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NEW POSSIBILITIES OF LOW-TEMPERATURE GENERATION OF ACTIVE CENTERS DURING HETEROGENEOUS-HOMOGENEOUS ACTIVATION OF PROPANE ON SILICA GEL SURFACE, MODIFIED WITH ZnO BY THE SOL-GEL AND CHEMICAL TRANSPORT REACTION METHODS

T. O. KAMALYAN [1*], P. S. GUKASYAN [2**], S. M. VARDAPETYAN [3***],
O. A. KAMALYAN[1****]

[1] *National Agrarian University of Armenia*
[2] *A.B. Nalbandyan Institute of Chemical Physics, NAS RA of Armenia*
[3] *Chair of Pharmaceutical Chemistry and Pharmacognosy,*
Institute of Pharmacy, YSU, Armenia

By the example of heterogeneous catalytic oxidation of propane the process of peroxide radicals transfer from the surface of catalysts into the reactor volume is studied. For comparison ZnO/SiO$_2$ contacts obtained by depositing the active phase on the silica surface by sol-gel and chemical transport reaction (CTR) were used. It was established that for the case both the temperature of the radicals transfer from the surface to the volume and the value of the activation energy are lower than in the case. It was shown that the modification of the silica gel surface with zinc oxide by the CTR method is more effective as compared with the sol-gel method. It is established that in both cases the active phase of the catalyst exhibits paramagnetic properties. On the basis of the given, semi-artificial kinetic method of radical detachment, the obligatory mechanism of activation failed.

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Introduction. Zinc oxide has wide applications in catalytic processes as an active phase of catalysts in the processes of dehydrogenation, dehydration, addition, and decomposition of pollutants [1]. Thin films and coatings of ZnO have a variety of physical and chemical properties, among which unique piezo- and pyro-effects, adsorption and reactions of gases on the ZnO surface, etc. [2, 3] occupy a prominent place. It is due to these properties that special attention is paid to the surface properties of ZnO [4] depending on the methods of its deposition on various solid contacts. A number of methods for surface modification with highly dispersed ZnO are known, including aerosol pyrolysis, gas deposition, sol-gel technology, etc.

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[*] E-mail: kamalyan@ysu.am
[**] E-mail: petros@ichph.sci.am
[***] E-mail: svardapet@ysu.am
[****] E-mail: kamalyan@ysu.am

One of the new and highly efficient methods of chemical modification of the surface of aerosil [4] and silica gel [5] with zinc oxide is the chemical transport reaction (CTR) method. In [6], the high activity of copper(II) oxide deposited on the solid surfaces of various carriers by the CTR method was demonstrated. It was shown in [4, 5], that when the surface of silica gel is modified with ZnO by the CTR method, the active component ZnO is deposited mainly in pores with sizes of 8–10 *nm*. Bearing in mind that one of the important characteristics of catalysts is their specific surface area, in this case the surface of the porous carrier was modified without a significant change of this parameter. The search for conditions leading to an increase in the catalytic activity of ZnO is urgent since this compound is widely using in various oxidation and hydrogenation processes.

Using the EPR method in [7] the process of peroxide radicals release from the surface to the reactor volume during propane oxidation on various surfaces modified with titanium carbides was studied. It was found that on active phases containing small amounts of oxygen, the release of peroxide radicals from the surface to the volume occurs with an activation energy of 56.3 *kJ*/*mol*, and the lower temperature limit for the detection of radicals is about 15–20 degrees lower than on a stoichiometric (oxygen-free) carbide. It was also shown that the activity of the carbide phase is conditioned by the deficiency of carbon and oxygen in the carbide sublattice of titanium. The mechanism of joint simultaneous activation of hydrocarbon and oxygen on this new active phase was also considered.

Based on the foregoing, in this work the task is to study the process of the release of peroxide radicals from the surface to the volume depending on the methods of ZnO deposition on various solid contacts by the example of propane oxidation.

The information obtained will make it possible to expand the field of ZnO application in various catalytic processes depending on the methods of surface modification with highly dispersed zinc oxide.

Experimental Part. Highly dispersed silica gel was used as a solid carrier, and ZnO of “Sigma Aldrich” trademark, 40% aqueous solution of hydrogen peroxide of “chemically pure” grade, surfactant “dodecyl chloride”, propane with a purity of 98.5%, oxygen with a putity of 99% were used in experiments. Chromatographic analysis was performed on a column packed with Chromaton with an OV-17 applied liquid phase. Analysis conditions: column length of 2 *m*, 2 *mm* in diameter, nitrogen as a carrier gas with flow velocity of 25 *mL*/*s*, temperature 433 *K*, flame ionization detector.

