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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Investigation of Catalyst Ni/K_2O–Al_2O_3 for Vapor Conversion of Methane

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Abstract—An effect of raw material (aluminum oxide and hydroxide), of amount, and of technique of KOH feed (solid or solution) on a composition of potassium aluminates formed at calcination. Reactivity of the obtaining catalysts at the vapor conversion of methane was studied.

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Catalysts of the vapor conversion of methane in apparatus of a large unit capacity in which nickel is active constituent, operate under exclusively severe conditions: temperature in a range of 800–1000°C, pressure 2–35 MPa, an oxidizing medium (H_2O, CO). As a whole this necessitates high requirements to used contacts. In addition to high activity it is necessarily that they possess required mechanical strength and thermal resistance, stability under working conditions, high selectivity to suppress such a side reaction as coal-formation. Often a carrier of such catalysts is alumina calcinated at temperature higher than 1000°C. On various stage of a catalyst preparation promoters are added in the catalyst composition for improving certain of the operational properties of the system.

For example, calcium aluminates, and (or) magnesium oxide or hydroxide are usual additives in the carrier composition that increase mechanical strength and main properties of the catalyst surface [1–3]. Disadvantage of such additives is an essential (up to 50%) loss of the strength as a result of hydratation of magnesium and calcium compounds accompanied by the increase in volume at feeding of a vapor–gas mixture on the catalyst layer. Also in [4, 5] compounds of titanium are suggested for employment. Aluminum titanate forming in the mechano-chemical synthesis and the following high-temperature treatment possesses a unique low coefficient of thermal linear dilatation that provides high stability of the catalyst. Alkaline and rare-earth metals, lanthanides are applied frequently as additives [2]. In particular, in [6, 7] it was showed that the stable operation of a catalyst, and suppression of the coal-forming even at low ratio of vapor–gas in a reaction medium were provided with help of these compounds. The attention should be paid to potassium since it possesses a high catalytic efficiency and it is the least expensive.

Actually an obligatory stage in a production of the catalyst for the conversion of hydrocarbons is the dispersion of raw materials where the mechano-chemical synthesis of different catalyst constituents may be facilitated. For example, calcium aluminates [8], aluminum titanate [9], and other compounds improving operating characteristics of the contacts [3] were obtained in this way. Thus synthesis of potassium aluminates in the course of the carrier production is very promising. The presence in the catalyst composition of potassium aluminates enables both preparation of sufficiently solid granules with a high porosity and a favorable influence on catalytic activity and selectivity due to intensification of the main properties of the surface.

For improving the technological properties of the system on the stage of granulation a paraffin input at grinding the raw components should be used [3, 5]. Moreover paraffin burning out in the course of calcination promotes formation of open porous structure of granules [3].

Production and investigation of physicochemical properties of nickel catalyst for the conversion of methane with water vapor on the potassium aluminum carrier prepared by various techniques is a purpose of the presented paper.

EXPERIMENTAL

For preparation of the catalyst carrier we used an alumina of G-00 grade containing 60 wt % of α-Al_2O_3, and the rest composed of γ- Al_2O_3, and aluminum hydroxide that represents practically 100% hydrargillite. We prepared samples by the following technique: Alumina and required amount of solid KOH (c.p.) that was grinded in the presence of 5% of paraffin of T-2 grade in the rolling ring crusher VM-4 (oscillation frequency 940 min^{-1}, energy supply 5.4 kW kg^{-1}) for 60 min. The content of paraffin and the grinding time were determined according to [3, 10]. Then we added water to the obtained system and agitated to formation of homogeneous plastic paste. Optimal plasticity moisture was controlled by a depth of submergence of a cone on Rehbinder plastometer [3] and was 28–30 wt %

From this paste with a ram extruder we formed granules of 10 mm diameter with the ratio of $d : h$ = 1:1. For preparation of other sample series alumina and aluminum hydroxide were also ground in the presence of 5 wt % paraffin during 60 min then in this powder 20 wt % solution of potassium hydroxide (KOH concentration of dry sample was 5 wt %) was added. An optimal moisture was governed by water addition. Granules were formed as noted above and then they were dryed at 100–110°C for about 4–6 hours till achievement of constant weight. The dryed samples were calcinated at 1200°C for 5 h. Depositing an active component was performed by multiple impregnation by a solution of nickel and aluminum nitrates (concentration of Ni was 140, Al 20 g dm^{-3} at temperature 50°C and stirring for 60 min). Impregnated samples were dryed and cacinated for 4 hours at 500°C. In the course of the thermal treatment the nitrates decomposed to nickel oxides and alumina whereas nitrogen and oxygen oxides transferred in the gas phase.

