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Торайгыров университета

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A. S. Krasilnikova[1], A. Zh. Kassanova[2]
[1,2]Toraighyrov university,
Republic of Kazakhstan, Pavlodar.
*e-mail: krasilkas12@mail.ru

SYNTHESIS OF METAL ORGANIC FRAMEWORKS AND THEIR APPLICATION AS PHOTOCATALYSTS

This article investigates the synthesis and catalytic applications of metal-organic frameworks (MOFs), with a detailed focus on their role in alcohol oxidation to carbonyl compounds, especially in converting isopropanol to acetone. MOFs like $[Cu_2(1,4\text{-chdc})_2]$ *offer high surface area, tunable pore structures, and reusability, making them ideal for various catalytic applications. This study explores the properties, synthesis, and catalytic mechanisms of MOFs, addressing challenges in conventional acetone production methods such as the cumene process. It highlights the use of hydrogen peroxide as an oxidizing agent, combined with titanium dioxide to enhance MOFs' oxidative capacity, demonstrating improved efficiency in UV-catalyzed reactions. Experimental findings indicate that titanium dioxide-modified MOFs achieve optimal performance with high catalytic activity and stability, providing an eco-friendly and economically viable solution for acetone production.*

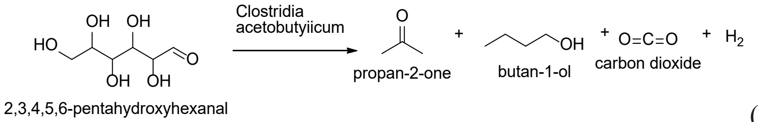
Keywords: metal-organic frameworks, alcohol oxidation, catalysis, acetone production, hydrogen peroxide.

Introduction

Metal-organic frameworks (MOFs) are an emerging class of materials with a crystalline structure, high surface area (up to 10,400 m^2/g), large pore sizes, and low density. Typically synthesized by combining hydrophilic metal and hydrophobic organic linkers through hydrothermal methods, MOFs offer customizable shape and size, making them valuable in industry and research. They act as effective heterogeneous catalysts with reusability and minimal leaching, suited for liquid-phase organic reactions [1]. Despite barriers like temperature limits (80–90 ºC) and competition with established materials, MOFs are promising for low-temperature oxidation reactions and applications in the oil industry, especially for reactions like alcohol oxidation to aldehydes or ketones.

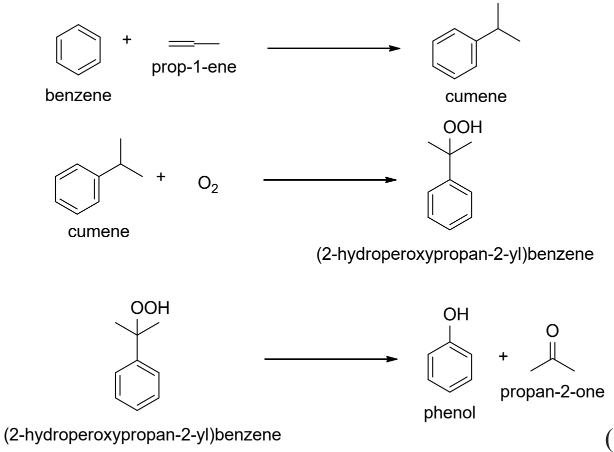
Methods for producing acetone in industry:

- acetone-butyl fermentation of carbohydrates (starch, sugars, molasses), caused by bacteria - clostridia, in particular Clostridium acetobutylicum by reaction scheme (1). During fermentation, acetone and butyl or ethyl alcohols are formed [1]. Acetone and butyl alcohol are obtained in a molar ratio from 2:1 to 3:1. The method is characterized by low yields [2].



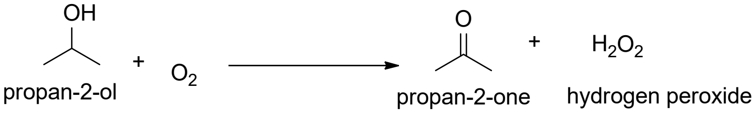
(1)

- cumene method - the main part of acetone is obtained as a co-product when producing phenol from benzene using the cumene method by reaction scheme (2). The process occurs in 3 stages [3]. At the first stage, benzene is alkylated with propene to produce isopropylbenzene (cumene), at the second and third (Udris-Sergeev reaction), the resulting cumene is oxidized with atmospheric oxygen to hydroperoxide, which, under the action of sulfuric acid, decomposes into phenol and acetone.



