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To the question of oxidation on the surface of oxides: temperature-programmed oxidation of cyclohexanol

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Temperature-programmed reaction (TPR) method with mass spectrometric control of the products was used to study of cyclohexanol oxidation into cyclohexanone on individual and mixed oxides supported by γ-Al_2O_3 and silica gel. In the TPR profiles the temperature of a maximum rate of cyclohexanone formation varies from 125°C for MoO_3/Al_2O_3 to 235°C for less active CuO/Al_2O_3. The catalytic activity of individual oxides decreases in the order $MoO_3/Al_2O_3 > V_2O_5/SiO_2 > Fe_2O_3/Al_2O_3 > Bi_2O_5/Al_2O_3 > TiO_2/SiO_2 \approx CeO_2/Al_2O_3 > TiO_2/Al_2O_3 > SnO_2/Al_2O_3$. As "reactive" oxygen in our TPR experiment was supplied only from oxide lattice, oxide activity is determined by different energy of the surface Me – O bonds. The approach to search for mixed active oxides based on decreasing coordination number of O^{2-} ions is proposed, that confirmed by the example of $CuO\text{-}WO_3/Al_2O_3$ catalyst. The mixed supported oxides, especially $CuO\text{-}CrO_3/Al_2O_3$, $CuO\text{-}MoO_3/Al_2O_3$, $MoO_3\text{-}SnO_2/Al_2O_3$ and $Bi_2O_3\text{–}SnO_2/Al_2O_3$, are more active in $C_6H_{12}O + 1/2O_2 \rightarrow C_6H_{10}O + H_2O$ oxidation. The synthesized $CuO\text{-}CrO_3/Al_2O_3$ catalyst provides cyclohexanone formation without side cyclohexanol dehydration and can be used for the oxidation of ethylene glycol – methanol mixture into methyl glycolate. $CuO\text{-}Cr_2O_3/Al_2O_3$ with a spinel structure of $CuCr_2O_4$ ($[CuO_4]^{6-}$ tetrahedra, Cu^{2+} sp^3-hybridization) is more active in cyclohexanol oxidation than CuO/Al_2O_3 with flat $[CuO_4]^{6-}$squares, Cu^{2+} dsp^2-hybridization. This is explained by the lower energy of Cu-O bonds at sp^3-hybridization of Cu^{2+} ions.

Keywords: heterogeneous catalysis, oxidation on oxides, supported catalysts, mixed oxides

Introduction

Even though many monographs and reviews have been written on the catalytic oxidation of various organic compounds on oxides [for example, [1-5]], the search for a suitable catalyst remains largely luck of a researcher. We have studied the reaction of cyclohexanol oxidation into cyclohexanone $C_6H_{12}O + 1/2O_2 \rightarrow C_6H_{10}O + H_2O$ on typical catalytic oxides at linear increasing temperature with mass-spectrometry product analysis. In particular, this TPR method has been applied for finding correlations between the ability of alcohols to be oxidized on CeO_2/AlO_3 and their chemical shifts $\delta(R^{13}COH)$ [6]. Usually, desorption mass-spectrometry is used to study monomolecular surface reactions such as the destruction of 1-butin-2-methyl-2ol (MBOH) test molecule or alcohol dehydrogenation on the Cu-catalyst [7]. However, the release of oxygen from the oxide lattice of a catalyst allows to study bimolecular reaction of alcohol oxidation. Obviously, it's possible to discuss Mars-Crevelen's mechanism only. In this communication, the TPR spectra of cyclohexanol oxidation on individual and mixed oxides supported by alumina and silica are presented, and the reaction schemes are discussed also.

Experiment

Numerous individual and mixed oxides supported by γ-Al_2O_3 and SiO_2 (30 samples) were used for the cyclohexanol (chromatography purity) TPR oxidation (Table 1, 2). The samples containing 2÷45 wt.% of supported oxides were prepared by usual incipient wetness impregnation of commercial γ-Al_2O_3 and silica gel with calculated aqueous solutions of correspondent metal salts. The supported oxides precursors were calcined at 400÷700°C for 1÷6 h. The samples were denoted as xMeO/Al_2O_3(SiO_2), where x is the MeO content in wt.%. The supported samples lose not more than 50% of initial high surface area of the γ-Al_2O_3 (260 m^2/g) and silica gel (380 m^2/g).

The TPR profiles of cyclohexanol products oxidation were registered on the modernized monopole mass-spectrometer MX-7304 (Ukraine). Previously oxide sample (1-2 mg) in a quartz cuvette was evacuated at 60-80°C, cooled to room temperature, and adsorption of alcohol vapor was provided. Then a sample was vacuumed at 30°C, and the TPR spectrum in the range, as a rule, of m/e = 39 -72 at sweep 2 a.u.m./s and temperature raising of 15°C/min was recorded.

