

GOLD AND PLATINUM-CATALYZED HYDROGENATION OF MONOTERPENOID OXIMES TO VALUABLE AMINES AND CARBONYL COMPOUNDS

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INTRODUCTION

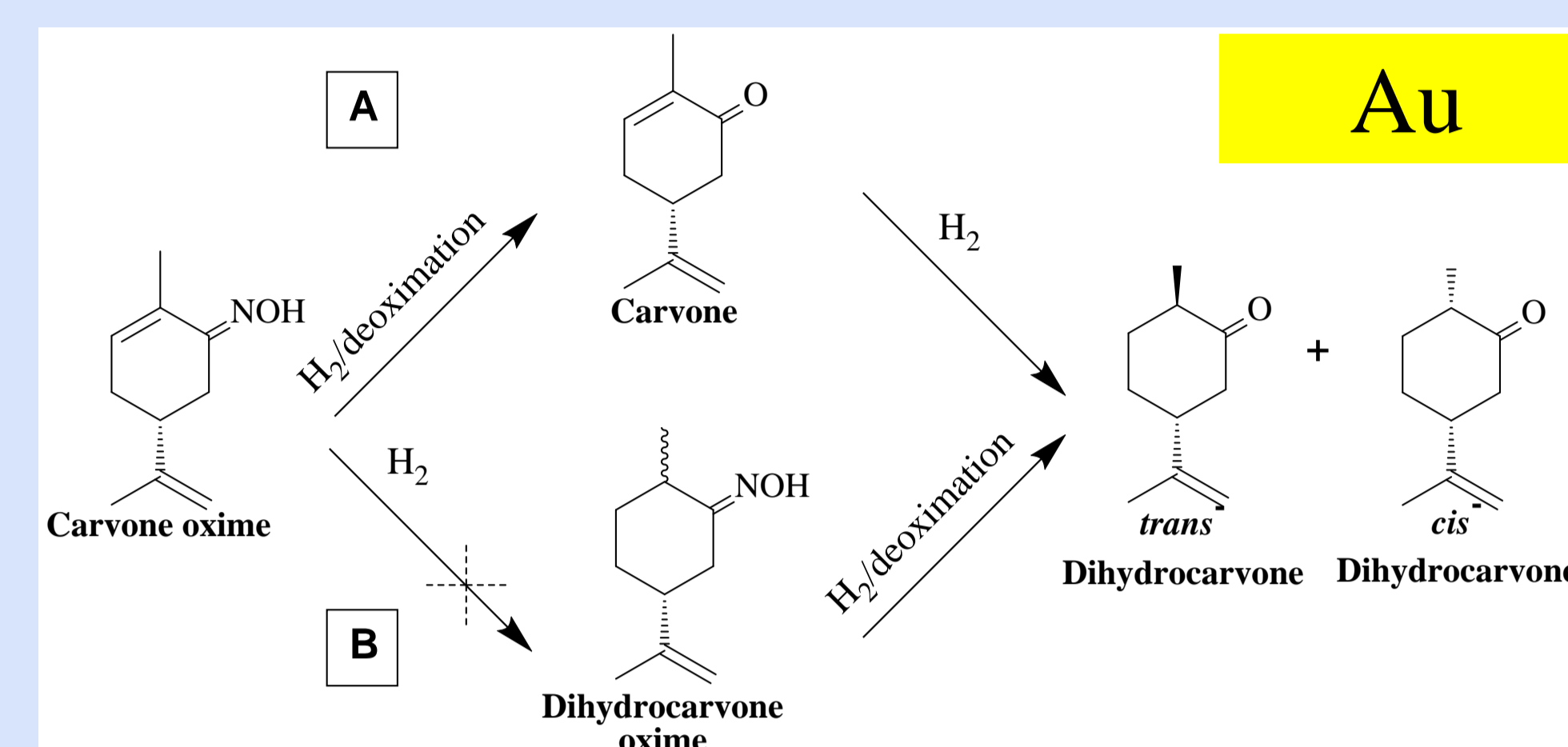
Widespread monoterpenoids are extensively applied as platform molecules in food, pharmaceutical and perfumery industries. Complicated structures of monoterpenoids with several functional groups and asymmetric centers allow synthesis of a broad range of the products. At the same time, development of selective catalytic processes for monoterpenoid transformations is a challenging task because of their high reactivity. Hydrogenation of monoterpenoid oximes is one of the key steps in the synthesis of valuable compounds, including those with carbonyl and amino groups. In the present work, the focus was on the catalyst design for direct transformation of monoterpenoid oximes into valuable amines or carbonyl compounds.

