

## Oxidative Conversion of Methane of Natural Gas to Oxygen Containing Compounds

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The search of new compositions of catalysts on carriers on the base of heteropoly compounds of molybdenum for oxidative conversion of methane, the identification of optimal conditions for the partial oxidation of methane to formaldehyde, as well as study the surface properties of catalysts by complex methods and their relation to catalytic properties were the aim of work. Physico-chemical properties of bulk and supported heteropoly compounds were investigated by complex methods. The optimum composition of thermal stable catalyst over carrier on the base of molybdenum heteropoly compounds for process of methane oxidation into formaldehyde was developed. It has been shown that the water vapor has a positive influence on the yield and selectivity by formaldehyde. Probably, the catalyst does not change the structure at the production stage of formaldehyde from methane at the abovementioned temperatures; only the transition of Mo<sup>6+</sup> into Mo<sup>5+</sup> is observed. Re-oxidation of this catalyst by oxygen of gas-phase or by oxygen with water vapor leads to the disappearance of Mo<sup>5+</sup> signals in EPR spectra and return of parameters specific to Keggin structure of HPA (773-873 K) (XRD, IRS, TPR).

### 1. Introduction

Natural gas is the most important alternative source of raw materials that can in the future compete with oil. Therefore, it is especially important to make rational use of C<sub>1</sub>-C<sub>4</sub> alkanes, which are used at present in significant amounts only as fuel or burned in a "torch". Gas processing to obtain important products facilitates the introduction of cleaner production. Alkanes can be a cheap raw material in organic synthesis for production of valuable compounds: olefins on usual (Patcharavorachot et al., 2013) and packed-bed membrane reactor (Esche et al., 2012), aldehydes (Dosumov et al., 2005), alcohols (Parfenov et al., 2014), hydrogen-containing fuel mixtures (Ismagilov et al., 2014), synthesis gas by partial oxidation (Tungatarova et al., 2010), steam reforming (Palma et al., 2016), dry reforming (Phongaksorn et al., 2015), complex steam and dry reforming (Siang et al., 2017), and from biogas (Authayanun et al., 2016). Obtaining of formaldehyde by direct oxidation of natural gas by oxygen is more preferable to a complex and multi-step synthesis of CH<sub>2</sub>O through synthesis-gas and CH<sub>3</sub>OH. Analysis of the literature shows that the compact oxide of acid type, as well as supported oxide catalysts on the base of Mo and V are mainly used for that process. Attempts to implement this way run into the problem of low selectivity of reaction caused by high strength of chemical bonds in the CH<sub>4</sub> molecule. Furthermore, the products of partial oxidation are more active, and more susceptible to further deep oxidation than the CH<sub>4</sub> under conditions of high temperatures required for activation of CH<sub>4</sub>. Stop the process at an intermediate stage is important task, whose solution allow solving the problem of selective production of CH<sub>2</sub>O from CH<sub>4</sub>. Reviews on the oxidation of CH<sub>4</sub> into the O<sub>2</sub>-containing compounds are presented in (Horn et al., 2015). The aim of our work was the search the new compositions of catalysts on carriers on the base of heteropoly compounds (HPC) of Mo for oxidative conversion of CH<sub>4</sub>, the identification of optimal conditions for the partial oxidation to formaldehyde (POMF), as well as studies the surface properties of catalysts by complex methods and their relation to catalytic properties.

## 2. Experimental

The studies were conducted in flow-type installation at atmospheric pressure in a tubular quartz reactor with a fixed bed reactor or in two flow reactors connected in series. The gas mixture containing CH<sub>4</sub> and O<sub>2</sub>, diluted with an inert gas Ar in the presence or absence of water vapor was used for oxidation. Ratio of the components of reaction mixture was varied widely. The methane content: CH<sub>4</sub> < 5 %, 20 % < CH<sub>4</sub> < 50 %. The oxygen content: 5 % < O<sub>2</sub> < 25 %. Mo-HPC catalysts with Si as central atom were prepared by incipient wetness impregnation of the different carriers, followed by drying at 393 K for 5 h in air. The concentration of the active phase on the carrier varied from 0.1 % to 20 %. The analysis was carried out on «Chromatec Crystal 5000.1» chromatograph with the «Chromatec Analyst 2.5» software on the capillary column. Physical-chemical properties of the bulk and supported HPC have been investigated by complex methods: IR spectroscopy, electron spectra of diffusion reduction (ESDR), temperature-programmed reduction (TPR), isotope analysis, differential thermal analysis (DTA), electron paramagnetic resonance (EPR).

