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Synthesis of Oxygenates by Oxidation of Light Alkanes on Modified Catalysts

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Supported polyoxide catalysts on the base of Mo and W, as well as natural Kazakhstan's clays were tested in the process of oxidative conversion of propane and propane-butane mixture. The influence of reaction temperature, contact time, composition and percentage of the active component of catalyst were determined. The important petrochemical products - acetone (500 - 550 °C) and acetaldehyde (300 - 350 °C) were the main liquid products of reaction on natural Kazakhstan's clays and also on clays modified by Mo, Bi, Cr, Ga ions.

1. Introduction

Partial oxidation of liquefied oil gas into ketones and aldehydes is important both in ecology and economy because 10 billion m^3 of casing-head gas is burned every year in the world and harmful exhaust into atmosphere measured by thousands of tons. Combustion process by means of huge consumption of oxygen and heat emission promotes strengthening of hotbed effect. The cost of 1000 m^3 of oil gas is about $30. Thus economy lost the great sum heating sky. More expensive product than raw substances is possible obtain from oil gas, for example, from isobutane (Wang et al., 2010), C_2-C_5 alkanes (Arutyunov et al., 2014) or methane (Palma et al., 2015). The rapid development of the petrochemical industry in the last decade has raised acute problems of the optimal choice of feedstock and catalysts for relevant processes. According to forecasts for the near future, saturated C_1-C_4 hydrocarbons not only will retain but also will strengthen their position as a raw material for the production of unsaturated hydrocarbons. Therefore, the problem of searching for ways of their effective conversion into different oxygen-containing compounds is also urgent. Unlike methane and ethane, which yield less complex compounds, propane and butane are expected to give unsaturated hydrocarbons, aldehydes, acids, and alcohols butane upon incomplete oxidation. Only the optimal choice of catalysts can ensure targeted synthesis with the predominant formation of a desired compound selected from these products.

Heterogeneous catalysts that are examined in light alkanes oxidation reactions are represented by both individual on the base of vanadyl phosphate (Casaletto et al., 2010), titanium pyrophosphate (Urlan et. al., 2008) and mixed La-Ni (Crapanzano et al., 2013), Ni-Co oxides (Phongaksorn et al., 2015), V/MgO in the complex with BiMo catalyst (O'Neill and Wolf, 2010), and BiVMo oxides (Yang et al., 2002) as well as by catalysts supported on different carriers, for example, γ-Al_2O_3, $ZnAl_2O_4$ spinel, $MgAl_2O_4$ spinel, and spheres of α-Al_2O_3 with a washcoating of γ-Al_2O_3 (Bocanegra et al., 2009), including zeolites modified with metal nanopowders (Erofeev et al., 2013), with Ga (Choudhary et al., 2000) on usual (Patcharavorachot et al., 2013) and packed-bed membrane reactor (Esche et al., 2012).

2. Experimental

The experiments were carried out at atmospheric pressure, 300 - 600 °C, WHSV = 300 - 15,000 h^{-1} in a continuous-flow unit with a fixed-bed quartz-tube reactor. The gas mixture used for oxidation contained propane and oxygen in a 1 : 2 ratio, as well as C_3H_8-C_4H_{10} mixture (14 - 80 %) and oxygen (4 - 18 %) in

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different ratios. As catalysts, we used a) 1 - 10 % Mo, Cr, Ga polyoxide catalysts with different composition and ratio supported on white natural clays (WNC) with kaolin structure and with admixture of hematite and α-quartz were dried at 120 °C for 5 h and calcined at 300 °C in air (Dossumov and Tungatarova, 2010), b) heteropoly compounds (HPC) of Mo and W with the Si and P central atoms deposited on supports by the incipient wetness technique followed by calcination at 120 °C for 5 h in air (Dossumov et al., 2005). The heteropoly compounds were synthesized according to procedures described in (Pope, 1990) for synthesis of Mo heteropoly acids and (Brauer, 1985) for synthesis of W heteropoly compounds. An Agilent 6890N gas chromatograph equipped with an FID and TCD was employed for the on-line analysis of the products. The catalysts were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD) analysis, and their surface area, porosity, and elemental composition were determined. Phase structure of catalysts was recorded on DRON-4-7, operating at 25 kV and 25 mA and employing Co-K_α radiation, covering 2θ between 5 and 80°. Morphology, particles size, chemical composition of initial and worked out catalysts for 56 h were performed on TEM-125K with enlargement up to 133,000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in vacuum universal station, and carrier of catalysts was dissolved in HF. Identification of micro diffraction patterns were carried out by means of ASTM (1986) cart index.

