

# Synthesis of acrylic acid and acrylic esters via oxidation and oxidative alkoxylation of acrolein under mild conditions with selenium-modified microgel catalysts

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## Synthesis of acrylic acid and acrylic esters *via* oxidation and oxidative alkoxylation of acrolein under mild conditions with selenium-modified microgel catalysts†

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Systematic studies of acrolein oxidation and oxidative alkoxylation catalyzed by Se-modified microgel catalysts under mild reaction conditions were conducted. Se-modified microgels proved to be highly active colloidal catalysts and exhibited high performance for the oxidation of acrolein to acrylic acid and oxidative alkoxylation to the corresponding methyl/ethyl/butyl acrylates using hydrogen peroxide as a green oxidant. Methyl acrylate or acrylic acid can be synthesized in high yield (89–91%) and with high selectivity (97–99%) simply by regulating the solvent type and the concentration of selenium moieties in the microgel structure. Se-microgels exhibit exceptional catalytic activity compared with other Se-containing molecules of organic and inorganic nature. Due to the unique properties of the microgels that combine advantages from homogeneous and heterogeneous catalytic systems in terms of activity and selectivity as well as re-use possibilities, Se-microgel catalysts can be easily separated and reused in several catalytic cycles and remain highly active.

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## 1. Introduction

Acrylic acid is a precursor for numerous chemicals that are used for textiles, paper treatment, surface coating, plastic additives, and superabsorbent polymer production. Acrylic esters are widely used for producing high quality water-based paints, synthetic rubbers, adhesives, and synthetic resins.<sup>1,2</sup> Annually more than six million tons of acrylic acid is produced by two-step gas-phase oxidation of propene.<sup>3</sup> It was expected that the acrylic acid annual production would increase to 8 million tons by 2020.<sup>2</sup>

Most of the acrylic acid is produced by a two-step gas-phase process that consumes a large amount of energy.<sup>4,5</sup>

According to this method, propylene is first oxidized to acrolein on metal oxide catalyst at a high reaction temperature, for example, the Bi/Mo–O catalyst at 320 °C. Then, the reaction mixture is directly converted into acrylic acid in a second reactor, using another type of catalyst, such as the Bi/V–O catalyst at 280 °C.<sup>1</sup> Production of acrylic acid largely depends on fossil fuel resources; therefore, since the price of propylene and the demand for polypropylene are constantly increasing,<sup>5</sup> manufacturers are now focusing on developing and commercializing alternative methods of acrylic acid synthesis,<sup>2</sup> such as synthesis based on renewable resources like glycerol and biomass. In particular, glycerol, the utilization of which still remains a major problem in biodiesel production, belongs to renewable resources and can be used as a resource for acrylic acid synthesis through the formation of acrolein.<sup>6</sup>

New green methods of aldehyde oxidation were established when hydrogen peroxide was used as an oxidant.<sup>7–10</sup> Certain aldehydes can be oxidized to carboxylic acids with 30–60% aqueous H<sub>2</sub>O<sub>2</sub> without organic solvents at moderate reaction temperatures (60–90 °C) in high yields (up to 95–100% (ref. 7, 8 and 10)). Largely stimulated by propene epoxide industrial synthesis, the boom in hydrogen peroxide production in the last three decades turned it into a large-scale affordable product, significantly lowering its cost.<sup>11</sup>

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Nowadays aqueous  $\text{H}_2\text{O}_2$  is a cheap and safe oxidant, which produces only water as a by-product,<sup>7</sup> but it requires the use of a suitable catalyst for the activation and promotion of the desired transformations with favorable reaction rates.<sup>8–10,12</sup>