EXPERIMENTAL

- Batch reactor
- T = 353-373 K, P(H₂) = 7.5-9 bar
- Monoterpenoid oximes: menthone, carvone (5 mmol)
- Solvent – methanol (15 ml); Catalysts 2% Au/Al₂O₃ (TiO₂); 2wt.% Pt/Al₂O₃ (TiO₂, ZrO₂, MgO)

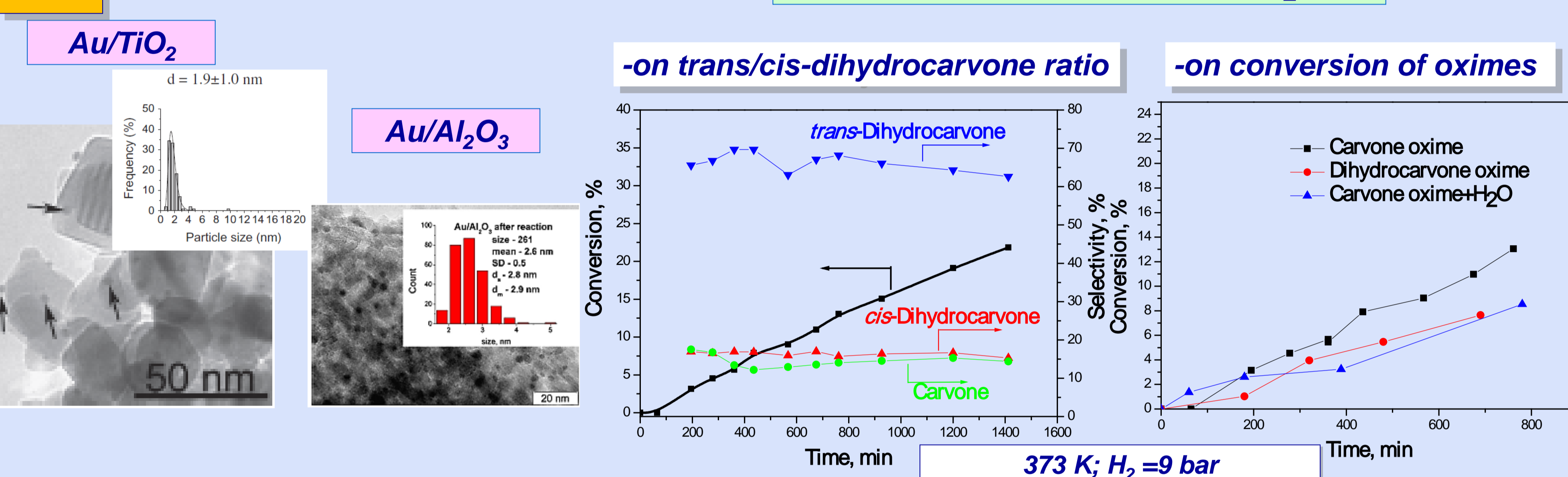
RESULTS

Carvone oxime hydrogenation over Au/TiO₂: Effect of substrate, support and water addition



