



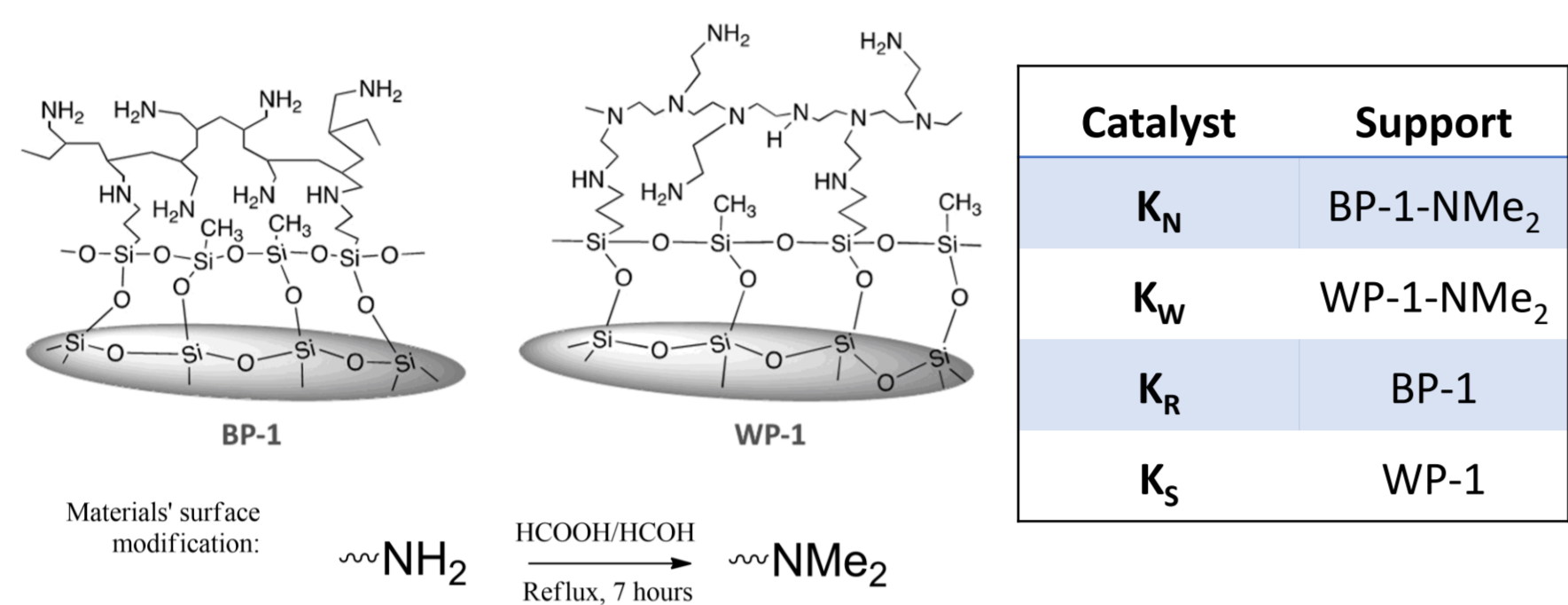
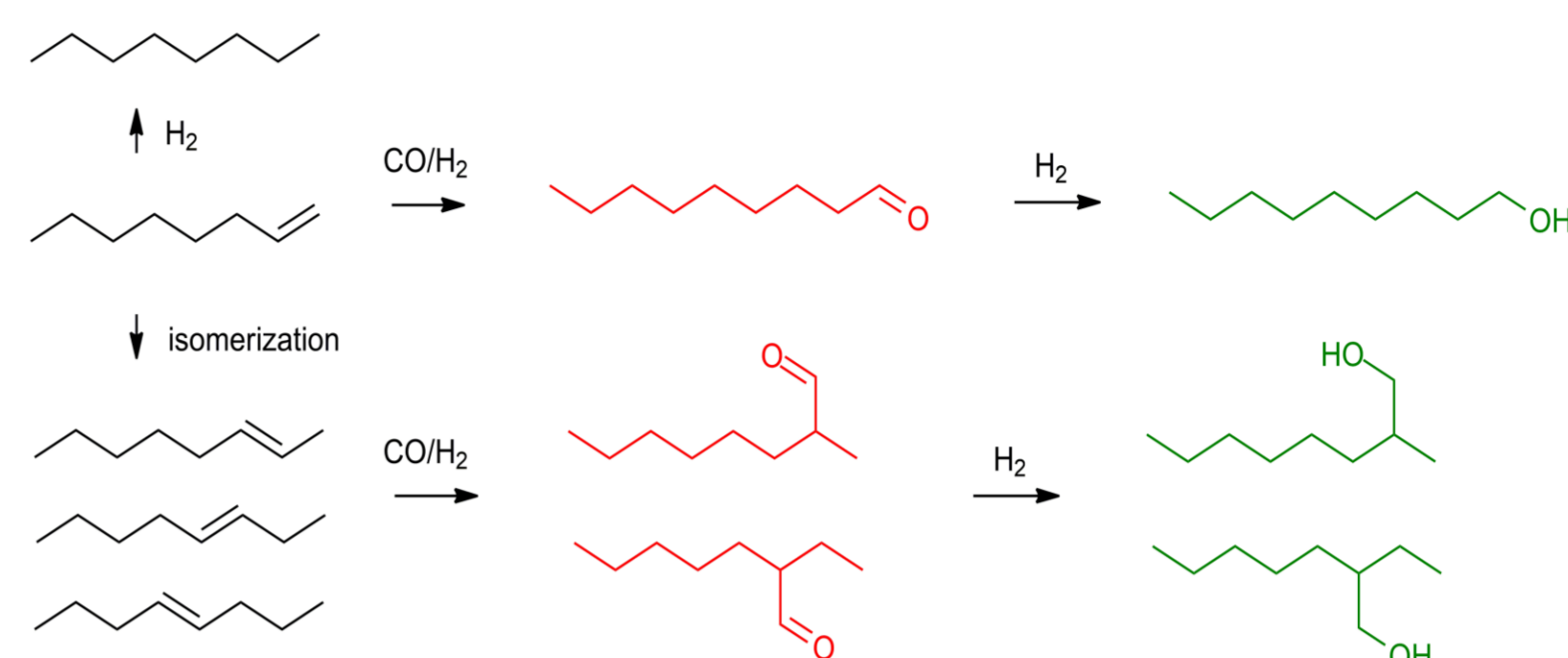
NITROGEN-CONTAINING CATALYTIC SYSTEMS FOR TANDEM REACTIONS BASED ON HYDROFORMYLATION

