

UDC 544.1

<https://doi.org/10.15407/kataliz2021.31.001>

Mechanochemistry as advanced methodology in green chemistry for applied catalysis

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In this survey we have assessed how mechanochemistry techniques comply with the aims of Green Chemistry to minimise the use of environmentally damaging reactants and unwanted by-products. In the publications the preparation of vanadium-phosphorus oxides as industrial catalysts for maleic anhydride production from n-butane and perspective catalysts of phthalic anhydride manufacture by direct n-pentane oxidation were analyzed. It is shown that mechanochemical activation and synthesis reduces the amount of harmful waste used in the production of the catalyst and increases its effectiveness. Improvement of a catalyst's properties, help limit production of harmful emissions such as carbon oxides and hydrocarbons. It was established that mechanochemical treatment can be successfully used in the process of industrial vanadium-phosphorus oxide catalysts modification or in the process of introduction in its composition of additives which lead to increase of activity and selectivity of hydrocarbons oxidation. The possibility of the mechanochemistry use in the vanadium-titanium oxide catalysts preparation which are the base catalysts in industrial phthalic anhydride production from o-xylene was determined. It was established that mechanochemical treatment of the vanadium and titanium oxides mixture permits to delete the nitrogen oxides emission in atmosphere and prepared catalysts demonstrate the same phthalic anhydride yield but at low reaction temperature. Catalysts, manufactured by mechanochemical treatment (on the base of molybdenum oxide), provide new techniques for producing compounds as exemplified by the direct oxidation of benzene to form phenol which can replace industrial two-step process from cumene or proposed process of benzene oxidation by N₂O. Mechanochemistry treatment could produce catalysts which eliminated the need to use highly toxic nitrogen oxides as reducing agents. The article describes activating Cu-Ce-O catalysts which reduce the temperature of the process for removing carbon monoxide from exhaust gases and as a method for purifying hydrogen used in fuel cells. Finally, there is a description of mechanochemically treated catalysts, containing metals and supported on stainless steel supports which are used to remove aromatic hydrocarbons from water sewers.

Keywords: green chemistry, catalysis, oxide catalysts, mechanochemistry

Introduction

Catalysis is crucially important to the economies of the developed world as shown by the following data. The cost of catalyst manufacture in the USA in 1992 for the fuel and chemical industry was estimated to be US\$ 1.5 billion dollars compare this with value of the products manufactured using catalysts which is approximately 600 times greater (US\$ 890 billion dollars) [1]. The cost of production of catalysts in 1995 was \$US 8.6 billion rising to \$US 11.4 billion by 2001 and \$US 16.2 billion by 2011 with one third of the money being spent on manufacturing catalysts used for environmental protection [2-3].

There are a large number of publications [e.g. 3-17] describing ecological problems where catalyst design could provide a solution. Developing new catalysts which minimise damage to the environment falls into the following categories:

1. Reducing toxic by-products (waste). Manufacturing catalysts using new techniques which reduce the quantity of damaging by-products.

2. Increasing the yield whilst reducing the number of harmful by-products. Improving catalyst designs in order to

increasing its efficiency and reducing the number of harmful by-products/waste.

3. Creating new efficient ecological catalysts.

4. Developing processes that produce the required product from non-toxic components and without toxic or harmful waste.

In this survey we present the results from a some of the work performed that extend the role of catalysts in the field of environmental protection.

Modern techniques for preparing catalysts include reactions carried out:

i) in solution using organic and inorganic solvents, oxidants, stabilisers:

- by impregnation,
- deposition-precipitation,
- sol-gel method,
- ion exchange,

ii) in gas phase:

- grafting,
- CVD,
- PVD,

- combustion,
- iii) in solid state by high-temperature process.

It is important to stress that all the methods generate significant quantities of liquid and gaseous waste including harmful/hazardous substances that, according to the Kyoto protocol, require additional processing to purify regenerate and reuse solvents [18-23]. Studies of existing data related to catalytic processes indicate there is much that can be improved [24–31].

Conventional methods for synthesizing catalysts including all the methods of optimisation don't always lead to increased efficiency. For these reasons it is important to explore new techniques and solutions in the field of catalyst technology [32–44] when trying to find solutions to environmental problems.

An alternative “Green Process” is mechanochemical treatment [45], which significantly reduces the quantity of solvent used. It also allows metals and their oxides to be used in reactions instead of salts. With these changes it is possible to completely eliminate gaseous waste (CO_x , NO_x , and SO_2) as well as increasing activity and selectivity of the catalyst.

A study into the possible applications of mechanochemical methods in catalysis is partly presented in papers [46–49]. Papers [50-52] deal with the synthesis and modification of solids.

Mechanochemical treatments have the following variants:

- 1) Mechanochemical activation of the reactants before conducting a traditional synthesis – MChA
- 2) Mechanochemical activation of the catalyst prepared in the traditional way (including doping) – MChA
- 3) Mechanochemical synthesis of catalyst by high energy reactive milling – MChS
- 4) Mechanocatalytic process as a result of mechanical treatment - MChCP

The following sections provide explanations and examples of all the techniques mentioned above, together with reasons as to why they should be considered as “Green Chemistries”.

Experimental

Catalyst preparation and characterization methods

Mechanochemical treatment was provided using two different high-energy laboratory planetary mills:

1. *Pulverisette 6* (by Fritsch GmbH) with vial and ball made of Si_3N_4 and WC with a rotation speed 550-600 rpm.
2. A mill with vial and balls of hardened steel with rotation speed of 3,000 rpm. The mass proportions of balls to sample were 10:1 and 10-20:1, respectively. The milling processes were performed in air and liquid media (water or ethanol).

The phase identification and physico-chemical characteristics of milling products were determined using the following methods:

- X-ray powder diffraction (XRD) patterns were recorded on a Philips X'Pert or Philips PW 1830 diffractometers ($\text{CuK}\alpha$).

- The binding energy was determined using X-ray photoelectron spectroscopy (XPS) with a VG scientific ESCA-3 X-ray photoelectron spectrometer (Al $\text{K}\alpha 1.2$). The binding energies were referenced to the C 1s line (284.8 eV) determination.

- Specific surface area (BET) of samples was determined using thermal method of nitrogen adsorption (Gazochrom-2).

- Morphology of the surface was pictured using a scanning electron microscope (SEM) Hitachi S-4000.

- Micro-Raman spectra were obtained by Dilor Labram spectrometer (He Ne laser – 632.8nm). The spectrometer was connected to the electron microscope to analyse the surface.

- The composition of catalysts surface was investigated using atomic force microscopy (AFM) with Nanoscope E Digital Instruments Scanning Probe Microscope Controller.

Catalytic oxidation processes of practical importance used for testing the reactivity of mechanochemically prepared metal oxide catalysts:

- partial oxidation of n-butane (1.6 vol. % in air) in apparatus with a flow reactor of stainless steel, described in detail [53];
- partial oxidation of o-xylene (0.9 vol. % in air) in analogous conditions;
- selective reduction of NO (900 pm) by ammonia (1000 ppm) with He containing 1 vol. % of O_2 ;
- partial oxidation of benzene (1.1 vol. % in air) in a quartz flow reactor;
- CO oxidation (1 vol. %) in combination with O_2 (1 vol. %) in He in a flow reactor of stainless steel.