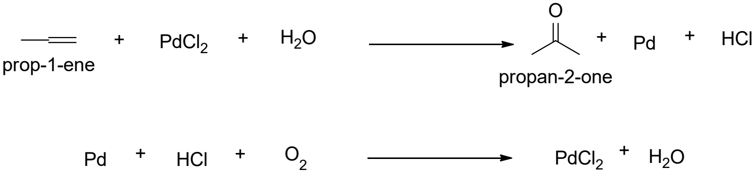
(2)

- from isopropanol – catalytic oxidation of isopropanol with air by reaction scheme (3). The thermal effect of the reaction is significant, which, along with the presence of a number of highly selective catalysts for this process (silver, copper, etc.), makes it more acceptable for industrial implementation. According to this method, isopropanol is oxidized in the vapor phase at temperatures of 450–650 °C on a catalyst (metallic copper, silver, nickel, platinum). Acetone with a high yield (up to 90 %) is obtained on a «silver on pumice» catalyst or on a silver mesh [4].



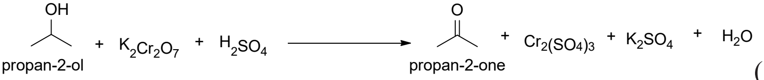
(3)

- method of direct oxidation of propene in the liquid phase in the presence of $PdCl_2$ in solutions of Pd, Cu, Fe salts by reaction scheme (4) at a temperature of 50–120 °C and a pressure of 50–100 atm [5].



(4)

In the laboratory, acetone is obtained by oxidizing isopropyl alcohol with potassium dichromate in an aqueous solution of sulfuric acid by reaction scheme (5) [6].



(5)

The reaction is carried out in a round-bottomed flask with a reflux condenser while heating (figure 1).

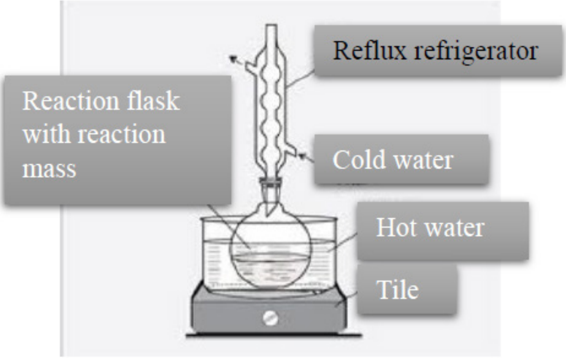
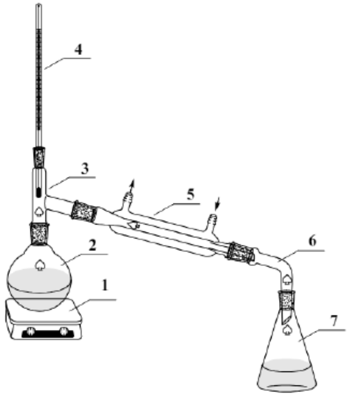


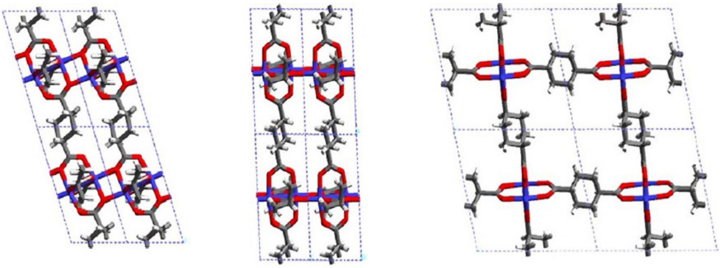
Figure 1 – Installation for acetone synthesis

Then the reflux condenser is replaced with a direct one and the fraction boiling in the range of 55–58 °C is distilled off in a water bath (figure 2).