Scheme of carvone oxime transformation over Au

TEM



Menthone oxime, Au catalysts

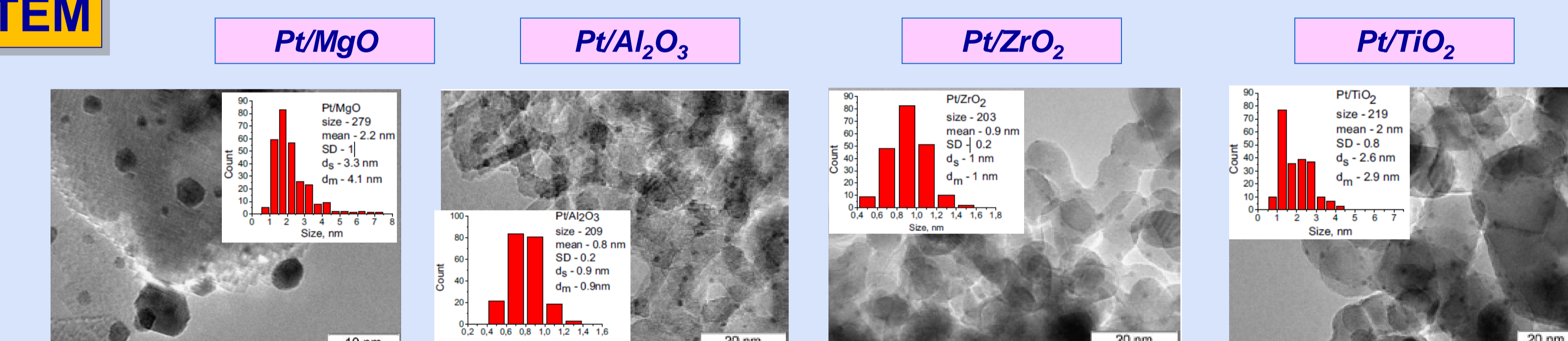
Sample	NPs size, nm	Solvent	TOF ^d , h ⁻¹	Conversion, %	Selectivity, %	
					Menthylamines ^e	Menthones ^e
TiO ₂	-	methanol	-	14	0	82
ZrO ₂	-	methanol	-	20	0	100
Al ₂ O ₃	-	methanol	-	38	0	92
MgO	-	methanol	-	22	0	91
Au/TiO ₂	3.0	methanol	21	73	62	13
Au/ZrO ₂	2.1	methanol	18	79	67	13
Au/MgO ^c	3.0	methanol	20	76	26	57
Au/Al ₂ O ₃	2.0	methanol	30	99	64	18
Au/Al ₂ O ₃	2.0	toluene	45	98	43	41
Au/Al ₂ O ₃	2.0	hexane	34	97	48	37
Au/Al ₂ O ₃	2.0	THF	19	65	45	48

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Yu.S. Demidova, E.S. Mozhaitsev, E.V. Suslov, A.A. Nefedov, A.A. Saraev, K.P. Volcho, N.F. Salakhutdinov, A. Simakov, I.L. Simakova, D.Yu. Murzin. Applied Catalysis A, General, 2020, 605, 117799.

Carvone and menthone oximes hydrogenation over Pt catalysts: effect of metal oxide support, SSA and NP size

