THE STUDY OF MAGNETIC-PHAZE STATE OF (Ni, SB, CR, K)/Y·Al_2O_3 CATALYSTS AND ELECTRON PROPERTIES OF PROMOTORS IN PROPAN DEHYDROGENATION REACTION

S.A. JAMALOVA
Institute of petrochemical processes of NAS of Azerbaijan
Baku, N. Rafiyev str., 30

The results of investigation on establishment of the changes in the catalysts magnetic properties depending on the conditions of their synthesis, incineration temperature and duration have been presented in the article for comparison of these properties with the catalysts activity in propane dehydrogenation reaction. The interaction of Ni^{2+} ions with a carrier is established.

The paper deals with the study of (Ni, Sb, Cr, K)/y·Al_2O_3 magnetic-phase state of catalysts and electron properties of promotors with purpose to find out their interaction with the carrier (y·Al_2O_3) in propan dehydrogenation reaction.

From the point if view of catalysts the special meaning has the character of metal oxides and ion distributions on the surface and in the volume of the carrier in the dependence on preparing conditions, thermotreatment of catalysts and the influence of reaction medium on the temperature of magnetic phase transfer in the Neel's point.

To solve these tasks it is necessary to apply magnetic and thermal methods (thermal capacity and temperature conductivity), allowing to study the structures of catalysts. The catalysts samples, taken for analysis are distinguished by the conditions of their preparing.

The catalysts were prepared under conditions of the atmospheric pressure and low atmospheric pressure (P=10-15mm·Hg).

The incineration time was variated from 1.5h to 5h. The incineration temperature was changed from 400°C to 650°C. For investigation of the influence of the dehydrogenation medium on the magnetic characteristics of catalyst, the propan dehydrogenation reaction at the temperature 580-620°C and propan valume velocity of feed 150-300h^{-1} is carried out on these catalysts.

The essential change of porouso-structural catalyst characteristics preparing in the conditions of lowed atmospheric pressure was established by the author earlier and in addition, the influence of these changes on the thermal conductivity and temperature conductivity (K) [1] was established also.

The magnetic permittivity (χ) of catalyst is investigated by Faraday method on the installation with photoelectric compensation [2] in the magnetic field strength interval 1000-7000 Gauss (Gs). The value χ of all investigated catalysts didn't depend on the field strength that shows on the absence of ferromagnetic impurities in the catalyst (metallic nickel). For calculation of χ and magnetic momentum (μ), the correction on the diamagnetism Al_2O_3, Sb_2O_3, K_2O and ions Ni^{2+}, Cr^{3+} was introduced.

The temperature change of magnetic phase transfer in the Neel's point (T_N) in the dependence on incineration temperature of samples was investigated by heat capacity method on the installation for measurements of thermal material coefficients by the impulse – light method [3,4].

The solution of the problem of the thermal distribution inside of the thermal isolated sample, boundered by two parallel is the base of this method.

The increase of the interaction between ions Ni^{2+} in the incinerated samples is confirmed by the increase of Neel's temperature and as a result the change of magnetic interaction energy is observed [5].

It is established by the author earlier, that the increase of incineration temperature of the catalyst up to 600°C increases the exchange interaction between ions Ni^{2+} and rises the catalyst activity [6].

The Bete-Payerlsa-Weissa (BPW) method was used for estimate of the change interaction.

The magnetic interaction energy of non-compensated spins of neighbouring ions at the room temperature is less, than value $kT(E_{magn}<kT)$, where k is Boltzmann constant, therefore the spins oriented almost antyparallelly and antiferromagnetism is observed. However, the energy, which equal to kT_2 is enough one to excite some fluctuations of summary magnetic moment of unpaired spin system. If the temperature is hire that Neel's temperature, then the magnetic interaction energy becomes more, than $kT(E_{magn}>kT)$ and therefore the ferromagnetism is destroyed and the system becomes paramagnetic one.