A mixture of gases in the measurements of temperature-programmed catalytic reaction (TPR) was used: CO (1 vol. %), H_2 (75 vol. %), O_2 (1 vol. %), He (23 vol. %). A quartz flow reactor with product analysis using quadruple mass-spectrometer was used.

The concentration of hydrocarbons in water after their oxidation during mechanochemical treatment was measured by chromato-mass spectrometry (Varian 3400 with Incos 50 Finnigan).

Results and Discussion

1. Vanadium-phosphorus oxide catalysts

The industrial process for manufacturing maleic anhydride is based on the oxidation of n-butane in the presence of vanadium-phosphorus oxide (VPO) catalysts different compositions but the base of these catalysts is the composition which contents vanadium and phosphorus oxides with atomic ratio V/P near to 1. [54-58]. The different nature additives to this composition which increase the activity and selectivity of the catalysts can be introduced in different steps of the catalyst synthesis. The most used method of VPO catalysts preparation based on reaction between V_2O_5 and H_3PO_4 in organic media (most used is butanol) with an addition of the reducing agent in this composition (most used is benzyl alcohol or oxalic acid). The molar ratio butanol/ V_2O_5 in the synthesis is 6-9 and reducing agent to V_2O_5 is equal to 1/1-2 [54-59]. The addition of reducing agent in reaction

mixture connected with low rate of the catalyst precursor $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ formation in the presence of butanol only. The big quantity of butanol used in the synthesis determines the necessity its reuse in this process. In same time partial oxidation of the butanol in synthesis process to aldehydes and acids affects in negative way the crystal structure of the precursor. So, the purification of the solvent becomes an essential step prior to its use in formation of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ in order to reduce the amount of the aldehydes and acids in solvent. It was noted that the using oxalic and benzyl alcohol partially reduces V^{5+} to V^{4+} ions which speeds up the reaction of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ formation but even with these enhancements the process still takes 12 -18 hours to complete.

1.1 Mechanochemical activation of reactants (MChA)

It is necessary to note that early we found that mechanochemical activation of V_2O_5 changes its morphology and undergoes a partial reduction to produce V^{4+} ions. Refer to Table 1 and papers [59-62] for details.

The obtained results permit to predicted that the use of the V_2O_5 after its mechanochemical treatment in $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ preparation can permit to excluded the participation of reducing agent in the synthesis. The properties of the VPO catalysts prepared on the base of V_2O_5 -MChA without reducing agent in n-butane oxidation to maleic anhydride presented in Table 2. The obtained results show that synthesized catalysts are not inferior the catalyst prepared by traditional method but demonstrate higher activity and selectivity. Further improvements, to the catalyst, were made by milling V_2O_5 in ethanol and water.

Table 1. Properties of V_2O_5 after mechanochemical treatment under different conditions

V_2O_5 sample	Medium/time, min	BET, m^2/g	XRD, I_{010}/I_{110}	XPS data		
				BE V 2p _{3/2} , eV		$\text{V}^{4+}/\text{V}^{5+}$ ratio
I	Initial sample	4.1	1.1	517.8	-	0.0
A	Air/30	19.2	0.8	517.7	516.4	0.10
E-1	Ethanol/20	8.0	4.1	517.9	516.5	0.13
E-2	Ethanol/30	8.2	4.2	517.6	516.1	0.37
W-1	Water/20	27.0	2.1	517.8	516.4	0.04
W-2	Water/30	1.6	*	517.6	516.2	0.41

* VO_2 reflexes were only observed

Table 2. Properties of VPO catalysts synthesized with V_2O_5 -MChA

Initial V_2O_5 sample	VPO synthesized catalysts						
	BET, m^2/g	XRD, I_{001}/I_{220}	BE, eV V 2p _{3/2}	n-Butane oxidation*			
				X_{C_4} , %	S_{MA} , %	C_{CO_x} , vol. %	$\text{C}_{\text{C}_{4\text{ex}}}$, vol. %
Traditional synthesis							
I	20.2	1.05	517.5	74	62	1.80	0.42
Synthesis without reducing agent							
A	21.4	1.07	517.6	70	62	1.70	0.48
E-1	30.2	1.92	517.4	85	78	1.20	0.24
E-2	14.1	1.32	517.5	81	76	1.24	0.30
W-1	24.6	1.47	517.4	81	78	1.14	0.30
W-2	17.5	0.96	517.3	77	68	1.58	0.37
Modified synthesis							
E-1	28.6	1.88	517.5	83	80	1.06	0.27
E-2	18.5	1.54	517.4	82	77	1.21	0.29
W-1	24.0	1.56	517.5	82	80	1.05	0.29

* X_{C_4} – n-butane conversion, S_{MA} – selectivity to maleic anhydride, C_{CO_x} – CO and CO_2 concentration in exhaust gases, $\text{C}_{\text{C}_{4\text{ex}}}$ – n-butane concentration in exhaust gases.

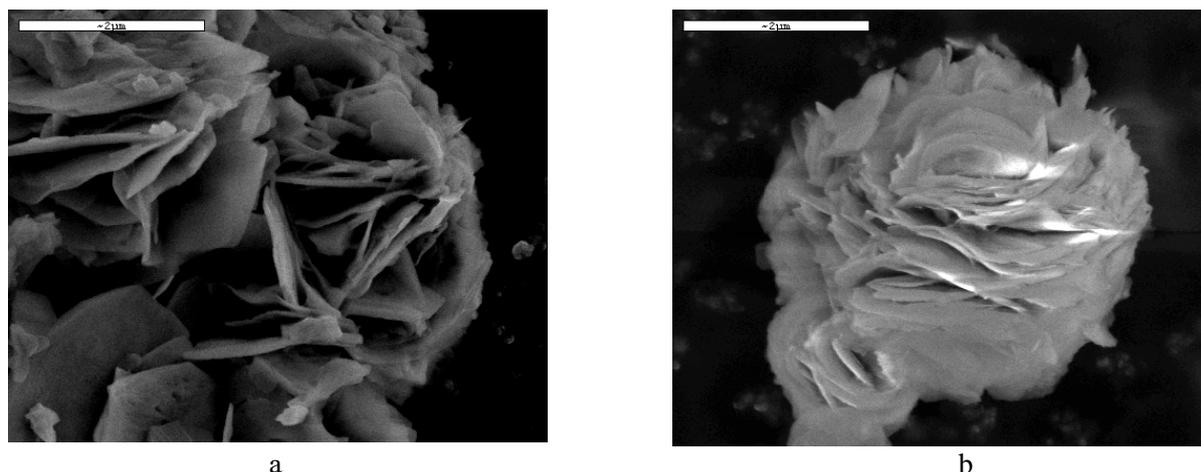


Fig.1. The samples of VPO catalysts prepared by traditional (a) and modified (b) methods.