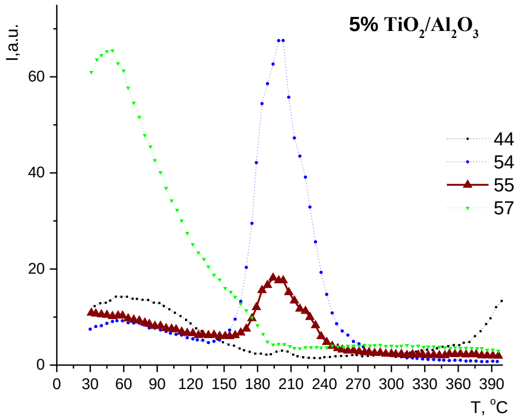
Results and discussion

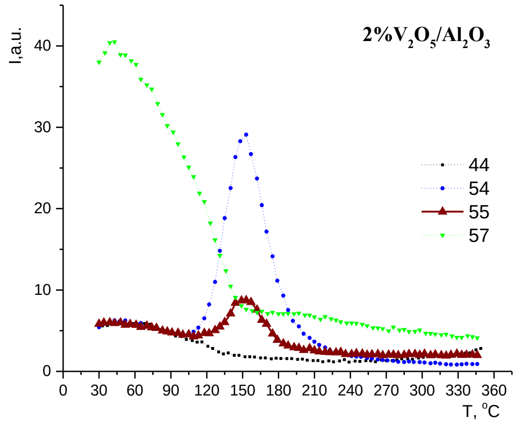
Individual supported oxides

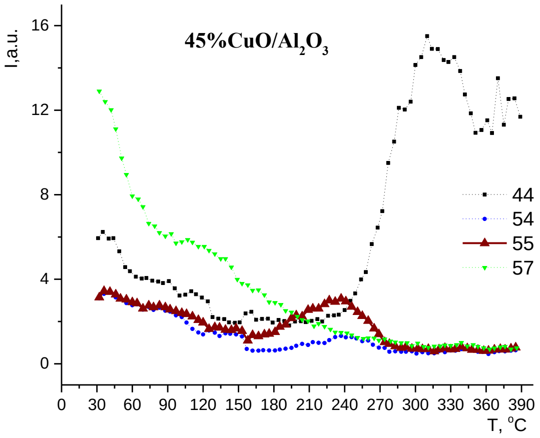
In Fig. 1 some typical TPR profiles of cyclohexanol oxidation on individual supported oxides are presented. Two main experimental facts should be noted:

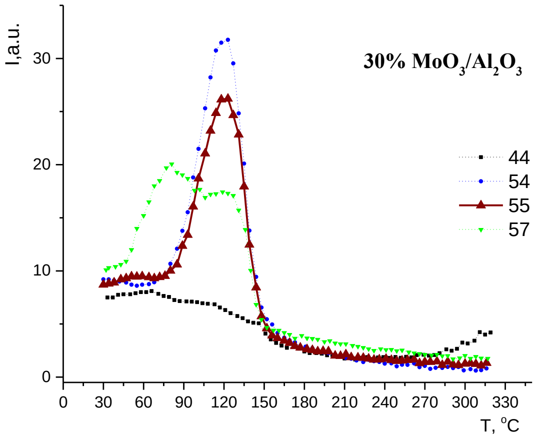
- the maximum rate of cyclohexanone formation is observed at various temperatures for several oxides in the range from 125 to 235°C (Table 1);
- in the TPR spectra three main products are fixed, namely, cyclohexanone (55, 42, 69 a.u.m.), cyclohexene (54, 67, 39 a.u.m.), and CO_2 (44 a.u.m.).

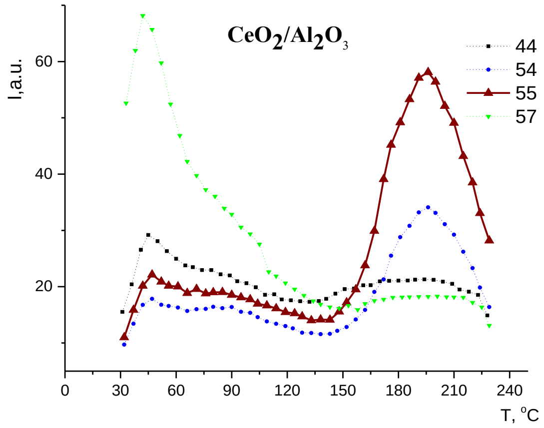
Cyclohexene forms at dehydration of cyclohexanol. This is the main side reaction chartered for alcohols, that proceeds on all studied oxides excluding CuO (Fig. 1). Interestingly, the peaks of cyclohexene and cyclohexanone formation often are observed at the practically same temperatures (Fig. 1, 2), i.e. exothermic oxidation of cyclohexanol stimulates its endothermic dehydration. Suppression of the dehydration of alcohols during their oxidation on solid catalysts is an important practical question.