## 3. Results and discussion

Studies have shown that 1 - 20 % catalysts based on Mo HPC supported on different carriers are active at temperatures above 673 K. The following sequence of formation of products with increasing reaction temperature is observed: CH<sub>2</sub>O (873 – 973 K), C<sub>2</sub>H<sub>6</sub> (973 – 1,123 K), C<sub>2</sub>H<sub>4</sub> (1,023 – 1,173 K). This sequence is based on theoretical studies of the mechanism of oxidation of CH<sub>4</sub> and our experimental results. It was established that the same catalysts could accelerate the reaction of POMF and oxidative dimerization of methane (ODM). The role of the catalyst is to generate CH<sub>3</sub> radicals; the selectivity is determined by the reaction conditions, i.e., C<sub>2</sub>H<sub>4</sub> and CH<sub>2</sub>O have as a precursor the same intermediate (CH<sub>3</sub> radical). Implementation of the reaction in either direction is determined by external parameters (temperature, pressure, space velocity). This suggests the competition of two reactions: recombination of CH<sub>3</sub> radicals with the formation of C<sub>2</sub>H<sub>6</sub> and oxidation to CH<sub>2</sub>O with the participation of surface oxygen. Studies on the effect of active component on the yield of CH<sub>2</sub>O have shown that molybdenum heteropoly acids (Mo-HPA) are more active than the W-HPA and H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> have been selected for further studies.

Significant effect on the yield of products of partial oxidation of methane has HPC content on the carrier. Studies on samples of catalysts with the content of active phase from 0.1 to 25.0 % on the carrier were carried out. The highest yields were obtained for 2 and 10 % samples (methane content in the mixture below the lower explosive limit) and 2 % and 1 % samples (methane content in the mixture above the upper explosive limit). It was shown that low-percentage catalysts are most active. The non-monotonic dependence of the yield from content of HPA on carrier may be due to the mutual influence of components in the catalyst system "HPA-carrier." Due to the fine distribution of HPA on carrier in low-percentage catalysts (XRD amorphous samples) assumed the formation of the structures of interaction "HPA fragment - carrier." This can be seen 1 – because of absence of exo-effect at 633 K on DTA curve corresponding to the destruction of individual HPA for the low percentage samples, 2 – because of coincidence of the a.b. of low percentage HPA and carrier in IR spectra at shift of characteristics on 1 - 20 cm<sup>-1</sup> to higher absorption frequencies (Table 1) and 3 – because of shift of TPR peaks of low percentage samples to higher temperatures area due to increasing the bond strength of structural oxygen. Consequently, the bidispersity of active HPC is specific to supported catalysts (> 10 %): the presence of the phase HPA (a.b. 780, 865, 915, 960 cm<sup>-1</sup> – IR spectra) together with the structure of interaction of "HPA fragment-carrier". Activity of the POMF is determined by existence of HPA on surface, and its contents shall not exceed a certain critical value.

*Table 1: The absorption bands specific to Keggin structure and samples of catalysts with different content of active component*

Type of bond	100 %	20 %	15 %	10 %	5 %	2,3 %	10 % with subtraction of carrier
Mo-O-Mo	780	810	810	810	810	820	815
Mo/O\Mo	870	-	-	-	-	-	-
Si-O-Mo	915	925	925	920	920	920	920
Mo=O	960	960	960	960	960	960	960