In the same it was established that the use of V_2O_5 -MChA as raw material in $VOHPO_4 \cdot 0.5H_2O$ preparation leads to a decrease of time this synthesis up to 2-4 h that is lower than in traditional method (see above). This fact permits to proposed the decrease of solvent quantity in synthesis of $VOHPO_4 \cdot 0.5H_2O$ at V_2O_5 -MChA using. The results obtained at $C_4H_9OH/V_2O_5 = 2.0-2.5$ (three times less than traditional method) presented in Table 2 (modified synthesis) and show that prepared samples have better properties in n-butane oxidation than the catalyst prepared in traditional conditions. A possible explanation for this increased activity is the formation of thin crystal plates (See Figure 1) which are predominantly vanadyl (VO^{2+}) plane which correspond to those found in mechanochemically pre-treated V_2O_5 (Table 1). The presence of V^{4+} ions in the initial oxide increases the formation of the precursor phase and because the time taken for the synthesis is reduced the crystals don't thicken in the (001) plane.

When looked at from the environmental perspective, this technique has some significant benefits:

- When producing the VPO catalysts the use of mechanochemical pre-treatment of V_2O_5 removes the need to add reducing agents oxalic and benzyl alcohol.
- During production of the catalyst less solvent is needed (reduce the ratio of n-butanol to V_2O_5 from 1:6-9 to 1:2.0-2.5) and fewer toxic by-products are produced.
- The resulting catalyst has greater selectivity and activity which reduces the quantity of un-reacted n-butane.
- The catalyst synthesized on the base of V_2O_5 -MChA reduces the quantity of carbon oxides (CO and CO_x) in the maleic anhydride production.

1.2 Mechanochemical activation of the catalyst obtained in a traditional way

The first data about mechanochemical activation (MChA) of VPO catalysts prepared by traditional method were reported in Patents [63, 64]. In our publications [65-67] the influence of medium nature on VPO precursor MChA at

treatment in high power mill (3000 rpm) was studied and it was shown that treatment in ethanol permits to an increase the catalysts activity and selectivity. The precursor treatment in water less influenced on its catalyst properties but MChA of the sample in air increases the catalyst activity only. These results were confirmed by the data published later [68].

In this paper the results obtained at VPO precursor treatment in less energetic mill (600 rpm) in ethanol media are presented. It was established that the MChA of the precursor prepared by traditional technique leads to an increase this properties in n-butane oxidation to maleic anhydride (Table 3).

In same time the quantity of CO_x and un-reacted n-butane as environmental harmful pollutants essential decreases. The sum of the CO_x emission in environment (with addition of necessity of un-reacted butane oxidation) decreases up to 1.4 vol. %.

The study showed that the improvements of the sample properties in the oxidation of n-butane are attributable to the formation of nano-dispersion areas of the active phase adjacent to amorphous vanadium phosphate (See Figure 2).

So, the mechanochemical activation of the catalyst precursor gives the following improvements: i) an increase of the catalyst properties in partial n-butane oxidation; ii) a decrease the quantity of CO_x produced as a by product; iii) a reduce the quantity of un-reacted n-butane.

1.3 Mechanochemical synthesis of the doped VPO catalysts

This section describes the benefits that accrue from mechanochemical synthesis of VPO catalysts containing additive elements. Well known that industrial VPO catalysts contain the additives of different transition metals with atomic ratio Me:V between 0.05–0.10 : 1 [53-58]. The most effective metals to use for this purpose are cobalt and bismuth [53, 55, 58, 69-73], which are introduced into the synthesis process of the VPO pre-cursor in the form of salts ($CoCl_2 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$).

Table 3. Properties of VPO catalysts after mechanochemical treatment of precursor

Time of MChA, min	XRD, I_{001}/I_{220}	BE, eV		n-Butane oxidation*			
		V 2p _{3/2}	P 2p _{1/2}	X _{C4} , %	S _{MA} , %	C _{COx} , vol. %	C _{C4ex} , vol. %
-	1.05	517.5	133.9	74	62	1.80	0.42
30	1.22	517.4	133.8	77	68	1.58	0.37
60	1.47	517.4	133.7	83	73	1.43	0.27
120	1.63	517.3	133.8	84	79	1.13	0.26
240	1.92	517.3	133.7	83	81	1.01	0.27
480	**	517.4	133.8	79	74	1.31	0.34

* symbols are analogous to Table 2.

** sample contains amorphous phase

Table 4. Properties of VPO catalysts doped by Co and Bi

Catalyst	Method of preparation	n-Butane oxidation			
		X _{C4} , %	S _{MA} , %	C _{COx} , vol. %	C _{C4ex} , vol. %
VPO	Traditional	74	62	1.80	0.42
VPO-Co	Traditional	85	62	2.07	0.24
VPO-Co	MChS-Water	87	64	2.00	0.21
VPO-Co	MChS-Ethanol	84	75	1.34	0.26
VPO-Bi	Traditional	76	68	1.56	0.38
VPO-Bi	MChS-Water	85	69	1.69	0.24
VPO-Bi	MChS-Ethanol	88	74	1.46	0.19

As result for every ton of catalyst synthesised in this way, 40kg of HCl and 80kg of NO₂ are produced as by-products.

We have explored the possibility of adding these elements by mechanochemical treatment of the VPO precursor with cobalt and bismuth oxides in water and ethanol. In papers [53, 73] we describe what happens to the bismuth and cobalt salts during the traditional process for synthesis VPO catalyst. The bismuth salt forms a BiPO₄ phase in the VPO structure and the cobalt salt disperses uniformly without forming a separate phase. The results obtained in process of MChS by treatment of the VPO precursor + Bi₂O₃ and VPO precursor + Co₂O₃ mixtures presented in Figure 3. These data show the increased dispersion of bismuth and cobalt salts that occur during mechanochemical synthesis compared with the traditional method.

The data of the Table 4 presented a comparison of the activity of the catalysts produced under different conditions. The study shows that mechanochemical synthesis of VPO catalysts, doped by additive elements, improves the oxidation of n-butane in comparison with doped samples prepared by traditional method. This improvement is accompanied by a reduction of CO_x in exhaust gases which formed as a by-product in maleic anhydride production. Taken together with the fact that mechanochemical preparation of the doped catalysts eliminate the production of harmful by-products HCl and NO₂, this procedure certainly qualifies as a "Green Chemistry".

In summary the presented results show that in the production of effective VPO catalysts n-butane oxidation to maleic anhydride by mechanochemical methods are the more environmentally acceptable for the following reasons:

- Reduce the volume of organic solvent (n-butanol) used in the catalyst manufacture process by 66%;
- Eliminate the addition of reducing agents (oxalic and benzyl alcohol) in catalyst production;
- Decrease the waste associated with solvent purification;
- Eliminate the formation of by-products HCl and NO₂ in synthesis of the catalyst;
- Reduce CO_x emission in maleic anhydride manufacture from n-butane on 8,000 tons per year for every 15,000 tons of maleic acid manufactured in a unite industrial reactor.

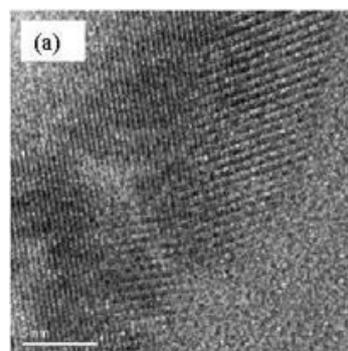


Fig. 2. The structure of the sample after 240 min of MChA.

