VERMICULITE-BASED CATALYSTS FOR OXIDATION OF ORGANIC POLLUTANTS IN WATER AND WASTEWATER

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ABSTRACT
In presented work natural expanded vermiculite was used as a starting material for synthesis of Fe-doped catalysts. Material was modified with increasing amount of Fe by ion-exchange and precipitation of iron oxide. Composite materials were characterized with respect to their structure (X-ray diffraction, Infrared spectra using Diffuse Reflectance), agglomeration state of Fe (Ultraviolet-Visible spectra using Diffuse Reflectance) and chemical composition. Activity in H_2O_2 decomposition as well as in phenol oxidation was studied in liquid phase at atmospheric pressure and temperature up to 70 °C. It was shown that doping with Fe increases catalytic activity. However, excess of iron resulted in formation of undesired side-products.

KEYWORDS: vermiculite, wastewater, advanced oxidation processes, phenol

1. INTRODUCTION

Phenols are frequently encountered organic molecules in contaminated surface water and groundwater. They are characterized by low biodegradability, high Chemical Oxygen Demand (COD) and high toxicity. Industrial wastewater (coke plant sewage, petrochemical industry, paints factories) and municipal wastewater are main sources of phenols. The effective removal of refractory organic pollutants can be achieved using catalytic oxidation of organic pollutants in aqueous solution – one of so called advanced oxidation processes (AOP) (Rokhina and Virkutyte, 2011).

Large group of emerging technologies consist on oxidation processes, such as: wet oxidation, catalytic wet air oxidation, advanced oxidation processes (Busca et al., 2008; Kim and Ihm, 2011; Luck, 1996; Luck, 1999; Biń, 1998; Tomaszewska, 2009). Wet oxidation process is destruction method for waste streams too diluted to incinerate or too concentrated for biological treatment (10-100 g/L of COD) and it may be used at high flow rates. Oxidation by oxygen or air takes place at elevated temperatures (e.g. 125-320 °C) and pressures (e.g. 0.5-20 MPa). For that reason those methods are considered as energy-consuming and expensive. Catalytic wet oxidation offers lower energy requirements and higher oxidation efficiencies (Liotta et al., 2009). Operating costs are about half that of non-catalytic process, due to milder reaction conditions and shortening of residence time. Despite high activity of commercial noble metal supported catalysts (Ru, Pd, Pt) or homogeneous systems (Cu salts), further development of high durability and low cost catalysts is necessary.

Catalytic wet air oxidation of organic compounds (Barbier et al., 2005) was studied on the CeO_2-based Ru-, Pd-, Pt-doped catalysts. It was shown that complete conversion of phenol was achieved after 3 h at 160 °C and 20 bar of oxygen on the Ru-containing catalysts. Similar results were obtained for the Ru-Ce γ-Al_2O_3-supported catalyst. However in both cases the catalysts were deactivated by the carbonaceous deposition on active sites and phase transformation of the support (Massa et al., 2007). Metal oxide catalysts are less susceptible to poisoning than noble metals and less expensive (Kim and Ihm, 2011). The Cu-based catalysts usually exhibit high activities due to high surface reducibility. Supported catalysts were also studied, because unique pore structure (e.g. mesoporous silicas, activated carbon) or surface morphology (e.g. ceria) increase accessibility of substrates and catalytic activity (Wu et al., 2001; Hocevar et al., 2000; Kim et al., 2007).

Strong oxidants used in the advanced oxidation methods, such as ozone or hydrogen peroxide, offer high conversions at lower temperatures and ambient pressure. Oxidants may be used simultaneously with other chemical compounds (O_3 and H_2O_2) and together with physical factors, such as UV, γ radiation or ultrasounds (Ledakowicz et al., 2001). Presence of a catalyst also improves the efficiency of the process. The most popular combinations of chemical agents are

$O_3 + H_2O_2$ together with Fenton reagent: the mixture of H_2O_2 and iron salts. In the latter case, problems with separation of dissolved metal cations may be overcome by application of heterogeneous source of iron.

Oxidation and advanced oxidation processes (AOP) belong to emerging technologies. Although right now application of such a methods on large scale is not possible due to high costs, formation of by-products and technical constrains, both afore-mentioned processes present strong advantages (Andreozzi et al., 1999). Oxidation which requires addition of chemicals is rapid and effective process. On the other hand, AOP require little or no consumption of chemicals, but it is effective for recalcitrant pollutants and no sludge is produced during the reaction (Crini, 2006).

In our previous studies it was shown that synthetic anionic clays are very effective in adsorption of phenol and humic acids (Węgrzyn et al., 2006; Węgrzyn et al., 2007), but they show poor mechanical stability in liquid phase. Much more promising seems to be application of silicate minerals in which case acid treatment may be used as an activation procedure (Chmielarz et al., 2010) and on the contrary to zeolites, they can accommodate in the interlayer space even bulky molecules. The following examples show variety of studies conducted on clays and metal oxides in catalytic conversion of some hazardous chemical organic compounds.

Numerous works have been devoted to iron-containing clays in Fenton and photo-Fenton process. HO• radicals, basically generated from H_2O_2 in the presence of Fe^{2+} ions, are highly oxidative, non-selective, and able to decompose many organic compounds including refractory pollutants. Incorporation of iron cations or oxides into porous support allows overcoming some drawbacks of the studied process. For example, the pH range for application of the Fenton is quite narrow, in the range 2.5-4.0 (Navalon et al., 2010). Additional separation steps in order to remove the iron sludges from the treated water after the reaction and neutralization step is necessary. It was observed that heterogeneous nanosize solid catalyst can accelerate the reaction rate (Soon and Hameed, 2011). Active centers are dispersed on surface in the form of iron oxides, polymeric iron species, and iron ions. On the contrary to homogeneous reaction, broad pH range may be used. Sludge treatment is not necessary or only minimal ferric hydroxide is formed due to leaching of the active components into the bulk solution. Catalysts loss is limited due to anchoring to the surface of porous solid materials. Recovery is easy and recycling is guaranteed.

Clay-based catalysts are characterized with high activity in the wide range of pH (3.0-9.5). Leaching of the active phases may occur after the formation of acidic intermediates in solution. Catalytic activity is enhanced under visible light irradiation; however it takes longer than in homogeneous solution to mineralize organic pollutants. In the clay-based catalysts iron occurs naturally or may be added in synthetic clays in controlled amounts. Acid activation can minimize leaching. High efficiency remains for many runs of catalytic reaction and regeneration.