The X-ray phase analysis was made with DRON-2 diffractometer with $Mo_{K\alpha}$ radiation (wavelength λ = 0.071 nm). A capture was performed by powder method in transparent mode by θ–2θ that enables widening a capture range from 1 deg of θ. A concentration of surface centers was determined by potentiometry data of a water extraction by decinormal solutions of HCl and NAOH taking into account an idler sample. A crusing strength of the granules and porosity of the carrier were measured by techniques in [11]. An activity of the produced catalyst was determined by a residual methane content in a dry gas after conversion with water vapor in a flow reactor at vapor : gas ratio = 2 : 1 and at flow equal to 6000 h^{-1}. The process temperature was varied from 500 to 800°C. Before a start of the experiments we reduced NiO in the catalyst to a nickel metal in the flow of a nitrogen–hydrogen mixture at 500°C. The experiments were executed according to [12].

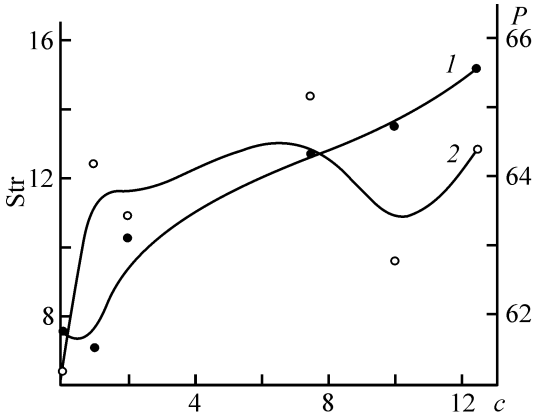

Fig. 1. The dependence (*1*) of the mechanical strength Str (MPa) and (*2*) of the granule porosity *P* (vol %) on the amount of potassiun hydroxide (*c*, wt %).

One of the main targets of the addition of potassium compounds to the composition of the alumina carrier for the nickel catalyst of the methane conversion with water vapor is increase in the crushing strength of the granules. Therefore a question about optimum potassium content is very important. Experimental data depicted on Fig. 1 showed that an increase in KOH amount, ranged from 2 to 35 wt %, put in the carrier composition in the course of its preparation after the calcinations led to a jumping growth of the crushing strength. The strength in this case rose more than by 10 MPa and that was a sufficiently acceptable result. Further increase in the potassium content did not lead to some visible effect.

It should be noted that as the strength increase at rise of the potassium content the granule porosity being in a range of 63–65 vol % did not change (Fig. 1). Comparing these data we concluded that the granule strength was determined both by strength of a crystallization bond between particles and by an amount of these bonds [3].

From geometrical considerations it is shown that an amount of the contacts is diminished. Therefore the growth of granule strength is caused just by the increase in the strength of intercrystalline bonds. This occurs in turn exclusively in the case of the formation of potassium aluminates. Thus from the point of view of a physical structure optimization for the carrier the potassium