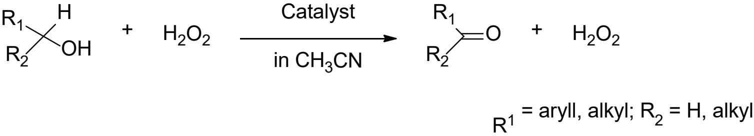
1 – heating device, 2 – round-bottomed flask, 3 – nozzle, 4 – thermometer, 5 – direct refrigerator, 6 – long, 7 – receiver
Figure 2 – Installation for distilling acetone from the reaction mass

The authors used MOF [$Cu_2(1,4\text{-chdc})_2$] as a heterogeneous catalyst for alcohol oxidation (e.g., 2-propanol, cyclohexanol) with H_2O_2. Unlike other copper carboxylates, this MOF remains stable in H_2O_2. Copper leaching was ruled out, confirming its role as a solid catalyst [7]. A green intermediate, identified as copper peroxide $H_2[Cu_2(1,4\text{-chdc})_2(O_2)]$, was isolated and found catalytically active, converting 2-propanol to acetone even without H_2O_2 [8].



a) axe a b) axe b c) axe c

Figure 3 – Unit-cell packing of complex [Cu2(1,4-chdc)2]



R^1 = aryll, alkyl; R_2 = H, alkyl

(9)

Materials and methods

Reagents used in the synthesis: 4-azido-1H-pyrazole, 3-azido-5-methyl-1H-pyrazole, 1-(5-methyl-1H-pyrazol-3-yl)-1H-1,2,3-triazole-4-carboxylic acid, 1-(1H-pyrazol-4-yl)-1H-1,2,3-triazole-4-carboxylic acid, cadmium nitrate tetrahydrate, cuprum nitrate dihydrate purchased from Sigma-Aldrich.

Solvents: dimethylformamide, diethylformamide, dioxane, dimethyl sulfoxide, ethanol, sodium hydroxide, hexane, propan-2-ol were classified as chemically pure and were used without further purification.

The progress of the reactions was monitored by TLC. To detect fluorescent traces on TLC plates, a BL-Black-Light UV lamp (365 nm), Vilber, France was used.

The solvent was distilled off using a PE-8920 rotary evaporator (OOO EKROSKHIM, St. Petersburg).

The melting point was measured with a device for determining the melting point PTP(M), V ~ 220 V, W = 500 VA, TU 92-891.001–90, 2006.

The thermosolvate synthesis of MOFs was carried out in an LF-25/350-VS2 oven with a power of 1200 W (AO LOIP, St. Petersburg).

Solids were dispersed using a GA008G ultrasonic bath (GRANBO, China).

NMR spectra were recorded using a Bruker Advance III instrument (500 MHz).

IR spectra in KBr granules were recorded in the range 4000–400 cm–1 on a Bruker Scimitar FTS 2000 spectrometer.

Thermogravimetric analysis was performed on a NETZSCH TG 209F3 TGA209F3A-0646-L instrument in an He atmosphere in the range from 30 to 850 °C, heating rate 10°C/min.

Powder X-ray diffraction (PXRD) analysis was performed at room temperature on a Shimadzu XRD-7000 diffractometer (Shimadzu Corporation, Kyoto, Japan, Cu-K α radiation, λ= 1.54178 Å).

Elemental analysis was performed on a Vario Microcube analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany).

The possible formation of acetone from isopropanol was monitored using a gas chromatograph Kristallux-4000M (Meta-Chrome, Republic of Mari El, Yoshkar-Ola).

Methods for the synthesis: thermosolvation method for the synthesis of MOFs using various solvents, metals and temperatures; modification of MOFs with titanium dioxide (TiO_2) nanoparticles; isopropanol oxidation in the presence of a catalyst (MOF) and hydrogen peroxide under the influence of ultraviolet radiation with constant stirring.

Results and discussion

After a series of thermosolvate syntheses, selecting a solvent, metal and temperature, a cadmium-containing frameworks $C_6H_3CdN_5O_2$ (MOF-1) (Mr = 289 g/mol) was obtained, which is based on the ligand 1-(1H-pyrazol-4-yl)-1H-1,2, 3-triazole-4-carboxylic acid and $C_7H_6CdN_5O_2$ (MOF-2) (M = 304 g/mol), which is based on the ligand 5-methyl-1H-pyrazol-3-yl-1H-1,2,3-triazole-4-carboxylic acid (figure 4).