3. Results and Discussion

It was shown that conversion of propane-butane mixture proceeds with the formation of gaseous and liquid products. It was found that the partial oxidation of propane-butane mixture with varying the catalytic mixture composition and the contact time yielded acetone, methyl ethyl ketone, methanol, acetaldehyde, croton aldehyde, butanol, and acetic acid, as well as C_2-C_3 unsaturated hydrocarbons. The results of propane oxidation on granulated catalysts made of PVW-HPC derivatives showed that the homogeneous oxidation of propane practically did not occur. The propane conversion (C) on the pure support is higher, and the use of catalysts sharply increases the conversion over the entire range of temperature. The main products are oxygen-containing compounds (mainly acetaldehyde), propylene, ethylene, and CO. The addition of water vapour decreases the propane conversion but increases the yield of olefins and oxygenated compounds over practically the whole range of temperatures (Table 1). The increase in the contact time by a factor of 2.5 reveals that the selectivity and their yield become somewhat lower with an increase in temperature, but the yield of CO increases. This is explained by the fact that the products of incomplete oxidative dehydrogenation and oxidation are further oxidized to CO and CO_2 at a longer contact time. The promotion of the catalysts with alkali or alkaline-earth metal salts increases the yield of ethylene. The admixture of water vapour significantly increases the rate of the process.

Table 1: Effect of space velocity on yield of acetaldehyde, acetone, methanol and methyl-ethyl-ketone at 500 - 550 °C

WHSV, h^{-1}	T, °C	Yield, %			
		Acetaldehyde	Acetone	Methanol	MEK
15,000	500	20.3	6.0	6.6	38.7
	550	34.5	25.0	0	8.6
9,000	500	29.2	5.4	8.5	33.1
	550	21.4	8.0	7.3	30.2
7,500	500	32.0	19.8	0	5.1
	550	34.4	20.3	5.8	9.2
2,700	500	32.3	9.7	4.9	8.2
	550	26.3	11.2	10.8	11.4
1,350	500	28.0	35.0	11.0	18.0
	550	21.4	35.3	12.7	22.0
900	500	27.6	30.0	11.3	21.7
	550	23.0	36.6	9.4	24.4
450	500	19.3	32.3	12.0	31.6
	550	14.2	50.9	0	36.3

For the oxidative conversion process, we also developed polyoxide low-metal-loading catalysts on the basis of molybdenum and tungsten HPC on monolithic (cordierite) supports. Cordierite, SiO_2, zeocar, Al_2O_3, and aluminosilicate were used as the second supports. Zirconium and SiO_2 were introduced as stabilizing additives in order to decrease the volatility and to stabilize the structure. The technology of deposition of polyoxide compounds on a porous block by varying the secondary support, the binder, and the protecting layer was developed. Figure 1 presents data on the yield of acetaldehyde plotted against the temperature of the reaction over monolithic catalyst specimens.

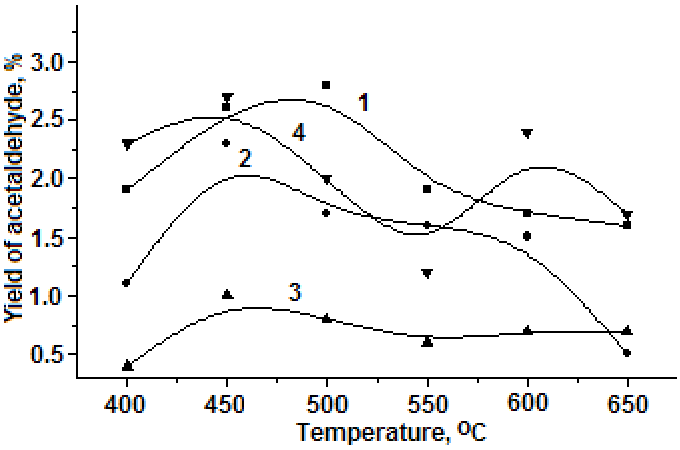

Figure 1: Dependence of the acetaldehyde yield from reaction temperature in the oxidation of a propane-butane mixture on different monolithic catalyst specimens: 1 - 5.5 % $Mg_2SiMo_{12}O_{40}$/cordierite/cordierite, 2 - 5.0 % $Mg_2SiMo_{12}O_{40}$/cordierite/cordierite with the secondary support stabilized with Zr, 3 - 4.9 % $Mg_2SiMo_{12}O_{40}$/cordierite/cordierite, with a Zr protective layer, and 4 - 5.0 % $Mg_2SiMo_{12}O_{40}$/cordierite/cordierite with a SiO_2 protective layer