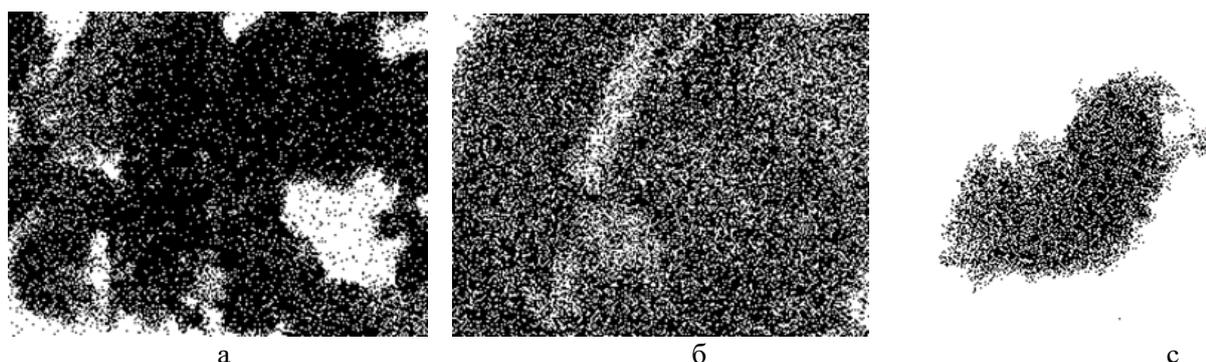


Fig. 3. The distribution of Me (white) in base VPO composition: Me = Bi (a, b) or Co (c). Traditional synthesis (a), MChS (b, c). SEM in BSE mode.

Table 5. Properties of V₂O₅ (10 %) and TiO₂ mixture after mechanochemical treatment

MChA treatment conditions		XRD, I ₀₁₀ /I ₁₁₀ (V ₂ O ₅)	XPS data		Ratio V/Ti
Medium	Time, min		B.E., eV		
			Ti 2p	V 2p	
-	-	3.1	459.2	517.7	0.76
Water	10	3.0	459.2	517.6	1.11
Water	30	3.2	459.3	517.8	1.17
Water	60	3.1	459.1	517.7	1.28
Ethanol	10	5.3	459.1	517.6	1.05
Ethanol	30	4.7	459.3	517.6	0.56
Ethanol	60	4.5	459.1	517.7	0.51
Ethanol*	10	15.3	459.2	517.6	0.85

* melted V₂O₅ with I₀₁₀/I₁₁₀ = 30 was used

2. Vanadium-titanium oxide catalysts

Catalysts based on vanadia (V₂O₅) and titania (TiO₂) are used in the industrial production of phthalic anhydride from *o*-xylene [74-76] and selective reduction of nitrogen oxides [10, 77-79]. The most active catalysts used in the production of phthalic anhydride are TiO₂ with 7-15% of the surface comprised of V₂O₅ and additional chemical elements. The catalyst is synthesized from aqueous NH₄VO₃ and produces NO_x (0.06 t per 1 t of the catalyst) in the preparation process. We conducted a study to find whether it was possible to produce vanadium-titanium-oxide catalysts by mechanochemical treatment of V₂O₅ and TiO₂ in different milling media. Previous study of the properties of the V₂O₅ and TiO₂ mixture subjected to mechanochemical treatment is described in papers [80-82]. Paper [82] describes the activity of the synthesized samples on the oxidation of toluene. These studies were shown the possibility of vanadium oxide dispersion on titania surface and its supporting on titanium oxide.

The data of the Table 5 show how the mechanochemical treatment affected the dispersal of V₂O₅ in the mixture with TiO₂ [83]. The breakdown of vanadium oxide in water does not change the morphology of the particles and partial dissolution to form “polyvanadia acids” with next their supporting accompanied by an increases the

ratio of vanadium to titanium of the surface layer. Mechanochemical treatment in ethanol results in isotropic disintegration of vanadium oxide (as shown by the XRD data) and after 10 minutes of milling the proportion of V₂O₅ to TiO₂ on the surface is increased as shown by the XPS data (Table 5). Increasing the treatment time leads to a sharp decline in the V₂O₅/TiO₂ ratio. This may be attributable to supporting of excess titanium oxide on the previously formed surface of the sample.

This explanation is supported by the study of the samples using a micro-Raman spectroscopy method (See Figure 4). Supporting of V₂O₅ after mechanochemical treatment in water is uniform as shown by the nearly identical spectra for point A and B on the surface area (Fragment 1). Secondary coating by TiO₂ (treatment in ethanol) is non uniform (seen as island structures with sharp edges) as shown by differences in the spectra for points A and B (See Figure 4, Fragment 2). In the case of ‘melted’ V₂O₅ (most oriented to vanadyl plane 010) coating of the

TiO₂ takes place instantly (due to the high resistance of melted V₂O₅ (Table 5).

2.1 Partial oxidation of *o*-xylene

The catalytic properties of V₂O₅/TiO₂ samples prepared by mechanochemical synthesis in the partial oxidation of *o*-xylene are given in Table 6. The obtained