The catalysts used in the Fenton-like system are natural iron-bearing earth materials, such as goethite, hematite, magnetite or ferrihydrite (Xu et al., 2009; Matta et al., 2007). Another interesting mineral of tourmaline group, shorl, was proposed (Xu et al., 2009). It exhibits unique properties, such as pyroelectricity and piezoelectricity. Tourmaline can generate an electrostatic charge, when a specimen is put under a tiny pressure or temperature change. Interesting results were also obtained for nanoparticulate zero-valent iron (Xu and Wang, 2011).

Typically montmorillonites, saponites, laponites or zeolites are doped with different Fe-species (Navalon et al., 2010; Dukkancı et al., 2010; Iurascu et al., 2009; Feng et al., 2006; Ramirez et al., 2007; Galeano et al., 2011). Iron may be introduced via ion-exchange, impregnation (Ramirez et al., 2007), intercalation of polycations (Iurascu et al., 2009; Tabet et al., 2006) or with multicomponent pillars (Carriazo et al., 2005). The most frequent applications of Fenton-like process are removal of dyes, phenols, organic acids, pesticides, endocrine disrupting compounds (Garrido-Ramírez et al., 2010).

For example, recently the vermiculite-based iron-pillared catalysts have been designed for photocatalytic degradation of azo dye (Chen et al., 2010). Under optimal conditions, at 30 °C, pH equal 3, oxidant concentration 3.93 mM, catalysts loading 0.5 g/L, 98.7 % decoloration and 54.4 % reduction of TOC was obtained in a solution of reactive brilliant orange X-GN (100 mg/L) after 75 minutes of UV irradiation. It was also shown that the catalyst exhibited long-term stability.

Up till now studies on materials like vermiculites are not as comprehensive or numerous as in the case of bentonites or metal oxides. The aim of presented work was preparation of a series of vermiculite-based catalysts doped with iron. Basic physico-chemical characterization was performed using X-ray diffraction, Diffuse Reflectance Infrared spectroscopy, Diffuse Reflectance Ultraviolet-Visible spectroscopy and analysis of Fe content in obtained materials. Oxidation of model pollutant (phenol) using H_2O_2 was studied. The influence of Fe content as well as parameters of catalytic test on activity of modified vermiculites was determined.

2. EXPERIMENTAL

2.1. MATERIALS

Commercial expanded vermiculite from South Africa (sample S0), fraction size 1 mm, was provided
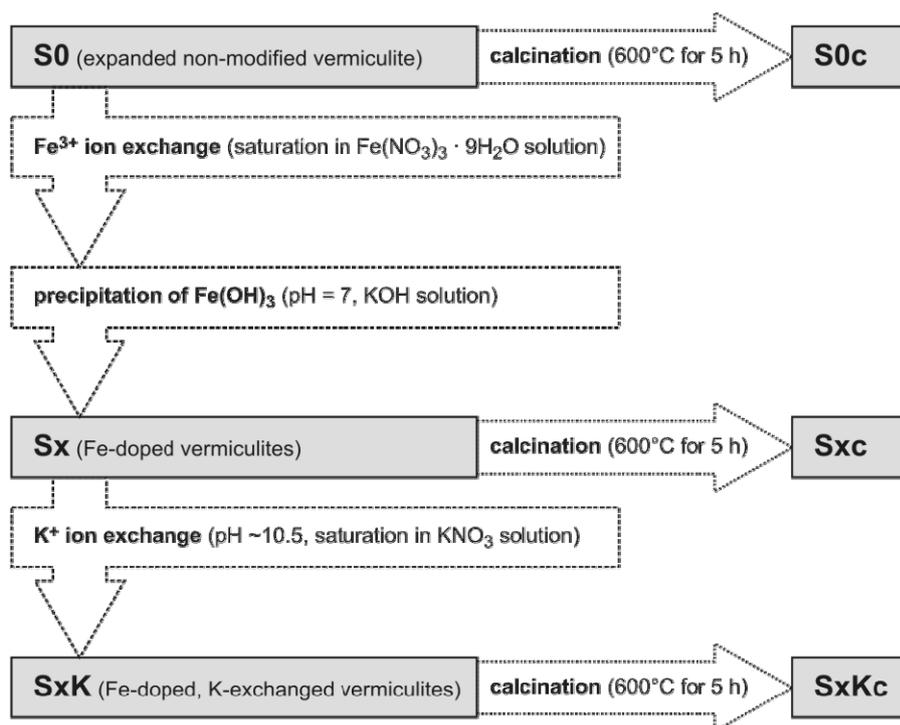
Fig. 1   Preparation of vermiculite-based catalysts.

by Romico Polska Sp. z o.o. A series of catalysts was prepared according to 4 steps procedure:

- 20 g of vermiculite was suspended in 600 mL of distilled water and then 400 mL of $Fe(NO_3)_3 \cdot 9H_2O$ (p.a., POCh) solution of increasing Fe concentration in each synthesis, was added stepwise; during ion exchange suspension was stirred continuously for 2 h,

- under constant stirring pH of the mixture was raised up to 7 by stepwise addition of 0.1-0.4 M KOH (p.a., POCh) depending on concentration of iron salt used in previous step; crystallization was continued for next 30 minutes (samples Sx),

- in each synthesis part of the filtered precipitate was submitted to additional ion exchange: interlayer Fe^{3+} cations were replaced by K^+; 0.1 M solution of KNO_3 (p.a., POCh) was added slowly and suspension was stirred again for 2 h at pH ~10.5 (samples SxK),

- in the last step, after filtering, washing with distilled water and drying at room temperature, small amount of each catalyst was calcined at 600 °C for 5 h (samples Sxc and SxKc).

As reference samples were used expanded non-modified vermiculite (S0) and iron oxide precipitated after the reaction of $Fe(NO_3)_3 \cdot 9H_2O$ with solution of KOH (the pH after the precipitation reached value 7) (sample S6).

Summary of the preparation procedure of vermiculite-based catalysts was illustrated in Figure 1.