The Mg salt of SiMo heteropoly acid deposited on the cordierite block with a cordierite secondary support turned out to be the most active. It was found that supported Ni-containing HPC were optimal for the synthesis of hydrogen-rich hydrocarbon mixture. The yield of H_2 in the oxidation of a propane-butane mixture was 60 - 64 %. It was found that there were two temperature ranges for the formation of hydrogen and C_2 hydrocarbons, which are determined by the occurrence of the oxidative-dimerization and cracking processes. The optimum contact time for the synthesis of H_2 and C_2H_4 is 0.45 - 0.9 s; T = 800 - 900 °C at the ratio of C_3H_8-C_4H_{10} : O_2 = 20 : 1 and the minimum content of water vapour in the mixture.

The tests on natural clays of Kazakhstan (Torgai white clay; the base phase is kaolin $Al_2[OH]_4Si_2O_5$ (ASTM-29-1488) and α-quartz (SiO_2), as well as Torgai red clay, which differs from the white clay by the presence of hematite (Fe_2O_3) and the absence of α-quartz (less than 1 %) showed that investigation in this direction is also of interest. The treatment of clay specimens with hydrochloric acid slightly changed their phase composition. The specific surface area and porosity of the sorbent specimens examined were determined by the Brunauer-Emmett-Teller low-temperature nitrogen adsorption technique. It was found that the clay surface area is 10 - 16 m^2/g and that the optimum pore radius ranges from 20 - 50 Å. The treatment of sorbents with 10 % HCl facilitated the development of pores and an increase in the pore radius. The elemental analysis of the initial sorbent specimens and those treated with 10 % HCl showed that the clay specimens predominantly contained oxide compounds of Si and Al, as well as Ca, Mg, Fe, and Na. Up to 20 other elements in amounts from 0.0008 to 0.4 % were found as concomitants. The SiO_2/Al_2O_3 ratio (silica modulus) was 5 - 0.4. The silica modulus increases after acid treatment.

Important petrochemicals, such as acetone (500 - 550 $^{°C}$) and acetaldehyde (300 - 350 $^{°C}$) are main liquid products. Ethylene is the main product of gas phase. Yield of ethylene increases beginning from 450 °C. Ternary catalyst is more active than two-component samples. Investigation of 1, 5 and 10 % MoCrGa/NC was shown that 5 % sample is active in forming of ketones (acetone, methyl ethyl ketone), 10 % - acetaldehyde and 1 % - ethylene. The yield of acetone was increased from 32 % at 400 °C to 50.9 % at 550 °C, WHSV = 450 h^{-1}, C_3-C_4 : O_2:N_2 : Ar = 5 : 1 : 4:5 over 5 % MoCrGa/WNC (Figure 2).

Optimal space velocities for catalysts with different content of active phase over carriers were determined. Up to 23 % of acetone and 35 % of methyl ethyl ketone on 1 % MoCrGa/NC were produced at WHSV = 1,350 h^{-1}. Increase of content of acetone up to 31 % in catalyzate was observed at reduction of propane-butane in reaction mixture. Dependence the yield of acetone from temperature at the different space velocity over 5 % MoCrGa/NC has shown on Figure 3. It was shown that more high yields of acetone were obtained at WHSV = 300 - 450 h^{-1} at 350 - 550 °C. The determination of the product composition showed that the process follows a complex mechanism including oxidation, oxidative dehydrogenation, and cracking.

