Catalytic oxidation of volatile organic compounds on Ni-containing catalysts

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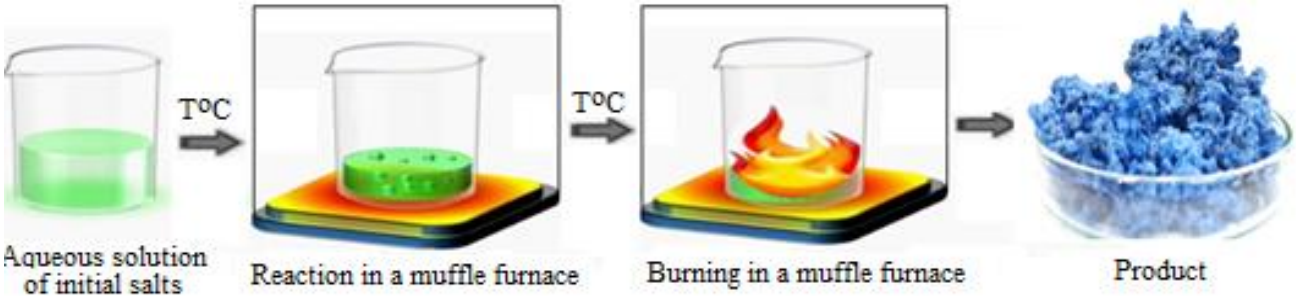
. Traditional incipient wetness impregnation from metal nitrate salts

Catalysts: **Ni-Cu-Cr/2% Ce/θ-Al_2O_3 Ni : Cu : Cr = 1.0 : 3.0 : 0.1**
Ni-Cu-Cr/θ-Al_2O_3
Ni-Cu/2% Ce/θ-Al_2O_3
Ni-Cr/2% Ce/θ-Al_2O_3
Ni/2% Ce/θ-Al_2O_3

The granulated θ-Al_2O_3 (S = 100 m^2 g^{-1}, particle size 40-50 μm) modified by Ce, which forms resistant surface $CeAlO_3$ perovskite up to 1,373 K

Self-propagating high-temperature synthesis



Reaction: **Deep oxidation of toluene was carried out on the flow type PKU-2VD catalytic nstallation.**