2.2. METHODS OF CHARACTERISATION

The structure of as prepared and calcined samples was studied using a powder diffractometer (Bruker, D2 PHASER) equipped with CuK_α radiation source. Infrared spectra of the samples diluted with KBr were recorded using diffused reflectance technique (Nicolet 6700 FT-IR, Thermo Scientific). The coordination and aggregation of iron present in the catalysts was studied by UV-Vis-DRS spectroscopy. The measurements were performed in the range of 200–900 nm with a resolution of 2 nm using an Evolution 600 (Thermo) spectrophotometer. Content of iron was measured using spectro-photometric technique at wavelength λ 510 nm (Thermo SCIENTIFIC EVOLUTION 220) as a complex with 1,10-phenanthroline after leaching of metal cations in 6 M HCl. Physico-chemical characterisation was also performed for selected spent catalysts (sample names Sx(r), SxK(r), Sxc(r), SxKc(r)).

2.3. CATALYTIC TESTS

Catalytic tests were carried out in a round-bottom flask equipped with reflux condenser (continuously stirred batch reactor). In each standard phenol (PhOH) oxidation test 150 mL of stock solution containing phenol (2.5 g/L) was mixed with 5 mL of oxidant solution (30 % H_2O_2, p.a. POCh) and total volume was made up to 175 mL with distilled water. Final concentration – 2 g/L of phenol was used with the aim to simulate raw wastewater from coking plant. For selected reactions solution of hydrogen

peroxide was added stepwise: 0.5/1 mL every 10/15 minutes until total volume of 5 mL was achieved. In tests of hydrogen peroxide decomposition phenol solution was replaced with water. Reaction was carried out for 2 h in the presence of 300 mg of the catalyst. H_2O_2 decomposition and PhOH oxidation reactions were studied at atmospheric pressure and temperature equal T = 30, 50, 70 °C. Phenol concentration was measured spectrophotometrically (Thermo SCIENTIFIC EVOLUTION 220) as a complex with 4-aminoantipyrine. For determination of H_2O_2 concentration titration with thiosulfate was used. Changes of pH were monitored throughout each experiment. Conversion (X [%]) of model pollutant (phenol) and oxidant (H_2O_2) was calculated according to equation (1):

$$X = \frac{C_0 - C}{C_0} \cdot 100\% \qquad (1)$$

in which C_0 is starting concentration and C is concentration at given reaction time of phenol or hydrogen peroxide.

3. RESULTS AND DISCUSSION

3.1. CHARACTERISATION OF THE CATALYSTS

Fresh catalysts, as prepared, before and after potassium ion exchange (Sx-SxK) were characterized with similar content of iron. This fact may be easily explained taking into account conditions in that step – pH was close to 10 and precipitation of iron oxide/hydroxide may be expected. The amount of iron in the samples before ion exchange is presented in Table 1. The amount of iron naturally observed in vermiculite is slightly higher than 6 wt.% and iron is present mainly in phyllosilicate layer. It cannot be

Table 1 Fe content in as prepared vermiculite-based catalysts.

sample name	[Fe_{total} wt.%]*	[Fe_{doped} wt.%]**
S0	6.02	0
S1	7.14	1.65
S2	8.57	3.24
S3	11.28	6.28
S4	16.26	11.82
S5	24.71	21.14
S6	69.94	n.a.

* - total Fe content,
** - Fe introduced in doping process.

also excluded however that some Fe cations are located in interlayer space. After Fe doping increasing amount of iron (between 1.65 and 21.14 wt.% of Fe) could be deposited on the vermiculite support as hydroxide/oxide clusters or intercalated into interlayer galleries in form of Fe^{3+} cations.

No significant difference was also observed in DRIFT (Fig. 2.) and UV-Vis-DRS (Fig. 3.) spectra between the samples before and after ion exchange. The broad bands in infrared spectra around 3600-3300 cm^{-1} were assigned as stretching vibrations of -OH groups in the mineral structure or water molecules. Two bands dominate in the starting material (3605 and 3320 cm^{-1}) and upon Fe-doping they become broader and finally overlap in one peak which should indicate higher heterogeneity of -OH species. Bending vibrations of interlayer and adsorbed water molecules result in formation of band around 1646-1650 cm^{-1}. Several other bands characteristic for aluminosilicate structure vibrations appear: band at 1085 and 988-996 cm^{-1} can be assigned to Si-O-Si
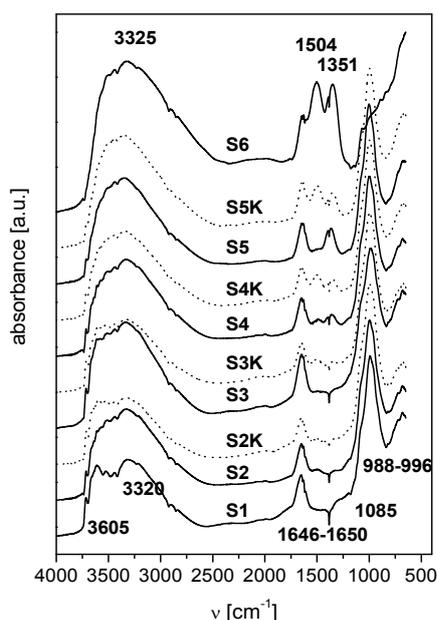

Fig. 2 DRIFT spectra of as prepared catalysts without (Sx) and with (SxK) potassium ion exchange.
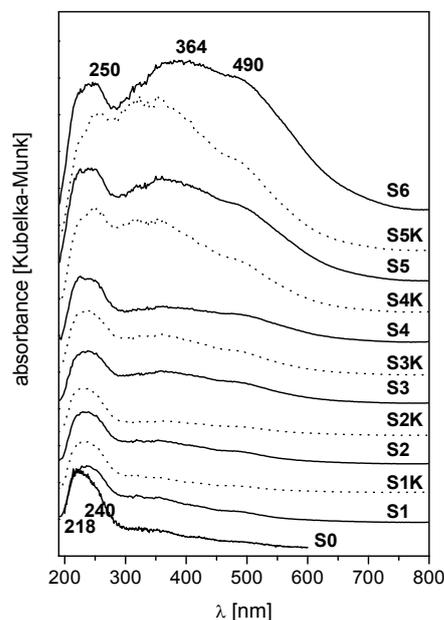