In the fifties, selenium dioxide was reported to be a promising catalyst for acrolein oxidation with hydrogen peroxide, though it was typically used in a non-water medium.<sup>13</sup> In 1970s, organoselenium compounds started to be used for catalytic activation of peroxides in oxidation reactions as an alternative to metals.<sup>10</sup> Organoselenium catalysts are well known to react with hydrogen peroxide to form the corresponding peracids that can be used as active oxygen transfer compounds<sup>12,14–16</sup> and can be utilized by green procedures under benign and neutral conditions.<sup>12</sup> Many recent studies have used diphenyl diselenide<sup>17–20</sup> and  $\text{SeO}_2$  for the oxidation of benzaldehyde as a test reaction.<sup>17–23</sup> High yields of benzoic acid were achieved (up to 99%).<sup>17–22</sup> In most cases though the catalyst couldn't be separated from the reaction mixture. In a previous work,<sup>19</sup> a reaction was performed under heterogeneous conditions (water was used as solvent), followed by precipitation and separation of benzoic acid and further reuse of the catalyst/water suspension. This approach allows performing the reaction under mild conditions and with a high yield of reaction products, but it cannot be applied for water-soluble substrates.

Therefore, research on organoselenium catalysis in oxidation reactions with  $\text{H}_2\text{O}_2$  should allow for the development of novel green, synthetic methods of acrylic acid production from propylene and glycerol by acrolein oxidation.

Even though organoselenium catalysts are highly effective for unsaturated aldehyde oxidation under mild reaction conditions in the liquid phase, by nature they are homogeneous. A significant disadvantage of homogeneous catalysts is the difficulty of their separation from the reaction mixture, which requires high energy consumption and a more complicated separation stage, and results in loss of catalyst.<sup>24</sup> One of the methods to solve this problem is to modify the catalyst structure in a way that will enable easy separation, for example, by incorporating catalytically active groups into the microgel. Microgels have the ability to swell or collapse under certain conditions that allow their easy separation from the reaction mixture.

Microgels have been proven excellent colloidal catalyst supports. Because of the availability of free spaces in the swollen gel networks, a good swelling degree of microgels in organic solvents,<sup>16</sup> and the possibility of post-modification of microgels with specific functional groups, they can provide excellent characteristics for the application of microgels as supports in catalysis.<sup>25–28</sup>

The high energy consumption of acrolein oxidation to acrylic acid in the gas phase prompted the research on acrolein oxidation with hydrogen peroxide in the liquid phase under mild reaction conditions. Microgels, consisting of diselenide crosslinkers and poly(*N*-vinylcaprolactam) (PVCL)

building blocks, are multifunctional crosslinked polymer colloids with an open porous structure and chemical functionality, and they are supposed to have unique properties like surface activity,<sup>29</sup> solvent resistance,<sup>30</sup> and adaptability. These characteristics should insure their high effectiveness in the oxidation reaction of acrylic acid production from acrolein due to their high selectivity and activity in organic solvents under mild reaction conditions. In previous works,<sup>31,32</sup> we described the synthesis and characterization of Se-modified microgels and confirmed that Se-microgels exhibit catalytic activity in the acrolein oxidation reaction.

Herein, to expand on previous results, we report the systematic study of the technological aspects of unsaturated aldehyde oxidation catalyzed by Se-microgels, such as the effect of catalyst concentration, reaction temperature, Se-unit concentration, Se-microgel composition, catalyst separation and reusability, and type of solvent on the reaction performance, namely, the yields of reaction products and their ratio.

## 2. Experimental section

### 2.1. Materials

Acrolein (purity >90%), dimethyl carbonate (purity >99%), acrylic acid (purity >99%), methyl acrylate (purity >99%), methylacrolein (purity >99%), 2-ethylacrolein (purity >99%), propionaldehyde (purity >99%), butyraldehyde (purity >99%), hexanaldehyde (purity >99%), nonanaldehyde (purity >99%), dioxane (purity >99%), isobutanol (purity >99%), hydrogen peroxide (60% wt), and methanol (purity >99%) were purchased from Merck. All chemicals were used as received.