Preparation of Catalysts. Initially, tablets were prepared from highly dispersed silica powder. A silica gel tablet weighing about 0.1 *g* and dimensions 1×1×0.1 cm^3 was prepared by pressing ultrapure silica gel under a pressure of 1500 kg/cm^3 without a binder. The catalyst 1, that is by the sol-gel method, was prepared according to the method described in [8, 9] by applying ZnO thin layer on the surface of the above-described tablets from alcohol suspension in the presence of a surfactant. The catalyst 2 was prepared by applying ZnO layer to the surface of silica pellets using CTR method described in [5].

The experiments were carried out on a flow vacuum installation. A cylindrical quartz reactor 16 *cm* long and 1.5 *cm* in diameter was installed in an electric furnace with a KVP-503 thermostat for temperature control. The accuracy of maintaining the temperature was ±0.5 *K*. Paramagnetic properties of the solid sample, as well as the radicals transfer to the volume, were studied by the method of electron paramagnetic resonance using SE/X-2543 radio spectrometer in the range of 3000–4000 *Oe* at a frequency of $\nu = 9.39$ *GHz*.

Two tablets of the sample under study were placed vertically on a quartz grid parallel to each other at a distance of 5 *mm*. The reaction mixture passed in a stream ($\tau_k = 0.1$ *s*) through the reactor with the catalyst and was directed to the finger-like extension of the Dewar flask with liquid nitrogen. The latter was in the resonator of an EPR radio spectrometer [10]. Experiments were carried out with mixtures of the reagents with a pressure ratio $P_{C_3H_8} : P_{CO_2} : P_{O_2} = 1 : 1 : 0.1$. The pressure of the mixture in the reaction zone was 0.05 *Torr*.

Results and Discussion. First of all, to obtain reproducible results, the reactor was rinsed with a 10% solution of hydrofluoric acid and dried. After that, oxidation reactions were carried out in the reactor in the high-temperature region (720 *K*). As experiments have shown, the activity of catalysts increases with time reaching a limiting value after 90 *min*. This ensured the reproducibility of the experimental results. It was shown in [2] by the EPR method that the catalytic activity of ZnO is mainly associated with oxygen vacancies formed during the process. For this reason, data on the EPR study of the active phase may be of interest. It should be noted that EPR is a very powerful method for studying point defects and deficiency states of the sublattice in complex solid-phase compounds. The fact is that compounds, where the spins of electrons responsible for chemical bonds are paired, do not have an EPR signal. Therefore, defect-free ideal crystals are diamagnetic. It should be noted that the effect of propane oxidation on the structure of such compounds should lead to the appearance of point defects and paramagnetic centers. This is directly demonstrated by the example of slow oxidation of propane in the reactors with salt-covered walls [10]. We carried out EPR studies with ZnO without and with activation. The EPR spectrum of ZnO before and after activation is shown in Fig. 1.

From the data, presented in Fig. 1, it follows that after activation the sample exhibits activity in a magnetic field 3340–3395 *Oe*, and *g*-factor was calculated by the formula $g = g_{\mathrm{DPPH}} (1 + \mathrm{H} / \mathrm{H}_{\mathrm{DPPH}})$. It was found that $g = 1.975$ *Oe*. The presence of an asymmetric signal with $g = 1.975$ *Oe* unambiguously indicates the presence of an oxygen vacancy (V_{o+}) in the oxide sublattice, and the shift of the *g*-factor towards low magnitudes is due to the anisotropy effect. As shown in [11], when chemically active particles interact with the surface of a solid, nonstoichiometric states are formed. Comparing the obtained result with the data of [12], we observe small changes in the values of the EPR spectrum parameters over the width and *g*-factor, which in turn is associated with the influence of the substrate. Zinc oxide is also widely used as a catalyst, filler, binder and decorative material. A feature of this compound is that it exhibits a deviation from the stoichiometric composition towards an excess of Zn in a fairly wide range. Some of the physical and chemical properties of ZiO, such as catalytic activity, are highly dependent on its stoichiometry.