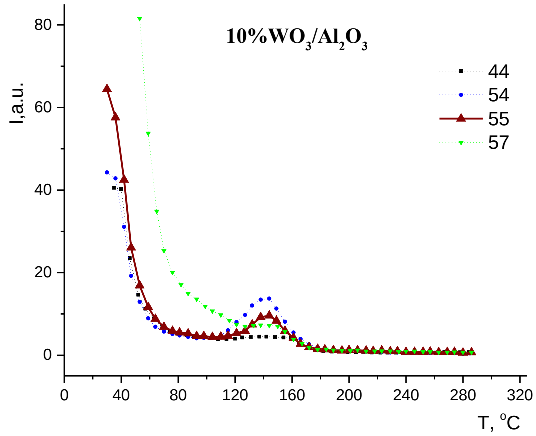












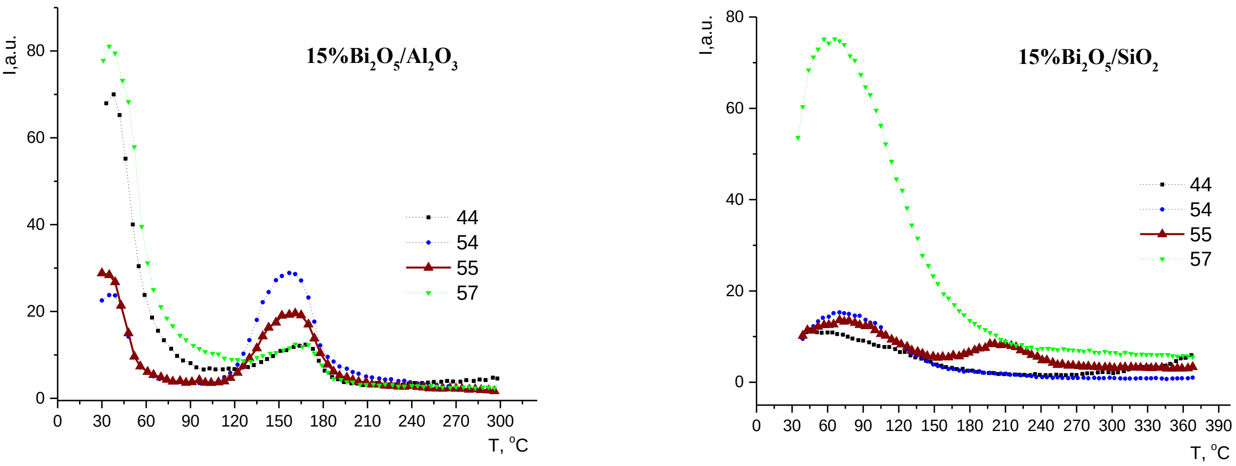


Fig.1. TPR profiles of cyclohexanol oxidation on individual supported oxides: 44 a.u.m. – CO_2; 54 a.u.m. – cyclohexene; **55 a.u.m. – cyclohexanone**; 57 a.u.m. - cyclohexanol.

Target cyclohexanone forms at 125°C on the most active MoO_3/Al_2O_3 and at 235°C for less active CuO/Al_2O_3 that corresponds to change activation energy of cyclohexanol oxidation reaction $E_a \approx 25\ RT_m$ [6], (where T_m in K), from 19.9 kcal/mol to 25.4 kcal/mol (Table 1). Obviously that this E_a difference could be associated with different energies of Cu-O and Mo-O bonds on the surface of oxides.

Table 1. **Temperatures of peak formation of cyclohexanone (T_m^{55}) and cyclohexene (T_m^{54}) from cyclohexanol adsorbed on studied oxides**

Sample	T_m^{55}, °C	$E_a=25RT_m^{55}$, kcal/mol *	T_m^{54}, °C	T^{44}, °C **
5wt%TiO_2/Al_2O_3	195	23.4	200	>300
5wt%TiO_2/SiO_2	190	23.2	190	>270
2 %V_2O_5/Al_2O_3	155	21.4	155	>330
2%V_2O_5/SiO_2	135	20.4	135	>350
2%MnO_2/ Al_2O_3	-	-	205	>180
2%MnO_2/ SiO_2	-	-	-	>160
7%Fe_2O_3/Al_2O_3	145	20.9	145	>270
5%Fe_2O_3/SiO_2	-	-	135	>270
45wt%CuO/Al_2O_3	235	25.4	240	>235
20wt%CuO/SiO_2	-	-	-	>170
30wt%MoO_3/Al_2O_3	125	19.9	125	>280
30wt%MoO_3/SiO_2	-	-	110	>290
10wt% SnO_2/Al_2O_3	205	23.9	205	>295
10wt%CeO_2/Al_2O_3	195	23.4	195	-
10wt%CeO_2/SiO_2	-	-	130	-
10wt%WO_3/Al_2O_3	145	20.9	145	-
10wt%WO_3/SiO_2	-	-	115	-
15%Bi_2O_5/Al_2O_3	160	21.7	160	>240
15%Bi_2O_5/SiO_2	-	-	-	>270

*) E_a –activation energy of cyclohexanol oxidation

**) temperature of CO_2 formation

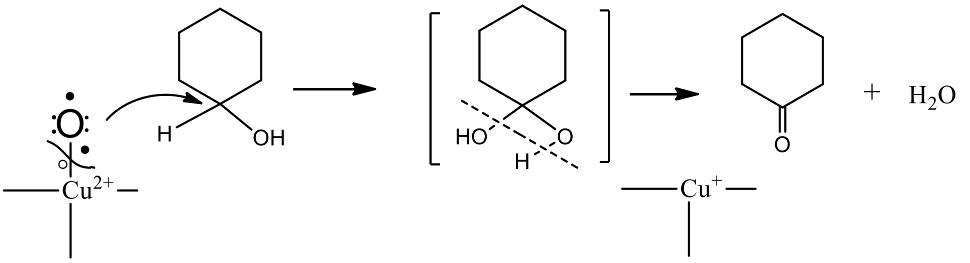
In TPR spectra for practically all studied samples the CO_2 formation, as a result of full cyclohexanol oxidation, is observed at temperatures higher 250°C as rule (Fig. 1, 2; Table 1, 3). More active towards CO_2 formation are $MnO_2/Al_2O_3(SiO_2)$ samples, unsuitable for selective alcohol oxidation. For the most part, the oxidation TPR spectra for alumina and silica as carriers are strikingly different, for instance, for supported Bi_2O_3 (Fig. 1). On the whole, oxides supported by alumina are more active (Table 1). A sample can be considered active if in its TPR spectrum the intensity of the fragment ion (55 a.u.m.) of cyclohexanone exceeds one of splinter cyclohexanol ion 57 a.u.m. at peaks. The influence of a carrier on the activity of supported catalytic oxide is a separate important question that is not discussed here.