The changes of the magnetic permittivity (χ), the magnetic moment (μ), the Neel's temperature (T_N) and catalytic activity (Ni-Cr-Sb-K)/Al_2O_3 of the catalysts of the propan dehydrogenation, prepared in the conditions of lowed atmospheric pressure in dependence on the incineration temperature change ($T_{inc.}$) are presented in the fig 1.

With the increase of the incineration temperature from 400 to 650°C, T_N shifts to the high temperatures and increases from 220 to 270°C. The symbat change of T_N and A (activity) in the dependence on $T_{inc.}$ is observed.

The shift of T_N to the high temperature, when $T_{inc.}$ increases, shows that the antiferromagnetic interaction degree between metal ions increases. From another side, the formation process of catalyst structure can take place with the formation of new magnetic phases of types: $NiAl_2O_4$ and $NiSb_2O_6$.

As it follows from fig.1, the $T_{N.}$ and C_3H_6 yield increase with the increase of $T_{inc.}$. The symbat change and activity are caused by the active centers, which are the analogical phases, being in non-antiferromagnetic state. The forming antiferromagnetic phases at the temperature more, than 300-400°C destroy with the increase of incineration temperature. They become paramagnetic at the temperature higher, than T_N. In the internal $T_{inc.}$=580-600°C where the reaction goes, the catalyst will be in the paramagnetic state.

The Neel's temperature states constant and activity decreases at the temperature higher, than 650°C. Probably, it is caused by the formation of catalyst structure and new antiferromagnetic phases leading to the decrease of paramagnetic centers concentration..

In the fig.1 the dependence of magnetic moment (μ) of catalyst on the incineration temperature is shown. As it follows from fig.1, the increase of the μ with the increase $T_{inc.}$ from 400 to 650°C is observed. In the incineration temperature interval $T_{inc.}$=750°C the essential decrease of the paramagnetic centers concentration is observed. However, in this interval T_N states constant. It shows that with the order of catalyst structure the T_N states unchangeable and the activity decreases.

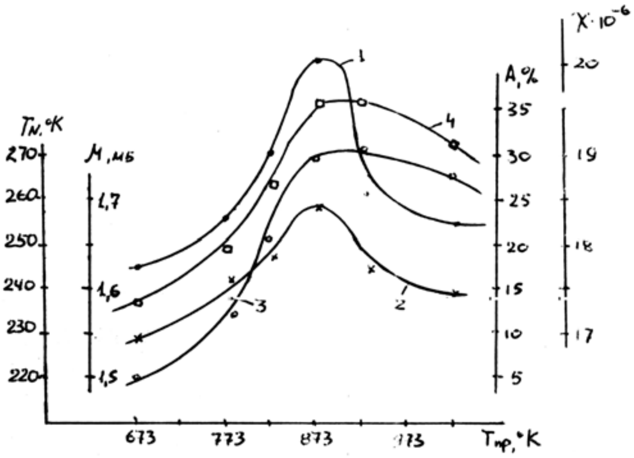

Fig.1. The dependence of magnetic characteristics (χ,μ) of (Ni-Cr-Sb-K)/γ·Al_2O_3 catalyst and Neel's temperature (T_N) on the catalyst incineration temperature ($T_{inc.}$°K)
1. magnetic permittivity (χ);
2. magnetic moment (μ, mB);
3. Neel's temperature (T_N°K);
4. catalyst activity (%mass.).

The decrease catalyst activity connects with the decrease of active catalyst surface in consequence of baking of catalyst poros in this case.

Thus, resuming the above mentioned, we can do the conclusion that the changes of activity and Neel's temperature allow to propose, that active centers in the propan dehydroqenation reaction are caused by the paramagnetic centers, which form at the increase of incineration temperature of catalyst higher, than $T_{N.}$

In the fig.2 the dependences of the magnetic permittivity and catalyst activity (Ni-Cr-Sb-K)/Al_2O_3 on the incineration time are shown. At the increase of the incineration time the magnetic permittivity increases and after 3,5 hours reaches the maximal value. The increase of the paramagnetic permittivity is caused by the increase of paramagnetic centers concentration. Later the decrease of χ value is observed (fig.2, curve 1.2). The identical picture is observed also for the dependence of the activity on the incineration time (fig.2, curve 3). Thus, the comparative date of permittivity and activity show, that catalyst activity is caused by the increase of the paramagnetic centers concentration. At this cause probably, the symbat change of activity and permittivity is observed.

