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Propylene glycol oxidation with hydrogen peroxide over Zr-containing metal-organic framework UiO-66

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ARTICLE INFO	A B S T R A C T
Keywords:	Zirconium-based metal-organic framework UiO-66 catalyzes oxidation of propylene glycol (PG) using hydrogen
Propylene glycol	peroxide as green oxidant. Hydroxyacetone (HA) is the main oxidation product, while the main side product is acetic
Selective oxidation	acid (AcA). The nature of the solvent drastically affects PG adsorption, oxidant utilization efficiency and product
Hydroxyacetone Alcohol oxidation	yields. The best catalytic performance (85% selectivity towards HA at ca. 10% PG conversion) was achieved with
Hydrogen peroxide	water-acetonitrile $(3/7 (v/v))$ mixture as a solvent. Additives of radical chain scavengers produce a rate-inhibiting
Metal-organic frameworks	effect, suggesting radical chain mechanism of the oxidation process. The PG oxidation over UiO-66 proceeds without

1. Introduction

Zirconium

UiO-66

Nowadays, a growing attention is being paid to the problem of replacing carbon sources by chemical synthesis from fossil hydrocarbons to biorenewable resources [1,2]. One of the products that could be obtained from mono- and polysaccharides extracted from biomass is propylene glycol (PG) [3]. A regioselective PG oxidation at secondary hydroxyl group leads to the formation of hydroxyacetone (HA). HA plays an important role in organic synthesis and finds application in food, textile, cosmetic industries as well as in the production of polymers [4]. However, selective oxidation of only one hydroxyl group in polyols is a challenging task in view of their close reactivity [5]. Traditionally, HA is manufactured by noncatalytic methods from sodium or potassium formate or acetate [6] or via direct oxidation of acetone [7]. However, these multistep procedures use toxic reagents in stoichiometric amounts and produce HA with low selectivities. Biosynthetic routes using various substrates are developing rapidly [8,9] but so far, low conversions and product yields, as well as long reaction times are characteristic of these methods.

Several groups reported the selective formation of HA in liquidphase PG oxidation [10–12], while the majority of publications were devoted to the production of lactic acid from PG using noble metalcontaining catalysts in alkaline conditions [13–16]. PG oxidation in a gas phase proceeded with preferential formation of methylglyoxal and C–C cleavage products [17–20]. Only small amounts of HA as an intermediate product were observed. At the same time, selective production of α -hydroxyketones in vapor phase was realized over copper catalysts [21]. Nevertheless, there is a growing demand in the development of effective catalytic systems for selective oxidation of alcohols, especially polyols, in liquid phase using environmentally friendly oxidants and easily recyclable heterogeneous catalyst [22–24].

leaching of the active metal into solution, and the catalysis has a truly heterogeneous nature. The catalyst can be

recycled without significant loss of activity and selectivity and retains its structure during at least five reuses.

The synthesis and application of metal-organic frameworks (MOFs) have attracted a great attention during the last two decades due to the possibility to obtain materials with a large variety of metal centers and structures. Very high surface areas and pore volume, crystalline structure and a large fraction of accessible metal centers make MOFs promising candidates to be used as heterogeneous catalysts [25-30]. Several examples of the selective oxidation of alcohols to carbonyl compounds over MOFs have been reported- [31-36]. Copper-based MOFs are the most widely used MOFs for alcohol oxidation due to the intrinsic activity of this transition metal in oxidation catalysis. Cu-MOFs revealed catalytic activity in the oxidation of various benzene ringcontaining alcohols in the presence of 2,2,6,6-tetramethylpiperidine-Noxyl (TEMPO) and/or organic base [31,32]. The use of Cu-MOF with NH₂-functionalized linkers has led to high activity without addition of any base [33]. Schiff base as an organic linker has allowed avoiding the addition of co-catalyst and led to the selective formation of benzyl aldehyde under mild temperature and solvent-free conditions [34]. Peng et al. have compared the activity of Co, Zn, Ni, and Cu-containing

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isostructural MOFs in aerobic oxidation of benzyl alcohol [35]. Co(bdc) (ted)_{0.5} showed higher benzyl alcohol conversion (81.8%) and selectivity towards benzaldehyde (> 99%) than the other systems. Benzyl alcohol oxidation over Ir-MOFs in the presence of inorganic base and iodobenzene afforded selective formation of benzaldehyde at moderate conversions [36]. Nevertheless, until recently there were no examples of selective oxidation of polyols over MOFs. Recently, we demonstrated that the selective oxidation of PG to HA could be realized over Cr-containing MOFs, MIL-100 and MIL-101, using *tert*-butylhydroperoxide as environmentally friendly oxidant [37]. However, use of green oxidants (molecular oxygen or hydrogen peroxide), which produce water as the only by-product, is more preferable for practical applications [38]. Moreover, the development of MOFs that can be used as truly heterogeneous catalysts in aqueous or quasi-aqueous media without any metal leaching is very attractive.