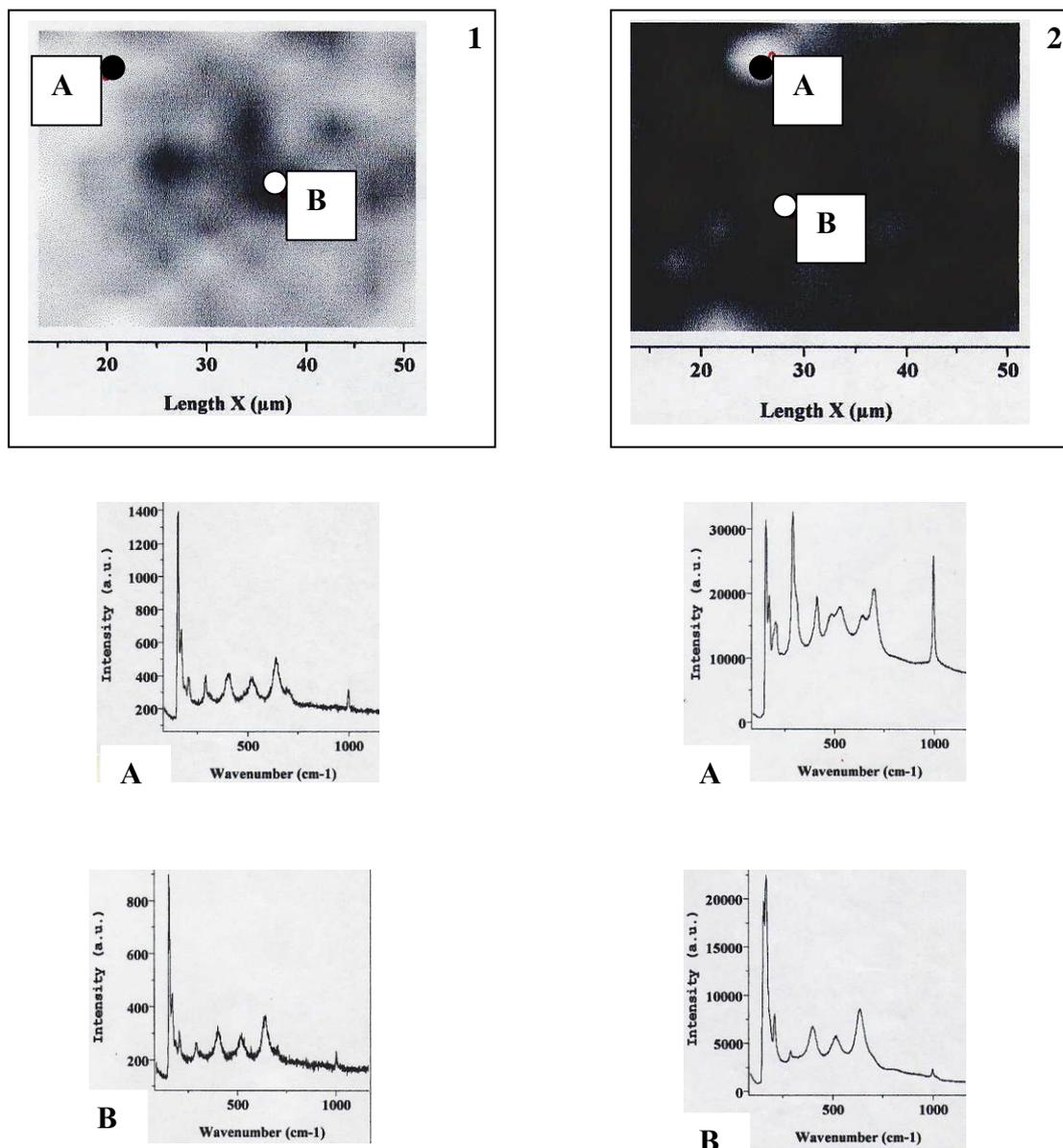


Fig. 4. Micro-Raman spectra for points A and B of the V_2O_5/TiO_2 samples after MChA in water (1) and ethanol (2) during 30 min.

results were compared with the patent data [84] and data of the study of the industrial catalyst 'XS'R-1211/2.

The difference in activity between samples obtained by mechanochemical treatment in ethanol and water can be explained by the following observation. V_2O_5 is dispersed less evenly and forms islands on the TiO_2 surface when ethanol is used. These islands reduce the likelihood that oxygen will diffuse from neighboring vanadium atoms the consequent oxidation of the product to form carbon oxides.

The data presented in Table 6 show that the catalysts, synthesized by mechanochemical treatment of V_2O_5 and TiO_2 in ethanol are active at temperatures of 70-1000 C lower than that required by the traditional method. In same time these catalysts demonstrate practically analogous phthalic anhydride yield that patented or industrial catalysts. It is necessary to

note that exploitation of the industrial catalyst at a temperature of 400 °C accompanied its deactivation [74, 75] and stabilization of the catalyst properties realized by addition of SO_2 to the reaction mixture. The catalyst synthesized by mechanochemical treatment doesn't require such a high reaction temperature and therefore eliminates the need to add SO_2 and its removal from phthalic anhydride manufacture gases.

To summarize, the mechanochemical synthesis of V_2O_5/TiO_2 catalysts proposed by us [85]: i) eliminates nitrogen oxides during catalysts preparation, ii) allows the reaction to take place at a lower temperature, iii) provide the same yield of phthalic anhydride as traditional catalysts, iv) eliminates the need to add and subsequently remove SO_2 .

2.2 Selective reduction of NO_x

The catalysts produced by mechanochemical treatment were studied with respect to their ability to remove nitrogen oxides (Selective Reduction SCR), especially in the outlet gases. The data in Table 7 shows that catalyst, prepared by milling in water, is the most effective at removing NO_x. It is assumed that even distribution of V₂O₅ as monolithic layer on the surface of

TiO₂ is an essential factor in the process which corresponded to proposed mechanism of the process [86]. The comparison results obtained on MChS prepared catalysts with literature data [86] shows that their properties are practically equivalent to traditional catalysts but their preparation method eliminate the formation of NO_x in this process.

3 Molybdenum oxide catalysts. Direct oxidation of benzene to phenol by molecular oxygen.

In our investigation [87] it was established that mechanochemical treatment of MoO₃ in ethanol leads to the formation of Magnelli phase χ -Mo₈O₂₃. It was shown that this sample demonstrates activity in direct benzene oxidation to phenol by molecular oxygen. It is well known [23, 24] that direct oxidation benzene to phenol is preferable to industrial process on the base of isopropyl benzene (cumene). The success in this direction was obtained in benzene oxidation by N₂O in the presence of Fe-containing zeolite catalysts (see, e.g. [88-89]). The drawback of this method is the use of N₂O, which is environmentally harmful and which must be added to the reaction mixture in excess. So, the direct oxidation of benzene using molecular oxygen is most promising method from green chemistry point.

Table 6. Properties of the V₂O₅/TiO₂ catalysts in o-xylene oxidation

Catalyst	o-Xylene oxidation*		
	T _r , °C	SV, h ⁻¹	Y _{PhA} , mol. %
MChS, water, 60 min	340	2700	71.6
MChS, ethanol, 30 min	280	3960	78.7
MChS, ethanol, 60 min	300	3960	81.4
MChS, ethanol, 10 min**	280	3960	82.0
US Pat [83]	370	2700	81.2
“XS” R-1211/2	380	3900	81.6

* T_r – reaction temperature, SV – space velocity, Y_{PhA} – yield of phthalic anhydride

** melted V₂O₅

Table 7. Selective reduction of NO by NH₃ on V₂O₅/TiO₂ catalysts*

Catalyst	T _r , °C	SV, h ⁻¹	X _{NO} , %
MChS, water, 60 min	340	9000	98
MChS, ethanol, 30 min	380	7000	96
MChS, ethanol, 60 min	380	7000	97
MChS, ethanol, 10 min**	400	7000	95

* T_r – reaction temperature, SV – space velocity, X_{NO} – NO conversion

** melted V₂O₅

Table 8. Properties of MoO₃/TiO₂ samples after mechanochemical treatment in ethanol

Catalyst	Time of MChA, min	Benzene oxidation*		
		T _r , °C	X _{C₆H₆} , %	S _{PhOH} , mol. %
MoO ₃	50	360	32	8
MoO ₃ /TiO ₂ (10 %)	50	360	28	12
MoO ₃ /TiO ₂ (10 %)	180	360	34	5
MoO ₃ /TiO ₂ (20 %)	30	340	28	11
MoO ₃ /TiO ₂ (20 %)	60	340	34	16
MoO ₃ /TiO ₂ (20 %)	120	330	35	17
MoO ₃ /TiO ₂ (40 %)	60	360	33	9
MoO ₃ /TiO ₂ (40 %)	120	350	35	7

* T_r – reaction temperature, X_{C₆H₆} – benzene conversion, S_{PhOH} – selectivity to phenol formation

In [87] it was shown that the addition of TiO₂ (10 wt. %) to MChT MoO₃ permits to an increase the selectivity of phenol formation in benzene oxidation. This result was the base for the study of mechanochemical treatment influence on the MoO₃/TiO₂ mixtures properties realization. Table 8 gives the composition of the mixtures, mechanochemical conditions and characteristics of the catalysts. It shows that a mixture comprised of 20 % TiO₂ and 80 % MoO₃ produced the catalyst with the highest activity and greatest selectivity. Catalyst activity was increased by extending the milling time from 60 – 120 minutes and decreased by increasing the proportion of TiO₂ in the mixture.