Nenasheva M.V., Gorbunov D.N.

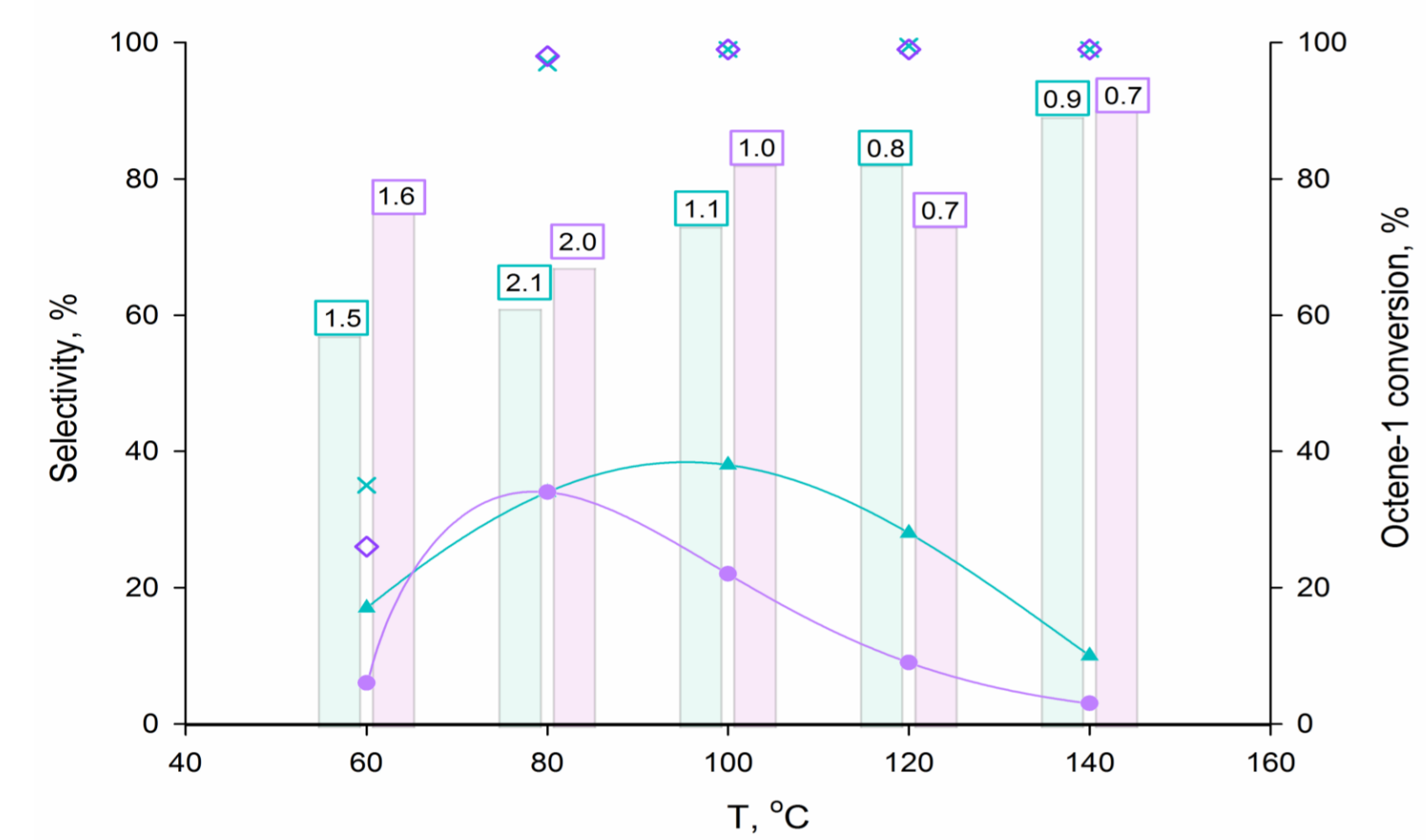
Department of Petroleum Chemistry and Organic Catalysis, Faculty of Chemistry, Moscow State University, Russia

mn2206@yandex.ru

Tandem hydroformylation-hydrogenation is a promising way to obtain primary alcohols from olefins. This reaction can be catalyzed by the complexes of Rh with tertiary amines [1]. Previous attempts to make a heterogeneous system of this type were mostly related to polymeric supports [2]. Here we report new heterogeneous catalysts for tandem hydroformylation-hydrogenation based on hybrid materials BP-1 and WP-1 [3], which are mesoporous silica with anchored nitrogen-containing polymers. The idea was in combining easy handling of the silica materials with high heteroatom concentration of the imine and enamine polymers to yield active and stable catalysts for the tandem process.