T = 523-773 K

GHSV = 5-15×10^3 h^{-1}

Toluene concentration (320 mg m^{-3})
in the initial mixture

Flow type PKU-2VD catalytic installation

Pilot plant

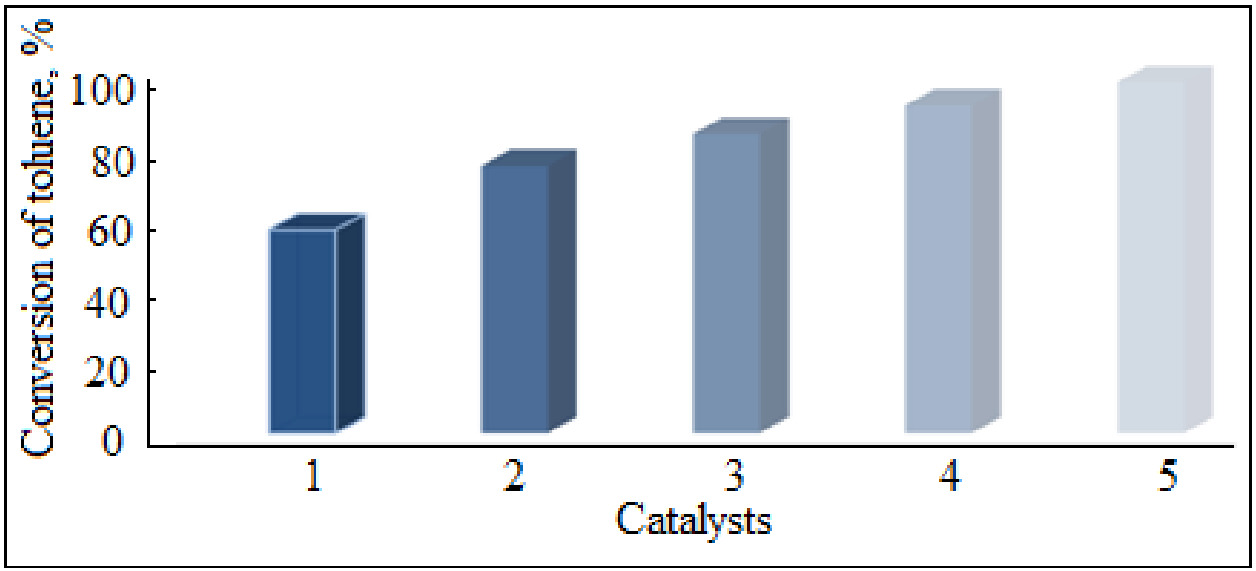


Fig. 1. The oxidation of toluene on oxide Ni-Cu-Cr catalysts at 723 K and GHSV 5×10^3 h^{-1}: 1 – 5% Ni/2% Ce/θ-Al_2O_3, 2 – 5% Ni-Cu/2% Ce/θ-Al_2O_3, 3 – 5% Ni-Cr/2% Ce/θ-Al_2O_3, 4 – 5% Cu-Cr/2% Ce/θ-Al_2O_3, 5 – 9% Ni-Cu-Cr/2% Ce/θ-Al_2O_3

Table 1. Effect of temperature and space velocity on the degree of conversion of toluene on the Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst

T, K	Space velocity, × 10^3 h^{-1}		
	5	10	15
	Degree of toluene conversion, %		
523	73.7	81.0	82.1
573	89.5	85.7	83.8
623	94.7	90.5	85.7
673	97.5	91.5	89.3
723	98.5	93.5	89.3
773	98.8	95.2	89.3

Table 2. Effect the content of toluene in the initial mixture with air on degree of its conversion on the various catalysts at 723 K; GHSV - 5×10^3 h^{-1}

Catalysts	Concentration of toluene, mg m^3	
	100	320
	Degree of conversion of toluene, %	
5% Cu-Cr/2% Ce/θ-Al_2O_3	68.0	67.9
5% Ni-Cr/2% Ce/θ-Al_2O_3	76.6	73.0
5% Ni Cu/2% Ce/θ-Al_2O_3	85.0	84.0
9% Ni-Cu-Cr/2% Ce/θ-Al_2O_3	98.5	98.8

Optimal conditions: degree of toluene conversion reaches 98.5-98.8% on the Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst at 723-773 K, GHSV – 5×10^3 h^{-1} and the concentration of toluene in the initial mixture with air – 100-320 mg m^{-3}.

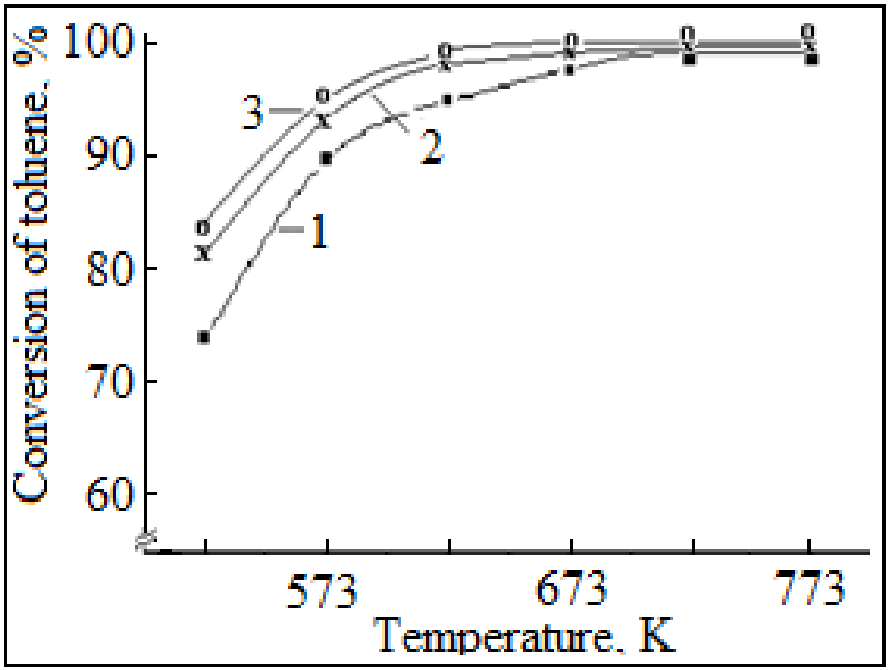


Fig. 2. Dependence of the degree of toluene oxidation from temperature and composition of catalysts at GHSV - 5×10^3 h^{-1} and toluene concentration - 320 mg m^{-3}: 1 – Ni-Cu-Cr/2% Ce/θ-Al_2O_3, 2 – Ni-Cu-Cr + Pd/2% Ce/θ-Al_2O_3, 3 – Ni-Cu-Cr + Pt/2% Ce/θ-Al_2O_3