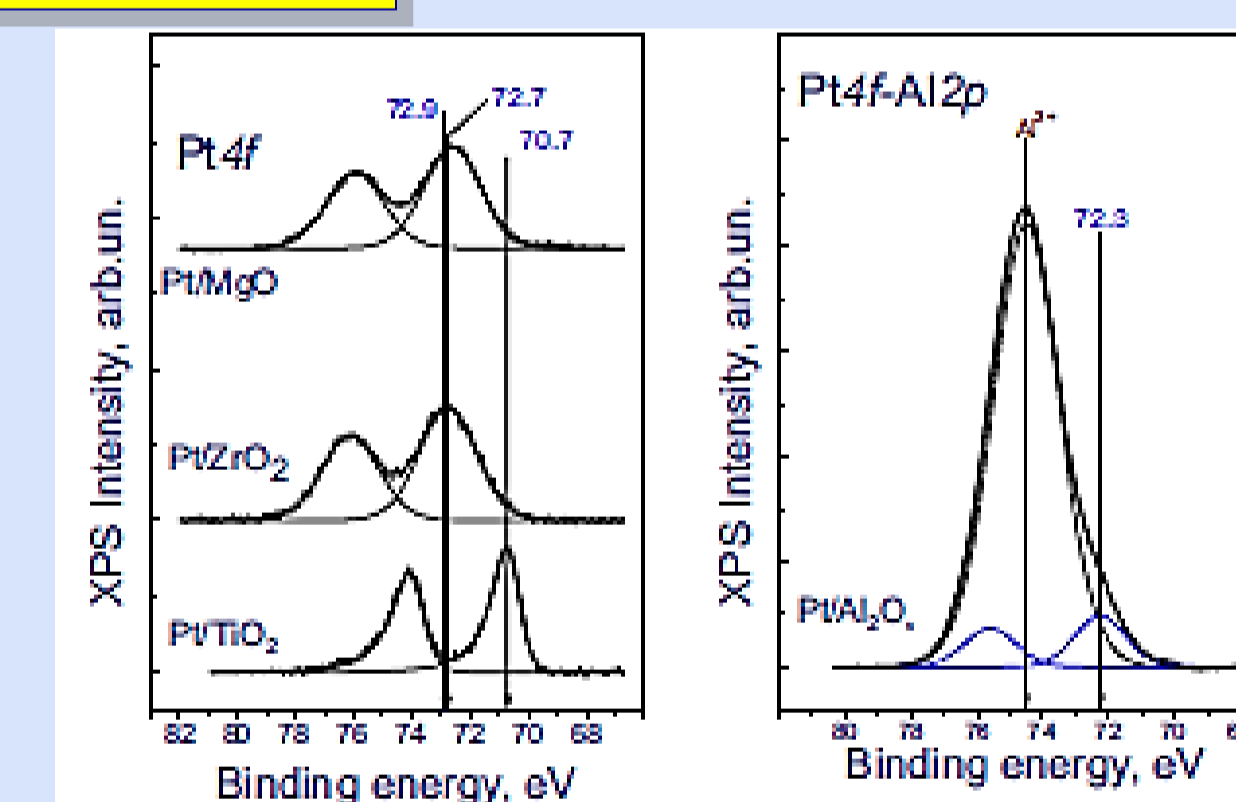
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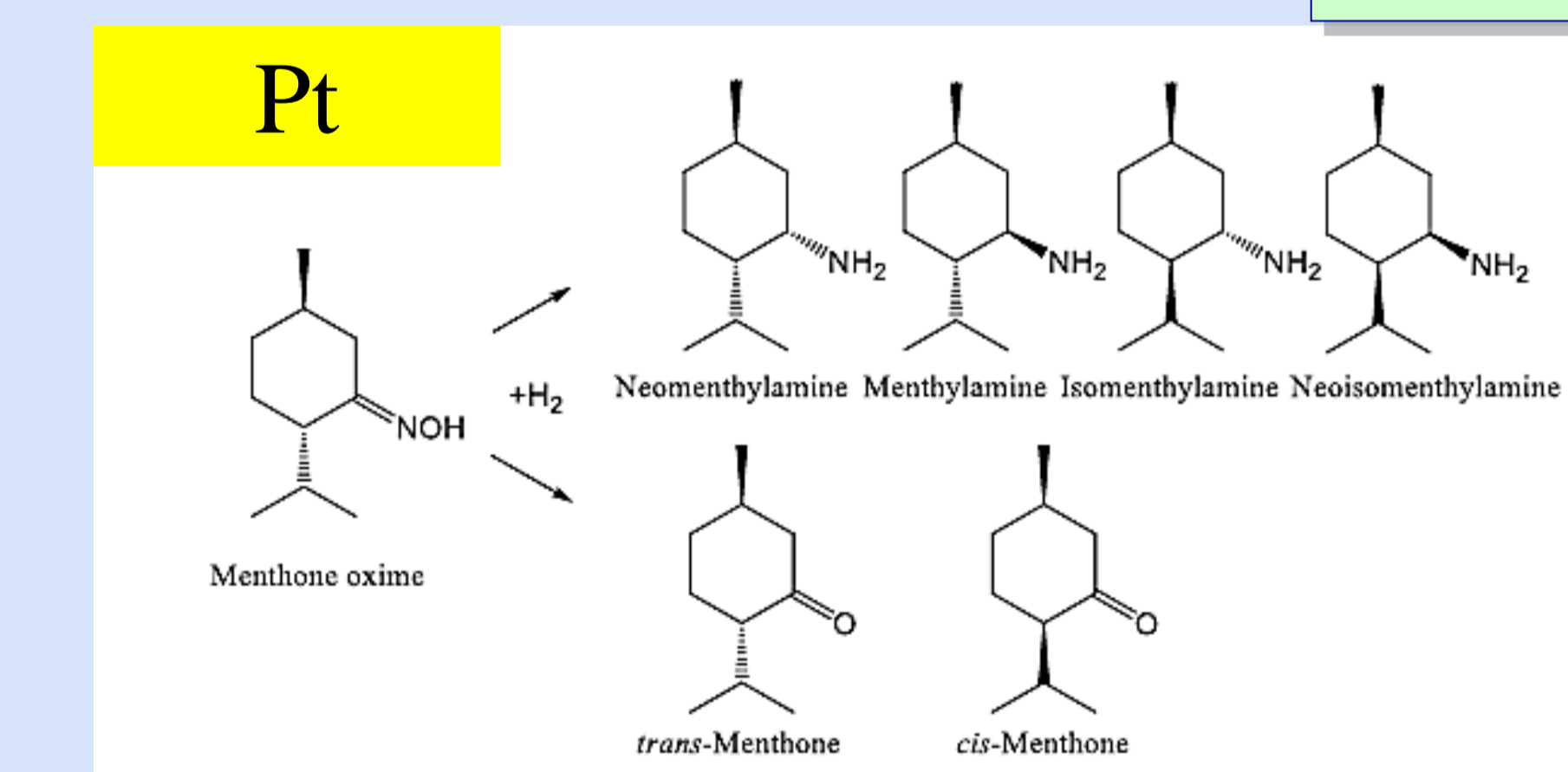
N₂ physisorption