Then two series of experiments were carried out using the catalyst 1 and the catalyst 2. The experiments were carried out using the mixtures $P_{C_3H_8} : P_{CO_2} : P_{O_2} = 1 : 1 : 0.1$. The mixture pressure in the reaction zone was 0.05 *Torr*, the temperature range was 620–720 *K* and the duration of the experiments was 30 *min*.

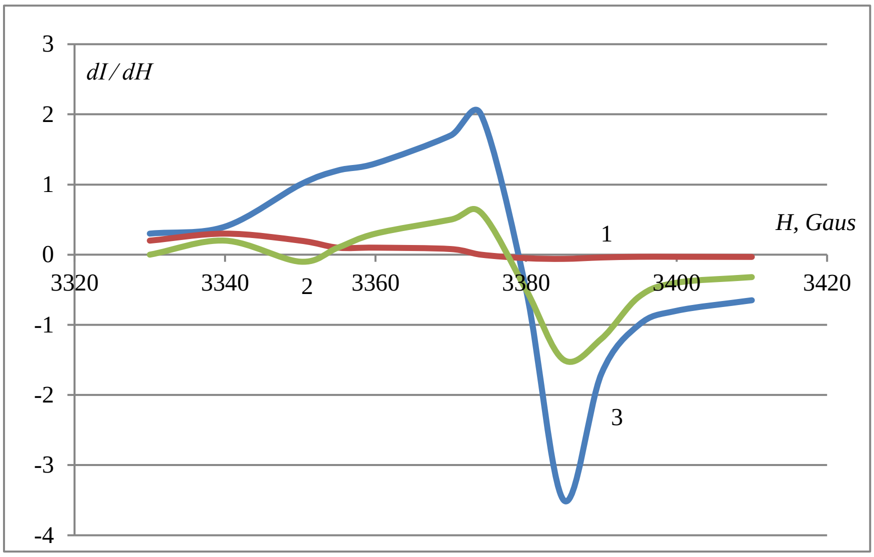

Fig. 1. EPR spectrum of ZnO: 1 – before activation; 2 – after vacuum thermal activation; 3 – activation by reaction, at *ν* = 9.39 *GHz*.

Experiments have shown that in both cases with the catalyst 1 and catalyst 2, alkyl peroxide radicals are detected, while hydroperoxide radicals are absent.

Fig. 2 shows the temperature dependence of radicals accumulation for two catalysts: 1 – catalyst 1; 2 – catalyst 2. It is evident from the data of Fig. 2, that the catalyst obtained by the CTR method is more active in comparison with the catalyst obtained by the sol-gel one. For the catalyst 1 the lower temperature limit for the detection of radicals is about 10–15 degrees lower, than for the catalyst 2.

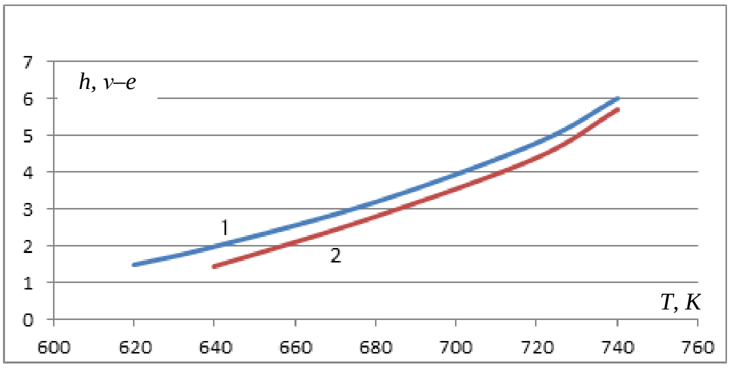

Fig. 2. Dependence of the accumulation of radicals (in arbitrary units) on temperature: $P_{C_3H_8} : P_{CO_2} : P_{O_2} = 1:1:0.1$; P_{total} = 0.05 *Torr*; 1 – catalyst 1; 2 – catalyst 2.

It was established that the release of alkyl peroxide radicals from the surface to the volume in the case of catalyst 1 occurs with an activation energy of 56.5 *kJ*/*mol*. In the second case it is 50.3 *kJ*/*mol*. An exemplary mechanism of joint simultaneous activation of hydrocarbon and oxygen on the catalysts 1 and 2 was considered. The HO_2 radicals formed on the surface decay faster [13] than are desorbed to the volume. Therefore, they were not detected, as shown in [14].