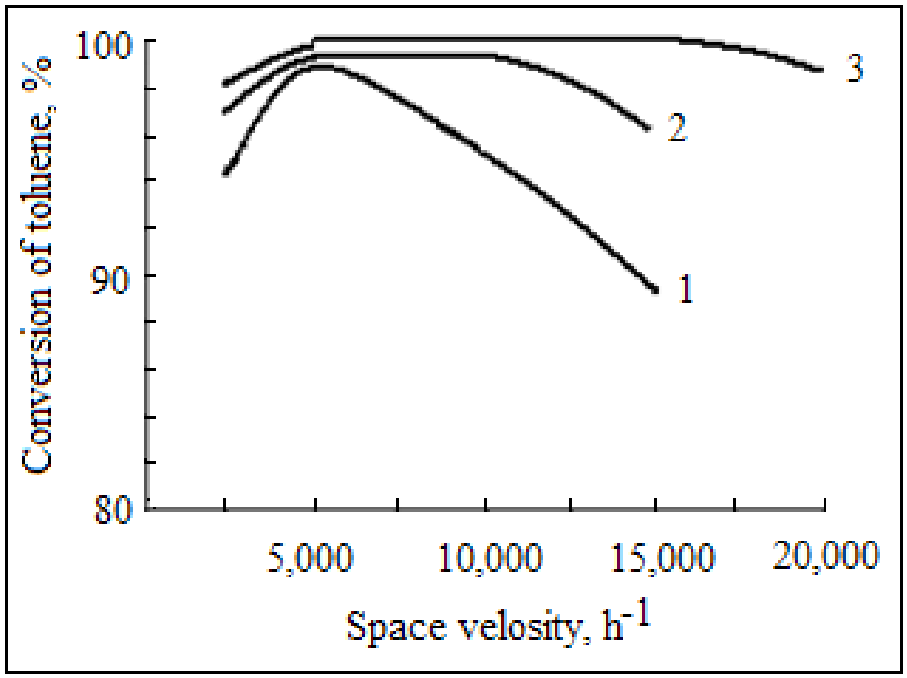


Fig. 3. Effect of space velocity on conversion of toluene at the toluene concentration of 320 mg m^{-3} in the initial mixture: 1 – Ni-Cu-Cr/2% Ce/θ-Al_2O_3, 2 – Ni-Cu-Cr + Pd/2% Ce/θ-Al_2O_3, 3 – Ni-Cu-Cr + Pt/2% Ce/θ-Al_2O_3

Table 3. X-ray analysis of polyoxide Ni_1-Cu_3-$Cr_{0.1}$/2% Ce/θ-Al_2O_3 catalysts

Promoter, %	T, K	CeO_2 1.91 Å	α-Al_2O_3 1.74 Å	θ-Al_2O_3 2.31 Å	$NiAl_2O_4$ $CuAl_2O_4$ 1.43 Å	Less intensive phases
	873	13	37	10		CuO (2.51; 2.31; 1.85) NiO (2.08; 2.42; 1.48)
	1,273	58	158	5	90	
	1,473	30	120	3	105	
0.3 Pt	873	10	9	22		CuO, Al_2O_3 (2.12), NiO (2.42)
0.1 Pt	873	14	20			CuO, Al_2O_3 (2.12), Ce_6O_{11}, Cr_5O_{12} (3.57)
0.1 Pt	1,073	26	20	10	10	CuO, NiO, Ce_6O_{11}, Al_2O_3
0.3 Pt	1,473	52	166	5	70	
0.05 Pd	873	20	13	7	7	CuO, Ce_6O_{11}, Al_2O_3 (2.12)
0.05 Pd	1,273	45	148	2	55	Pd (2.25)
0.05 Pd	1,473	60	177	5	105	$NiAl_{10}O_{16}$ (1.99)