Since between the activity of catalysts and their acidity there is a relationship, it is important to determine what strength acid sites are involved in the partial oxidation reaction, and what their energy distribution. Method for determination of the electron-acceptor properties of the surface centers on adsorption of different aromatic hydrocarbons has been used for this purpose. It is based on the adsorption of 0.05 M solution of benzene,

naphthalene or anthracene in hexane, with the ionization potentials (IP) 9.24, 8.12 and 7.4 eV. They form cation-radicals with the surface of the carrier. This gave a set of electronic tests. Samples of catalysts were dried at 423 K before adsorption. Adsorption was carried out for three days. The concentration of paramagnetic centers has been registered by the EPR spectrometer on catalysts with different content of active ingredient. Molecules with a lower IP are able to displace a molecule with a large IP at adsorption on the active sites of previously formed radical cations. That is, molecules with lower IP are able to form cation radicals with both strengths and more weaknesses active centers. This helps determine the number of centers that belong to a certain energy interval, based on the difference between the amount of adsorbed radicals with smaller and larger IP. Figure 1 shows the dependence of number of cation radicals from concentration of  $H_4SiMo_{12}O_{40}$  supported on  $SiO_2$ .

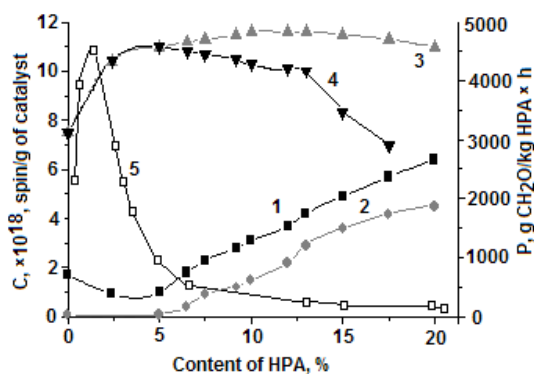


Figure 1: Influence of the content of HPA on concentration of cation-radicals defining acidity of a surface, and on productivity by  $CH_2O$ : 1- benzene (enlarged in 200 times), 2 – naphthalene, 3 – anthracene, 4 – difference curve of concentration ( $C_{14}H_{10}-C_{10}H_8$ ), 5 – productivity by formaldehyde

Supporting of HPC promotes the formation of centers with predominantly IP = 8.12 eV (naphthalene), since the concentration of centers with IP = 9.24 eV (benzene) increases symbatically with the centers stabilization of naphthalene (8.12 eV), but the total concentration of about two orders less which reduces their contribution to zero. The concentration of the weakest centers with IP = 7.47 eV depends on the concentration of HPC which is associated either with the same concentration of them on HPC and carrier, or almost full belonging to acidic centers of carrier. The concentration of cation-radicals of benzene and naphthalene passes through a minimum for low percentage catalysts, whereas for anthracene reaches its plateau. The concentration of strong electron-acceptor centers (8.12 - 9.24 eV) for high percentage catalysts increases with the concentration of HPC, and concentration of the weaker active centers (7.4 - 8.12 eV) passes through a maximum at low concentrations of HPA in catalyst. The difference curve between the centers of IP = 7.47 eV and 8.12 eV is an extreme nature and correlates with the curve of productivity by  $CH_2O$ , Figure 1. This indicates that the active acid sites in POMF reaction are in the area of IP = 7.4 - 8.12 eV, i.e. in the weak-medium strength, but not in the medium-medium strength. It was also shown that the yield of  $CH_2O$  symbatically varies with variation the content of I and II oxygen forms determined by TPR of hydrogen method, Figure 2. It is known that I and II oxygen forms are characterized by presence of HPC on surface of samples.

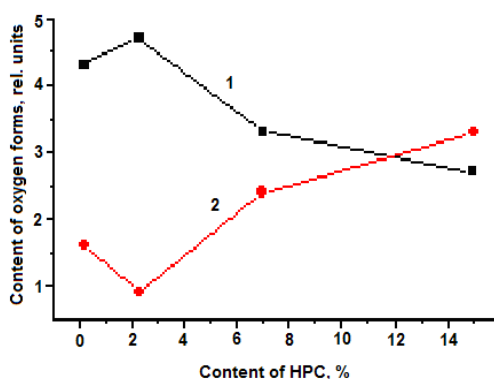


Figure 2: Influence of HPA content on intensity of TPR signal: 1 - I + II forms, 2 - III form of oxygen