The supported $Cr_2O_3/Al_2O_3(SiO_2)$ samples were not active in the oxidation of alcohol, but unexpectedly for us supported SnO_2 and Bi_2O_3 oxides showed not bad activity towards cyclohexanone formation (Table 1). Thus, among the studied samples, some individual oxides are suitable for the oxidation of cyclohexanol into cyclohexanone. Their activity decreases in such order: $MoO_3/Al_2O_3 > V_2O_5/SiO_2 > Fe_2O_3/Al_2O_3 > Bi_2O_5/Al_2O_3 > TiO_2/SiO_2 \approx CeO_2/Al_2O_3 > TiO_2/Al_2O_3 > SnO_2/Al_2O_3$.

Reaction proceeding

In our experiments at low pressure (~ 10^{-3-5} Tor in cuvette), oxygen for the reaction can be generated from oxide lattice only according to the equation $2CuO = Cu_2O + 1/2O_2$, for instance. A possible oxidation scheme could be written as

$$-^{IV}Cu^{2+}\ -^{III}O^{-} + C_6H_{11}OH \rightarrow -^{IV}Cu^{+}\square + C_6H_{10}O + H_2O \quad (1)$$



Active surface oxygen ion returns an electron to Cu^{2+} ion and formed O atom attacks the adsorbed cyclohexanol molecule. Note, the formed oxygen atom is easier attached to alcoholic $-CH_2OH$ group with a reduced electron density (or a large chemical shift) on the carbon atom [6]. As result, molecules of cyclohexanone and water, and a virtual oxygen atom vacancy □ or a hole are formed. Obviously, that activation reaction energy is determined by the energy of broken surface Me-O bonds. Studied samples changed their color after the experiment, for instance, light yellow CeO_2/Al_2O_3 turned brown that chartered for Ce_2O_3.

How is it possible to estimate the energy of Me-O bond in the surface-active site? There are many data on the heat of oxygen chemisorption Q_{O2} on oxides, and the known correlation between Q_{O2} and activation energy $E_a = E_0 – 0.5\ Q_{O2}$ or $lgW = a - bQ_{O2}$, where W –reaction rate, has been determined [8]. We have tried to obtain TPD profiles of O_2 chemisorbed on studied oxides, as $E_{des} = Q_{O2\ max}$, but reliable, repeatable results did not obtain, even after preliminary calcining samples and adsorption of pure oxygen. Boreskov with co-workers [8] have measured the O_2 pressure (10^{-1}-10^{-4} Tor) above several oxides heated at various temperatures (150-600°C) and calculated using the Clapeiron equation the q_o values named “binding energies of oxygen”. These q_o values are useful for estimating the ability of oxides to lose oxygen (Table 2).

The estimation of energy of surface Me-O bond could be based on a standard enthalpy formation of oxide but necessary to consider the coordination number (CN_o) of oxygen ions in lattice and the circumstance that for O^{2-}ion on the surface its coordination number decreases by 1. For instance, for $^{IV}Cu^{IV}O$ with $[OCu_4]$ tetrahedrons (O sp^3-hybridization) and flat $[CuO_4]^{6–}$ squares (Cu dsp^2), the binding energy of surface Cu-O could be calculated as $E_{Cu\text{-}O} = \Delta H^0_f\ (CN_o\text{-}1)/CN_o^2 = 37^*\ 3/16 = 7$ kcal/mol, and for $^{VI}Mn^{III}O_2$ with rutile’s structure $E_{Mn\text{-}O} = 125^*2/9 = 28$ kcal/mol. Such calculated $E_{Me\text{-}O}$ values for studied oxides are presented in Table 2. These values are varied from 51 kcal/mol for WO_3 to 7 kcal/mol for CuO (Table 2).

The calculated enthalpies (ΔH_R) of the reactions of decomposition of higher oxides into lower ones with the release of oxygen are changed within 90-20 kcal/mol (Table 2). Electron affinity (EA) of higher oxides is undoubtedly a useful parameter because it reflects their ability to change a charge of Me-cation ($Me^{n+1} + e \rightarrow Me^{n+}$), but such data are available for some oxides only (Table 2). Standard electrode potentials also are useful. For example, comparison of E_0=0.77 v for Fe^{3+} +e =Fe^{2+} and E_0 = 0.15 v for $Cu^{2+} + e = Cu^{+}$ allows to say that Fe_2O_3 is a stronger oxidizer than CuO.

However, the comparison of experimental T_m^{55}, E_a results (Table 1) and $E_{Me\text{-}O}$, ΔH_R values, presented in Table 2, does not show any correlations.

Consider a possible way for the oxidation of adsorbed alcohol molecule with the participation of surface oxygen ion of oxide, for instance, CuO. A surface oxygen ion with an unpaired electron can exist either as

-CuOH group or as a strained $-Cu-O^{*}-Cu-$ bridge. Such sites “sleep” until they are attacked by adsorbed alcohol molecules. In the case of bridging structure, the sum reaction is written as

$$-Cu^{2+}\text{-}O^{*}\text{-}Cu^{2+}\text{-} + C_6H_{11}OH = 2\ –Cu^{+}\square + C_6H_{10}O + H_2O.$$

In the case of –Cu-OH group, split-off $OH^{\bullet}$ radical could attack the hydrogen atom of β-CH_2 group of cyclohexanol, forming water and 3-cyclohexene-1-ol (m/e=54). Of course, hydroxyl groups and strained bridges may affect oxidation only at the beginning of a reaction that proceeds with the participation of molecular O_2 in the gas phase.