### 2.2. Synthesis of the microgel catalyst

Poly(*N*-vinylcaprolactam) (PVCL) microgels modified with diselenide functional groups (diselenide crosslinker, Fig. 1a) were synthesized by precipitation polymerization in aqueous/DMSO media at 70 °C along with a conventional crosslinker, *N,N'*-methylenebis(acrylamide) (BIS), according to a reported procedure.<sup>31,32</sup> Diselenide bonds inside the microgels were cleaved through oxidation by  $\text{H}_2\text{O}_2$  and converted into seleninic peracid whilst maintaining the microgel microstructure intact (Fig. 1). A series of selenium-containing PVCL microgels (Table S1†) with various diselenide concentrations were previously synthesized and characterized by Raman spectroscopy.<sup>32</sup> Also, new PVCL microgels with various diselenide and BIS concentrations were additionally synthesized (Table S1†).

### 2.3. Catalyst characterization

<sup>77</sup>Se high-power proton decoupled NMR spectra were measured by direct polarization under static conditions and magic angle sample spinning (MAS) using a solid-state Bruker AVIII 700 NMR spectrometer operating at a <sup>77</sup>Se

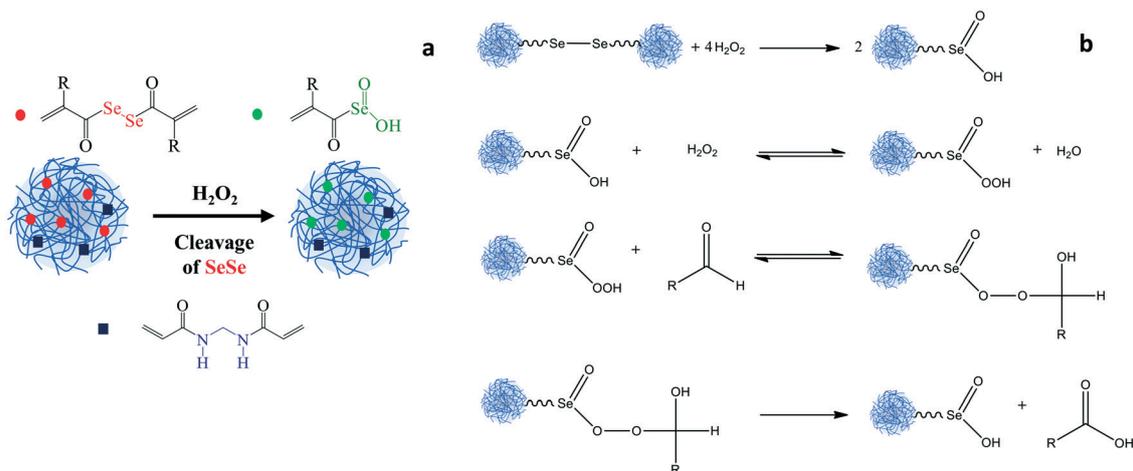


Fig. 1 a) Structure of selenium modified microgel catalysts. b) Possible mechanism for the oxidation of aldehyde with the selenium catalyst.

frequency of 133.651 MHz. <sup>77</sup>Se spectra high-power <sup>1</sup>H decoupling was applied during the free induction decay of <sup>77</sup>Se, using the SPINAL64 pulse sequence. This phase shifted train of pulses was applied at a proton frequency of 700.282 MHz with a pulse length of 20 μs (120 W). The chemical shift reference of the <sup>77</sup>Se spectra was (CH<sub>3</sub>)<sub>2</sub>Se. All the measurements were made at 23 °C with 16, 1024, and 4096 scans. The spectra were recorded using a <sup>77</sup>Se pulse length of 3 μs, a dwell time of 2 μs, and a recycle delay of 10 s. The dead time was set to 6.5 μs, the receiver gain was 181, the line-broadening was 5 Hz, the time domain was 32k, and the acquisition time was 65.5 ms. The spectral width was 1870 ppm. Selenium-77 spectra were processed using the Bruker TopSpin 3.2 and MestReNova® (Mestrelab Research UK) NMR programs.