It is known that titanium dioxide nanoparticles are widely used in organic synthesis in the processes of complete oxidation of organic substances. Selective oxidation of isopropanol was carried out in the presence of:

a) MOF-1 (5 mol %) and titanium dioxide nanoparticles (10 mg);

b) MOF-1 (5 mol %) and 43,8 % hydrogen peroxide (5 mol %);

c) MOF-2 (5 mol %) and 43,8 % hydrogen peroxide (5 mol %);

d) MOF-2 (5 mol %) and titanium dioxide nanoparticles (10 mg).

In a previously presented article, the authors described the oxidation of alcohols catalyzed by copper-containing MOFs in the presence of hydrogen peroxide [9]. The oxidation reaction of isopropanol (3 ml) with obtained frameworks (5 mol %) and hydrogen peroxide (5 mol %) was carried out under the influence of ultraviolet radiation of 24 W and during constant stirring. Then, we performed flash chromatography for (c) and (d) on the resulting mixture of isopropanol and acetone to separate the water contained in the added hydrogen peroxide solution and recorded a gas chromatogram.

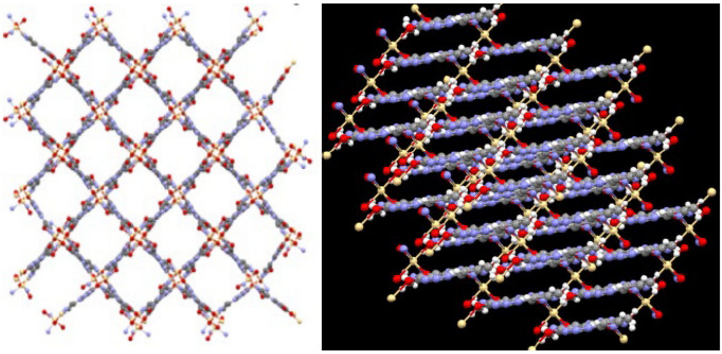
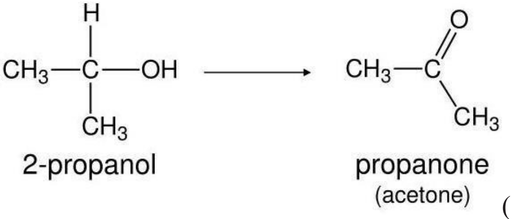


Figure 4 – MOF-1 and MOF-2 structure obtained after X-ray diffraction

Alcohol oxidation to carbonyl compounds is key in organic chemistry, especially for eco-friendly processes and material production. Acetone, essential in labs and industries, serves as a solvent and precursor for various products like adhesives and coatings. Industrial acetone production is primarily via cumene hydroperoxide oxidation, producing both acetone and phenol. However, alternatives to this method are needed to balance the phenol market.

Titanium dioxide nanoparticles are known for catalyzing complete organic oxidation. Using this, the authors modified a previously synthesized MOF (with cadmium and 1-(1H-pyrazol-4-yl)-1H-1,2,3-triazole-4-carboxylic acid ligand) by adding titanium oxide nanoparticles through solvothermal synthesis. The modified MOF showed distinct absorption properties and was tested for isopropanol oxidation to acetone as a model reaction (10).



(10)

The oxidation reaction of isopropanol (3 ml) in the presence of modified MOF (5 mol %) and hydrogen peroxide (5 mol %) was carried out under the influence of ultraviolet radiation of 24 W and during constant stirring [10].

We tested different catalytic systems for the oxidation of isopropanol,

under which conditions we obtained different results of the reaction, presented in table 1.

Table 1 – results of the isopropanol oxidation reaction

Catalytic system	Products of the reactions			
	Initial substance	Content, %	Obtained substance	Conversion, %
MOF-1 (5 mol %) and titanium dioxide nanoparticles (10 mg)	Isopropanol	100	Acetone	61,8
MOF-1 (5 mol %) and hydrogen peroxide (5 mol %)	Isopropanol	100	Acetone	0
MOF-2 (5 mol %) and hydrogen peroxide (5 mol %)	Isopropanol	100	Acetone	0
MOF-2 (5 mol %) and titanium dioxide nanoparticles (10 mg)	Isopropanol	100	Acetone	0

Then, we performed flash chromatography on the resulting mixture of isopropanol and acetone to separate the water contained in the added hydrogen peroxide solution and recorded a gas chromatogram.