Support	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Pt particle size (nm)
MgO	33	0.2	22.6	2.2
Al ₂ O ₃	204	0.5	10.3	0.8
ZrO ₂	103	0.3	10.8	0.9
TiO ₂	45	0.2	7.6	2.0

XPS



Menthone oxime, Pt catalysts



Scheme of Pt-catalyzed transformation of menthone oxime: two ways – Cis/Trans-menthones or menthylamines

Sample	TOF ^a (h ⁻¹)	Conversion (%)	Selectivity (%)		
			Menthylamines	Menthones	trans-/cis-Menthone
TiO ₂	-	14	0	82	3.9
ZrO ₂	-	20	0	100	3.0
Al ₂ O ₃	-	38	0	92	4.0
MgO	-	22	0	90	3.0
Pt/TiO ₂	9	67	2	70	3.7
		80 ^b	11	62	2.6
Pt/ZrO ₂	8	46	47	34	2.8
		52 ^b	44	40	3.0
Pt/Al ₂ O ₃	32	100	90	2	1.0
Pt/MgO	56	98	72	13	1.6

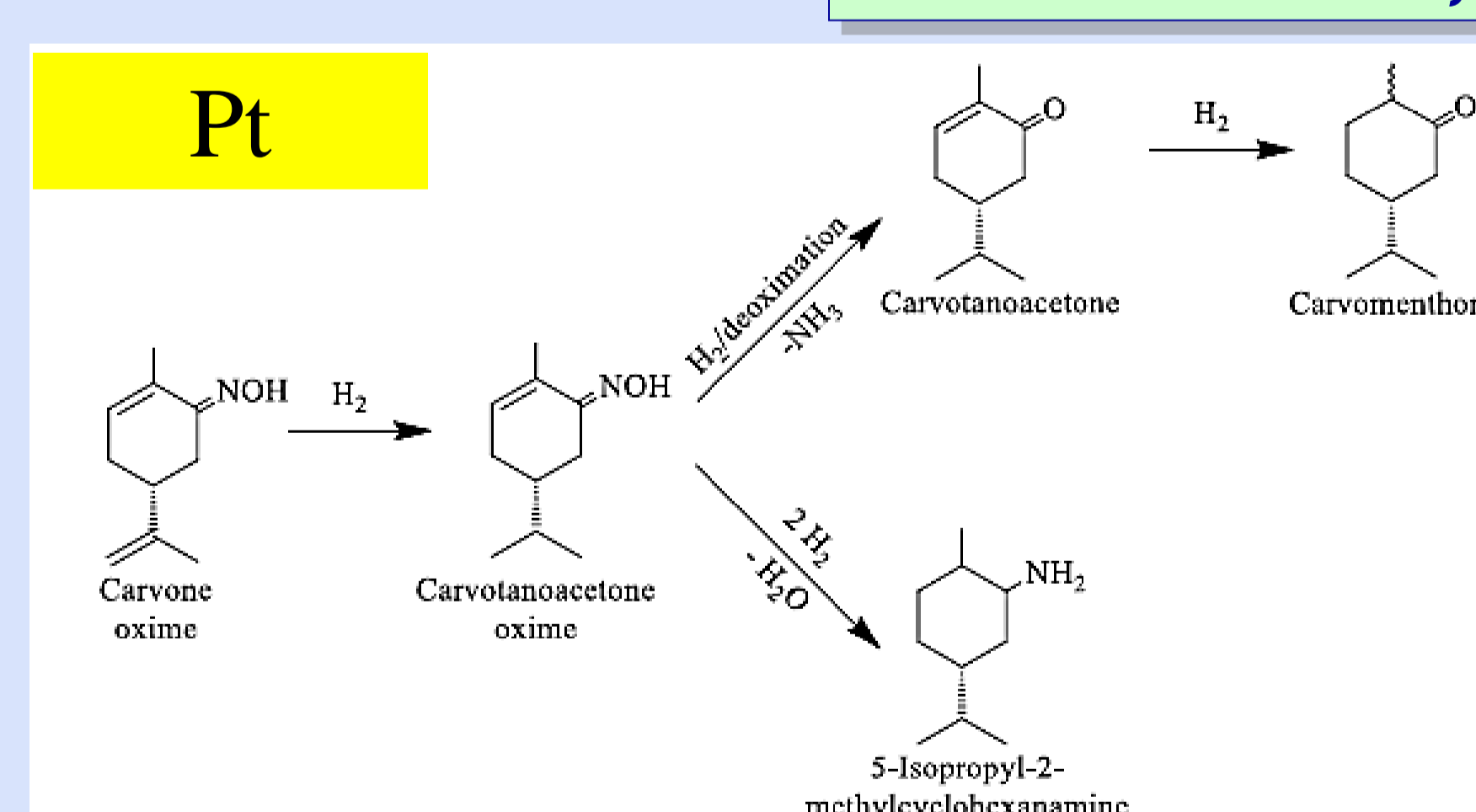
The reaction conditions: T = 100 °C, p (H₂) = 7.5 bar, menthone oxime 1 mmol, methanol 10 ml, catalyst 150 mg (Me/menthone oxime = 1.5 mol%)

^aTurnover-frequency was calculated after 1 h;