The Figure 5 compares the surface morphology of the catalysts obtained by MChA using the AFM method. They show that the MoO₃/TiO₂ (20 %) mixture, with a 120 minute

treatment time (Fig. 5 c), has a surface with the most peaks and these are jagged when compared with the surface of the MoO₃/TiO₂ (40 %) mixture (Fig. 5 d). The comparison with catalytic properties of the samples shows the maximal selectivity to phenol formation observed for MoO₃/TiO₂ (20 %) with most pointed peaks on surface.

The theoretical model for the reaction mechanism can be follows. The peaks are where the χ -Mo₈O₂₃ Magnelli phase is formed with Mo⁵⁺ ions present which fix the oxygen in the form of O⁻ ions [90 – 93] which then directly oxidise benzene to phenol. TiO₂ is crucial to the process of dispersing the active MoO₃ and the formation of the active sites where oxidation takes place.

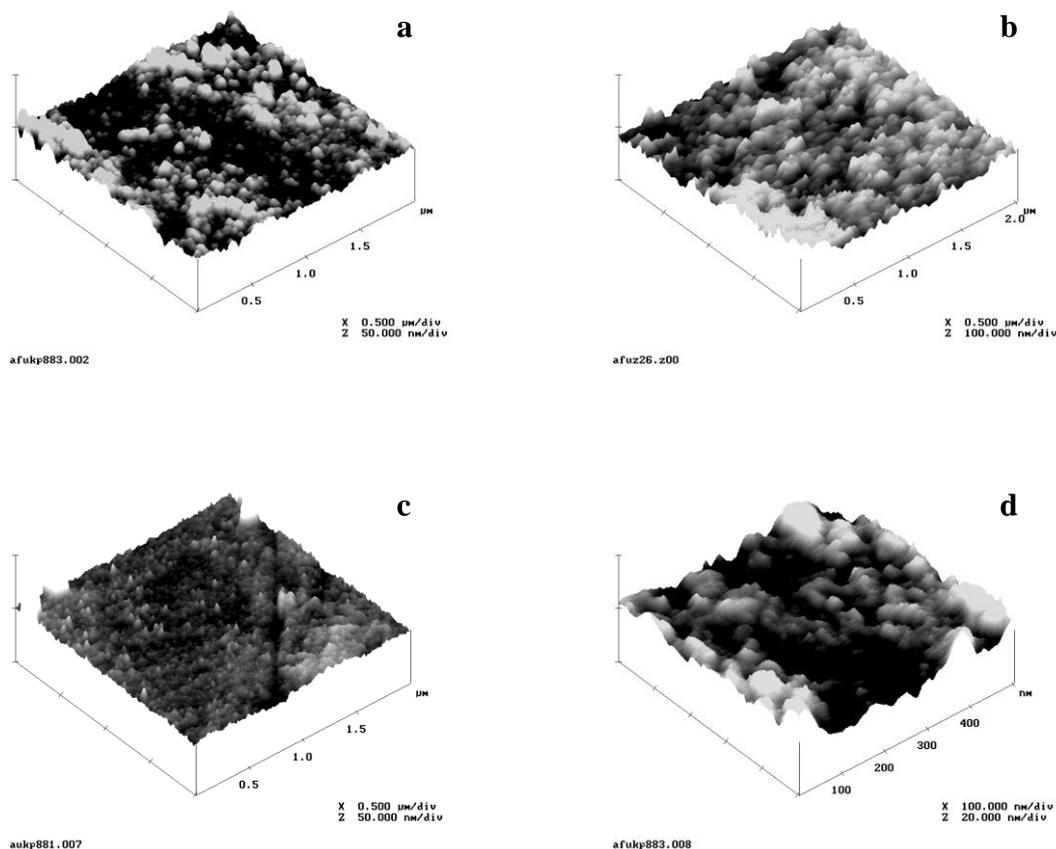


Fig. 5. Surface morphology (AFM) of the samples: a – MoO₃/TiO₂ (10 %) – 50 min, b – MoO₃/TiO₂ (20 %) – 30 min, c – MoO₃/TiO₂ (20 %) – 120 min, d – MoO₃/TiO₂ (40 %) – 60 min.

Our work, presented here, gives a possible alternative process for producing phenol from the direct oxidation of benzene. The reaction is catalysed by mechanochemically activated mixture of MoO₃/TiO₂ which creates a surface with a χ -Mo₈O₂₃ Magnelli phase which presents Mo⁵⁺ ions which fix O⁻ ions. However more research is needed to fully understand the mechanism involved but developed catalysts

permit to realize process of phenol production from benzene without participation of harmful N₂O.

4. Oxide catalysts based on copper and cerium

It is known [94-97] that catalysts formed from the oxides of copper and cerium are suitable for removing CO from exhaust gases which do not contain the metals nickel,

palladium and platinum. They are also suitable for purifying hydrogen, used as a liquid fuel, by removing CO [98-103].

Hydrogen is proposed as a Green Chemistry method for producing electro-energy in fuel cell. The disadvantage of these catalysts is that in excess hydrogen is oxidized to water which decreases its selectivity to CO and subsequent deactivation.

We have explored how preparation methods and catalyst mixtures affect the activity of the oxidation of CO [104, 105]. The material shows that the catalyst with the

greatest activity is a mixture comprised of 25 % CuO and 75 % CeO₂. In this communication the influence of mechanochemical treatment on its properties presented. Figure 6 shows how mechanochemical activation of the catalyst increases activity in the oxidation of CO. The catalyst with the greatest activity was obtained by treatment conducted in ethanol medium. In observing the activity of the catalyst with benzene, we were able to show that it was capable of catalysing the oxidation of other pollutants.