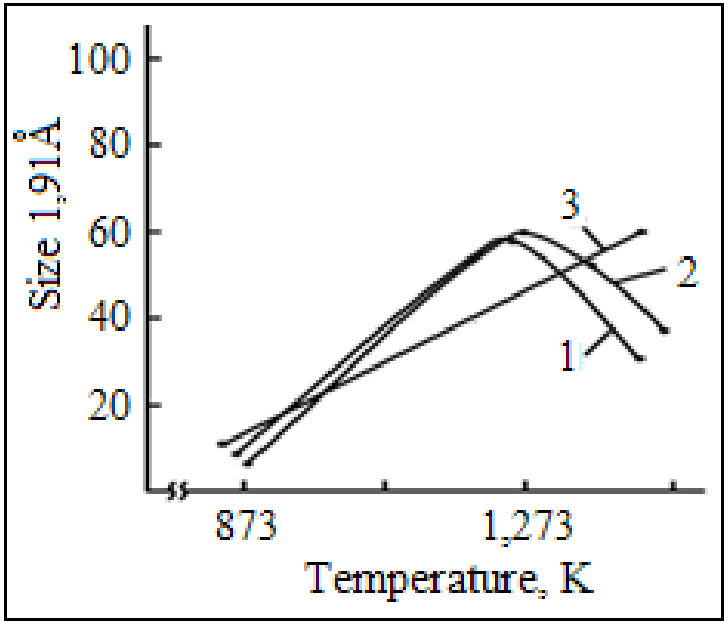


Fig. 4. Dependence of the intensity of CeO_2 reflection (1.91 Å) from the heating temperature: 1 – Ni-Cu-Cr, 2 – Ni-Cu-Cr + Pt, 3 – Ni-Cu-Cr + Pd

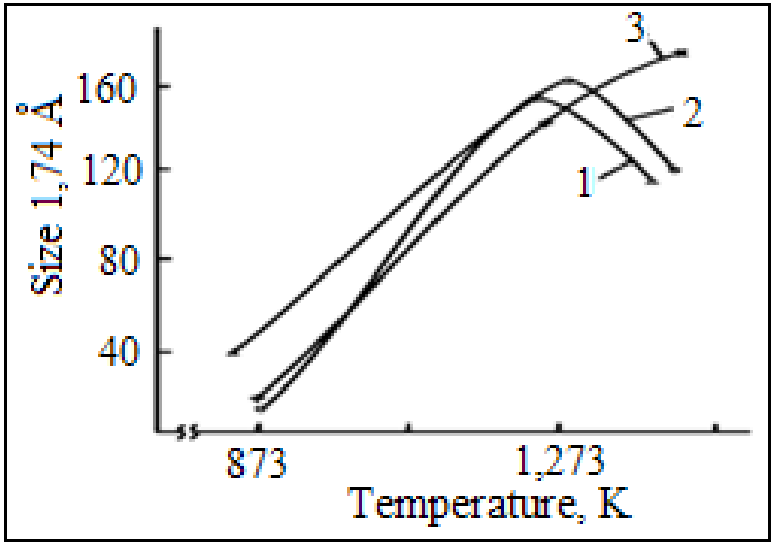


Fig. 5. Effect of the heating temperature on relative content of the α-Al_2O_3 (1.74 Å) in polyoxide Ni-Cu-Cr/2% Ce/θ-Al_2O_3 catalyst: 1 – Ni-Cu-Cr, 2 – Ni-Cu-Cr + Pt, 3 – Ni-Cu-Cr + Pd

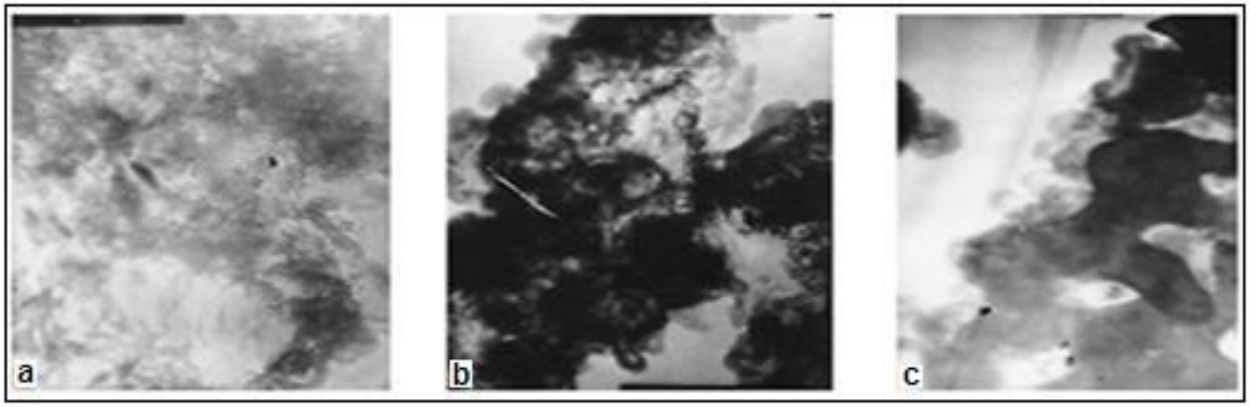


Fig. 6. TEM images of the supported three-component catalyst: a – Ni-Cu-Cr (873 K), b – Ni-Cu-Cr + Pd (873 K), c – Ni-Cu-Cr + Pd (1,473 K)