Fig. 3 UV-Vis-DRS spectra of as prepared catalysts without (Sx) and with (SxK) potassium ion exchange.
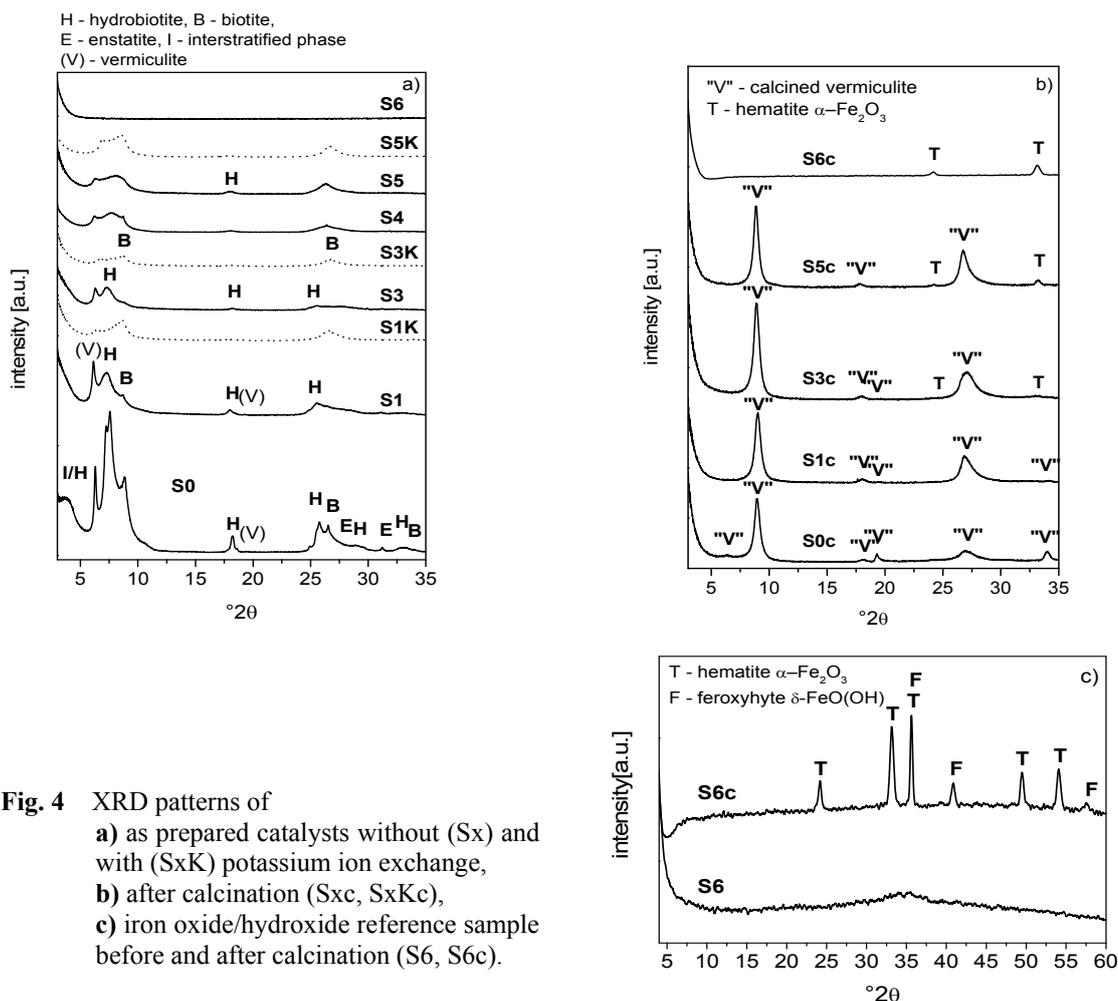
Fig. 4 XRD patterns of
a) as prepared catalysts without (Sx) and with (SxK) potassium ion exchange,
b) after calcination (Sxc, SxKc),
c) iron oxide/hydroxide reference sample before and after calcination (S6, S6c).

units, two weak bands at 1144 and 1124 cm^{-1} are due to stretching of Si-O (Steudel et al., 2009; Chmielarz et al., 2010; Chmielarz et al., 2011; Chmielarz et al., 2012). Bands with low intensity at 907, 820 and 725 cm^{-1} result from bending and deformation vibrations in octahedral layer (e.g. Al-OH, Al-Mg-OH) (Liu et al., 2011). Peak at 678 cm^{-1} can be assigned as R-O-Si vibrations (R = Al, Mg, Fe). It was observed that with increasing iron content increases intensity of two peaks at 1504 and 1351 cm^{-1} as a result of formation of inorganic Fe carbonates (probably due to contact with air during synthesis) and nitrates (probably due to incomplete washing of the precursor after synthesis).

Iron is natural component of vermiculite. Furthermore, its coordination and agglomeration state can be determined using UV-Vis spectroscopy. Cations built in octahedral and tetrahedral layers are isolated and the latter coordination is dominating – peak at 218 nm is more intense than peak at 240 nm. Upon Fe doping bands assigned to octahedral coordination become more intense and are shifted to higher wavelengths (250 nm). Increases also the intensity of bands about 360 nm related to small Fe$_x$O$_y$ clusters and above 400 nm – bulk Fe$_2$O$_3$ oxide (Chmielarz et al., 2008, Chmielarz et al., 2009,

Chmielarz et al., 2010, Chmielarz et al., 2012). After calcination (selected results shown in section 3.5., Fig. 9) all peaks become more intense. It was also observed that both peaks assigned as small clusters and bulk iron oxide are shifted to higher wavelengths: from 360-364 to 385-390 nm and from 490 to 520 nm, respectively.

XRD results (Fig. 4a) indicate that fresh materials are characterized with similar phase composition, however basal reflections positions are strongly influenced by cations introduced during synthesis. In the case of all samples two main phases of hydrobiotite (peaks of high intensity at 1.223, 0.349, 0.491, 0.272 nm) (Downs, 2006) and biotite (peaks of high intensity at 1.01, 0.337, 0.266 nm) (Downs, 2006) were identified, although it seems that hydrobiotite is dominating in the samples without K$^+$ ion exchange. On the contrary, biotite is the main phase after exchange with potassium. Additional peaks at 0.317, 0.288, 0.254 nm could be related to enstatite (Downs, 2006); others at ~1, 0.457, 0.261, 0.257 nm could be related to vermiculite (Downs, 2006), however in expanded material these peaks might also correspond with mica-like structure (probably muscovite) (Marcos et al., 2009; Marcos et al., 2010).