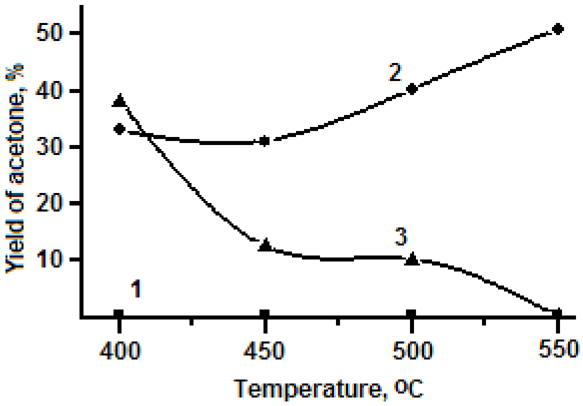

Figure 2: Dependence of the acetone yield on the reaction temperature in the oxidation of a propane-butane mixture. C_3-C_4 : O_2 : N_2 : Ar = 5 : 1 : 4:5; τ = 8 s; WHSV = 450 h^{-1}. 1- 1 % MoCrGa/NWC; 2 – 5 % MoCrGa/NWC; 3 – 10 % MoCrGa/NWC

The multipeaked character of change in the catalytic properties during the oxidation of propane-butane mixture and the highest activity of low-loading supported catalysts are due to the existence of both crystalline and amorphous phases of heteropoly acids on the supports (Tungatarova et al., 2003) and to the appearance of strong interaction in the heteropoly acid-support system (Tungatarova, 2010).

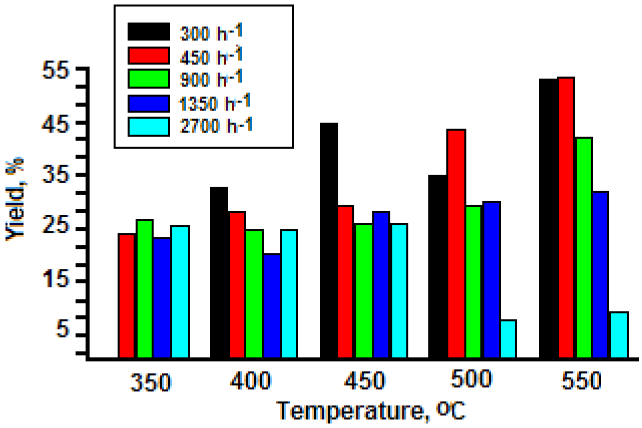

Figure 3: Dependence the yield of acetone from temperature at the different space velocity over 5 % MoCrGa/NC. C_3-C_4 : O_2 : N_2 : Ar = 33.3 : 7.0 : 26.4 : 33.3

Modification of carrier by zeolite ZSM-5 in the presence of aluminium oxynitrate promoted increase the content of acetone in catalyzate up to 70 - 80 %, but decreased the content of acetaldehyde, Figure 4. The content of acetone was higher the whole temperature interval. C_3-C_4 : O_2 = 33.3 : 7.0 ratio is more optimal for selective obtaining of acetone and acetaldehyde.

Large particles and aggregates from large dense particles are characteristic for initial MoCrGa/NWC catalyst. Micro-diffraction picture of particles is submitted by the separate rare reflexes referred to Cr_2O_3 (JCPDS, 6 - 508), CrO (JCPDS, 6 - 532), and also translucent lamellar type a particle, micro-diffraction picture from which is submitted by the reflexes which are settling down on hexagonal motive, referred to $CrMoO_4$ (JCPDS, 34 - 474). For the Mo-containing phase processed in reaction conditions the dense large crystals (500 - 1,000 Å) with attributes of rectangular motive the facets corresponding Mo_4O_{11} (JCPDS, 13 - 142) are characteristic. For a Cr-containing phase the large translucent lamellar particles of α-Cr_2O_3 (JCPDS, 6 - 503), small congestions made from disperse particles in the size ~ 30 Å, referred to Cr_2O_5 (JCPDS, 36 - 1329), aggregates from translucent particles with the minimal sizes 200 - 400 Å and more, characteristic for CrO_2 (JCPDS, 9 - 332), congestion of translucent lamellar particles of Cr_5O_{12} (JCPDS, 18 - 390) in the size 300 - 600 Å with rectangular motive of a facet are characteristic. Besides small congestions, characteristic for the joint phases consisting of particles in the size 30 - 50 Å and large lamellar particles are found. Micro-diffraction is submitted by a mix of rings and separate reflexes. Rings correspond to a phase of disperse particles of $CrMoO_4$ (JCPDS, 29 - 452), and large lamellar crystals correspond to Cr_2MoO_6 (JCPDS, 33 - 401). For a Ga-containing phase the various phases for oxidation of Ga down to a metal phase are characteristic: α-Ga_2O_3 (JCPDS, 6 - 503), φ-Ga_2O_3 (JCPDS, 20 - 426), ε-Ga_2O_3 (JCPDS, 6 - 509) in a mix with Ga (JCPDS, 31 - 539), Ga (JCPDS, 25 - 345). Comparison with EM pictures of initial samples of catalysts has allowed to determine, that as a result of their processing in reaction conditions there is the new phase Cr_2O_5 corresponding to transition Cr^{2+} and Cr^{3+} into Cr^{5+}, and also joint phases of Mo with Cr in various valent conditions. The physical sense and role of them should be determined.