In 2008, Cavka et al. reported the first synthesis of a porous zirconium terephthalate UiO-66 [39]. This material attracted a lot of attention due to unprecedentedly high thermal (up to 540 °C) and solvothermal stability among MOFs. It consists of Zr-oxo-hydroxo clusters $Zr_6O_4(OH)_4$ coordinated by terephthalate ligands (Fig. 1). This MOF possesses two types of pores with windows of 0.6 and 1 nm, the surface area of ca. 1200 m²/g, and pore volume of 0.7 cm³/g. It has found wide application in adsorption and gas storage [40,41] as well as an active and selective catalyst for Lewis-acid catalyzed transformations [42,43]. However, to the best of our knowledge, UiO-66 was not used as a heterogeneous catalyst for oxidation reactions, particularly, with hydrogen peroxide as oxidant.

The aim of this work was to explore the potential of UiO-66 for the selective oxidation of PG with hydrogen peroxide. The effects of reaction conditions (solvent nature, temperature, concentrations of reagents and atmosphere) on the selectivity and yield of HA and acetic acid (AcA) have been studied. The nature of catalysis was addressed, and the catalyst reusability was evaluated.

2. Experimental

2.1. Materials

Propylene glycol (Vekton, 99%) was distilled under vacuum. Acetonitrile was dried and stored over activated 4 Å molecular sieves. Terephthalic acid (Acros Organics, 99%), zirconyl (IV) nitrate hydrate (Acros Organics, 99.5%), *N*,*N*-dimethylformamide (DMF, ECOS-1, 99.8%), hydrochloric acid (Vekton, 38% aqueous solution) were used without additional purification. The concentration of hydrogen peroxide (~35%) was determined by iodometric titration prior to use.

2.2. Catalyst preparation and characterization

UiO-66 was synthesized by solvothermal method following the procedure reported by Cavka et al. [39] with some modifications. Equimolar





amounts (3 mmol) of terephthalic acid and $ZrO(NO_3)_2$ ·2H₂O were dispersed in DMF (60 mL) and then hydrochloric acid (99 mmol) was added. The mixture was placed into Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. The obtained white solid was washed with DMF and ethanol. Prior to characterization, the sample was degassed under vacuum at 90 °C during 1 h and at 150 °C during 5 h.

Textural characteristics of the catalyst were determined from nitrogen adsorption isotherms (-196 °C; 3Flex instrument, Micromeritics). Horvath-Kawazoe sphere pore geometry method was used to calculate pore size distribution. The structure of the UiO-66 material was confirmed by XRD (Riguku Miniflex 600 X-ray diffractometer) and FT-IR spectroscopy (SCIMITAR FTS 2000 spectrometer).

Zirconia was synthesized by thermal decomposition of $ZrO(NO_3)_2 2H_2O$ in air at 500 °C for 4 h. According to XRD, the resulting material consists of a mixture of monoclinic and tetragonal ZrO_2 phases (see Supporting information (SI), Fig. S1). Low-temperature nitrogen adsorption revealed the formation of a mesoporous material with S_{BET} 47 m²/g, pore volume 0.24 cm³/g, and average pore diameter 17 nm (Fig. S2 in SI).

2.3. Catalytic experiments and product analysis

Catalytic oxidation tests were carried out in a thermostatted glass vessel at 40–70 °C under vigorous stirring (500 rpm). Typically, the reaction was initiated by the addition of H₂O₂ to a mixture containing 1 mmol of PG, 1 ml of solvent and 3.7 mg (0.013 mmol Zr) of catalyst. Samples (1 µL) were removed periodically through a septum and analyzed by GC (Chromatec Crystal 5000.1, flame ionization detector, 30 m × 0.22 mm × 0.5 µm ZB-WAX capillary column, chlorobenzene as an internal standard). At the end of the reaction, the catalyst was separated and the filtrates were analyzed by GC-MC (Agilent 7000B system with triple-quadrupole mass-selective detector Agilent 7000 and GC Agilent 7890B, 30 m × 0.25 mm × 0.25 µm ZB-WAX capillary column), and HPLC (Shimadzu Prominence-I LC-2030C, Rezex ROA-Organic Acid H + column). Each experiment was reproduced 2–3 times. ¹H NMR spectra were collected using Bruker Avance-400 spectrometer (400.13 MHz). The concentration of hydrogen peroxide was determined by iodometric titration.

