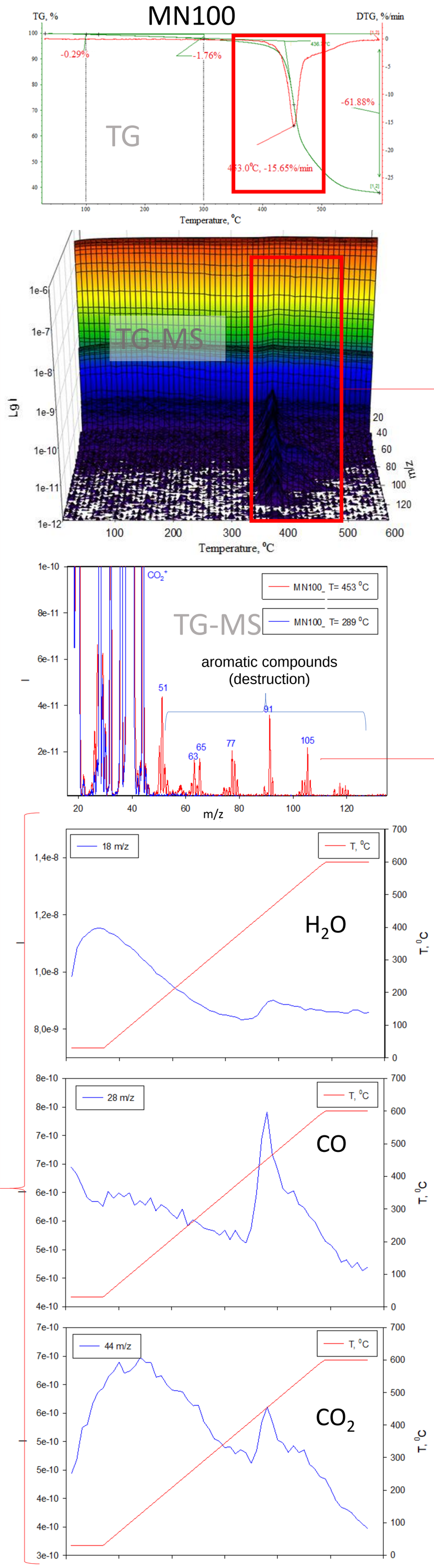
Reduction time	Rui/ΣRui, %		
h	RuO2	$RuO2*nH_2O$	$Ru(OH)Cl_3$
0	13.2	65.3	21.5
3	55.0	45.0	0.0
12	61.4	38.6	0.0
24	60.2	39.8	0.0

Naphthalene hydrogenation in supercritical conditions

1,5 g NL+ 40 ml hexane, 0,1 g Pt/MN100



Element and Band	Surface Content, at.%						
	Initial (Unreduced) Catalyst	After the Reduction		After the Use in NL Hydrogenation			
		3 h	12 h	24 h	3 h	12 h	24 h
Pt 4f	1.6	1.4	1.4	1.4	1.2	1.1	1.1
Cl 2p	1.4	0.4	0.3	0.1	0.2	0.2	0.1
C 1s	83.6	91.8	92.3	92.9	91.0	90.4	90.9
O 1s	10	5.2	5.0	4.9	6.6	7.0	6.7
N 1s	3.4	1.2	1.0	0.9	1.0	1.3	1.2

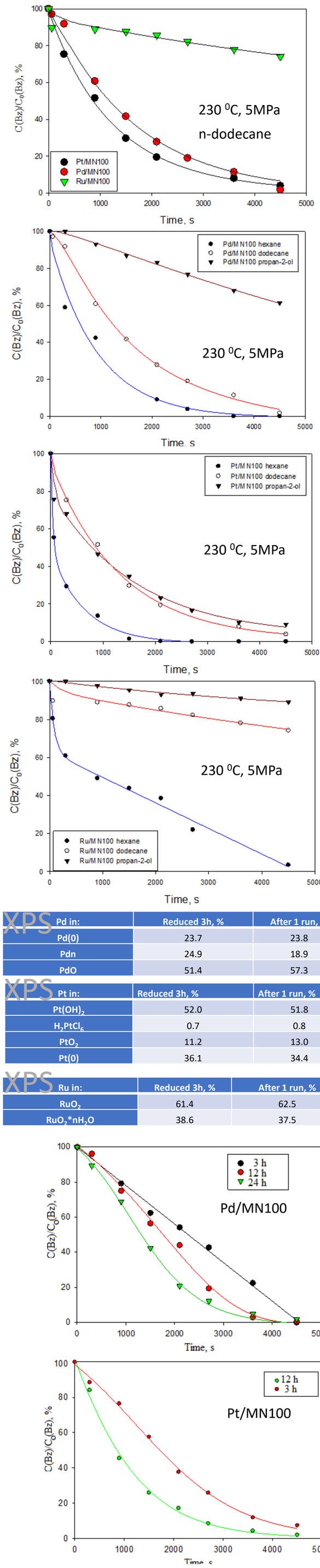


This study is devoted to the investigation of catalytic behavior of noble metals (Pd, Pt, Ru) stabilized in the aromatic polymeric network in liquid-phase hydrogenation of arenes.

Catalytic systems were synthesized by the impregnation of metal compounds dissolved in suitable solvents in the polymeric matrix of hypercrosslinked polystyrene of MN100 type. Before the experiments, all the catalytic systems were reduced in hydrogen flow at 300°C. Catalytic testing was carried out in a liquid-phase using hexane or dodecane as solvents at elevated hydrogen pressure. Benzene, aniline, and naphthalene were used as hydrogenation substrates.

Benzene hydrogenation in liquid phase

0,14 mol/L Bz + 40 ml hexane, 0,1 g catalyst



XPS

Pd in:	Reduced 3h, %	After 1 run, %
Pd(0)	23.7	23.8
Pdn	24.9	18.9
PdO	51.4	57.3

XPS

Pt in:	Reduced 3h, %	After 1 run, %
$Pt(OH)_2$	52.0	51.8
H_2PtCl_6	0.7	0.8
PtO_2	11.2	13.0
Pt(0)	36.1	34.4

XPS

Ru in:	Reduced 3h, %	After 1 run, %
RuO_2	61.4	62.5
RuO_2*nH_2O	38.6	37.5

Acknowledgments This work was funded by the Russian Foundation for Basic Research according to the research project № 18-08-00435.