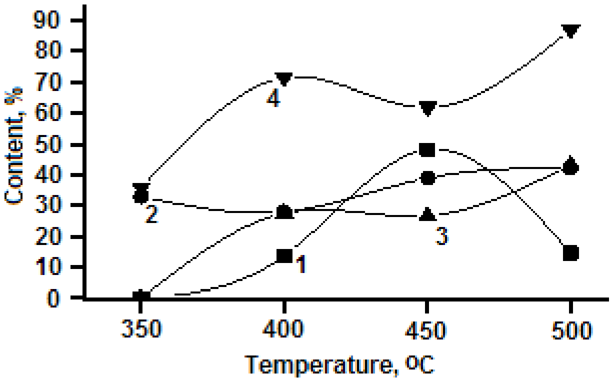

Figure 4: Influence of the temperature on content of acetone in catalyzate at oxidation of propane-butane mixture. C_3-C_4 HC : O_2 : N_2 : Ar = 33.33 : 7.0 : 26.0 : 33.67 (%). WHSV = 1350 h^{-1}. 1 – 1 % MoCrGa/WNC; 2 – 5 % MoCrGa/WNC; 3 – 10 % MoCrGa/WNC; 4 – 5 % MoCrGa/WNC+ZSM-5 + $Al_n(OH)_{3n-1}NO_3$

4. Conclusions

The determination of the product composition showed that the process follows a complex mechanism including oxidation, oxidative dehydrogenation, and cracking. The optimal conditions for synthesis of products were detected:

- 50.9 % of acetone was produced on 5 % MoCrGa/TWC catalyst at 550 °C and WHSV = 450 h^{-1} in reaction mixture C_3-C_4 : O_2 : N_2 : Ar = 5 : 1 : 4 : 5;
- 41.0 % of acetaldehyde was produced on 10 % MoCrGa/TWC catalyst at 450 °C and WHSV = 450 h^{-1} in reaction mixture C_3-C_4 : O_2 : N_2 : Ar = 5 : 1 : 4 : 5;
- 80.0% of methyl ethyl ketone was produced on 5 % MoCrGa/TWC+ZSM-5+$Al_n(OH)_{3n-1}NO_3$ catalyst at 450 °C and WHSV = 3150 h^{-1} in reaction mixture C_3-C_4 : O_2 : N_2 : Ar = 1 : 1 : 4 : 1;
- 71.4 % of ethylene was produced on 1 % MoCrGa/TWC catalyst at 450 °C and WHSV = 450 h^{-1} in reaction mixture C_3-C_4 : O_2 : N_2 : Ar = 5 : 1 : 4 : 5;
- 83.0 % of benzene was produced on 1 % MoCrGa/TWC catalyst at 550 °C and WHSV = 750 h^{-1} in reaction mixture C_3-C_4 : O_2 : N_2 = 7 : 1 : 4.

This screening study aimed at searching for appropriate compositions and technological parameters of the oxidative conversion of propane and the propane-butane mixture show that the chosen line of research is promising and makes it possible to obtain good results in the synthesis of hydrocarbons and oxygenated compounds.

References

Arutyunov V.S., Magomedov R.N., Proshina A.Y., Strekova L.N., 2014, Oxidative conversion of light alkanes diluted by nitrogen, helium or methane, Chem. Eng. J., 238, 9-16.

Bocanegra S., Ballarini P., Zgolicz P., Scelza O., de Miguel S., 2009, Highly selectiveand stable bimetallic catalysts supported on different materials for n-butane dehydrogenation, Catal. Today, 143, 334-340.

Brauer G., Eds., 1985, Handbook on Preparative Inorganic Chemistry, Mir, Moscow, Russian Federation (in Russian).