Recycling experiments were performed under the optimized reaction conditions. After the reaction the catalyst was filtered off, washed with water or acetone, dried at room temperature overnight, and then reused. The amount of zirconium in the filtrates was determined by microwave plasma atomic emission spectroscopy (Agilent 4100 microwave spectrometer).

2.4. Adsorption measurements

All adsorption measurements were carried out at room temperature (25 °C). A concentrated (3.3 M) solution of PG (HA or AcA) was added by portions (30 μ L) to a solution containing 2 ml of solvent, 8 μ L of chlorobenzene (internal standard) and 20 mg of activated (150 °C, 5 h) UiO-

Fig. 1. Metal-oxide cluster (a) and representation of 3D framework structure of UiO-66 (b). Zr atoms are shown in dark purple, O atoms in light purple and C atoms in orange. Hydrogen atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article). Adapted from [54].

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Table 1

Effect of solvent nature on PG oxidation with H2O2 over UiO-66.

Solvent	Conversion, %		H ₂ O ₂ utilization	Selectivity, %	
	PG	H ₂ O ₂	enciency, %	НА	AcA
H ₂ O	8	60	14	63	14
MeCN	6	18	34	68	12
2/8(v/v)H ₂ O/MeCN	6	22	32	75	13
3/7(v/v)H ₂ O/MeCN	8	27	36	85	13
4/6(v/v)H ₂ O/MeCN	8	25	39	83	14

66. After the addition of each portion, the mixture was stirred for 20 min (this time is sufficient to reach the adsorption equilibrium) and then the MOF was separated by centrifugation (6000 rpm, 15 min), and the concentration of organic substance was determined by GC (3-5 measurements) using a gas chromatograph Chromos GC-1000 equipped with a flame ionization detector and a quartz capillary column BPX5 $(30 \text{ m} \times 0.25 \text{ mm})$. Parallel, blank experiments (without MOF) were performed. The amount of adsorbed PG (HA or AcA) was determined as a difference between the concentrations of PG (HA or AcA) in the solutions with and without MOF multiplied by the solution volume. Adsorption constants were estimated using the Langmuir adsorption model.

3. Results and discussion

3.1. Synthesis and characterization of UiO-66

Traditionally UiO-66 is synthesized by the solvothermal method using terephthalic acid and zirconium chloride [39]. However, the major drawback of ZrCl₄ is its high corrosive and hygroscopic behavior resulting in the formation of a mixture with unknown proportions of ZrCl₄ and ZrOCl₂. As a result, the synthesis procedure has low reproducibility. To avoid these drawbacks, Ragon et al. [44] used different zirconium precursors, such as ZrOCl₂·8H₂O, (Zr[acac]₄), Zr(SO₄)₂·xH₂O, $(CH_3CO_2)_x Zr(OH)_y$ (x + y = 4), $Zr(OH)_2 CO_3 ZrO_2$, and $Zr(O^{-i}Pr)_4^{-i}PrOH$. Only the use of ZrOCl₂·8H₂O in DMF led to pure UiO-66 solid.

When we attempted to employ a more available reactant, ZrO (NO₃)₂·2H₂O, instead of ZrCl₄ or ZrOCl₂·8H₂O in the standard synthetic procedure, an amorphous material with low surface area was obtained. The low-temperature nitrogen adsorption isotherm revealed a hysteresis in the region of average relative pressures, showing the presence of mesopores (Fig. S3 in SI), which could correspond to mesoporous ZrO₂. This can be rationalized if we remember that ability of zirconium to attract ions and molecules into its coordination sphere decreases in the following order: $OH^- > carbonate$ and α -oxycarboxylates > F-> HSO₄⁻, NO₃⁻, carboxylate > H₂O > alcohols > halide ions (Cl⁻, Br⁻, I⁻) [45]. Thus, if we start from ZrO(NO₃)₂·2H₂O, terephthalic acid