The nature of used carrier can have a decisive importance for obtaining of highly active and selective catalysts. It was found that activity of carriers for the same catalysts used in POMF process is increased in the following series:  $\text{Al}_2\text{O}_3 < \text{C} < \text{CaAZ} < \text{KCM-5} < \text{cordierite} < \text{aluminosilicate}$ . Samples deposited on the Si-containing carriers were the best catalysts. This is due to the large amounts of hydroxyl groups on their surface, which cause high proton acidity of surface. In addition, Si is available both in carrier and in active phase which determines some "cross-link" in interaction of  $[\text{SiMo}_{12}\text{-HPA}]$  with  $\text{Si}^{4+}$  cations of carrier, the interaction of HPA with surface OH-groups of aluminosilicate or  $\text{SiO}_2$ . This follows from the data on decrease of the concentration of Si-OH groups at applying of HPA. Thus, there is distortion of the structure of HPA at interaction with carrier. Suggestion about the possible neutralization of HPA with surface OH-groups is rejected in literature. It is assumed that the sorption of HPA on hydroxylated surface should be "multipoint", that is strong enough.

As a result of studies, it has been established that activity of POMF is determined by the presence of HPA or heteropoly-like structure (dehydrated form or anhydride of HPA) on surface of acidic carrier. Oxides remain on the surface at destruction of structures; their activity in the synthesis of formaldehyde is low. The process changes the direction toward the formation of  $\text{C}_2\text{-C}_3$  hydrocarbons.

It was shown that the presence of steam sharply increases the yield of  $\text{CH}_2\text{O}$  and reduces the optimum reaction temperature, Figure 3. The presence of water vapor in mixture, increasing the yield of  $\text{CH}_2\text{O}$ , stabilizes catalyst as occurs development of catalytic activity after steam-air treatment of them between experiments (Figure 4) and increasing the duration of catalytic operation in the presence of water vapor in contrast to the similar composition of oxide catalyst.

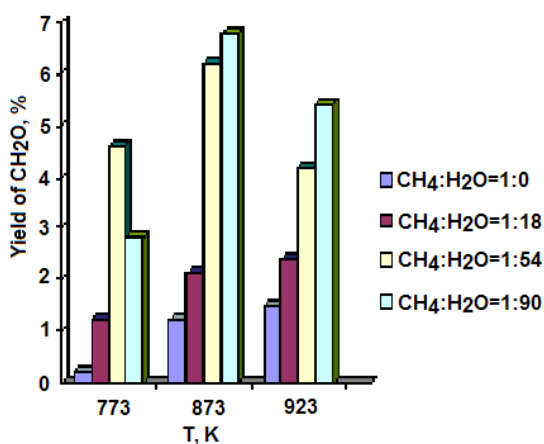


Figure 3: Effect of addition of water vapor on yield of formaldehyde at different content of  $\text{H}_2\text{O}$  in the initial mixture

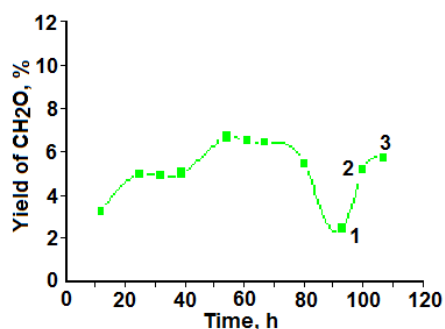


Figure 4: Effect of addition of water vapor on yield of formaldehyde in long-term test for 115 h and after regeneration in steam-air mixture: 1 - 473 K, 2 - 673 K, 3 - 923 K

Investigation of the role of concentration of water vapor (in mixtures with the content of  $\text{CH}_4$  lower than lowest explosive limit) allowed to develop the optimal conditions for selective action of catalysts to produce products of POMF and ODM. Optimal conditions for formation of  $\text{CH}_2\text{O}$  and parallel formation of  $\text{C}_2$  hydrocarbons were observed in small quantities under the action of excess of water vapor ( $\text{CH}_4 : \text{H}_2\text{O} = 1 : 90$ ;  $\text{CH}_4 - 0.5\%$ ,  $\text{O}_2 -$

10.0 %). Reducing the concentration of water vapor decreased the yield of formaldehyde, ceased ethylene formation in the presence of small amounts of ethane. There was a significant formation of trimerization products - propylene. Further decrease the content of water vapor decreased the yield of  $\text{CH}_2\text{O}$ , inhibited the formation of  $\text{C}_3\text{H}_6$  and resulted mainly to the formation of  $\text{C}_2$  hydrocarbons.