So as the result of the first catalytic acts, surface $-Cu^{+}\square$ ions are formed that are capable to chemisorb O_2 molecules, forming $-Cu^{2+}$-O-$O^{\bullet}$, and then 2 $-Cu^{2+}$-$O^{\bullet}$ sites. As the energy of single Cu-O and -O-$O^{\bullet}$ bonds is approximately two times less than in O_2 molecule (118 kcal/mol), obviously that these surface sites are a source of active oxygen for oxidation. At forming active sites by reaction $-Me^{n+}\square + O_2 \rightarrow -Me^{n+1}$-O-$O^{\bullet}$, one O-O bond in O_2 (~54 kcal/mol) is brooked and $-Me^{n+1}$-O one is formed. If $E_{Me\text{-}O} < E_{O\text{-}O}$, the chemisorption could be endothermic, but the $2-Me^{n+}\square + O_2 \rightarrow 2-Me^{n+1}$-$O^{\bullet}$ oxygen chemisorption is always exothermic. The regeneration of active sites is a complicated question that is not discussed here.

Table 2. **Several physical-chemical parameters of individual oxides.**

Oxide	- ΔH_f^{0s},* kcal/mol	$E_{Me\text{-}O}$,** kcal/mol	q_o[8], kcal/mol	Oxide – O	ΔH_R, kcal/mol	EA, eV***
$^{VI}Ti^{III}O_2$	226	50	59	$2TiO_2 = Ti_2O_3 + O$ $Ti^{4+}[Ar] \rightarrow Ti^{3+}[Ar]3d^1$ $Ti^{4+} + e = Ti^{3+}$, E_0=-0.04v	87	1.59
$^{V}V_2{}^{II}O_5$	378	92	43	$V_2O_5 = V_2O_3 + O_2$ $V^{5+}[Ar] \rightarrow V^{3+}[Ar]3d^2$	80	-
$^{VI}Mn^{III}O_2$	125	28	20	$2MnO_2 = Mn_2O_3 + O$ $Mn^{4+}[Ar]3d^3 \rightarrow Mn^{3+}[Ar]3d^4$	20	2.06
$^{VI}Fe_2{}^{IV}O_3$	197	38	33	$Fe_2O_3 = 2FeO + O$ $Fe^{3+}[Ar]3d^5 \rightarrow Fe^{2+}[Ar]3d^6$ $Fe^{3+} + e = Fe^{2+}$, E_0=0.77v	68	3.06
$^{IV}Cu^{IV}O$	37	7	19	$2CuO = Cu_2O + O$ $([Cu^{3+}\text{-}O]^{+} = [Cu^{2+}\text{-}O])$ $Cu^{2+}[Ar]3d^9 \rightarrow Cu^{+}[Ar]3d^{10}$ $Cu^{2+} + e = Cu^{+}$, E_0=0.15v	34	1.78
$^{IV}Mo^{II}O_3$	181	45	53	$2MoO_3 = Mo_2O_5 + O$ $Mo^{6+}[Kr] \rightarrow Mo^{5+}[Kr]4d^1$	-	3.17
$^{VI}Sn^{III}O_2$	140	31	-	$SnO_2 = SnO + O$ $Sn^{4+}[Kr]4d^{10} \rightarrow Sn^{2+}[Kr]4d^{10}5p^2$ $Sn^{4+} + 2e = Sn^{2+}$, E_0=0.15v	72	-
$^{VIII}Ce^{IV}O_2$	261	49	-	$2CeO_2 = Ce_2O_3 + O$ $Ce^{4+}[Xe] \rightarrow Ce^{3+}[Xe]4f^1$ $Ce^{4+} + e = Ce^{3+}$, E_0=1.61v^1	90	-
$^{VI}W^{II}O_3$	202	51	55	$WO_3 = WO_2 + O$ $W^{6+}[Xe]4f^{14} \rightarrow W^{4+}[Xe]4f^{14}5d^2$	60	3.30
$^{VI}Bi_2{}^{IV}O_3$ BiO_2 $[BiO][BiO_3]$	140	26	-	$[Bi^{3+}O][Bi^{5+}O_3] = {}^{VI}Bi_2{}^{IV}O_3$ $Bi^{5+}[Xe]4f^{14}5d^{10} \rightarrow$ $Bi^{3+}[Xe]4f^{14}5d^{10}6p^2$	60	3.30

* from: Turova N. Ya. Reference tables on inorganic chemistry. “Khimiya”, 1977; https://webbook.nist.gov/chemistry/.

** $E_{Me\text{-}O} = \Delta H^0_f\,(CN_o\text{-}1)/CN_o^2$

***https://webbook.nist.gov/chemistry/

It should be noted such an interesting option. With an excess of adsorbed alcohol, its chemisorption on the $-Cu^{+}\square$ sites with dehydrogenation to aldehyde (or ketone) is not excluded. The mechanism may be similar to that described in [7]: an oxygen atom of alcoholic -OH group exchanges the hydrogen atom for an electron from $-Cu^{+}$ ion, forming $-Cu^{2+}$-O-CH_2-R species; formed $H^{\bullet}$ atom attacks the C-H bond forming H_2 and aldehyde with the return of the “borrowed” electron to Cu^{2+} ion. The hydrogen will be oxidized in the presence of oxygen to water so that the total reaction (1) does not change. Known data on the oxidation of methanol to formaldehyde confirm this pathway.