The investigation of magnetic properties NiO-Al_2O_3 of catalyst gives the important information about the ions Ni^{2+} interactions and their localization in a lattice Al_2O_3.

The obtained results of magnetic moments are very interested. We propose, that Ni in the catalyst is as in the microcrystals NiO form, as ion Ni^{2+} form, introduced in a lattice Al_2O_3. As well known, that the theoretical value μ of the ion Ni^{2+} is equal to 3.4 mB in the octahedron empties, but the experimental one is equal to 3.0-3.2mB. The hydrate of protoxide of Ni has the layer structure, in which the every ion is in the octahedron, having six OH-groups.

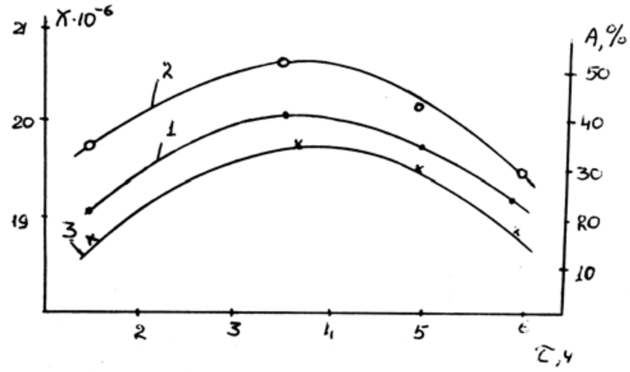

Fig.2. The dependence of magnetic permittivity and activity of (Ni-Cr-Sb-K)/γ·Al_2O_3 catalysts of propan gehydrogenation reaction on the incineration time of catalyst. 1. magnetic permittivity of fresh catalyst;
2. magnetic permittivity of waste catalyst;
3. catalyst activity (%mass.).

The results of the defining of magnetic permittivity (χ), calculated on 1 gr., and the magnetic moment (μ) for (Ni-Cr-Sb-K)/Al_2O_3 catalysts are given in the table 1.

The magnetic permittivity value (χ_{Ni}) of the catalyst, obtained under the usual conditions before the reaction (sample №1) is equal to $55{\cdot}10^{-6}$SGSE, but the magnetic moment value, calculated on the ion Ni^{2+} is equal to μ=2.81mB, that well agree with μ of ion Ni^{2+} for the pure spin value (2.83mB).

For the catalyst, prepared at the low atmospheric pressure (sample №2) the μ is equal to 3.1mB, that is accordance with μ for Ni^{2+}, being in the octahedron positions (μ=3-3.2mB).

The weak enough interaction between ions Ni^{2+} states constant in the non-incinerated samples of catalyst.

The magnetic properties of the systems (Ni-Cr-Sb-K)/γ·Al_2O_3, prepared at the low atmospheric pressure and incinerated from 400°C to 650°C, differ abruptly from the magnetic properties of catalysts, prepared under the usual conditions (sample №1). The differences are caused by the presence of antiferromagnetic microcrystals NiO. For the catalysts before and after the work in the propan dehydrogenation reaction, the χ_{Ni} and μ change from $16\text{-}22{\cdot}10^{-6}$ SGSE to 1.53-2.83mB correspondingly. The magnetic moments of samples before and after reaction, and incinerated up to 680C during 5 hours also are essentially less, than the magnetic moment value *(μ)* of the ion Ni^{2+}/μ=2,83 mB).

The obtained results show, that in the catalyst the big part of NiO is in the form of the large enough crystals of antiferromagnetic phase NiO with strong interaction between Ni ions, that explains the low values of χ_{Ni} and μ.

Table 1.