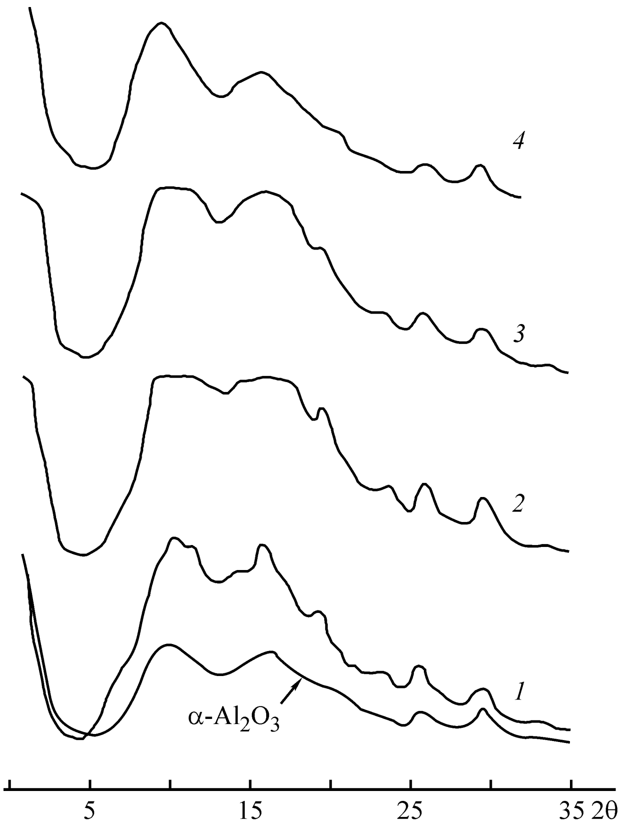

Fig. 2. X-ray charts ($Mo_{K\alpha}$-radiation) of the samples of the catalyst carrier. (2θ) the diffraction angle (deg); the same for Fig. 4. The curve numbers are the sample numbers in Table 1, the same for Figs. 3, 4.

content in the sample with respect to KOH should be in the range of 2–5 wt %.

It should be considered what kind of aluminates formed in the system in the dependence on the potassium content and on the way of potassium input. The raw composition for the carrier preparation was presented in Table 1. So addition of 2 wt % solid KOH on the grinding stage and the following calcinations lead to a registering on charts series of reflexes in a range of diffraction angles of 7–12, 14–17, and 19.2° 2θ (Fig. 2, curve *1*). By reflex series and intensity relations of characteristic peaks we may conclude that the sample in addition to α-Al_2O_3 contains such potassium aluminates as $K_2O{\cdot}9Al_2O_3$ ($K_{0.67}Al_6O_{9.33}$, Mullite), and $K_2O{\cdot}11Al_2O_3$ ($KAl_{11}O_{17}$, Potassium Aluminum Oxide). Here and hereinafter an order of a phase enumeration corresponds to decrease in its content. Unfortunately all the most intensive reflexes are placed very closely to each other and so an accuracy determination of their content in the sample is not possible.

Table 1. Concentration of the surface centers

Sample no.	Composition of raw for preparation of the carrier, wt %	Concentration of the surface centers, mmol g^{-1}			
		on the carrier		on the catalyst	
		acid	base	acid	base
1	$A1_2O_3 + 2KOH_{solid}$	0.166	0.071	0.100	0.022
2	$A1_2O_3 + 5KOH_{solid}$	0.172	0.062	0.097	0.027
3	$A1_2O_3 + 5KOH_{sol}$	0.119	0.067	0.117	0.020
4	$A1(OH)_3 + 5KOH_{sol}$	0.369	0.075	0.218	0.051

At the increase of the potassium constituent up to 5 wt % KOH the new reflexes appear in the same areas of the diffraction angles (Fig. 2, curve *2*) that can be related to formation in the system in addition to $K_2O.9Al_2O_3$, and $K_2O{\cdot}11Al_2O_3$ the aluminate $3K_2O{\cdot}16Al_2O_3$ ($K_2Al_{10.67}O_{17}$, Alumina).[1]

In the case of thr use instead of the solid KOH its solution changes in X-ray spectra were not found (Fig .1, curve *3*) but we observed redistribution of the intensities. This evidences that the prevailing phase among aluminates is $K_2O{\cdot}11Al_2O_3$, and other potassium compounds form in the less are amount.

For the sample where Al_2O_3 was charged as hydroxide the sufficiently intensive reflexes of $K_2O{\cdot}11Al_2O_3$ were recorded on the diffractogram (Fig. 2, curve *4*). In this case a synthesis of other aluminates is very insignificant. In the course of the preparation of the paste an extremely undesirable effect of a fast cementation due to a small value of an induction time caused by a formation of potassium hydroaluminates as a result of a hydraulic solidification.