Casaletto M.P., Land G., Lisi L., Patrono P., Pinzari F., 2010, Effect of the support on the catalytic prpperties of vanadil phosphate in the oxidative dehydrogenation of propane, J. Mol. Catal. A. Chem., 329, 50-56.

Choudhary V.R., Mantri K., Sivadinarayana C., 2000, Influence of zeolite factors affecting zeolitic acidity on the propane aromatization activity and selectivity of Ga/H–ZSM-5, Micropor. Mesopor. Mater., 37, 1-8.

Crapanzano S., Babich I.V., Lefferts L., 2013, The influence of over-stoichiometry in $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ on selective oxidative dehydrogenation of propane, Catal. Today, 203, 17-23.

Dossumov K., Tungatarova S.A., Kuzembaev K.K., Massalimova B.K., 2005, Oxidative C_3–C_4 hydrocarbon conversion to olefins and oxygen-containing compounds in the presence of molybdenum and tungsten polyoxometalates, Petroleum Chemistry, 45, 261-263 (in Russian).

Dossumov K., Tungatarova S.A., 2010, Synthesis of acetone and acetaldehyde from propane-butane mixture, Materials Research Society Symposium Proceedings, August 15-19, Cancun, Mexico, Warrendale, Pennsylvania, 1279, 215-221.

Erofeev V.I., Medvedev A.S., Khomyakov I.S., Erofeeva E.V., 2013, Conversion of gas-condensate straight-run gasolines to high-octane gasolines over zeolite catalysts modified with metal nanopowders, Russian Journal of Applied Chemistry, 86, 979-985.

Esche E., Arellano-Garcia H., Biegler L.T., Wozny G. 2012, Two-dimensional modeling of a packed-bed membrane reactor for the oxidative coupling of methane, Chemical Engineering Transactions, 29, 1537-1542.

O'Neill C., Wolf E.E., 2010, Partial oxidation of propane to acrolein in a dual bed inert membrane reactor, Catal. Today, 156, 124-131.

Palma V., Ricca A., Meloni E., Miccio M., Martino M., Ciambelli P., 2015, Methane steam reforming intensification: experimental and numerical investigations on monolithic catalysts, Chemical Engineering Transactions 43, 919-924.

Patcharavorachot Y., Tiraset S., Saebea D., Arpornwichanop A., 2013, Optimization of a membrane-based oxidative coupling of methane reactor using surface response methodology, Chemical Engineering Transactions, 35, 121-126.

Phongaksorn M., Tungkamani S., Dharmasaroja N., Sornchamni T., Chuvaree R., Kanjanabat N., Siri-Nguan N., 2015, Elucidation of the influence of Ni-Co catalytic properties on dry methane reforming performance, Chemical Engineering Transactions, 43, 925-930.

Pope M.T., Eds., 1990, Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983, Nauka, Novosibirsk, Russian Federation.

Tungatarova S.A., Savelieva G.A., Dossumov K., 2003, Oxidative conversion of methane over supported molybdenum heteropoly compounds, Proceedings of NATO Advanced Study Institute. Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges, and Opportunities, July 6-19, Vilamoura, Algarve, Portugal, 345-350.

Tungatarova S.A., 2010, Transformations of supported heteropoly compounds in oxidative conversion of alkanes, Materials Research Society Symposium Proceedings, August 15-19, Cancun, Mexico, Warrendale, Pennsylvania, 1279, 27-39.

Urlan F., Marcu I.C., Sandulescu I., 2008, Oxidative dehydrogenation of n-butane over titanium pyrophosphate catalysts in the presence of carbon dioxide, Catal. Commun., 9, 2403-2406.

Wang G., Dai H., Zhang L., Deng J., Liu C., He H., Au Ch.T., 2010, CrO_x/nano-$Ce_{0.60}Zr_{0.35}Y_{0.05}O_2$ catalysts that are highly selective for the oxidative dehydrogenation of isobutane to isobutene, Appl. Catal., A, 375, 272-278.

Yang H.P., Fan Y.N., Feng L.Y., Qiu J.H., Lin M., Xu B.L., Chen Y., 2002, The structure and catalytic properties of Bi-V-Mo-O composite oxide catalysts for selective oxidation of propane, Huaxue xuebao, 60, 1006-1010.