does not tend to replace hydroxyl and NO3- ions in the zirconium coordination sphere to form the required MOF structure. On the other hand, the formation of UiO-66 structure is expected to be favorable for halide compounds such as ZrCl₄. However, it was reported that acid modulators, such as hydrofluoric, hydrochloric, formic and other acids, can be used to improve the crystallinity of MOFs during the solvothermal reactions [46-48]. The amounts of both acid and water had impact on the crystallization kinetics of the UiO-66 formation [44]. We found that the addition of a 33-fold excess of HCl relative to ZrO (NO₃)₂·2H₂O yielded a highly crystalline porous solid. The BET surface area $(1260 \text{ m}^2/\text{g})$ was close to that of the UiO-66 material prepared by Cavka [39] while the pore size distribution curve had two maximums (Fig. S4 in SI), corresponding to two types of micropores (0.6 and 0.9 nm in diameter). The XRD and FT-IR data (Figs. S5 and S6 in SI) confirmed the formation of the UiO-66 phase. No unidentified reflections were observed in the XRD pattern.

3.2. Catalytic performance of UiO-66 in PG oxidation

3.2.1. Effect of solvent nature

The results of catalytic experiments of PG oxidation with hydrogen peroxide over UiO-66 in different solvents are presented in Table 1. Initially, water and a polar organic solvent, acetonitrile, were employed. In both cases, HA was the main product while predominated side products were C-C cleavage products, including AcA, formic acid, acetaldehyde, and formaldehyde. Scheme 1 shows possible routes for their formation. No other overoxidation products, such as methylglyoxal or pyruvic acid, were found in the reaction mixture (Sheme 1).

In water, at equimolar concentrations of PG and hydrogen peroxide, conversion of the oxidant was much higher relative to conversion of the substrate, which indicated that unproductive decomposition of the oxidant was significant. Selectivity towards HA was 63%. In acetonitrile, H₂O₂ conversion did not exceed 18%, but PG conversion was also low. At the same time, H₂O₂ decomposition was significant in the absence of organic substrate, but it did not occur without catalyst (Fig. 2). This fact confirmed the ability of UiO-66 to activate hydrogen peroxide.



Scheme 1. Possible routes of PG transformation over UiO-66.



Fig. 2. H₂O₂ decomposition in MeCN over UiO-66 (○), ZrO₂ (●), and without catalyst (■). Reaction conditions: [H₂O₂] = 1 M, 14.8 mg of catalyst, 4 ml of solvent, 50 °C.



Fig. 3. Adsorption of PG on UiO-66 from MeCN solution (), its fitting with Langmuir model (O), and adsorption of PG from 7/3(v/v) MeCN/H₂O solution (

To clarify the observed effect of solvent on the PG oxidation over UiO-66, we studied PG adsorption from different solvents on this MOF (Fig. 3). Indeed, UiO-66 is able to adsorb PG from MeCN and the adsorption constant evaluated using Langmuir model is quite high (290 \pm 60 M⁻¹). This allowed us to suppose that adsorbed PG molecules block zirconium active sites and thereby suppress adsorption and activation of the oxidant. On the other hand, no adsorption of PG occurred from a mixed solvent H₂O/MeCN 3/7(v/v) (Fig. 3).

In order to optimize adsorption of the reactants, different amounts of water were added to acetonitrile (Table 1). The replacement of 20 vol.% of acetonitrile by water led to a slight increase in H₂O₂ conversion and HA yield. Increase in water amount up to 30 vol.% resulted in enhancement of both PG conversion (to the level of that attained in water) and H₂O₂. Moreover, HA selectivity increased markedly (85 versus 63% in water) and carbon mass balance (HA + AcA) became close to 100%. The oxidant utilization efficiency also enlarged from 14 to 36%. Additional increase in water concentration (40 vol.%) produced no significant changes of PG conversion and product selectivities. Further optimization of the reaction conditions was performed using the optimal mixture of the two solvents.

3.2.2. Effect of catalyst loading

The corresponding kinetic curves for PG oxidation with H₂O₂ acquired using different amounts of UiO-66 are presented in Fig. 4. Enlarging of the catalyst amount increased initial reaction rates, but just slightly influenced on the substrate conversion and product yields. Without catalyst, the reaction was much slower and PG conversion did not exceed 7% after 24 h. HA selectivity in this case was about 70%.