Fourier transform infrared spectroscopy (FTIR) spectra (resolution 4 cm<sup>-1</sup>) were recorded using a Nicolet NEXUS 670 Fourier transform IR spectrometer. Samples were mixed with KBr powder and then pressed to form a transparent KBr pellet before measurement.<sup>31,32</sup>

Raman spectra were recorded on a Bruker RFS 100/S spectrometer. The laser used was Nd:YAG at 1064 nm wavelength at a power of 250 mW. On average, 1000 scans were taken at a resolution of 4 cm<sup>-1</sup>. For sample holding, aluminum pans of 2 mm thickness were used. The software used for data processing was OPUS 4.0.

Transmission electron microscopy (TEM) was performed with a Zeiss LibraTM 120 (Carl Zeiss, Oberkochen, Germany). One drop of sample (approximately 10 μL) was deposited onto a carbon-coated copper grid and then air-dried. The

electron beam accelerating voltage was set to 120 kV and images were recorded using a CCD camera system (UltraScan 1000, Gatan, Germany).<sup>31,32</sup>

Dynamic light scattering (DLS) data (hydrodynamic radii) were obtained with a laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and an ALV/CGS-8F S/N 025 laser goniometry system with a helium–neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as a light source.<sup>31,32</sup>

The hydrodynamic radii of all the microgels are shown in Table 1. Methanol and dioxane are good solvents for PVCL microgels, but they eliminate their thermal-responsive properties. The experimental data presented in Table 2 indicate that upon heating to 50 °C the hydrodynamic radii of the microgels increase due to swelling. This effect might contribute to better diffusion of the reagents and improved accessibility of the Se-groups in the microgel structure.

The viscosities of the microgel solutions in dioxane and methanol were investigated with a Discovery HR-3 hybrid rheometer with a temperature control system from TA Instruments. The measurements were performed at 25 °C with a 20 mm cone-plate geometry with a cone angle of 2° and a shear rate ramp procedure. The shear rate was increasing from 0.1 to 1000 1/s.

#### 2.4. Oxidation and oxidative alkoxylation of acrolein

Oxidation and oxidative alkoxylation reactions were carried out in a 25 ml two-necked glass flask with a reflux condenser

Table 1 Hydrodynamic radii (Rh) of selenium containing PVCL microgels in methanol–water and dioxane–water mixtures

Sample	Rh, nm									
	PVCL		Se1.0		Se2.0		Se3.0		Se5.0	
Temperature	20 °C	50 °C	20 °C	50 °C	20 °C	50 °C	20 °C	50 °C	20 °C	50 °C
Dioxane/H <sub>2</sub> O	502	534	194	208	173	189	196	218	140	158
Methanol/H <sub>2</sub> O	588	676	224	264	210	240	298	356	205	242

**Table 2** Effect of the microgel hydrodynamic radius (measured after oxidation) on the yield of acrylic acid

Sample	$R_h$ , nm	Acrylic acid yield, %			
		0.5 h	1.0 h	3.0 h	8.0 h
B1.5Se2.0	235	12.5	23.6	58.6	79.1
B1.5Se2.0	65	4.8	15.1	50.7	89.6
B0.5Se5.0	54	6.9	11.3	30.0	61.8
B0.5Se5.0	3.5	10.3	22.9	51.3	94.7

and a magnetic stirrer (400 rpm). Initial concentrations of reagents ( $\text{mmol ml}^{-1}$ ): hydrogen peroxide (in the form of 60% wt aqueous solution) – 2.6; acrolein – 2;  $\text{H}_2\text{O}$  – 3.3. Hydrogen peroxide: acrolein ratio – 1.3:1. The volume of the reaction mixture was 7.5 ml. First, the catalyst (diselenide crosslinker, Se-microgels (Se 1.0, Se 2.0, Se 3.0, Se 5.0)) or pure PVCL was added to the flask; the catalyst concentration was  $0.0044 \text{ mmol ml}^{-1}$ . Then the solvent (methanol or dioxane) was added. After that, the flask with the catalyst and solvent was heated to the reaction temperature ( $50^\circ\text{C}$  if not specified otherwise) and left to stir until the catalyst was dissolved. Then, acrolein and hydrogen peroxide (in the form of 60% water solution) were added, and the resulting mixture was stirred under reflux for 8 h. The moment of hydrogen peroxide addition was considered as the beginning of reaction. Periodic probes after the sample preparation procedure were analysed using a gas chromatograph with a SUPELCOWAX 10 capillary column ( $30 \text{ m} \times 0.53 \text{ mm}$ ) and an FID detector using isobutanol as solvent and dimethyl carbonate as internal standard.