Variation of the methane content from 10 to 45 % vol (in mixtures with the content of  $\text{CH}_4$  upper than highest explosive limit) and oxygen from 5 to 22.6 % in the reaction mixture, and water vapor from the ratio of  $\text{CH}_4$ :  $\text{H}_2\text{O} = 1 : 0.25$  to  $\text{CH}_4$ :  $\text{H}_2\text{O} = 1 : 0.60$  shows that the ratio of  $\text{CH}_4$ :  $\text{H}_2\text{O}$ :  $\text{O}_2 = 1 : 0.53 : 0.45$  is optimum ( $\text{CH}_4 - 39.0\%$ ,  $\text{O}_2 - 17.6\%$ ) for the single reactor of oxidative conversion of  $\text{CH}_4$ .

The test of the process in cascade of two reactors connected in series, equipped with condenser to trap the reaction products, where the reaction mixture at the optimum ratio was fed into the first reactor and at the same time further into the second reactor was fed water vapor and methane to save gas volume ratios and enrichment by reacting components of partially reacted mixture. It was shown that on catalyst 2.3 %  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}/\text{AlSi}$  can be obtained 6 – 8 %  $\text{CH}_2\text{O}$  in a single pass at productivity 10 – 14 kg  $\text{CH}_2\text{O}/\text{kg HPC}\cdot\text{h}$  and 60 – 85 % selectivity by  $\text{CH}_2\text{O}$ . Studies have shown that the catalyst works stable up to 120 h at a periodic treatment of catalyst in steam-air mixture at 923 K. Processing at lower temperatures (473 – 673 K) reduces the process parameters; only retreatment at 923 K returns the initial activity of sample, Figure 4.

The stability of catalysts in POMF reaction confirmed by IR spectroscopy, ESDR and TPR methods. 2 and 10 % catalysts treated in the steam-air mixture at 873 K kept the typical absorption bands of Keggin structure (820, 925  $\text{cm}^{-1}$ , but disappeared a weak shoulder at 960  $\text{cm}^{-1}$ ), and charge-transfer band at 390 nm (ESDR). This suggested that for the other samples in the range of 2 – 10 % HPA at temperatures up to 873 K HPA structure kept on the surface.

At the same time, these data indicate about changes in the structure of supported catalysts. In this case, most likely formed dehydrated HPA associated with the surface of carrier. This is a great stabilizing factor, as it is known that a massive HPA decomposes at 633 K.

Analysis of the data showed that all bonds typical for Keggin structure present in the samples with the contents of active component from 2.3 % to 20 % except for the a.b. at 870  $\text{cm}^{-1}$ , which was low-intensity even in the original sample  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ . The a.b. became more resolved with increase the content of active component, and low-intensity a.b. at 960  $\text{cm}^{-1}$  for catalyst samples with the contents of 2.3 – 5 % HPA gradually increased his intensity on more high-percentage samples. This indicates that at high concentration of HPA on carrier, it crystallized with the formation of the initial Keggin structure. The spectrum of 2.3 % HPA / aluminosilicate is close to the IR spectrum of carrier indicating on fine distribution of HPA on the surface of carrier. Supporting of  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  on the carrier moves slightly a.b. to longer wavelengths (a.b. at 915  $\text{cm}^{-1}$  - to 920 - 925  $\text{cm}^{-1}$ , a.b. at 780  $\text{cm}^{-1}$  - up to 810 - 820  $\text{cm}^{-1}$ ). At the same time, the imposition of a.b. of HPA and carrier took place at the 800 - 870  $\text{cm}^{-1}$ . On the spectrum of 10 % HPA with the dedication of carrier which had its own absorption at 800 - 870  $\text{cm}^{-1}$  were observed more intensive signals of a.b. specific to  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  with a shift to high-temperature region on 10 - 40  $\text{cm}^{-1}$ .