^bCatalytic activity after 9 h

Carvone oxime, Pt catalysts

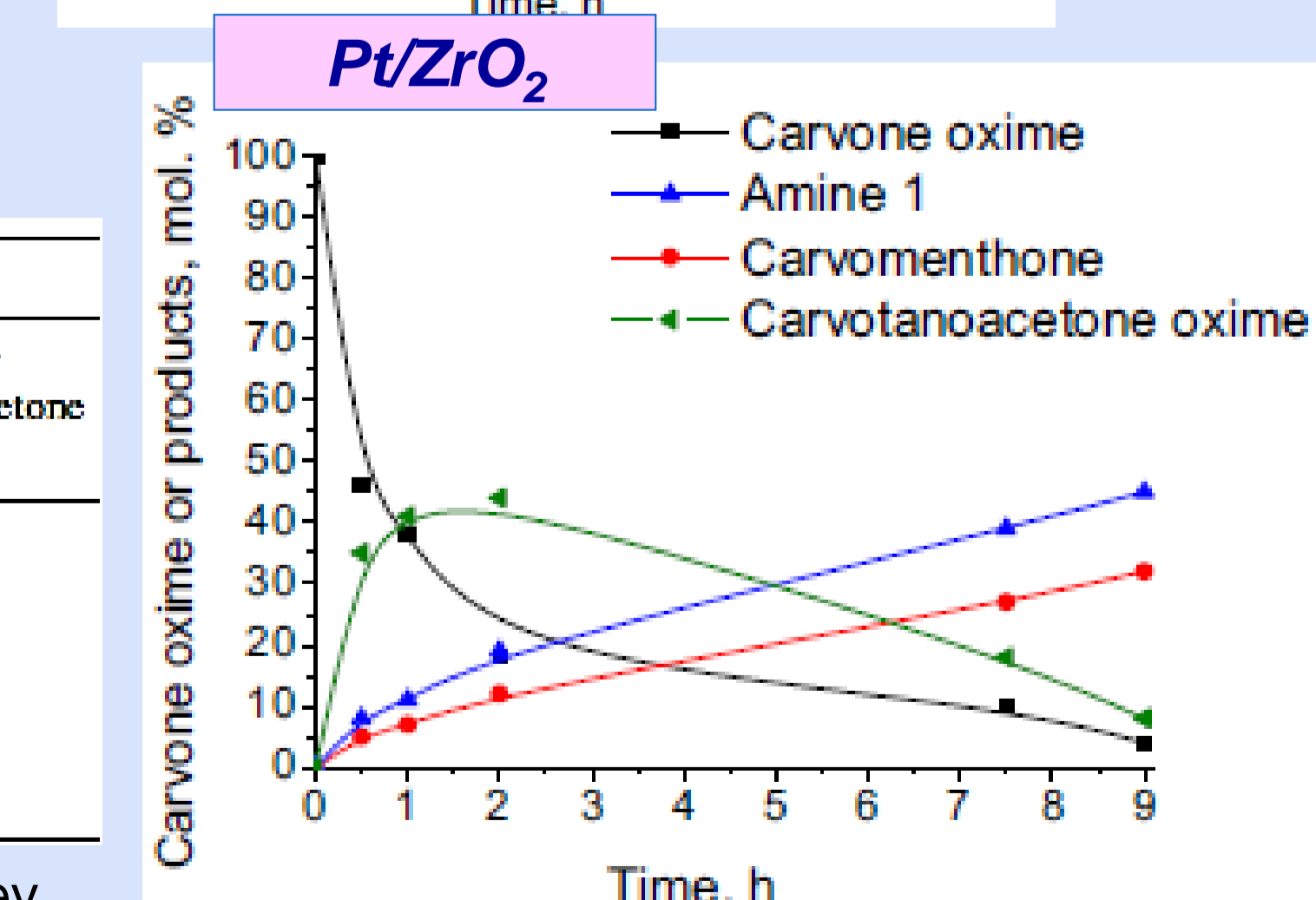