Table 2 Interlayer distance of Fe-modified vermiculite-based catalysts.

sample name	d [nm]	d [nm]	d [nm]	d [nm]	d [nm]	(d [nm]*)
S0 (S0c*)	2.37	1.40	1.22	1.17	1.00	(0.988)
S1 (S1c*)	2.47	1.44	1.21		1.02	(0.981)
S1K		1.37		(…)	1.01	
S3 (S3c*)	2.31	1.40	1.21		1.00	(0.993)
S3K		1.30			1.02	
S4		1.43		1.15	1.01	
S5 (S5c*)		1.40		(…)	1.09	(0.996)
		dominating in Sx samples			dominating in SxK samples	calcined samples
	inter-stratification	2 layers of water Mg^{2+}/Fe^{3+}	inter-stratification	1 layer of water Mg^{2+}/Fe^{3+}	0 layers of water K^+ in non calcined samples	mica-like structure

* - results for calcined samples

Table 2 presents interlayer distances calculated for all obtained samples. In case of the samples without K^+ ion exchange one should expect that interlayer space is occupied mainly by Fe^{3+} cations. It cannot be excluded that original cations such as Mg^{2+} were not removed completely. It was reported before (Helsen, 1975; Argüelles et al., 2011) that ion exchange of the Mg^{+2} cations with Fe^{3+} results in small decrease of d-spacings (from 1.44 to 1.42 nm) related both to changes in the interaction between interlayer Fe ions and the cations in the octahedral layers as well as changes in the configuration of the water molecules. However, in both cases calculated interlayer distances are related to 2 layers of water and are dominating in the series Sx. Heterogeneity of cationic composition may result in appearance of additional shoulder in the range of 7.0-7.5°2θ. On the other hand, potassium exchanged samples are characterized with lower interlayer distances usually assigned as 0 layers of water molecules and typically associated with the presence of interlayer K^+ (Chmielarz et al., 2010, Chmielarz et al., 2012). Interstratified phase was detected only at low Fe loadings in the samples S0-S3. After calcination (Fig. 4.b) the main phase is more uniform in all samples and was indicated as calcined vermiculite. In this case the interlayer distances should be described as, most probably, mica-like structure (Marcos et al., 2009; Marcos et al., 2010).

Iron oxide, which is component of composite catalysts, is characterized with completely amorphous structure. After calcination at 600°C two phases were identified in the reference sample S6c (Fig. 4c): hematite and feroxyhyte. Traces of those phases were identified only in the samples with higher Fe doping after calcination: S3c-S5c.

3.2. THE INFLUENCE OF TEMPERATURE ON SUBSTRATE CONVERSION

Results of catalytic tests, presented in Figure 5, confirm that catalytic activity in both studied reactions (H_2O_2 decomposition and phenol oxidation using H_2O_2) strongly depends on temperature. It was shown that samples doped with iron are active in decomposition of hydrogen peroxide (Fig. 5a). However time of 50 % conversion (Table 3.) is shorter for the samples without K^+ ion exchange. It cannot be excluded that Fe^{3+} cations are released from interlayer spaces of the samples and play role of catalysts.

Similar conversions of H_2O_2 playing role of oxidant in oxidation of phenol (Fig. 5b) were obtained for the sample S4. Although it should be noted that in the case of all studied catalysts, due to the presence of second substrate (phenol), the time necessary for 50 % conversion is significantly longer. The non-modified sample S0 is characterized with very low conversions at temperatures 30 and 50 °C – not higher than 10 %. Low conversions of phenol (Fig. 5c) were also measured for the sample S0 at temperatures below 70 °C and S4 at 30 °C. Another interesting obser-vation, shorter time necessary for 50 % phenol conversion than H_2O_2, may be explained by the reaction mechanism. OH• radicals are obtained on the catalyst from H_2O_2 and they initiate chain reactions of organic radicals. From that point phenol is converted in reactions with radicals until those reactions are terminated (Bielicka-Daszkiewicz, 2008; Rivas et al., 1999; Magario et al., 2012). It should be also taken into account that hydrogen peroxide was used with excess with respect to organic substrate.

3.3. THE INFLUENCE OF IRON CONTENT AND POTASSIUM EXCHANGE ON PHENOL CONVERSION

Selected results of catalytic tests carried out at 70 °C over iron doped vermiculite-based materials with increasing amount of Fe are presented in Figure 6. In all tests it was shown that conversion of phenol as well as H_2O_2 strongly depends on Fe con-tent. In the case of non-calcined materials without K^+ ion exchange (Sx series) the higher Fe doping the shorter time of α 50 % (Table 4). Within 60 minutes
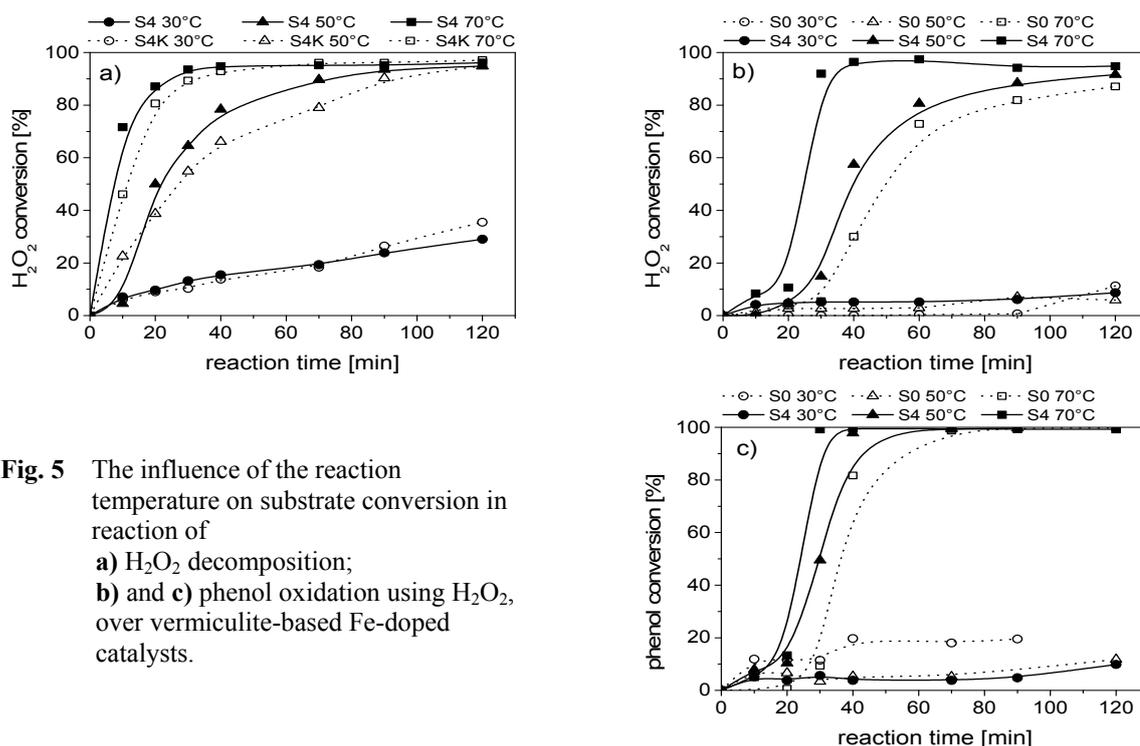
Fig. 5 The influence of the reaction temperature on substrate conversion in reaction of
a) H_2O_2 decomposition;
b) and **c)** phenol oxidation using H_2O_2, over vermiculite-based Fe-doped catalysts.