It is essential that for all samples very intensive peaks corresponding to interplanar distances of more than 1.1 nm should be observed for potassium aluminates in the range of the diffraction angles of 3–4° 2θ according to ASTM data whereas very weak reflexes are observed in this area on the experimental X-ray spectra (Fig. 2). The following feature is the significant widening of all peaks. As a whole this picture can be understood through the formation of potassium aluminates with poorly crystallized structure that has only a short range order.

Investigation of acid–base properties of the carrier surface shows (Table 1) that Lewis acid centers are

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[1] Formulas and names according to ASTM classification are noted in the parentheses.

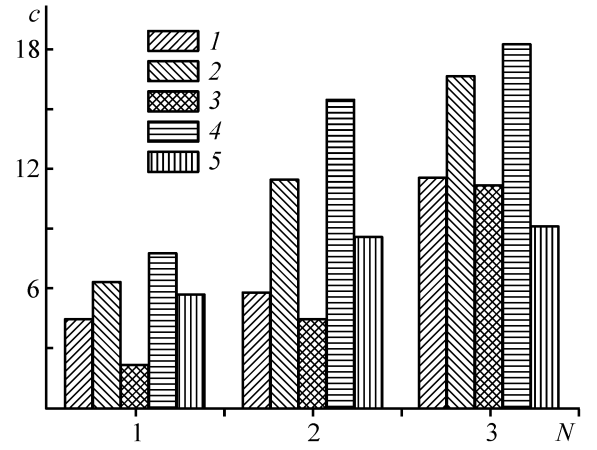

Fig. 3. Dependence of NiO content in the catalyst (*c*) on the number of the impregnations (*N*) (*5*) Al_2O_3.

prevailing. The presence of these centers caused by existence of aluminum atoms which have not unshared electon pair [3], on the surface.

Sufficiently high concentration of the main Brønsted center is quite natural as K–$O_{surface}$ bonds are capable to easy proton bonding.

The next stage of the catalyst preparation is impregnation by nickel salts that naturally in many respects determines the properties of the product. As shown in [4, 6, 12] an optimum content of NiO in the catalyst is 10–15 wt %. Nickel totally coats the carrier surface at this concentration with a layer close to monomolecular completing pores without excess and that provides maximum possible use of the surface at a minimum consumption of the active component.

Experimental data show (Fig. 3) that in dependence on carrier composition the required content of NiO can be provided by to a various amount of the impregnations. Since a volume of the open pores of all the samples is about equal [water absorption is 27–29 wt %, a specific surface according to BET (Brunauer–Emmett–Teller equation) is 10–12 $m^2 g^{-1}$] the observed occurrence evidently relate to the surface properties. Comparison of the data from Table 1 and Fig. 3 enables correlation between concentration of Lewis acid centers and the amount of the deposited Ni: the higher acidic properties of the carrier are the smaller amount of the impregnations is required to reach a desired result.

X-ray phase analysis of the catalyst sample recorded only peaks corresponding to NiO on the diffractogram (Fig. 4). Only in the sample prepared with use of aluminum hydroxide the reflexes of potassium aluminate $K_2O{\cdot}11Al_2O_3$ occur. Potentiometry data evidence that the amount of the base and acid centers decreases and becomes practically equal (Table 1). The sample 4 is an exclusion in the quantitative respect.