Fig. 4. PG oxidation with H_2O_2 without catalyst (\blacklozenge), over 1.9 (\blacklozenge), 3.7 (\blacktriangle), 7.4 (■), and 11.1 mg (▼) UiO-66. Filled symbols – PG, open symbols – HA. Reaction conditions: 1 mmol PG, 1 mmol H₂O₂, 1 ml 7/3(v/v)MeCN/H₂O, 50 °C.

The dependence of the initial reaction rate on the catalyst amount was linear (Fig. S7 in SI), indicating that the reaction is first order in catalyst, which suggests the absence of external diffusion limitations. Additionally, we performed an experiment using mesoporous zirconia instead of UiO-66 as catalyst. Previously, Jung and Bell investigated structure of active sites on the surface of ZrO₂ for samples with monoclinic and tetragonal modification and their mixture and found that all the zirconia samples have coordinatively unsaturated Zr⁴⁺ cations and possess Lewis acidity [49]. Studies on hydrogen peroxide decomposition in the absence of organic substrate showed that zirconia is more active in this reaction than UiO-66 (Fig. 2). Nevertheless, PG conversion over zirconia did not exceed 1% although oxidant conversion was close to 100%. On the other hand, the structure of UiO-66 [39] as it is does not imply the presence of coordinatively unsaturated Zr^{4+} . but namely this MOF enabled PG oxidation to HA. This may indicate the crucial role of the specific microporous confinement of UiO-66 in this reaction. We may assume that both enlarged PG concentration in the MOF pores and the spatial arrangement of the Zr active sites therein are significant for the observed catalysis. We cannot also exclude that some defects present in the structure of UiO-66 [50] may contribute to the activation of H₂O₂. However, further studies are needed to elucidate their role.

3.2.3. Effect of H_2O_2 and PG amount

Although complete conversion of hydrogen peroxide was not attained under the condition of the experiments presented in Table 1, a two-fold reduction of its amount led to decreasing PG conversion and HA yield (Table 2). In turn, augmentation of H₂O₂ concentration did

Table 2					
Effect of H ₂ O ₂	amount o	on PG	oxidation	over	UiO-66.

[H ₂ O ₂], M	PG conversion, %	Selectivity, %		H ₂ O ₂ utilization efficiency,
		HA	AcA	, , , , , , , , , , , , , , , , , , ,
0.5	5	92	9	41
1	8	85	13	36
1.5	9	72(80 ^a)	12(20 ^a)	> 34
1 ^b	10	85	10	34
1	10 ^c	-	95	54

Reaction conditions: 1 mmol PG, 1 mmol H₂O₂, 3,7 mg UiO-66, 1 ml 3/7(v/v) H₂O/MeCN, 50 °C, 2 h.

Selectivity in 1 h.

 $^{\rm b}$ Concentration corresponding to the total amount of $\rm H_2O_2$ added (slow addition during 1.5 h).

^c HA (0.2 mmol) was used as substrate.

Та



Fig. 5. Arrhenius plot for PG oxidation with H₂O₂ over UiO-66.

not affect the substrate conversion but it decreased the selectivity towards HA and resulted in increasing amount of C–C cleavage products, including AcA. It is noteworthy that the kinetic curves of HA and AcA accumulation had maximum (Table 2, entry 3), indicating that further oxidation (probably to CO_x) takes place. When HA was used as substrate instead of PG, the selective formation of AcA was observed (Table 2). The initial rate of PG oxidation was proportional to the H₂O₂ amount and independent on PG concentration, demonstrating that the reaction is first reaction order in oxidant and zero order in substrate (Fig. S8 in SI). Thus, we can infer that PG does not participate in the rate-limiting step of the oxidation process.

Gradual addition of H_2O_2 into the reaction mixture did not improve significantly oxidant utilization efficiency, but it slightly increased PG conversion and HA yield (see Table 2). We may suppose that the oxidant addition by portions disfavors the formation of C–C cleavage products.

3.2.4. Effect of temperature

The increase in the reaction temperature from 40 to 60 °C accelerated the reaction but had only little effect on the PG conversion and product selectivities. Further rising of the temperature led to decreasing selectivity towards HA. The initial rates of PG oxidation over UiO-66 exhibited a typical Arrhenius dependence (Fig. 5). The activation energy estimated from the corresponding plot equaled to 88 kJ/mol. Such value is typical of reactions controlled by the chemical interaction rather than diffusion of reactants [51].