Table 3 Time of 50% conversion (time α 50%) of substrates in decomposition of H_2O_2 and phenol oxidation over vermiculite-based Fe-doped catalysts.

reaction	H_2O_2 decomposition		phenol oxidation			
substrate	**H_2O_2**	H_2O_2	H_2O_2	PhOH	**H_2O_2**	**PhOH**
catalyst	**S4**	S4K	S0	S0	**S4**	**S4**
temperature [°C]	time α 50% [min]	time α 50% [min]	time α 50% [min]	time α 50% [min]	time α 50% [min]	time α 50% [min]
30	**-**	-	-	-	**-**	-
50	**22**	28	-	-	**40**	**30**
70	**7**	12	50	37	**25**	**24**

Table 4 The influence of iron content on substrate conversion in phenol oxidation over vermiculite-based Fe-doped catalysts – time of 50 % conversion.

catalysts series	Sx		Sxc		SxK		SxKc	
substrate	H_2O_2	PhOH	H_2O_2	PhOH	H_2O_2	PhOH	H_2O_2	PhOH
catalyst number	time α 50 % [min]	time α 50 % [min]	time α 50 % [min]	time α 50 % [min]	time α 50 % [min]	time α 50 % [min]	time α 50 % [min]	time α 50 % [min]
0	50	36	-	-	50	36	-	-
1	46	33	-	-	48	36	-	-
2	41	34	-	104	n.d.	n.d.	n.d.	n.d.
3	37	32	**68**	**28**	25	13	106	87
4	25	24	102	77	10	**5**	113	95
5	15	**14**	-	101	**5**	**5**	**103**	**82**
6	**11**	24	-	-	n.a.	n.a.	n.a.	n.a.

complete conversion of phenol is achieved over all tested catalysts with the exception of S6 – pure iron oxide (Fig. 6a). Surprisingly for that catalyst reaction is not fully effective and final phenol conversion is equal 91 %. Similar result was obtained for calcined catalyst in studied series (S6c). After fast increase up to 30 % conversion is stable and increases to 39 % after 120 minutes of the reaction. Induction phase was also observed for the calcined samples S2c, S4c, S5c (Fig. 6b). On the contrary the sample S3c was very active and total conversion of phenol was observed between 70 and 90 minutes. Nevertheless calcined samples were less active than as prepared catalysts.

In the series of the samples submitted to ion exchange with potassium and without calcination (Fig. 6c) high phenol conversion was achieved in
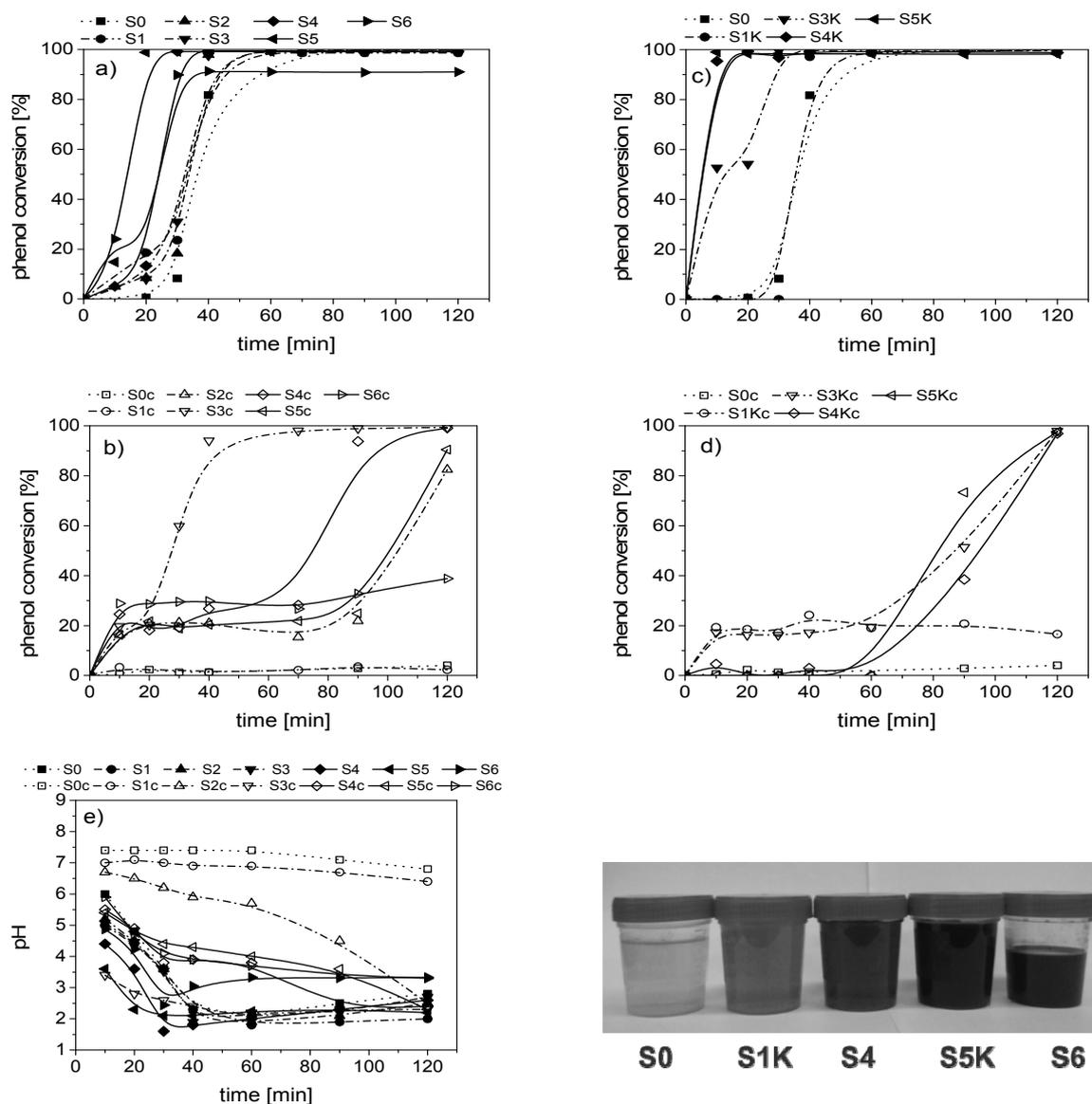
Fig. 6 **a)** and **b)** The influence of iron content and calcination on phenol conversion over catalysts without potassium exchange, Sx and Sxc;