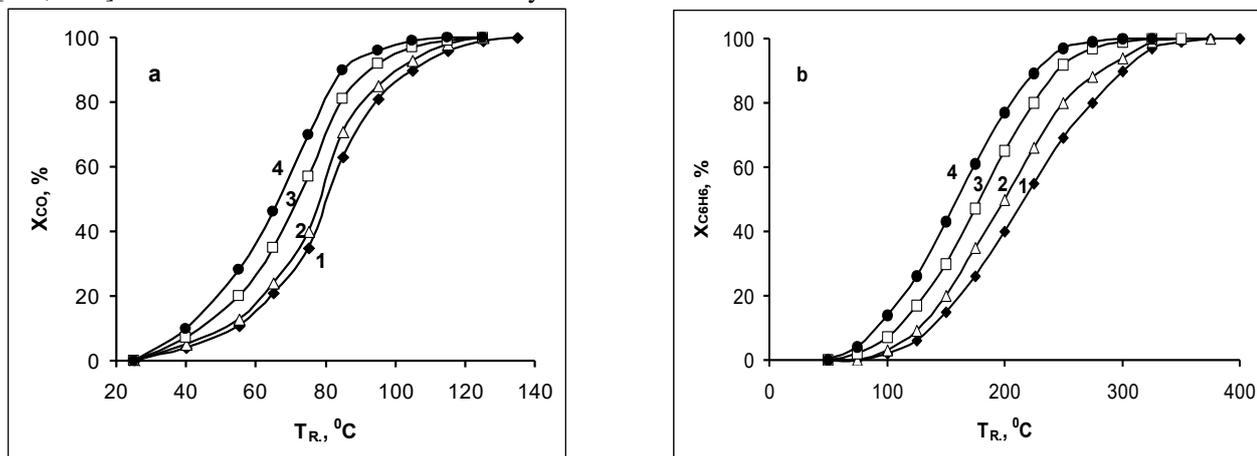


Fig. 6. Dependence of CO (a) and C₆H₆ (b) conversion on Cu-Ce-O catalysts from reaction temperature: 1 – initial, 2 – MChA in water, 3 – dry MChA, 4 – MChA in ethanol.

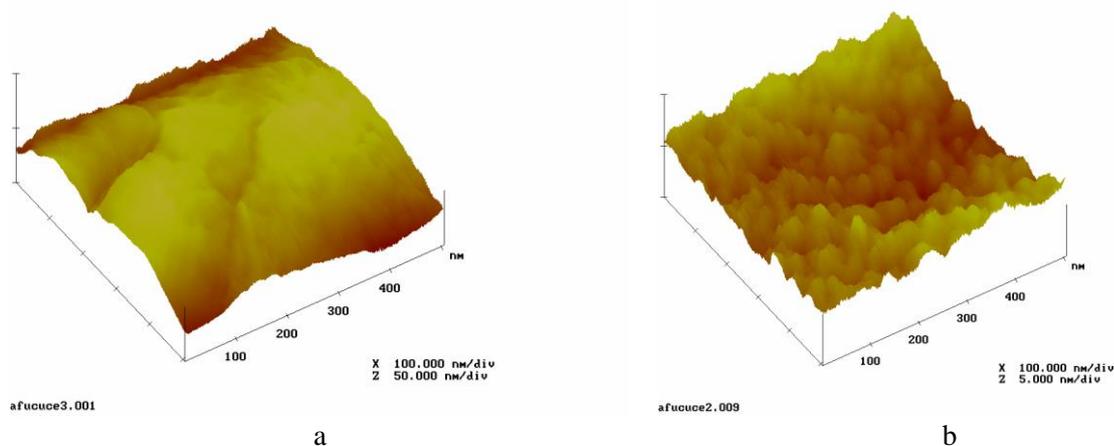


Fig. 7. Surface morphology (AFM) of Cu-Ce-O samples: a- initial, b – MChA in ethanol.

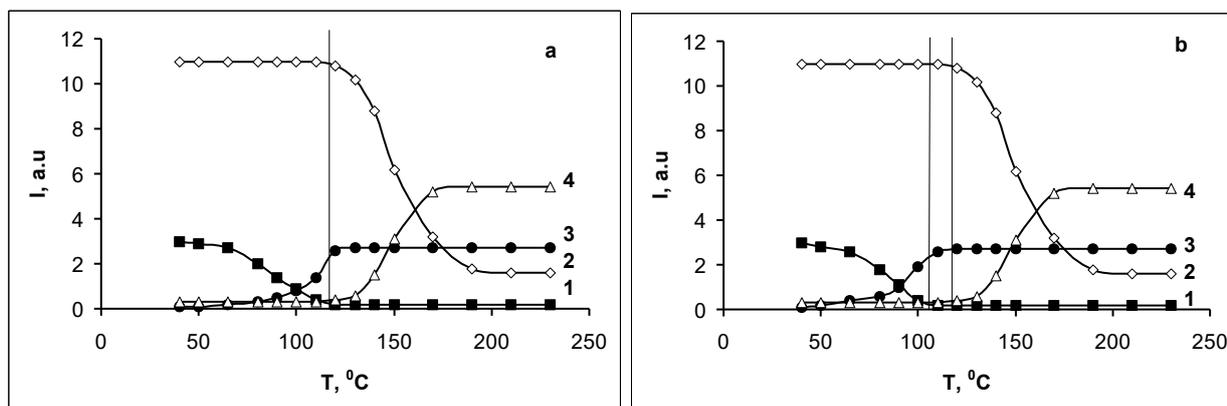


Fig.8. Thermo-programmed reaction mixture H₂ (75 %) – CO (1 %) – O₂ (1 %) – He on traditional Cu-Ce-O catalyst (a) and after MChA in ethanol (b). Intensity of the masses: 1 – CO, 2 – H₂, 3 – CO₂, 4 – H₂O.

Table 9. Mechano-catalytic oxidation of hydrocarbons (0.3 wt. %) in water

Catalyst	Hydrocarbon concentration after mechanochemical treatment (MChT)					
	Benzene		Toluene		Phenol	
	15 min	60 min	15 min	60 min	15 min	60 min
V ₂ O ₅	0.004	0.00003	0.001	0.0004	0.004	0.0002
CuO	0.008	0.0005	0.04	0.008	0.003	0.0003
TiO ₂	0.006	0.0008	0.002	0.001	0.006	0.0004
Ti/SS*	0.0003	traces	0.006	0.0001	0.0003	traces
Ni/SS	0.0001	traces	0.002	traces	0.0001	traces
Mo/SS	0.0001	traces	0.007	0.0002	0.0003	0.0001

*SS – stainless steel

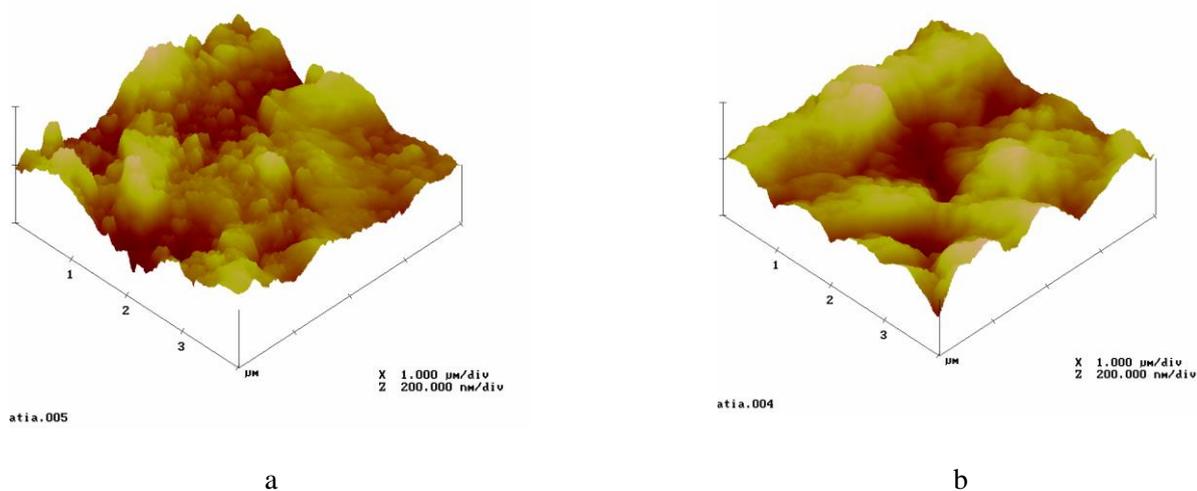


Fig. 9. Surface morphology Ni/SS sample: a – initial, b – after MChT 60 min.