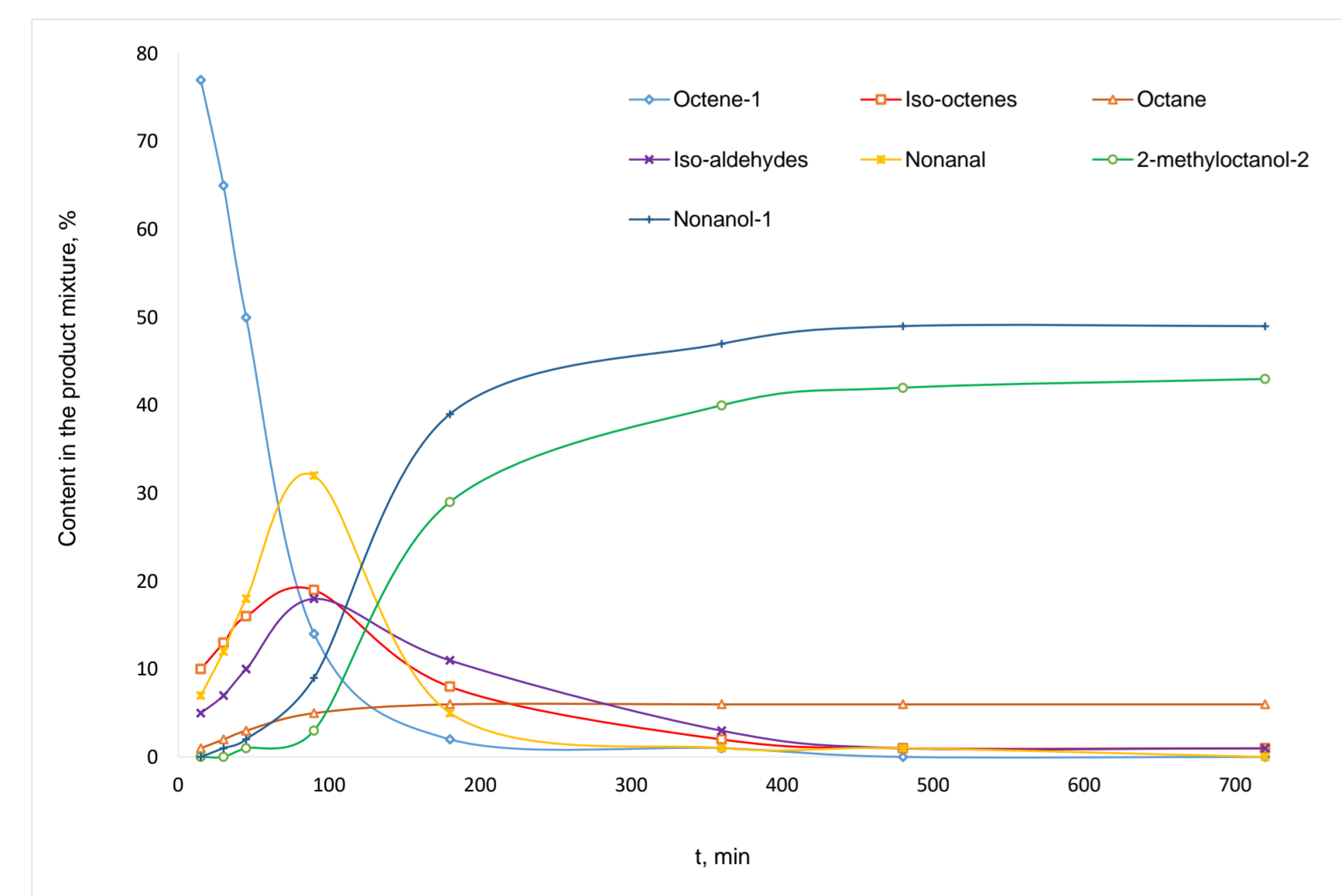


The catalysts were obtained by stirring the supports with the solution of Rh(acac)(CO)₂ in DCM for 12 h (r.t.)
In all the catalysts, Rh content was about 2% wt (ICP-AES)



Legend for the graph:
 × Octene-1 conversion (first use)
 ◇ Octene-1 conversion (reuse)
 Total oxygenates (first use) - light blue bar
 Total oxygenates (reuse) - pink bar
 ▲ Alcohols (first use)
 ● Alcohols (reuse)
 n:iso ratio (C₉ aldehydes and alcohols)
 - first use - light blue bar
 - reuse - pink bar

Conditions: K_N 30 mg, octene/Rh (mol.) = 670, octene-1 0.6 mL (4 mmol), toluene 2 mL, syngas (CO:H₂=1:3) 6.0 MPa, 5 h.



Conditions: K_N* 50 mg (reused after the first reaction cycle under the same conditions, 5 h), octene-1 0.9 mL (6 mmol), octene/Rh (mol.) = 600, toluene 3.3 mL, 80°C, syngas (CO:H₂=1:3) 6.0 MPa

Conclusion:

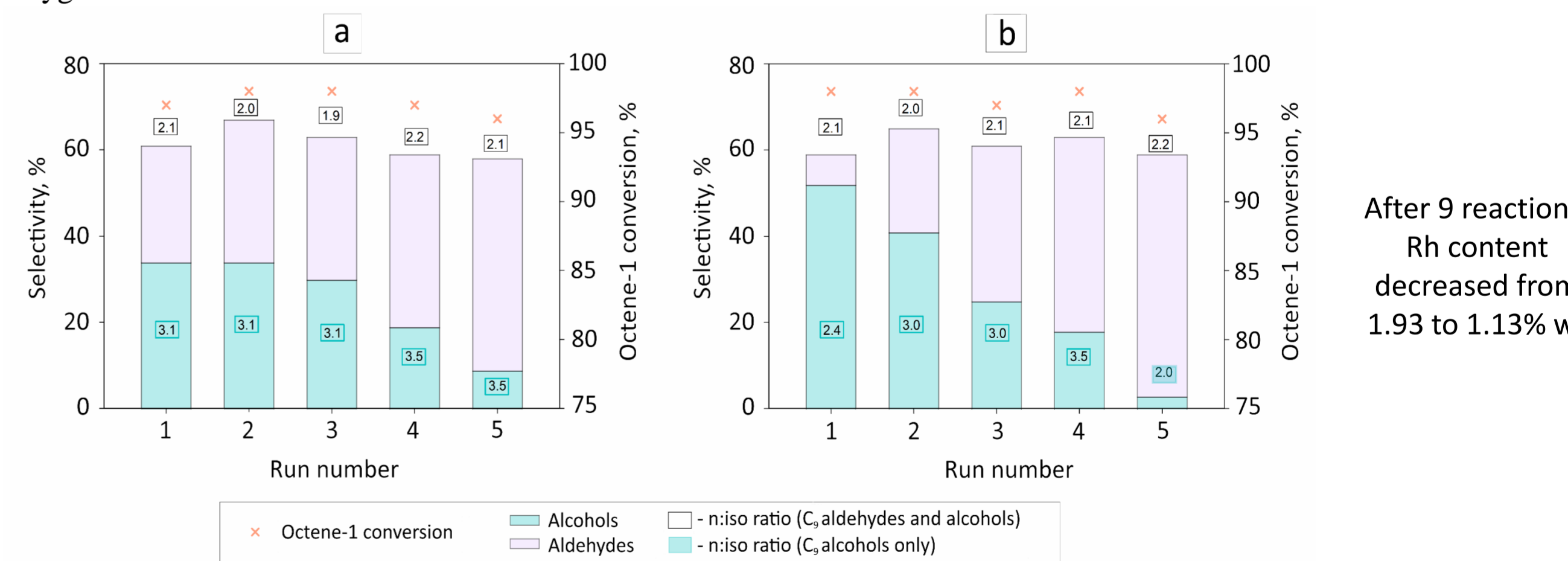
- The catalysts K_N and K_W containing a sufficient share of tertiary nitrogen atoms are effective in tandem hydroformylation-hydrogenation and can be reused
- K_N is more stable, however, both catalysts gradually lose their hydrogenation activity due to rhodium leaching
- Rhodium in K_N catalyst is in +1 oxidation state, and no reduction or agglomeration during the reaction is observed.

Catalyst	Conv., %	Selectivities					
		Int. octenes, %	Octane, %	Aldehydes, %	n:iso _{ald+alc}	Alcohols, %	n:iso _{alc}
Rh(acac)(CO) ₂ ^[a]	100	<1	2	97	0.9	-	-
Rh(acac)(CO) ₂ /PPh ₃ ^[b]	100	<1	<1	99	2.4	<1	-
Rh(acac)(CO) ₂ /TMPDA ^[c]	97	25	3	56	2.0	16	3.0
K _N ^[d]	97	29	10	27	2.1	34	3.1
K _N * ^[d]	98	22	11	32	2.0	34	3.1
K _W ^[d]	94	21	18	7	2.1	52	2.4
K _W * ^[d]	98	23	10	24	2.0	41	3.0
K _R ^[d]	98	24	7	62	1.9	6	5.0
K _R * ^[d]	98	23	7	70	1.9	-	-
K _S ^[d]	71	30	4	56	2.1	10	2.5
K _S * ^[d]	96	29	5	61	2.0	5	4.0