To monitor the progress of the reaction, we used a Kristallux-4000M gas chromatograph.

First, pure isopropanol was analyzed to determine its retention time. The chromatogram of pure isopropanol is shown in Figure 5.

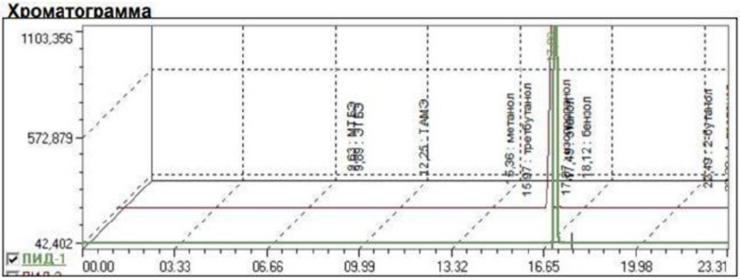
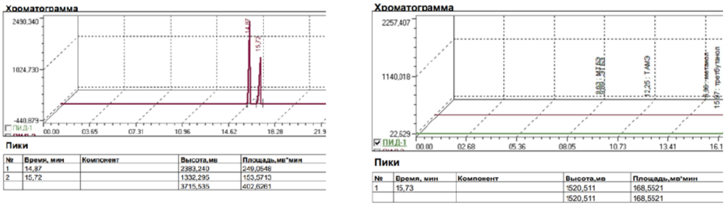


Figure 5 – Chromatogram of the starting substance – isopropanol

Chromatograms of samples of the resulting substance taken from catalytic systems are presented in figure 6.



Пики

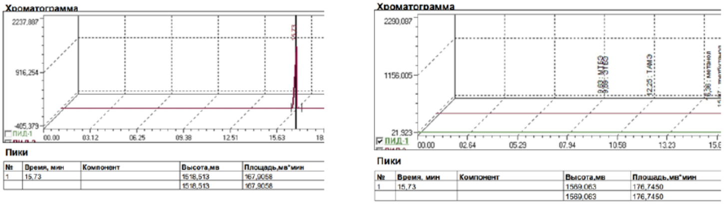
№	Время, мин	Компонент	Высота,мв	Площадь,мв*мин
1	14,87		2383,240	249,0548
2	15,72		1332,295	153,5713
			3715,535	402,6261

MOF-1 (5 mol %) and
titanium dioxide nanoparticles (10 mg)

Пики

№	Время, мин	Компонент	Высота,мв	Площадь,мв*мин
1	15,73		1520,511	168,5521
			1520,511	168,5521

MOF-1 (5 mol %) and
hydrogen peroxide (5 mol %)



Пики

№	Время, мин	Компонент	Высота,мв	Площадь,мв*мин
1	15,73		1518,513	167,9058
			1518,513	167,9058

MOF-2 (5 mol %) and
hydrogen peroxide (5 mol %)

Пики

№	Время, мин	Компонент	Высота,мв	Площадь,мв*мин
1	15,73		1569,063	176,7450
			1569,063	176,7450

MOF-2 (5 mol %) and
titanium dioxide nanoparticles (10 mg)

Figure 6 – Chromatograms of resulting product in different catalytic systems

Conclusion

During this thesis, the following practical results with industrial potential were achieved:

a) A cadmium-based MOF with 1-(1H-pyrazol-4-yl)-1H-1,2,3-triazole-4-carboxylic acid as the linker was synthesized. Characterized by IR, X-ray diffraction, and TGA-DSC, the MOF has a near-cubic cell structure with 49 % free volume (1286.55 Å^3), offering strong sorption capabilities. Its porous, tetragonal tunnel structure makes it suitable for storing, separating, and transporting liquids and gases. However, it is catalytically useful only in low-temperature reactions due to mass loss above 400 °C.

b) Modifying this MOF with titanium dioxide may enhance its oxidative ability, enabling its use as a catalyst for alcohol-to-ketone oxidation.