What is a typical number of active sites on the oxide surface? According to the results on chemisorption of methanol on numerous individual oxides [9], the typical concentration of active sites is ~ 7 10^{14} site/cm^2 [10]. In work [11] the reasonable concentrations of active oxygen $[O^{*}]$~$[Cu_{surf}]$ = 1.2-

2.6 site/nm^2 (1.2 - 2.6 10^{14} site/cm^2) for CuO-CeO_2 mixed oxides have been determined. The best CuCeOx–CP catalyst was capable to oxidize of CO at 60°C with rate $1.2 \cdot 10^{-8}$ mol CO/m^2/s, $7 \cdot 10^{-7}$ mol CO/g$_{cat}$/h, TOF = 10^{-3}–10^{-2} s^{-1} [11] that corresponds to $7.2 \cdot 10^{11}$ molecule/cm^2/s ($7.2 \cdot 10^{-3}$ molecule/ nm^2/s, TOF = $3 \cdot 10^{-3}$ s^{-1}) or to space yield time SYT= 5mmol/g$_{cat}$/h. Note, that for an industry catalyst productivity, as rule, must be higher than this SYT value. The turnover frequency TOF = $3 \cdot 10^{-3}$ s^{-1} means that during 1 sec the 300 sites are capable to oxidize only one molecule of CO as follows from the calculation of 2.1 10 ^{14} (site/cm^2) / $7.2 \cdot 10^{11}$ (molecule/cm^2/s) = 300 site s/molecule.

It’s possible to calculate the collisions number of CO with the active sites in the experiment performed in [11]: 333 K, 1 vol% CO at normal pressure (partial $P_{CO} = 10^{-1}$ bar [N/cm^2]), using Hertz-Knudsen formula $F = P/(2\pi mkT)^{1/2} = P\,N_A/(2\pi MRT10^{-3})^{1/2}$ [molecules/cm^2/s], where N_A – 6.02 10^{23} Avogadro number [molecules/g-mol)], P -partial pressure [N/cm^2], $M=mN_A$ molecular weight [g/mol], R= 8.3 [J/(mol K]. Calculated collisions $F_{CO\text{-}Cu} = 2.7 \cdot 10^{22} P_{CO}/[Cu_{surf}] = 2.7 \cdot 10^{21}/2 \cdot 10^{14} \sim 10^7$ [CO collisions/site/s]. This calculation demonstrates the possibility of proceeding TPR reaction of absorbed cyclohexanol with the Me-O• sites even under 10^{-3} Tor vacuum ($P \sim 10^{-6}$ bar) when the collision number exceeds the [Me-O•] sites by 2-3 orders.

The observed in [11] CO oxidation rate was $7.2 \cdot 10^{11}$ molecules/cm^2/s, i.e. the proportion of active, reacting CO molecules is $N^*/N = 7.2 \cdot 10^{11}/3 \cdot 10^{21} \sim 2 \cdot 10^{-10}$. By Boltzmann distribution, $N^*/N = e^{-E/RT} = 2 \cdot 10^{-10}$, and the active CO molecules must have the energies

$E \geq RT \ln 2 \cdot 10^{10} \sim 11$ kcal/mol, significantly exceeding average thermal energy of molecules $\varepsilon = 3/2 \cdot RT \sim 1$ kcal/mol at 333 K.

Mixed oxides

As known, slow desorption of reaction product is capable to brake oxidizing reaction, and for a selective catalyst must observe “consistency between the rates of formation and desorption of oxidized product” [5]. In the case of gas-phase alcohol oxidation, reaction temperatures > 150°C are suitable for the quick desorption of formed aldehydes (ketones). Therefore, a question on the synthesis of oxide systems capable of effectively releasing active oxygen at 150-200°C is greatly actual. We have used the way for search of active mixed oxides based on a decrease in the coordination number of O^{2-} ions (CN_O) in the framework of mixed oxide in comparison with individual active oxide. At that, the bond Me^{n+}-$O^{\bullet}$ in the surface species could be weakened, and the oxidation reaction accelerated. An O^{2-} ion has different coordination numbers in oxide lattices equal to 4 (sp^3-hybridization, CuO), 3 (sp^2, TiO_2), or 2 (sp, WO_3). Decreasing CN_O formally leads to increasing electron density on O^{2-} ion, that should weaken Me-O bond. For instance, the formation of copper tungstate by formal reaction ${}^{IV}Cu^{IV}O + {}^{VI}W^{II}O_3 \rightarrow {}^{IV}Cu^{VI}W^{8/3}O_4$ decreases formal CN^f_O from 4 to 8/3 in comparison with CuO, but increases one from 2 to 8/3 according to WO_3. The formal CN_O value is calculated from an electrical neutrality of the lattice: $(2^+/4) + (6^+/6) + 2\,(2^-/CN^f_O) = 0$, whence $CN^f_O = 8/3$. Obviously, the O^{2-} ions are characterized by the integer CN_O= 2 or 3. The proportion of ${}^{II}O^{2-}$ions (X) with CN_O=2 is calculated from the equality $2X + 3(1-X) = 8/3$, whence $X = 1/3$, and the proportion of ${}^{III}O^{2-}$ions is 2/3. Then, a probability of the ${}^{IV}Cu$-${}^{II}O$ –${}^{VI}W$ (bond) species formation in $CuWO_4$ lattice is equal $W = 1/2\ 1/3 = 1/6$, i.e. [${}^{IV}Cu$- ${}^{II}O$ –${}^{VI}W$] ≤ 1/6 [$Cu_{\Sigma}{}^{2+}$]. With existence of such species on the surface, the –Cu_s-${}^{II}O^{\bullet}$ sites could be more active in comparison with pure CuO.

In work [12] the crystalline dark gray $CuWO_4$ samples from copper nitrate and sodium tungstate have been obtained as effective photocatalyst ($E_g \sim 2.2$ eV). In calculated lattice, the double [CuO_4] squares and [WO_6] octahedrons are present [12], i.e. Cu^{2+} and W^{6+} ions keep their coordination numbers in the structure of mixed oxide. Also, the proportion of ${}^{IV}Cu$-${}^{II}O$ – ${}^{VI}W$ structures in the lattice is equal to 1/3 [12].