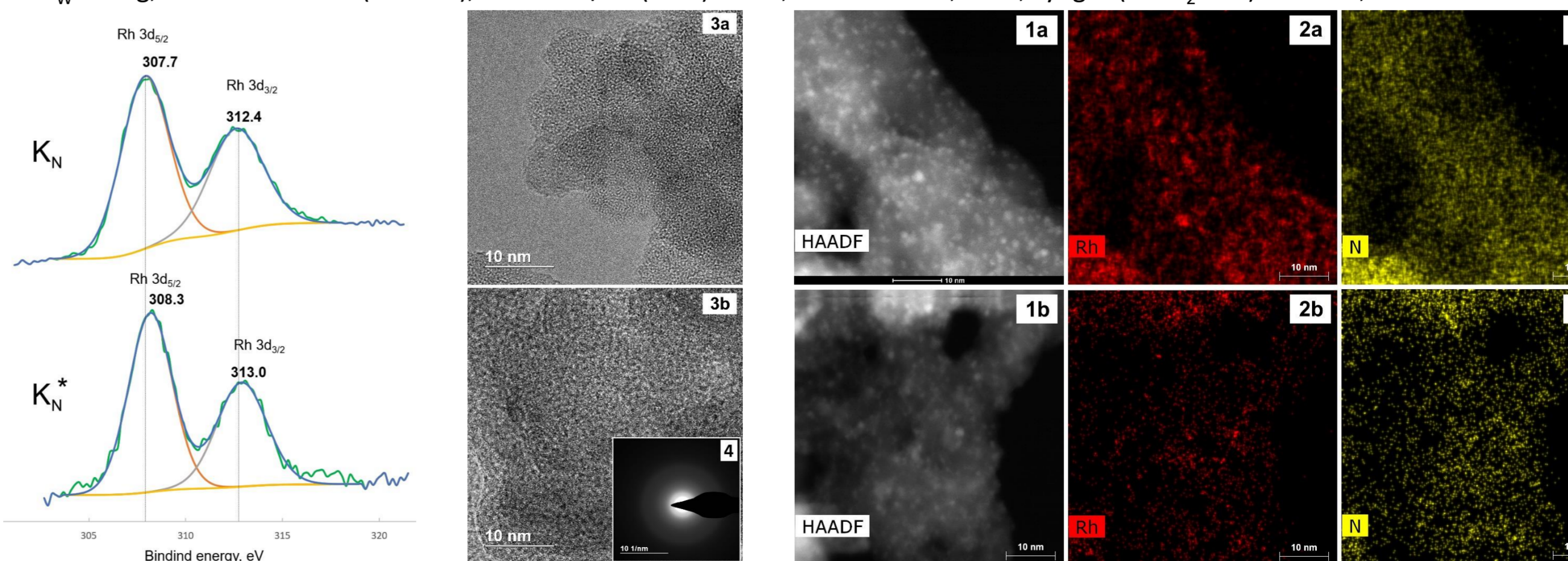
General conditions: octene-1 0.6 mL (4 mmol), toluene 2 mL, 80°C, syngas (CO:H₂=1:3) 6.0 MPa, 5 h; [a] Rh(acac)(CO)₂ 2 mg (0.008 mol); [b] Rh(acac)(CO)₂ 2 mg (0.008 mmol), PPh₃ 6 mg (0.023 mmol); [c] Rh(acac)(CO)₂ 2 mg (0.008 mmol), N,N,N',N'-Tetramethyl-1,3-propanediamine 0.005 mL (0.03 mmol); [d] heterogeneous catalyst 30 mg, octene/Rh (mol.) = 670, * - recycle.

Substrate	Conv./ %	Selectivities					
		Int. olefins/ %	Hydrogenated substrate/ %	Aldehydes/ %	n:iso _{ald+alc}	Alcohols/ %	n:iso _{alc}
Octene-1	97	29	10	27	2.1	34	3.1
Hexene-1	94	29	2	37	2.3	32	3.3
Cyclohexene	55	-	<1	3	-	97	-
Styrene	77	-	13	23	0.3	64	0.3
Ethylene ^[b]	70 ^[c]	-	n/a	99	-	1	-

K_N 30 mg, substrate 4 mmol, toluene 2 mL, 80°C, syngas (CO:H₂=1:3) 6.0 MPa, 5 h. [b] p (CH₂CH₂) = 0.5 MPa; [c] conversion to oxygenates



Activity of K_N (a) and K_W (b) in tandem hydroformylation/hydrogenation of octene-1 in five consequent reactions. Conditions: K_N or K_W 30 mg, octene-1 0.6 mL (4 mmol), substrate/Rh (mol.) = 670, toluene 2 mL, 80°C, syngas (CO:H₂=1:3) 6.0 MPa, 5 h



X-ray photoelectron spectra

TEM images of K_N (3a), K_N* (3b) and SAED pattern of K_N* (4)

HAADF-STEM images of K_N (1a-3a) and K_N* (1b-3b) with corresponding element mapping analysis