Conclusion. Thus, the modification of the silica gel surface with ZnO by the CTR method is more efficient as compared with the sol-gel method. Consequently, catalysts obtained by applying an active phase on the surface of various carriers using a chemical transport reaction can be successfully used for low-temperature generation of active radicals. As a result, new prospects for the application of the CTR method are opening up, as one of the simple and effective methods for obtaining new heterogeneous catalysts.

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Տ. Օ. ՔԱՄԱԼՅԱՆ, Պ. Ս. ՂՈՒԿԱՍՅԱՆ, Ս. Մ. ՎԱՐԴԱՊԵՏՅԱՆ, Օ. Ա. ՔԱՄԱԼՅԱՆ

ԶՈԼ-ԺԵԼ ԵՎ ՔԻՄԻԱԿԱՆ ՏԵՂԱՓՈԽՄԱՆ ՌԵԱԿՑԻԱՅՈՎ ZnO –ՈՎ ՄՈԴԻՖԻԿԱՑՎԱԾ ՍԻԼԻԿԱՀՈՂԻ ՄԱԿԵՐԵՎՈՒՅԹԻՆ ՊՐՈՊԱՆԻ ՀՈՄՈԳԵՆ–ՀԵՏԵՐՈԳԵՆ ՑԱԾՐՋԵՐՄԱՍՏԻՃԱՆԱՅԻՆ ԱԿՏԻՎԱՑՄԱՆ ԱԿՏԻՎ ԿԵՆՏՐՈՆՆԵՐԻ ՍՏԱՑՄԱՆ ՆՈՐ ՀՆԱՐԱՎՈՐՈՒԹՅՈՒՆՆԵՐԸ

Պրոպանի տարասեռ-կատալիտիլ օքսիդացման ռեակցիայի օրինակով ուսումնասիրվել է կատալիզատորի մակերևույթի ակտիվ կենտրոններից պերօքսիդ ռադիկալների ծավալ դեսորբվելու գործընթացը: Համեմատելու համար օգտագործվել է սիլիկահողի մակերևութային ակտիվ ֆազի նստեցումից ստացված ZnO/SiO$_2$-ը զոլ-ժել և քիմիական տեղափոխման ռեակցիայիյ (ՔՏՌ) եղանակներով: Հաստատավել է, որ ՔՏՌ-ով ZnO-ով նախապես մոդիֆիկացված սիլիկաժելի մակերևույթի կատալիտիկ ակտիվությունն ավելի բարձր է, քան զոլ-ժել եղանակով մոդիֆիկացված սիլիկաժելի մակերևույթի ակտիվությունը: Հաստատվել է նաև, որ ստացված ակտիվ ֆազը երկու դեպքերում էլ ցուցաբերում է պարամագնիսական հատկություն: Ելնելով ռադիկալների սառեցման կինետիկական մեթոդով ստացված տվյալներից, քննարկված է պրոպանի ակտիվացման մեխանիզմը:

Т. О. КАМАЛЯН, П. С. ГУКАСЯН, С. М. ВАРДАПЕТЯН, О. А. КАМАЛЯН

НОВЫЕ ВОЗМОЖНОСТИ НИЗКОТЕМПЕРАТУРНОЙ ГЕНЕРАЦИИ АКТИВНЫХ ЦЕНТРОВ ГЕТЕРОГЕННО-ГОМОГЕННОЙ АКТИВАЦИИ ПРОПАНА НА ПОВЕРХНОСТИ КРЕМНЕЗЕМА, МОДИФИЦИРОВАННОЙ ZnO МЕТОДАМИ ЗОЛЬ-ГЕЛЬ И ХИМИЧЕСКОЙ ТРАНСПОРТНОЙ РЕАКЦИИ

На примере гетерогенно-каталитического окисления пропана изучен процесс переноса пероксидных радикалов с поверхности катализаторов в объем реактора. Для сравнения использовались контакты ZnO/SiO$_2$, полученные осаждением активной фазы на поверхность кремнезема методами золь-гель и химической транспортной реакции (ХТР). Установлено, что в случае кантакта, полученного с использованием ХТР, как температура перехода радикалов с поверхности в объем, так и значение энергии активации ниже, чем в случае контакта, полученного золь-гель методом. Установлено также, что в обоих случаях активная фаза катализатора проявляет парамагнитные свойства. На основании данных, полученных кинетическим методом замораживания радикалов, обсужден механизм активации пропана.