Magnetic characteristics of (Ni-Cr-Sb-K)/Al_2O_3 catalysts

Sample №	Catalyst composition, %	Treatment conditions ($T_{c.}$=650°C)				Makeweight m, mg	f	$A_{av}=\frac{f}{m}$	$\chi\cdot 10^{-6}$	μ, mB
		Incineration time	Pressure, mmHg	fresh	waste					
1	NiO – 3 Sb_2O_3 - 3 Cr_2O_3 – 7.5 K_2O – 2.5	5	760	fresh	-	6.6	12.21	1.85	55	2.81
2	- « -	5	15	fresh	-	5.21	13.96	2.68	68	3.11
3	NiO – 6 Sb_2O_3 - 8 Cr_2O_3 – 8 K_2O – 3.0	5	760	fresh	-	2.655	2.86	1.076	21	4.71
4	- « -	5	760	-	waste	6.515	5.798	0.89	16.46	1.53
5	- « -	5	15	fresh	-	5.75	6.38	1.109	21.4	1.79
6	- « -	1.5	15	fresh	-	3.76	3.61	0.96	19.75	1.67
7					waste	8.8	9.06	1.03	21.13	1.73
8	- « -	3.5	15	fresh	-	4.32	4.31	0.997	20.03	1.704
9		3.0		-	waste	6.3	6.34	1.006	20.65	2.23
10	- « -	5.0	15	fresh	-	11.6	12.59	1.085	19.9	1.68
11				-	waste	1.165	1.14	0.98	20.14	2.2

[1] *S.A. Jamalova, O.N. Novruzov, A.A. Gasimov, V.A. Quseinova, M.M. Seidrzayeva.* Fizika, Izvestiya AN Azerb., 1998, №1, p. 40-43.

[2] *A.T. Pilipenko, L.I. Savrinskiy, A.I. Zubenko.* “Koordinatsionnaya khimiya”, 1981, v.7, №1, p.25-33.

[3] *D.A. Jogolev, V.B. Volkov*. “Naukovo dumka”, Kiev, 1976.

[4] *D.W. Klark, P.S. Hush, J.R. Jandle*. J. Chem. Plys, 1972, v.57, p.3503.

[5] *J.A. Pople, G.A. Segal*. J. Chem. Phys, 1987, v.47, p.158.

[6] *S.A. Jamalova, A.A. Gasimov, O.N. Novruzov, S.A. Zeinalova, Kh.A. Amrakhova*. Fizika, Izvestiya AN Azerb., 1999, №3, p. 72-74.

S.Ə. Camalova

PROPANIN DEHİDROGENLƏŞMƏ REAKSİYASINDA (Ni-Cr-Sb-K)/γ-Al_2O_3 KATALİZATORUNUN MAQNİT FAZA HALININ VƏ PROMOTORLARIN ELEKTRON XASSƏLƏRİNİN ÖYRƏNİLMƏSİ

Məqalədə katalizatorların maqnit xassələrində baş verən dəyişikliklərin onların sintez şəraitdən, közərtmə temperaturundan və müddətindən asılılığını müəyyən etmək üçün, həmçinin, bu xüsusiyyətlərin propanın dehidrogenləşmə reaksiyasında katalizatorların aktivliyi ilə müqayisə məqsədi ilə, çökdürücü ilə Ni^{2+} ionları arasında qarşılıqlı təsir dərəcəsinin müəyyən edilməsi aparılan tədqiqatların nəticəsi əks olunur.

С.А. Джамалова

ИЗУЧЕНИЕ МАГНИТНО-ФАЗОВОГО СОСТОЯНИЯ (Ni-Cr-Sb-K)/ γ-Al_2O_3 КАТАЛИЗАТОРОВ И ЭЛЕКТРОННЫХ СВОЙСТВ ПРОМОТОРОВ В РЕАКЦИИ ДЕГИДРИРОВАНИЯ ПРОПАНА

В статье представлены результаты исследования по выявлению изменений, происходящих в магнитных свойствах катализаторов в зависимости от условий их синтеза, температуры прокалки и ее продолжительности и сопоставление этих свойств с активностью катализаторов в реакции дегидрирования пропана.

Установлена степень взаимодействия ионов Ni^{2+} с носителем.

Received: 05.04.03