Single, double and triple metal oxides, the particle size of which are decreased from 50-80 Å (Ce/Al_2O_3) to 20-30 Å (Ni-Cu-Cr) are formed at complication the composition of three-component catalyst. Two types of particles: fine oxides (60-150 Å) and larger aluminates are formed at introduction of Pt and Pd into Ni-Cu-Cr catalyst. Interaction of elements with θ-Al_2O_3 carrier with formation of larger copper and nickel aluminates of the AB_2O_4 and ABO_3 type occurs when the temperature rises.

Table 4. Data of TEM studies of polyoxide Ni_1-Cu_3-$Cr_{0.1}$/2 % Ce/θ-Al_2O_3 catalysts

Catalysts	T, K	Particle size, Å	Diffraction data
Ni_1-Cu_3-$Cr_{0.1}$	873	20-30	$NiCr_2O_4$, $CuCrO_4$, $CuAl_2O_4$, $CuAlO_4$, $NiAl_2O_4$,
	1,473	20-100	CrO_2, Cr_2O_3, $CuAlO_2$, AlCu, $NiCrO_4$, Cr_2O_3
		>200	$CuAl_2O_4$, $NiAl_2O_4$, $CeAlO_3$
Ni_1-Cu_3-$Cr_{0.1}$+Pd	873	100	Cu, Ni, Cr oxides, CeO_2
	1,473	200-500	Cu, Ni aluminates, $CuCr_2O_4$, Pd, PdO, Ce_2O_3,
		(flaky particles)	CrO_2, $NiCrO_3$, $CuAl_2O_4$, $CuCr_2O_4$,
		>1000	$NiCrO_3$, $CeAlO_3$, Cu, Ni, Cr oxides, $NiAl_{26}O_{42}$,
			Cu_2O, Ni_2O
Ni_1-Cu_3-$Cr_{0.1}$+Pt	873	60-150	Cu, Ni, Cr oxides, Pt°
	1,473	200-500	Cu_2O, Ni_2O, PtO, $NiAl_2O_3$
		(dispersing and	$CuAl_2O_4$, CrO_4, Cr_2O_3, Ni_2O_3
		enlarging)	Cu_2O, Pt°, $NiCrO_4$, Ni_2O