c) and **d)** The influence of iron content and calcination on phenol conversion over catalysts with potassium echange, SxK and SxcK;

e) pH of reaction mixture in phenol oxidation over vermiculite-based Fe-doped catalysts;

f) the examples of post-reaction mixtures containing colored side-products.

short time intervals and again it was possible to convert substrate completely in less than 60 minutes. On the other hand, calcined samples after K$^+$ ion exchange SxKc (Fig. 6d) were less active. It could be concluded that optimum composition of the catalyst is necessary to obtain high efficiency of phenol removal. The excess of iron oxide, especially in the form of bulk species and big clusters do not enhance reaction. Moreover the higher Fe doping was used the more side-products were formed (Fig. 6f). Conversion of H$_2$O$_2$ in studied series of the catalysts SxK and SxKc is again lower for calcined materials. Taking into account obtained conversions, K$^+$ ion exchange seems beneficial for the samples with higher Fe loadings in non-calcined samples. On the contrary, potassium

exchanged samples and calcined are less active then K$^+$ non-exchanged counterparts.

In each test the increase of conversion was followed by drop of pH of the reaction mixture to value equal 2 (Fig. 6e). This clearly indicates formation of acidic products (Bielicka-Daszkiewicz, 2008; Liotta et al., 2009).

3.4. THE INFLUENCE OF STEPWISE ADDITION OF OXIDANT ON SUBSTRATE CONVERSION

For selected catalyst additional tests were carried out in order to improve reaction efficiency. It was reported before that incomplete oxidation may result in formation of colored side-products such as hydroquinone, quinhydrone or even polymeric species
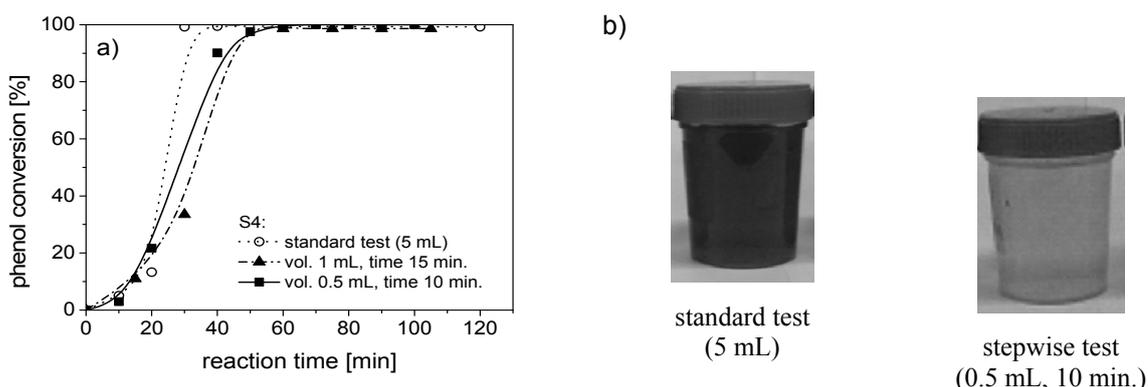
Fig. 7 **a)** The influence of the stepwise addition of oxidant on substrate conversion in phenol oxidation over vermiculite-based Fe-doped catalyst (phenol conversion;
b) formation of colored transition products during standard test and with stepwise addition of oxidant (H_2O_2 volume 0.5 mL, feeding ratio: 10 minutes – right) over Fe-doped vermiculite (S4).

(Alejandre et al., 1999). In standard test total volume of oxidant was added at the beginning of the reaction and as it was described above, significant amount of side products was observed. In alternative tests oxidant solution was added stepwise (0.5 or 1 mL) in constant intervals (10 or 15 minutes). Conversion of phenol (Fig. 7a) was only slightly inhibited – time of α 50 % was extended from 24 minutes to 28 or 33, respectively. However at 60 minutes of the reaction total conversion of product was achieved. Moreover transparency of post-reaction mixture was significantly improved (Fig. 7b).

3.5. *CHARACTERIZATION OF SPENT CATALYSTS*

After catalytic reaction in XRD patterns (Fig. 8) significant changes were observed mostly in lower range of °2θ. Basal reflections at 6.18°2θ became very sharp and intense (this phenomenon can be related to structural reconstruction), with an exception of the calcined sample with high Fe loading S5c(r). Moreover, no peaks of hematite or feroxyhyte were detected in the sample S4(r) after reaction. Those two facts may indicate that during reaction part of iron oxide is dissolved and takes part in reaction in homogeneous phase as well as is intercalated between layers. Depending on reaction conditions Fe release measured in post-reaction mixtures was equal 1.1-7.7 mg for the non-calcined samples (S4-S6) and 2.1-8.7 mg for the calcined samples (S2Kc-S5Kc). In experimental conditions no leaching of Fe from the structure of non-modified vermiculites (S0-S0c) was detected.

Unclear is the origin of small peak at 8.55°2θ in the sample S4(r). On the other hand peaks at 18.56°, 24.85°, 28.8° and 31.2°2θ could be assigned to hydrobiotite. Interstratified phase was observed mostly for catalysts with low Fe doping. At higher Fe doping disappears also basal reflection assigned to 1 layer of water molecules. Basal spacings are presented in Table 5. Traces of iron oxides are not-detectable in spent catalyst S4c(r), but characteristic peaks of hematite, traces of hydrobiotite and another

phase, most probably muscovite, were observed for S5c(r) (Marcos et al., 2009; Marcos et al., 2010).