Figure 7 shows the surface morphology of the catalyst with and without mechanochemical treatment. The gentle hills observed in initial sample change on pointed peaks with nanodimensions top and base of these peaks. It is possible to suppose that the formation of these nanoforms determines an increase of the catalyst activity. The X-ray photoelectron spectroscopy (XPS) measurements indicate that the oxidation state of the elements is unaffected by the mechanochemical treatment of the mixture. The literature data [106-109] describes that the formation of nano-sized oxide clusters significantly increase the catalytic activity of the oxide catalysts in the oxidation of CO. The mechanochemically treated Cu-Ce-O catalyst displays the same surface morphology and this is the likely explanation for its increased activity.

The results obtained on this catalyst in CO oxidation predetermine its study in purifying hydrogen. Figure 8 compared the results from thermo-programmed reaction on: i) traditionally synthesized sample and ii) mechanochemically treated sample. The curves show the changes in relative mass intensity ($H_2 = 2$, $H_2O = 17/18$, $CO = 28$, $CO_2 = 44$). It can be seen that for the first sample (initial) the temperature of maximum oxidation CO and the start of H_2 oxidation (Figure 8, a) practically have not difference (vertical line). The sample

after MChA (Figure 8, b) demonstrates difference between temperature of full CO oxidation and beginning of hydrogen oxidation ($\Delta T = 15$ °C). This difference indicates that Cu-Ce-O after mechanochemical activation is suitable as a means of eliminating CO from hydrogen fuel.

The results of this study show that mechanochemical activation has provided the solution to several problems facing “Green Chemistry”: i) increases the activity of catalysts used to oxidise CO in Industrial outlet gases, ii) eliminate aromatic hydrocarbons referred to as VOC, iii) it provides a suitable method for purifying hydrogen which is used in low temperature processes related to “fuel cells”.

5. Mechanochemical reactions – “green chemistry” in water medium

In [60] it was observed the water decomposed and hydrogen peroxide generation when metal oxides were treated in water. This fact formed the basis for postulating a hypothesis that hydrocarbons could be removed from water during its mechanochemical treatment in the presence of oxide catalyst. The first data obtained at benzene-water mechanochemical treatment [110,111] confirmed this hypothesis. The drawback of oxide catalysts in this process is connected with their reduction in process and their partial destruction.

In result using the low temperature implantation method, catalysts containing metals deposited onto a stainless steel support were synthesized [112-115]. The data of Table 9 show that catalysts prepared in this way are highly effective when it comes to removing aromatic hydrocarbons from water.

The results obtained from atomic force microscopy (AFM), show that in the process of mechano-catalytic reaction there is no significant alteration to the surface of the catalyst (See Figure 9).

In addition to these studies we have investigated the decomposition of distilled water in the presence of catalysts containing metals supported on stainless steel. In these experiments we recorded the release of molecular hydrogen which results from this process. This phenomenon is being investigated as a method for splitting water and releasing molecular hydrogen as a way of producing fuel.

Research into mechanocatalytic processes in water provides another route for "Green Chemistry" to follow and provide possibilities for removing traces of hydrocarbons from water and alternative methods for producing of fuel.

Conclusions

In this review of our work we have attempted to show how mechanochemistry techniques contribute to the principle of "Green Chemistry".

Our research has centered on the preparation of catalysts which reduce the quantities of environmentally damaging materials used and created as by-products in essential production processes.

Mechanochemical activation and synthesis have proved themselves to be very effective techniques for improving the performance of existing catalysts.

Benefits that accrue from this work are:

- Increased activity which increase of the productivity of desired product,
- Increased selectivity which means reactions are far more efficient, allowing more conversion to main product and fewer unwanted by-products,
- The possibility that catalyst could provide a method for producing a clean source for fuel cell.

Acknowledgements

The financial support of the National Academy of Science – Programme "New functional substances and materials for chemical manufacture" (Project 13/19-21).

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Надійшла до редакції 16.04.21 р.

Механохімія як перспективна методологія зеленої хімії для промислових каталізаторів

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В даному огляді показано, як механохімічна обробка може бути включена до технологій зеленої хімії, що пов'язано з зниженням використання небезпечних вихідних речовин та утворення супутних продуктів. В роботі проаналізовано приготування оксидних ванадій фосфорних каталізаторів, які використовують в промисловому процесі одержання малеїнового ангідриду з н-бутану та розглядають перспективність їх використання в реакції одержання фталевого ангідриду з н-пентану. Показано, що механохімічна активація вихідних реагентів для синтезу каталізаторів знижує кількість шкідливих речовин в їх виробництві та підвищує їх каталітичні показники. Підвищення селективності каталізаторів веде до зниження утворення оксидів вуглецю, а підвищення активності – до зменшення кількості непрореагованої речовини в вихідних газах процесу каталізу. Показано, що механохімічна обробка може бути також успішно використана для модифікування відомих промислових оксидних ванадій фосфорних каталізаторів, або введення до їх складу домішок які підвищують активність та селективність в окисненні вуглеводнів. Розглянуто можливість використання механохімії до синтезу оксидних ванадій титанових каталізаторів, на яких базується сьогодні промисловий процес одержання фталевого ангідриду з о-ксилолу. Встановлено, що механохімічна обробка оксидів ванадію та титану дозволяє виключити викиди оксидів азоту в процесі синтезу каталізатора, синтезовані каталізатори дозволяють одержати такий самий вихід фталевого ангідриду, що відомі промислові зразки, але при температурі реакції значно нижчій. Показано, що механохімія дозволяє синтезувати каталізатори для нових процесів, наприклад одержання фенолу окисненням бензолу молекулярним киснем (в присутності каталізаторів на основі оксиду молібдену). В результаті, виникає можливість замінити промисловий двостадійний кумольний процес або конкурувати з пропонуємим процесом окиснення бензолу оксидом азоту N₂O. Показано, що механохімічна активація Cu-Ce-O каталізатора дозволяє знизити температуру окиснення СО в вихідних газах та цей каталізатор може бути використаний для очищення водню від монооксиду вуглецю для його подальшого використання в паливних комірках. Також продемонстровано, що використання оксидних каталізаторів, краще нанесених на металічні носії, дозволяє реалізувати механо-каталітичне окиснення ароматичних вуглеводнів в водних стоках.

Ключові слова : зелена хімія, каталіз, оксидні каталізатори, механохімія