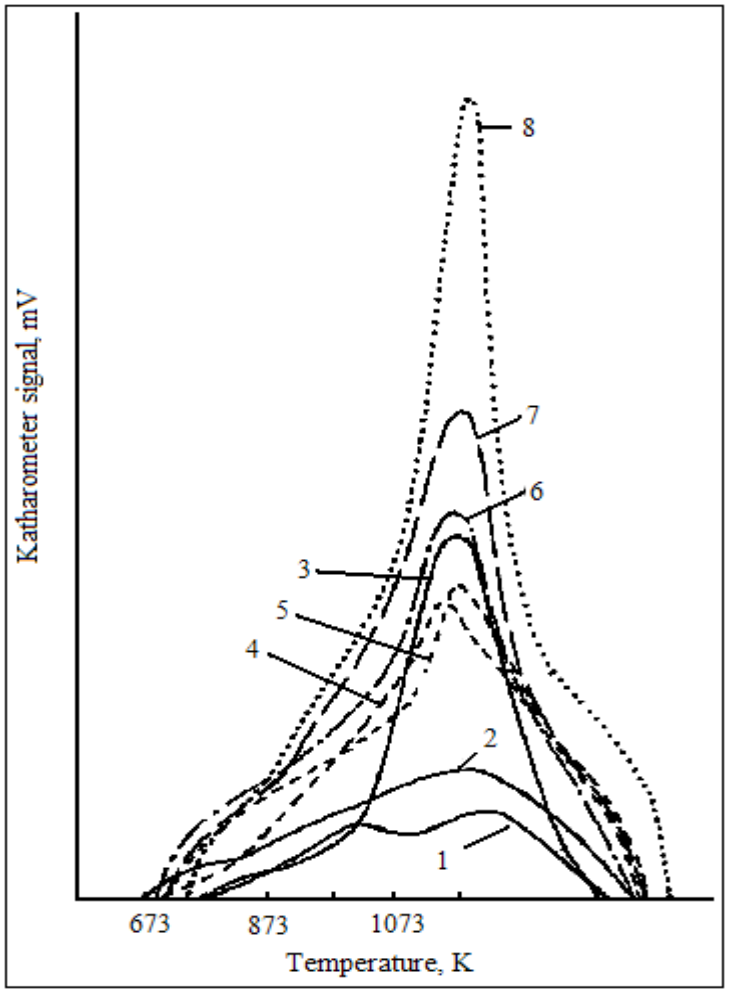


Fig. 7. Thermal desorption of oxygen from the catalysts on Al_2O_3 after heating in air: 1 – 5% Ni, 2 – 5% Cu, 3 – 5% Cr, 4 – 5% (Ni + Cr), 5 – 5% (Cu + Cr), 6–8 – 10% Ni-Cu-Cr at varying the deposition methods of catalysts: 6 - NH_4HCO_3, 7 - $Al(NO_3)_3$, 8 - NH_4HCO_3 + $Al(NO_3)_3$, T – 873 K, 1 h

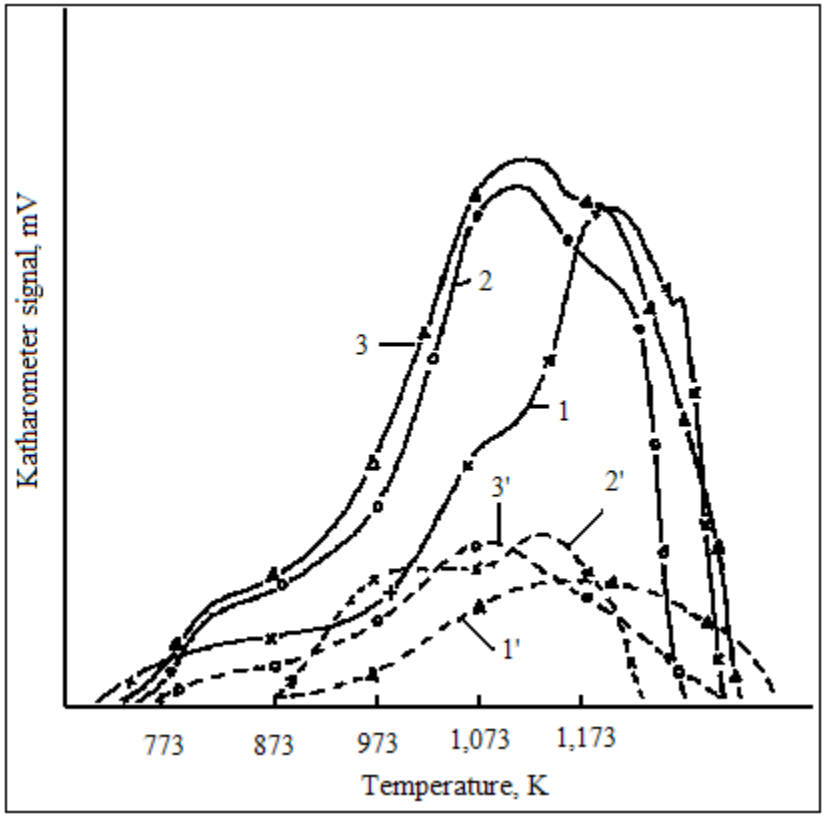


Fig. 8. Thermal desorption of oxygen from the Ni-Cu-Cr/2% Ce/Al_2O_3 catalyst heated in oxygen and promoted with Pd and Pt: 1 - Ni-Cu-Cr/2% Ce/Al_2O_3, 2 - Ni-Cu-Cr/2% Ce/Al_2O_3 + Pd, 3 - Ni-Cu-Cr/2% Ce/Al_2O_3 + Pt. 1^1, 2^1, 3^1 - catalysts after heating at 1,473 K, T – 873 K