### 3. Results and discussion

#### 3.1. Study of the reaction mechanism of acrolein oxidation with the Se-modified microgel

According to the literature review<sup>10,12,15,20,33,34</sup> and our preliminary results,<sup>32,33</sup> the obligatory condition for the reaction to occur is the presence of a seleninic group, which, when interacting with hydrogen peroxide, gives a perseleninic group that acts as a catalyst<sup>20</sup> (Fig. 1b).

In order to confirm the proposed scheme of diselenide bond transformation, Raman and FT-IR spectroscopy methods were employed to analyze the chemical structure of the microgel before and after the oxidation reaction (Fig. S1 and S2†). The Raman spectra confirm the efficient reaction of hydrogen peroxide with the Se–Se group, so that at the 5th minute of reaction, the absorbance band that corresponds to the Se–Se group ( $290 \text{ cm}^{-1}$ )<sup>35</sup> is not observed (Fig. S1†). Preliminary treatment of the catalyst with hydrogen peroxide does not contribute to increasing the yield of the product (acrylic acid).

The FT-IR spectra of the microgels analyzed during reaction (Fig. S2†) show an absorbance band at around  $890 \text{ cm}^{-1}$ , which corresponds to the Se=O bond,<sup>36</sup> and a band at around  $715 \text{ cm}^{-1}$ , which corresponds to the Se–OH bond.<sup>36</sup> However, the microgel before oxidation (MG\_0) also has a

band at  $894 \text{ cm}^{-1}$ , since PVCL itself has a band in that area. If we compare the peak intensity at  $890 \text{ cm}^{-1}$  for the microgels before and after oxidation and for PVCL (Table S2†), we can see the increase of the ratio that proves the formation of the Se=O bond. The  $^{77}\text{Se}$  NMR spectra (Fig. S1 of the ESI†) show a peak at 1043 ppm which corresponds to seleninic acid. These altogether prove the diselenide bond transformation by hydrogen peroxide into seleninic acid (Fig. 1b) which is then transformed into a catalytically active peracid.

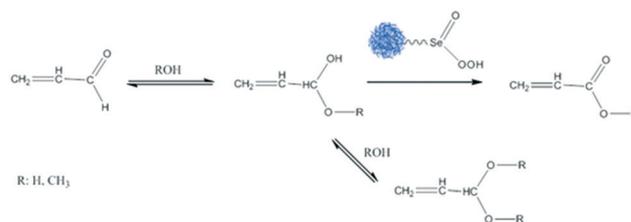
#### 3.2. Se-MG oxidation and oxidative alkoxylation