In Fig. 2 and Table 3 the results of testing mixed oxides supported by alumina are presented. All prepared mixed oxides, including CuO-WO_3/Al_2O_3, are more active in comparison with individual supported oxides (Table 1, 3). Quite unexpected for us were the successful combinations of Bi_2O_3 and MoO_3 with SnO_2, and WO_3 and MoO_3 with CuO (Fig. 2, Table 3). We also managed to synthesize a quite good composition of CuO-CrO_3 on Al_2O_3 that oxidizes cyclohexanol into cyclohexanone at 110°C without its dehydration in fact (Fig. 2). Also, this sample catalyzes the oxidation of ethylene glycol – methanol vapour mixture into methyl glycolate at 200°C with high selectivity [14].

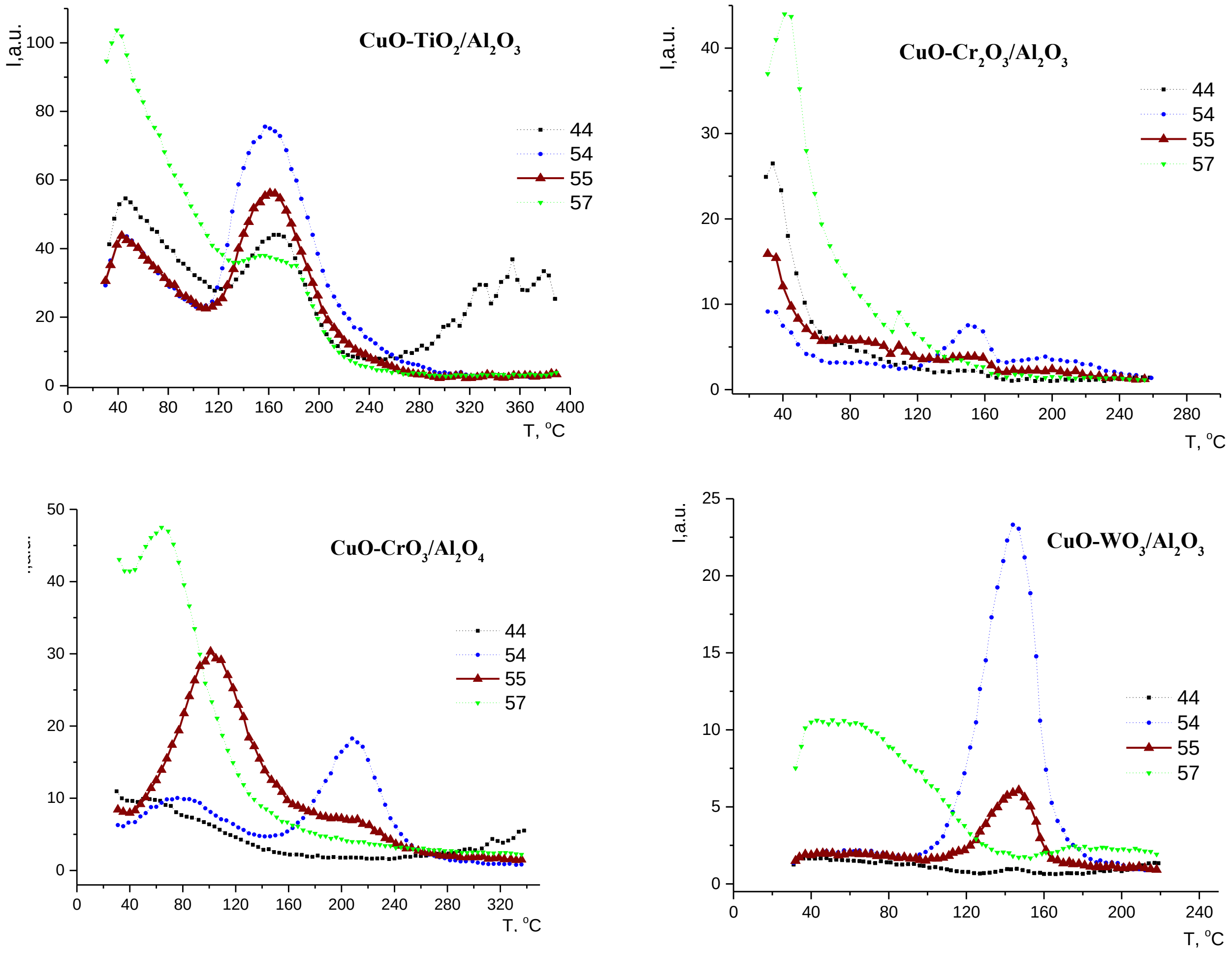


Fig.2. TPR profiles of cyclohexanol oxidation on mixed supported oxides: 44 a.u.m. – CO_2; 54 a.u.m. – cyclohexene; **55 a.u.m. – cyclohexanone**; 57 a.u.m. - cyclohexanol.

Table 3. **Temperatures of peak formation of cyclohexanone (T_m^{55}) and cyclohexene (T_m^{55}) from cyclohexanol adsorbed on mixed supported oxides**

Sample	T_m^{55}, °C	T_m^{54}, °C	T^{44}, °C *
$CuO\text{-}TiO_2/Al_2O_3$	160	160	>240
$CuO\text{-}Cr_2O_3/Al_2O_3$	155	155	>260
$CuO\text{-}CrO_3/Al_2O_3$	110	210	>260
$CuO\text{-}Fe_2O_3/Al_2O_3$	140	140	>250
$CuO\text{-}MoO_3/Al_2O_3$	200	200	>240
$CuO\text{-}WO_3/Al_2O_3$	150	150	>200
$MoO_3\text{-}SnO_2/Al_2O_3$	150	150	>270
$Bi_2O_3\text{-}SnO_2/Al_2O_3$	165	165	>250