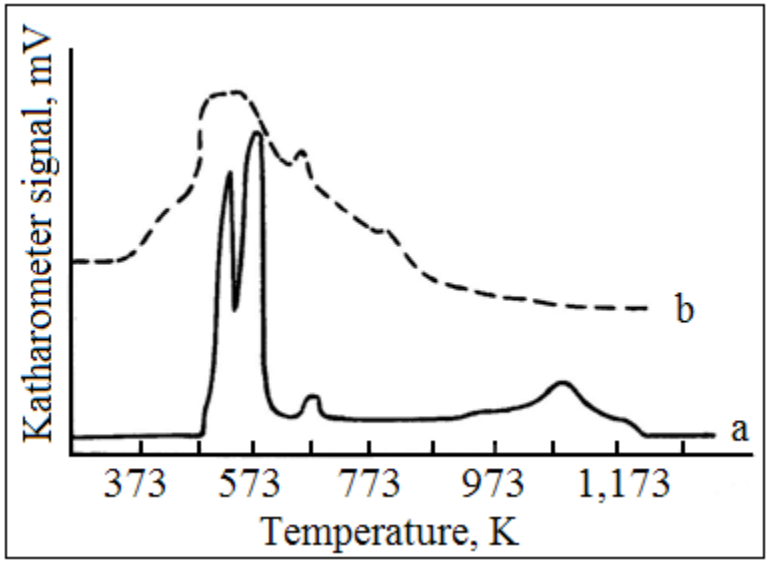


Fig. 9. TPR and TPO spectra of the initial Ni-Cu-Cr/Ce/θ-Al_2O_3 catalyst: a - TPR of the initial catalyst, b - TPO after TPR up to 1,225 K

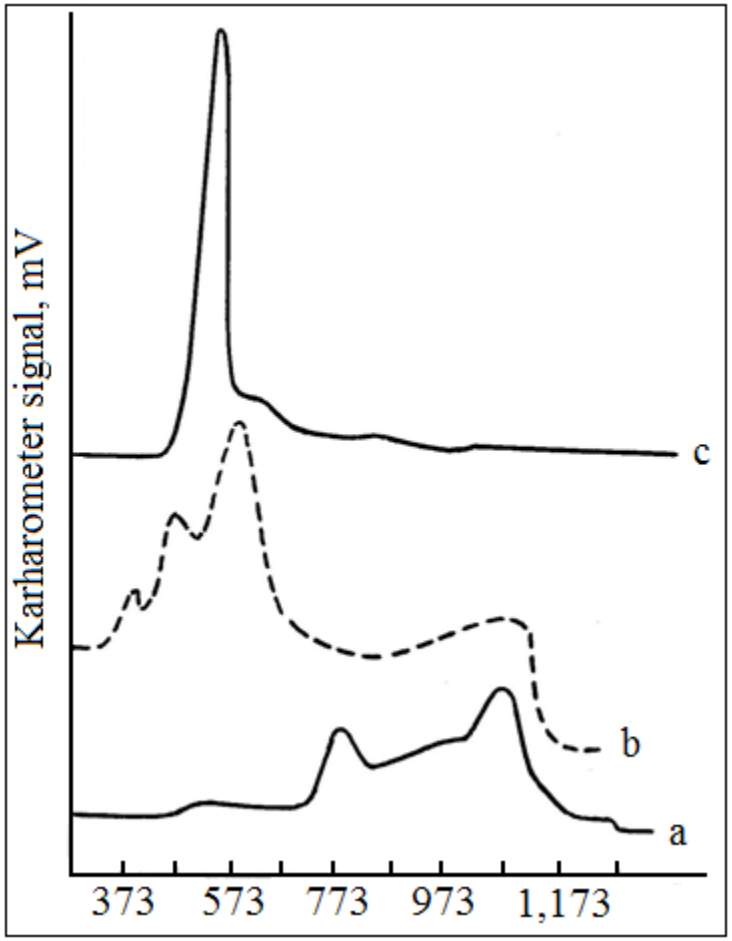


Fig. 10. TPR and TPO spectra of the Ni-Cu-Cr/Ce/θ-Al_2O_3 catalyst: a - TPR of the initial catalyst, b - TPO of catalyst reduced up to 1,223 K, c - TPR of catalyst after treatment in oxygen to 973 K, T – 1,473 K, 5 h