Leaching of Fe could be additionally confirmed using UV-Vis-DRS results (Fig. 9). In the case of non-modified vermiculites (calcined and non-calcined) there is no significant difference in peak positions, however it should be noted that in starting vermiculite (before calcination S0) dominating species are Fe isolated cations in tetrahedral coordination. On the contrary, in the calcined sample S0c ratio of octahedral Fe cations is higher. After reaction the opposite distribution may be observed – in the sample S0 cations in octahedral coordination are more numerous, but in the calcined sample – in tetrahedral.

As it was described in section 3.1., in the samples doped with iron (both calcined and non-calcined) isolated Fe cations are more likely to accommodate octahedral coordination. After catalytic reaction, in all samples, regardless calcination or K^+ ion exchange, large number of isolated cations in tetrahedral coordination was observed. It results in the increase of relative intensity of peak at about 224 nm. At the same time the decrease of relative peak intensity is observed for small Fe_xO_y clusters as well as bulk iron oxide. Moreover, both peaks are shifted to lower wavenumbers (about 10-15 nm). The most extensive leaching of Fe was observed for non-calcined sample S4. Nevertheless, the precise and quantitative analysis of UV-Vis spectra may be hindered by significant change of hydration state of the studied samples.

Those facts are in an agreement with previous observations that interlayer space is strongly altered – probably by Fe^{3+} cations released from introduced iron oxide. It cannot be excluded that, in minor proportion, Fe^{3+} cations were also introduced in the octahedral layers (Argüelles et al., 2011).

In presented studies only traces of organic compounds, possible reaction products, were identified using DRIFT technique (results not shown). As it was shown in section 3.3., all transition products have acidic character (Bielicka-Daszkiewicz, 2008,
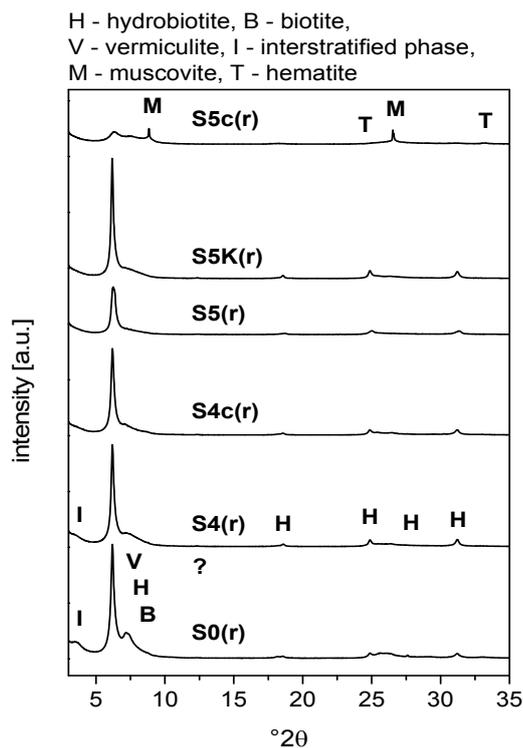
H - hydrobiotite, B - biotite,
V - vermiculite, I - interstratified phase,
M - muscovite, T - hematite

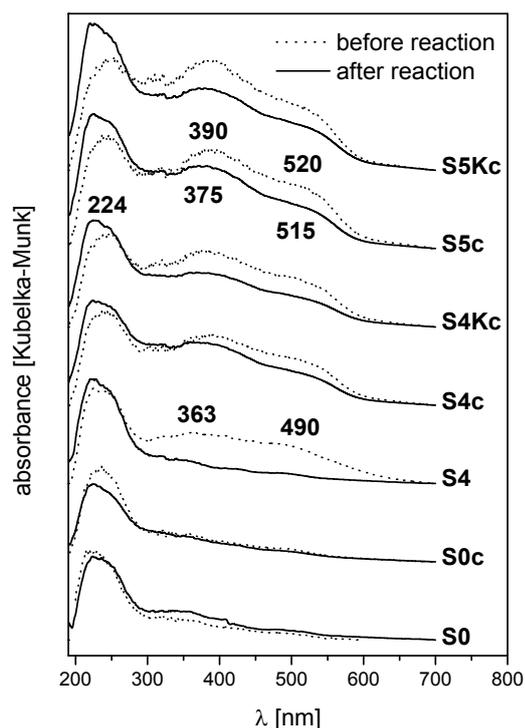**Fig. 8** XRD patterns of catalysts after reaction.

Fig. 9 UV-Vis-DRS spectra of catalysts after reaction.

Table 5 Interlayer distance of Fe-modified vermiculite-based catalysts after reaction.

sample name	d [nm]	d [nm]	d [nm]	d [nm]	d [nm]
S0(r)	2.48	1.43	1.24	1.20	1.01 *w
S4(r)	2.49	1.43	1.23		1.01 *w
S4c(r)		1.43	1.25		1.01 *w
S5(r)		1.41		1.18 *w	
S5K(r)		1.43		1.19 *w	
S5c(r)		1.40		1.18	1.00 *s
	inter-stratification	2 layers of water Mg^{2+}/Fe^{3+}	inter-stratification	1 layer of water Mg^{2+}/Fe^{3+}	0 layers of water K^+ possible mica-like structure

*w – weak, low intensity peaks, s – sharp peak

Liotta et al., 2009) and one cannot expect significant adsorption or its intercalation in interlayers.

4. CONCLUSIONS

In presented paper it was shown that vermiculites may be used as catalysts of phenol oxidation. The catalytic activity can be increased by additional doping with Fe compounds. Upon modification Fe cations were probably introduced into interlayer spaces and in minor proportion in octahedral layers, and metal oxide cluster are deposited on the surface. Depending on iron content four different species were identified: isolated cations in tetrahedral and octahedral coordination, small clusters of Fe_xO_y and bulk Fe_2O_3. It was shown that the presence of isolated ions and small clusters is the most beneficial for the reaction efficiency. Optimum catalyst composition also allowed to avoid formation of large amounts of undesired side-products. Additionally those products could be avoided by stepwise addition of oxidant during reaction. Potassium exchange seems beneficial in the case of non calcined samples – 50 % conversion was achieved in shorter time in comparison to their K-non-exchanged counterparts. The opposite effect was observed in the case of calcined samples: potassium exchanged samples were characterized with lower conversions than non-exchanged catalysts. Characterisation of the spent catalysts revealed that partial degradation of deposited iron oxide may occur. Released Fe^{3+} cations occupied probably interlayer spaces and sites in octahedral layers and may play role of catalysts of the studied process.

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