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**А. С. Красильникова*[1]*, А. Ж. Касанова*[2]
[1,2]Торайғыров университеті,
Қазақстан Республикасы, Павлодар қ.

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МЕТАЛДЫҚ ОРГАНИКАЛЫҚ ПОЛИМЕРЛЕРДІҢ СИНТЕЗІ ЖӘНЕ ОЛАРДЫ ФОТОКАТАЛИЗАТОР РЕТІНДЕ ҚОЛДАНУ

Бұл мақалада спирттің карбонилді қосылыстарға тотығуындағы, әсіресе изопропанолдың ацетонға айналуындағы рөліне баса назар аудара отырып, металл-органикалық координациялық полимерлердің (МОКП) синтезі мен каталитикалық қолданылуы қарастырылады. [$Cu_2(1,4\text{-}chdc)_2$] сияқты МОКП-тердің үлкен бетінің ауданы, реттелетін кеуекті құрылымы және қайта өңдеу мүмкіндігі бар, бұл оларды әртүрлі каталитикалық қолданбалар үшін өте қолайлы етеді. Бұл зерттеу МОКП қасиеттерін, синтезін және каталитикалық механизмдерін зерттейді, кумен процесі сияқты дәстүрлі ацетон өндіру әдістеріндегі мәселелерді шешеді. Ол УК-катализделген реакциялардағы тиімділікті жоғарылатып, МОКП тотығу қабілетін арттыру үшін сутегі асқын тотығын титан диоксидімен бірге тотықтырғыш ретінде пайдалануды көрсетеді. Эксперименттік нәтижелер титан диоксиді модификацияланған МОКП жоғары каталитикалық белсенділік пен тұрақтылықпен оңтайлы өнімділікке қол жеткізіп, ацетон өндірісі үшін экологиялық таза және үнемді шешімді қамтамасыз ететінін көрсетеді.

Кілтті сөздер: металлорганикалық координациялық полимерлер, спирт тотығуы, катализ, ацетон алу, сутегі асқын тотығы.

**А. С. Красильникова[1], А. Ж. Касанова[2]*
[1,2]Торайгыров университет,
Республика Казахстан, г. Павлодар.

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СИНТЕЗ МЕТАЛЛООРГАНИЧЕСКИХ КООРДИНАЦИОННЫХ ПОЛИМЕРОВ И ИХ ПРИМЕНЕНИЕ В КАЧЕСТВЕ ФОТОКАТАЛИЗАТОРОВ

В этой статье исследуется синтез и каталитическое применение металлоорганических координационных полимеров (МОКП) с акцентом на их роли в окислении спирта до карбонильных соединений, особенно в превращении изопропанола в ацетон. МОКП, такие как [$Cu_2(1,4\text{-}chdc)_2$], обладают большой площадью поверхности, настраиваемой пористой структурой и возможностью повторного использования, что делает их идеальными для различных каталитических применений. В этом исследовании изучаются свойства, синтез и каталитические механизмы МОКП, решая проблемы в традиционных методах производства ацетона, таких как кумольный процесс. В нем подчеркивается использование перекиси водорода в качестве окислителя в сочетании с диоксидом титана для повышения окислительной способности МОКП, демонстрируя повышенную эффективность в реакциях, катализируемых УФ-излучением. Экспериментальные результаты показывают, что модифицированные диоксидом титана МОКП достигают оптимальной производительности с высокой каталитической активностью и стабильностью, обеспечивая экологически чистое и экономически выгодное решение для производства ацетона.

Ключевые слова: металлорганические координационные полимеры, окисление спиртов, катализ, производство ацетона, пероксид водорода.

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«Toraighyrov University» баспасынан басылып шығарылған
Торайғыров университеті
Павлодар мемлекеттік университеті
140008, Павлодар қ., Ломов к., 64, 137 каб.

«Toraighyrov University» баспасы
Торайғыров университеті
140008, Павлодар қ., Ломов к., 64, 137 каб.
8 (7182) 67-36-69
e-mail: kereku@tou.edu.kz
www.vestnik-cb.tou.edu.kz