The research on determination the role of water vapor by means of isotopic exchange with water, labeled by oxygen or by hydrogen showed that in the reaction products in the presence of deuterated water deuterium is included in the initial methane (due to exchange of isotopes), and into the reaction products with a high degree of exchange. The use of labeled oxygen in water  $\text{H}_2^{18}\text{O}$  led to the appearance of isotopic oxygen atoms in oxygen-containing products; the degree of entry of  $^{18}\text{O}$  in the products increased with increasing reaction temperature. Obtained data are evidence of the participation of water molecules as a mild oxidant. This is possible through the exchange of oxygen of OH groups of water with active oxygen (structural) of HPC. Oxygen of OH groups of water entering directly into the structure of HPC (pseudo-liquid phase), in the hydroxyl cover of support and structures of the interaction of HPA-carrier may also be involved in the reaction. High stability of low percentage catalysts based on HPA can be explained by the fact that surface of carrier in low-percentage catalysts (not more than  $\geq 10\%$  HPA on carrier) is covered by HPA (close to the monolayer, fine dispersed cover - 0.8  $\text{Mo}/\text{nm}^2$  where there is interaction with carrier). Bulk HPA, which blocks the carrier and layer with close interaction of "HPA-carrier" is formed on the surface of high-percentage catalysts. Samples with high content of HPA exposed to destruction with the formation of oxides on the surface under the experimental conditions. In this case, the stability of catalyst depends on the properties of bulk and thermally unstable HPA. Low percentage catalysts, as shown by IR spectroscopy, DTA, TPR and ESDR methods are thermal stable as a result of the interaction of "HPA-carrier" and steam-air treatment (steam is also necessary to maintain the structure HPA).

#### 4. Conclusions

Thus, the activity of low-percentage catalysts from Mo-HPC at high temperatures and reaction medium caused by:

- the optimal value of catalytic acidity. In the low-percentage catalysts even after the destruction of HPA to oxides as a result of the high acidity of carrier, the re-synthesis of HPA probably takes place. It is known that at supporting of MoO<sub>3</sub> on silica gel on the surface is formed not only oxide phase, but also HPC, as the pH of carrier is sufficient for synthesis of HPA on surface of sample, especially at processing by water vapor. High-percentage catalysts are difficult to regenerate, as decomposed HPA forms on the surface significant amounts of oxides. To regenerate HPA in water vapor, apparently, is not enough acidity of carrier although on the surface are likely to be small amounts of HPC, but the content of decomposition products likely would prevail. It is clear that the stabilizing influence of the carrier acts only for low percentage samples;
- preservation of structural fragments of HPA in the steam-air processing up to 873 – 923 K which is confirmed by immutability of the bands in IR spectra, ESDR and TPR peaks;
- micro fine distribution of HPA on carrier that provides bidisperse of catalysts. The formation of small crystallites of HPA, their thermal decomposition is not in DTA regime up to 873 K;
- micro fine distribution of HPA on carrier that provides hardening of Mo-O bonds in structural fragments of Mo=O, Mo-O-Mo, and Mo-O-Si of HPA (shift of TPR peaks by hydrogen to high temperatures area compared with TPR of pure HPA), which determines the thermal stability of catalysts at prolonged high-temperature operation.

Thus, at the stage of synthesis of CH<sub>2</sub>O from methane under the above temperature, the catalyst does not change the structure; there is only a transition of Mo<sup>6+</sup> into Mo<sup>5+</sup>. Re-oxidation of this catalyst by oxygen of gas-phase or oxygen with water vapor leads to the disappearance of Mo<sup>5+</sup> signals in EPR spectra and return of parameters specific to Keggin structure of HPA (773 – 873 K) (XRD, IRS, TPR).

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