*) temperature of CO_2 formation

The TPR experiments show that $CuO\text{-}Cr_2O_3/Al_2O_3$ sample with spinel structure of supported $CuCr_2O_4$ ($[CuO_4]^{6-}$ tetrahedra) is more active in cyclohexanol oxidation (T_m^{55} =155°C) than CuO/Al_2O_3 with flat $[CuO_4]^{6-}$ squares (T_m^{55} = 235°C) (Table 1, 3). Ion Cu^{2+} has 9 electrons at 3d level, and for forming 4 σ-bonds in square of $[CuO_4]^{6-}$ are suitable $3d_{x2-y2}$, 4s and $4p_x$, $4p_y$ orbitals [13]. For forming $[CuO_4]^{6-}$ tetrahedron the 4s and $4p_x$, $4p_y$, $4p_z$ orbitals of Cu^{2+} are suitable only [13]. An O^{2-} ion with 8 electrons at 2s, 2p levels forms 4 equal σ-bonds at sp^3-hybridization. The electrons density is shifted to more electronegative oxygen atoms. As energy of 4p level is higher than 3d one [13], the Cu_{sq} –O bond is stronger than Cu_{tetr}–O according to the experiment (Table 3).

Conclusions

TPR method with mass-spectrometric control of reaction products is useful for the study of oxidizing reactions on oxides. Some individual oxides supported on alumina and silica oxidize cyclohexanol into cyclohexanone at 130 – 240°C. Their activity decreases in the following order: MoO_3/Al_2O_3 > V_2O_5/SiO_2 > Fe_2O_3/Al_2O_3 > Bi_2O_5/Al_2O_3 > TiO_2/SiO_2 ≈ CeO_2/Al_2O_3 > TiO_2/Al_2O_3 > SnO_2/Al_2O_3.

Some mixed oxides, especially CuO-CrO_3/Al_2O_3, CuO-MoO_3/Al_2O_3, MoO_3-SnO_2/Al_2O_3, Bi_2O_3–SnO_2 /Al_2O_3, are more active in the cyclohexanol oxidation and could be applied for selective oxidation of other alcohols including glycerol and ethylene glycol. In search of a suitable catalyst, a coordination number of O^{2-} as well as Me^{n+} ions in oxide framework could be taken into account.

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Окиснення на поверхні оксидів: термопрограмоване окиснення циклогексанолу

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Метод термопрограмованої реакції (ТПР) з мас-спектрометричним контролем продуктів застосовано для дослідження реакції окиснення циклогексанолу до циклогексанону на індивідуальних та змішаних оксидах, нанесених на γ-Al_2O_3 та силікагель. В зареєстрованих ТПР профілях окиснення циклогексанолу температура макси-мальної швидкості утворення циклогексанону (55 а.о.м.) змінюється від 125°C для MoO_3/Al_2O_3 до 235°C для менш активного CuO/Al_2O_3, що відповідає зміні енергії активації реакції від 19.9 до 25.4 ккал/моль. В ТПР мас-спектрах спостерігаються також піки утворення циклогексену (54, 67 а.о.м.), як продукту дегідратації циклогесанолу, та CO_2 (44 а.о.м.), як продукту його повного окиснення за температур > 200°C. Каталітична активність нанесених індивідуальних оксидів щодо утворення циклогексанону зменшується в ряду $MoO_3/Al_2O_3 > V_2O_5/SiO_2 > Fe_2O_3/Al_2O_3 > Bi_2O_5/Al_2O_3 > TiO_2/SiO_2 \approx CeO_2/Al_2O_3 > TiO_2/Al_2O_3 > SnO_2/Al_2O_3$. Оскільки «реакційний» кисень в умовах нашого ТПР експерименту може постачатись тільки граткою оксиду, їх активність обумовлюється різною енергією поверхневих Me – O зв'язків. Запропоновано підхід до пошуку змішаних активних оксидів, що базується на зменшенні координаційного числа іонів O^{2-}, який підтверджено на прикладі $CuO\text{-}WO_3/Al_2O_3$ каталізатора. Встановлено, що змішані оксиди, нанесені на γ-Al_2O_3, особливо, $CuO\text{-}CrO_3/Al_2O_3$, $CuO\text{-}MoO_3$ /Al_2O_3, $MoO_3\text{-}SnO_2/Al_2O_3$ та $Bi_2O_3\text{–}SnO_2/Al_2O_3$, є більш активними в $C_6H_{12}O + 1/2O_2 \rightarrow C_6H_{10}O + H_2O$ окисненні. Слід зазначити, що синтезований $CuO\text{-}CrO_3/Al_2O_3$ каталізатор забезпечує утворення циклогексанону практично без побічної дегідратації циклогексанолу і може застосовуватись для окиснення етиленгліколю з метанолом до метилгліколату. ТПР експеримент показує, що $CuO\text{-}Cr_2O_3/Al_2O_3$ з шпінельною структурою нанесеного $CuCr_2O_4$ ($[CuO_4]^{6-}$ тетраедри, Cu^{2+} $4s4p^3$-гібридизація) є більш активним в окисненні циклогексанолу (T_m^{55} =155°C), ніж CuO/Al_2O_3 з пласкими $[CuO_4]^{6-}$ квадратами, Cu^{2+} $3d4s4p^2$-гібридизація (T_m^{55} =235°C). Це пояснюється меншою енергією Cu-O зв'язків при $4s4p^3$-гібридизації іонів Cu^{2+}.

Ключові слова: гетерогенний каталіз, окиснення на оксидах, нанесені каталізатори, змішані оксиди