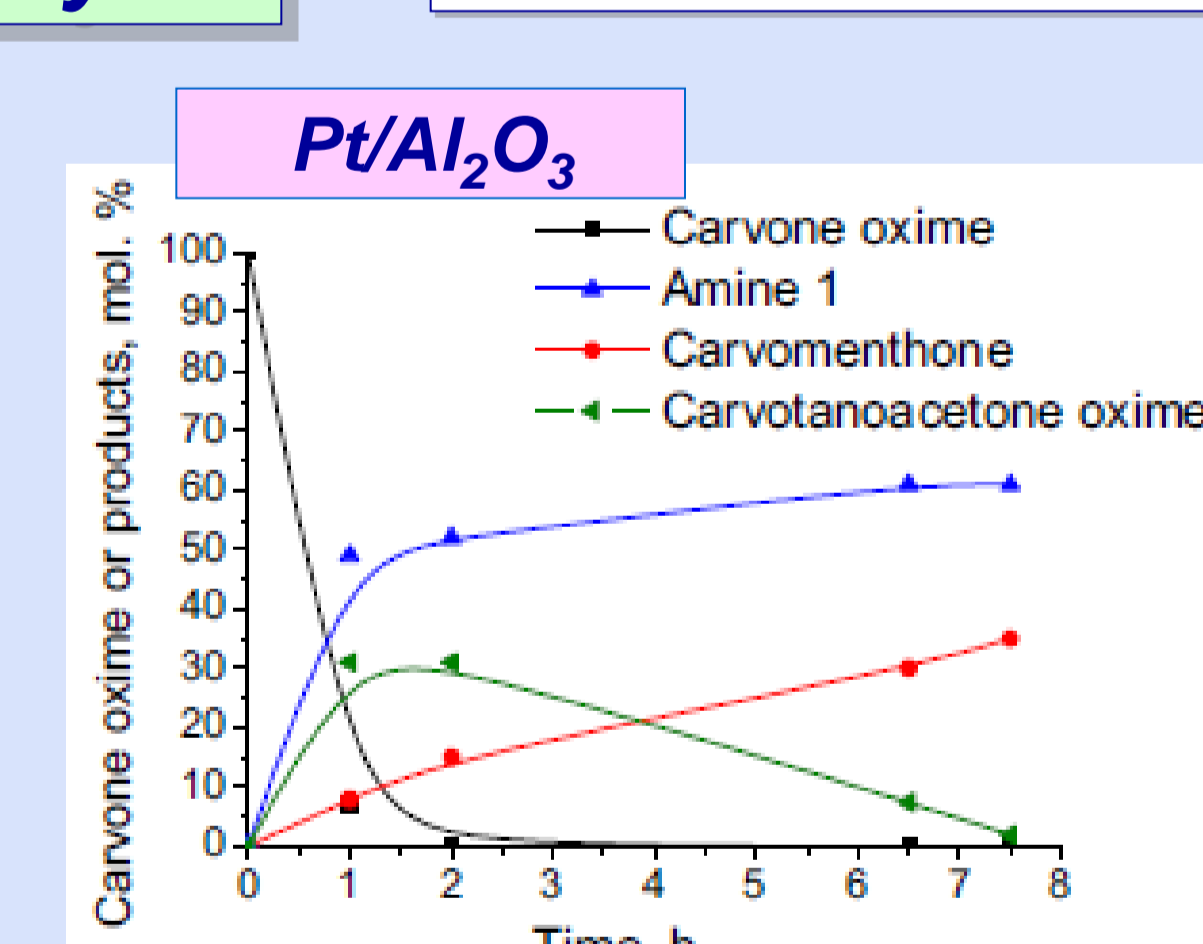
373 K; H₂ = 7.5 bar