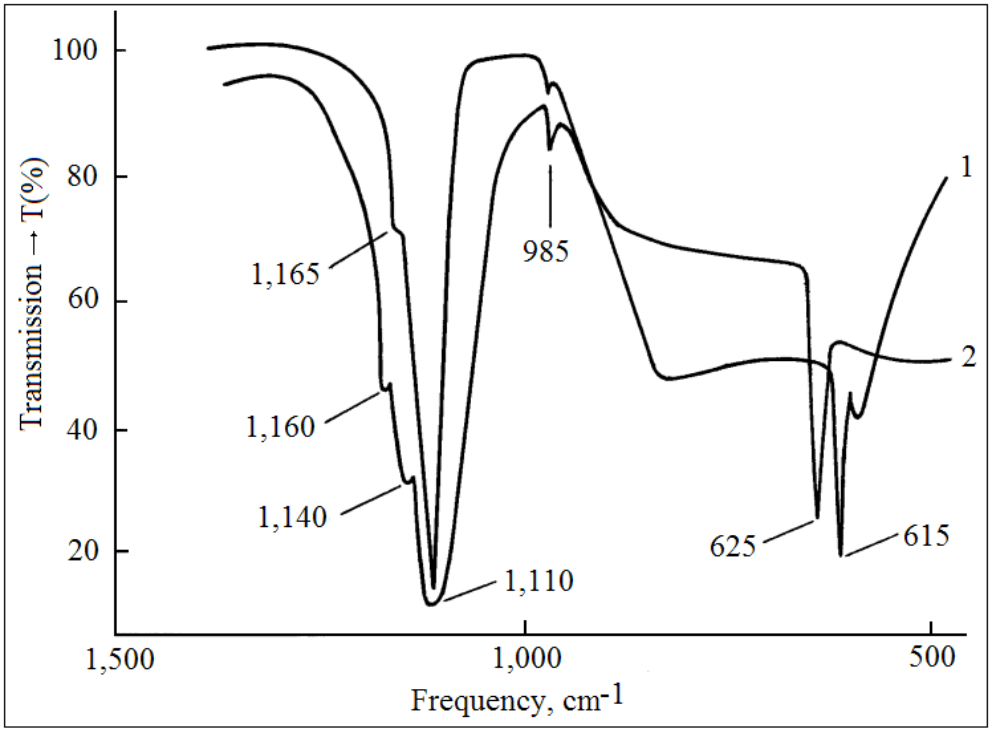


Fig. 11. IR spectra recorded after the reaction of the $SO_2 + O_2$ mixture at 673 K (4 h) with θ-Al_2O_3 (1), 2% Ce/θ-Al_2O_3 (2)

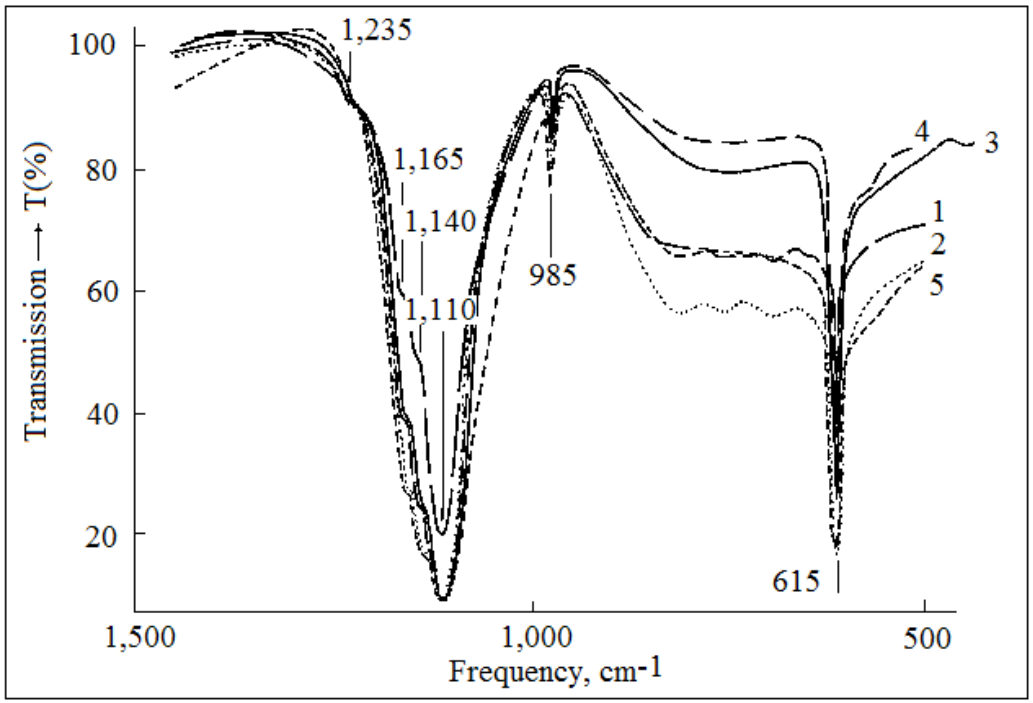


Fig. 12. IR spectra recorded after the reaction of the $SO_2 + O_2$ mixture at 673 K (4 h) with catalysts on 2% Ce/θ-Al_2O_3: 1 - Cr, 2 - Ni, 3 - Cu, 4 – Ni-Cu, and 5 – Ni-Cu-Cr

Thank you for your attention