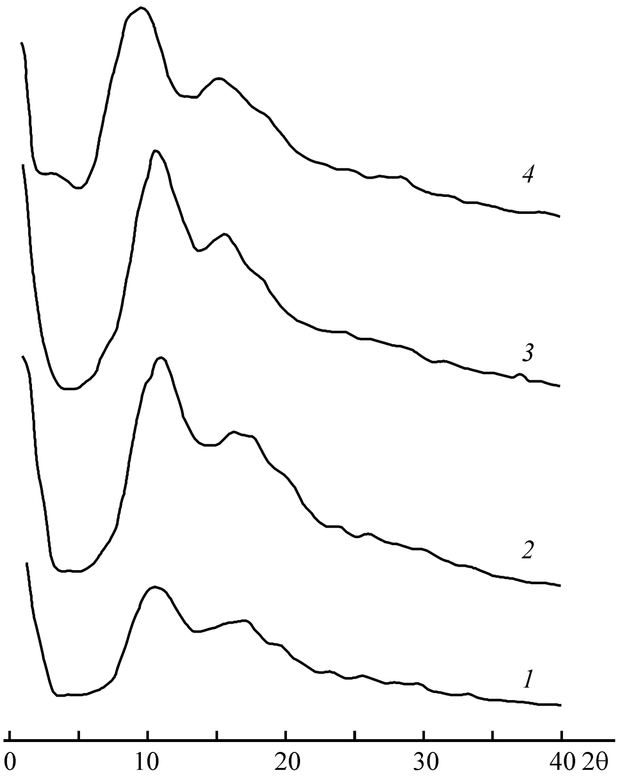

Fig. 4. X-ray charts (Mo*K*α-radiation) of the samples of the catalyst.

Thus we can conclude that after achievement of the optimum concentration of the active constituent in the catalyst the whole surface is covered by a layer of nickel oxide whose force of Lewis acid centers as known is lower than that of Al_2O_3. The distinction of sample 4 is apparently undestood through prevalence of potassium aluminate kind of $K_2O{\cdot}11Al_2O_3$, and also through a sort of the raw material. In this case for preparation of the carrier $Al(OH)_3$ (hydrargillite) was used that at calcilantion consistently decomposed to bayerite, boehmite, γ-Al_2O_3 recrystallizing in α-form at temperature of more than 900°C, was used [3]. The recrystallization under conditions of the carrier preparation proceeds incompletely and γ-Al_2O_3 presents in the system that data of X-ray analysis confirm (Fig. 2, curve *4*).

Test of the catalysts in the methane conversion with water vapor shows that all studied samples have more activity than industrial analogs (Table 2). It is important that at low temperatures (500°C) the residual content of methane is about 1.5 time less. That once again

Table 2. Catalyst activity in the course of the vapor conversion of methane. The vapor : gas ratio = 2 : 1, the flow 6000 h^{-1}, the temperature 700°C

Sample no. (Table 1)	NiO content, wt %	Residual content of methane, vol %, at the temperature, °C		
		500	650	800
1	11.49	24.7	3.4	0.3
2	11.45	33.1	8.0	0.6
3	11.15	26.9	2.2	0.5
4	15.45	53.6	7.8	3.8
Industrial samples				
GIAP-8(K)	8.0	35.0	5.0[a]	1.0
DKR-1(K)	12.0	35.0		

[a] At 700°C.

emphasizes a good work of the catalyst thereby in industry the process starts at temperature that is not higher than 550°C. An exception is the sample prepared with the use of hydrargillite possessing low activity (less than required activity). That is clarified by the presence of γ-Al_2O_3 characterized by cubic lattice since α-phase possesses a hexagonal structure poor cryslaillized.

The hexagonal lattice enabling achievement of a structural stability of the active constituent on the carrier surface that is particularly important under conditions of high temperatures, is energy favorable.

Moreover it is important that a thermal resistance of the catalysts (number of a thermal regime change of 1200 $\leftrightarrows$ 20°C) is more than 20 and that exceeds standard indices for the studied catalysts.

CONCLUSIONS

(1) Aluminun oxide and hydroxide where solid KOH on the stage of the grinding or solution of KOH in the course of the preparation of the paste is input as promoting additives, are used for producing the carrier of the nickel catalyst of the methane conversion with water vapor. The optimum content of KOH is 2–5 wt %.

(2) Emploiment of aluminum oxide and hydroxide as raw material, and also the amount and technique for the input of potassium after the calcinations lead to formation of potassium aluminates of the various compositions.

(3) The correlation between the way of catalyst carrier preparation, acid-base properties of the surface, and the amount of nickel oxide deposited by impregnation were established.

(4) The nickel catalysts on the aluminum potassium carrier are more active than their industrial analogs at the methane conversion with water vapor.

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