Scheme of Pt-catalyzed transformation of carvone oxime: two ways via intermediate carvotanoacetone oxime – carbonyl carvomenthone or 5-isopropyl-2-methylcyclohexanamine

Sample	TOF ^a (h ⁻¹)	Conversion (%)	Selectivity (%)		
			5-Isopropyl-2-methylcyclohexanamines	Carvomenthones	Carvotanoacetone oxime
Pt/TiO ₂	6	46	0	28	33
Pt/ZrO ₂	16	90	41	29	23
		98 ^b	45	33	8
Pt/Al ₂ O ₃	34	100	61	35	2
Pt/MgO	21	100	8	15	20

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Contrary to menthone oxime, carvone oxime has a double bond conjugated with the oxime group and an isolated C=C bond, which does not have a steric hindrance from the oxime group. In the presence of Pt supported on Al₂O₃ and ZrO₂ non-selective hydrogenation of carvone oxime was observed resulting in predominant 5-isopropyl-2-methylcyclohexanamine (1) formation. The reaction proceeded through first hydrogenation of the C=C bond in isopropyl substituent of carvone oxime. Subsequent hydrogenation and deoxygenation of carvotanoacetone oxime gave amine 1 as well as carvotanoacetone and carvomenthones, the latter was the main product.

CONCLUSIONS

- Catalytic activity and product distribution depend on the oxime structure, acid-base properties of the support and the nature of active metal.
- One-pot synthesis of dihydrocarvone comprising sequential transformations of carvone oxime to dihydrocarvone over Au/TiO₂ catalyst, which is a novel approach to obtain a valuable additive in food industry, was developed.
- Carvone oxime, containing several reducible functional groups and a conjugated oxime group, seems to be activated over Pt catalysts in the way leading to non-selective hydrogenation. Pt catalysts based on metal oxides were successfully applied for menthone oxime hydrogenation into valuable menthylamine. Pt/Al₂O₃ provided higher activity and selectivity to the desired amine.