3.3. Mechanistic tests

The presence of molecular oxygen can significantly influence on the oxidation reactions with peroxides over MOF catalysts [52]. Recently, we demonstrated participation of dioxygen as an oxidant together with *tert*-butylhydroperoxide in the PG oxidation over Cr-MIL-100 and Cr-MIL-101 [37]. Therefore, an experiment under inert atmosphere was carried out to clarify the effect of O_2 on PG oxidation with hydrogen peroxide over UiO-66. The replacement of air for Ar produced no changes in the rates of PG consumption and product accumulation (Fig. S9 in SI) indicating that hydrogen peroxide was the sole oxidant in the system.

Additives of conventional radical chain scavengers (2,6-di-*tert*butyl-4-methylphenol (BHT), hydroquinone and chloroform) led to different rate-limiting effects, depending on the scavenger nature (Fig. 6). The smallest effect was observed in the case of bulky BHT. It is not surprising if we take into account that the kinetic diameter of the BHT molecule exceeds the pore entrance of UiO-66 (0.6 nm) [38]. Nevertheless, based on the shape of the kinetic curves in the presence of three different inhibitors, we can conclude that PG oxidation with H_2O_2 over UiO-66 proceeds through radical chain mechanism. The absence of



Fig. 6. PG oxidation over UiO-66 with addition of BHT (\bigcirc), chloroform (\bigtriangleup), hydroquinone (\blacksquare), and without addition of any inhibitor (\blacktriangledown). Filled symbols – PG, open symbols – HA. Reaction conditions as in Fig. 4, inhibitor 0.03 mmol.

PG adsorption on UiO-66 from mixtures of MeCN/H₂O (Fig. 3) coupled with zero reaction order in substrate (Fig. S8 in SI), we may suggest that the first step of the catalytic reaction is homolytic decomposition of H₂O₂ on the active zirconium sites. The hydroxyl radicals formed during H₂O₂ degradation abstract H atom bound to C₂ atom of the substrate molecule, resulting in the formation of PG secondary radicals, followed by their further transformations (Scheme 2). Given that mesoporous ZrO₂ is more active in H₂O₂ decomposition than UiO-66 (see Fig. 2) but, in contrast to the Zr-MOF, it is not able to perform selective conversion of PG to HA, we may assume that UiO-66 ensures an optimal rate of H₂O₂ decomposition and concentration of PG within the micropores.

3.4. Comparison of UiO-66 with other catalysts

Comparison of the catalytic performance of UiO-66 with other catalytic systems reported in the literature for liquid-phase PG oxidation to HA with H_2O_2 is presented in Table 3. The attainable level of PG conversion was lower for UiO-66, but selectivity to HA was higher than in case of PG oxidation over Pd nanoparticles [12] or Ti-containing polyoxometalate (Ti-POM) [11]. TS-1 enabled higher HA selectivity at higher PG conversion, but reusability of this catalyst and its stability under the reaction conditions was not reported [10]. Moreover, milder reaction conditions (50 °C) and shorter reaction times could be used for oxidation of PG over UiO-66 (Table 3).

3.5. Catalyst stability and reusability

High thermal and hydrothermal stability of UiO-66 was documented [39], but its stability under turnover conditions of a catalytic reaction in the presence of high amounts of polar organic substances and hydrogen peroxide has not yet been addressed. To verify the nature of the catalysis in PG oxidation over UiO-66, we performed a hot filtration test [53] during the reaction course. After catalyst separation, the reaction in the filtrate stopped, which confirmed the truly heterogeneous nature of the catalysis over UiO-66 (Fig. 7). The amount of zirconium in the filtrate did not exceed 2 ppm. The retention of MOF structure was confirmed by the FT-IR and XRD techniques (Figs. S10 and S11 in SI). An increase in the relative intensity of the IR absorption band in the range of 3000–3600 cm⁻¹ can be due to an increased amount of guest water molecules after catalysis in the water-containing medium. The surface area of UiO-66 after the catalytic experiment slightly decreased from 1260 to 1101 m^2/g . The reason for that could be small amounts of unwashed adsorbed components of the reaction mixture. The corresponding pore size distribution plots (Fig. S12 in SI) confirm

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Scheme 2. Tentative mechanism of PG oxidation with H₂O₂ over UiO-66.

preservation of the specific porosity of UiO-66 after the catalysis.

Given that the structure of UiO-66 is stable under the turnover conditions, we may suppose that a possible reason for incomplete conversions of substrate and H_2O_2 could be adsorption of the reaction products of the active Zr(IV) sites and/or blocking of the micropores. Adsorption experiments revealed no adsorption of the main oxidation product (HA) from the mixed solvent MeCN/H₂O (Fig. S13 in SI). On the other hand, additives of acetic acid produced a strong rate-inhibiting effect on the PG oxidation over UiO-66 (Fig. 8). In turn, adsorption measurements confirmed the ability of UiO-66 to adsorb acetic acid (Fig. S13 in SI). Therefore, we may conclude that adsorption of AcA on the MOF surface is, most likely, responsible for the incomplete conversion of the reactants observed during one catalytic run.

The recycling performance of UiO-66 strongly depends on the activation method used between operation cycles (Table 4). While catalyst washing with water led to progressive decrease in PG conversion and HA yield, catalytic activity and selectivity of UiO-66 remained at the same level during, at least, 5 reuses if the catalyst was washed with acetone. Overall, after five operation cycles, ca. 50% of the starting PG could be converted to HA with ca. 85% selectivity.

4. Conclusions

In this work, we first demonstrated that the metal-organic framework UiO-66 can be successfully synthesized using zirconyl nitrate as the Zr source with the addition of an appropriate amount of HCl and the resulting material can be employed as a heterogeneous catalyst in liquid-phase selective oxidation using H₂O₂ as oxidant. In particular, we found that this MOF catalyzes selectively oxidation of the challenging substrate, propylene glycol. The reaction proceeds with high regioselectivity, leading to the formation of hydroxyacetone as the main product. After optimization of the reaction conditions, we managed to obtain HA with 85% selectivity at 10% PG conversion. Under these conditions, zirconia is highly active in H₂O₂ decomposition but it gives PG conversion below 1%. The optimal solvent for PG oxidation over UiO-66 is a mixture of MeCN and H₂O with 30% vol. water content. PG oxidation with hydrogen peroxide over UiO-66 proceeds via radical chain mechanism, but molecular oxygen does not participate in the oxidation process. The nature of the catalysis over UiO-66 is truly heterogeneous, and no metal leaching into solution occurs. The progressive formation of the by-product acetic acid leads to deactivation of UiO-66 caused by strong adsorption of the acid on the catalyst. Importantly, UiO-66 can be recycled with the

Table 3

PG oxidation with H ₂ O	2 over various catalysts.
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Fig. 7. Hot catalyst filtration test at 50 °C. \blacksquare and \blacksquare symbols correspond to kinetic curves acquired without and with catalyst separation, respectively. Filled symbols – PG, open symbols – HA.



Fig. 8. PG oxidation over UiO-66 with (\blacksquare) and without (\blacktriangledown) addition of 0.2 mmol AcA. Filled symbols – PG, open symbols – HA. Reaction conditions as in Fig. 4.

maintenance of the catalytic performance and MOF structure during, at least, five operation cycles, provided the catalyst is washed with acetone prior to reuse. The excellent recycling performance of UiO-66 partially compensates the relatively low PG conversion acquired during one operation cycle.

	5 5	5						
Catalyst	Solvent	Molar ratio		T, °C	time, h	PG conversion, %	HA selectivity, %	Refs.
		PG/Metal	PG/H_2O_2					
TS-1 Ti-POM Pd-black	H ₂ O MeCN H ₂ O	150 12.5 7	2.5 0.25 0.025	90 70 95	8 5 10	32 35 35	94 77 60	[10] [11] [12]
UiO-66	H ₂ O/MeCN	75	1	50	2.5	10	85	This work

 Table 4

 Recvcling of UiO-66 in PG oxidation.

Washing solvent	Cycle	PG conversion %	HA vield %
Washing sorrein	eyele	i e conversion, vo	ini jiciu, /o
water	I	10	8.5
	II	6	5.0
	III	4	3.2
acetone	I	10	8.5
	II	10	8.7
	III	10	8.7
	IV	10	8.5
	v	10	8.6

Reaction conditions: 1 mmol PG, 1 mmol H_2O_2 (slow addition during 1.5 h), 3.7 mg UiO-66, 1 ml $3/7(v/v)H_2O$ /MeCN, 50 °C, 2.5 h.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2018.11.063.

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