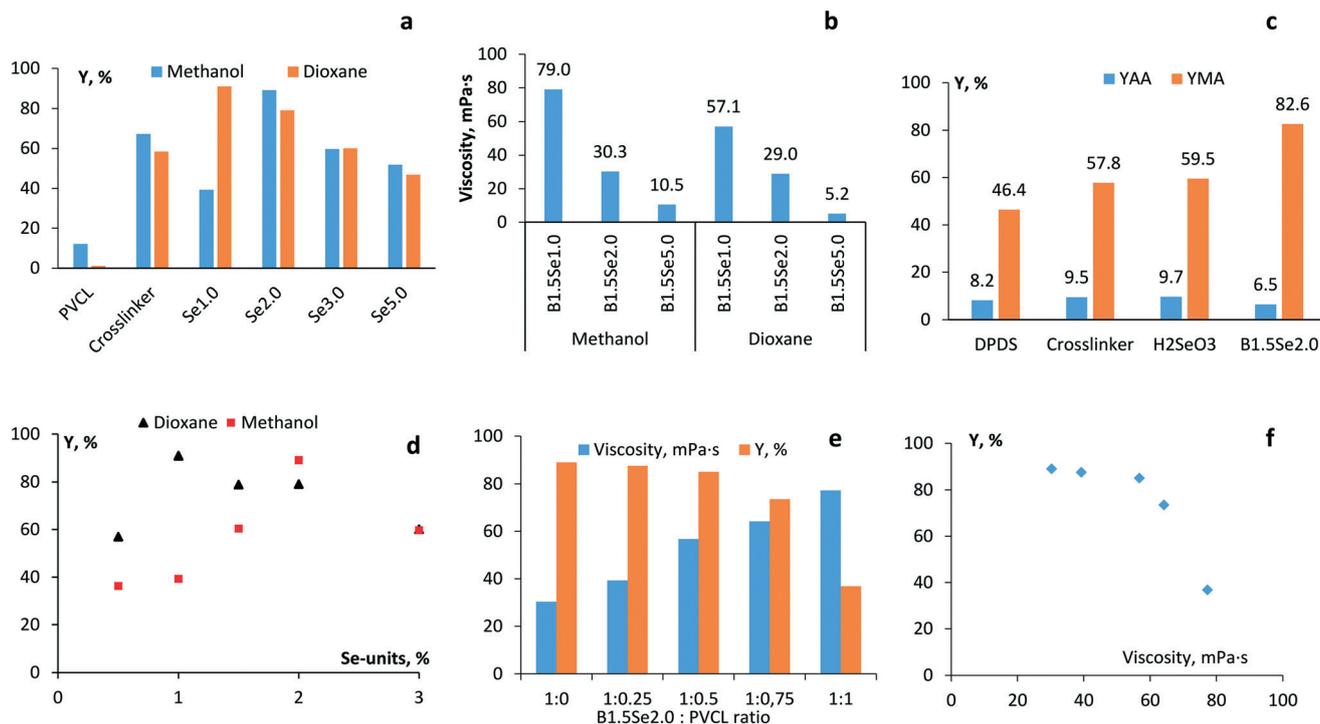
The amount of Se-units in the microgels is the key performance parameter for acrolein oxidation and oxidative alkoxylation in the presence of  $\text{H}_2\text{O}_2$  in methanol and dioxane. To prove this hypothesis experimentally, we performed catalytic runs at a constant overall Se-unit concentration in the reaction mixture and compared the results with those of the diselenide crosslinker and pure PVCL microgel.

The PVCL microgel itself had no effect on reaction performance: acrolein conversion, methyl acrylate, and acrylic acid yields were close to those of a non-catalytic reaction (Table S3†) regardless of the solvent. This confirms that PVCL has no catalytic activity.

Nevertheless, even in the absence of the catalyst, there was some conversion of acrolein (Table S3†) but the formation of the final product (acrylic acid) was not observed. The mass spectroscopic analysis of the reaction mixture with methanol as solvent shows the presence of acrolein methyl acetal and acrolein dimethyl acetal. Based on these data, we can suggest the following reaction scheme of acrolein oxidative alkoxylation:

This mechanism of oxidative alkoxylation differs from the oxidation mechanism described in Fig. 1b due to intermediate stages of acetal formation in the presence of alcohol. The formation reactions of acrolein methyl acetal and acrolein dimethyl acetal are equilibrium reactions (Scheme 1) and, as was found, they can proceed without catalysts. So, acrolein methyl acetal is formed first and then it is catalytically oxidized to form acrylic acid. Acrolein dimethyl acetal can be considered as a “buffer” compound. In the case of the dioxane solvent, instead of acetals, their respective hydrates are formed due to the presence of water

**Scheme 1** Reaction sequence for oxidative alkoxylation of acrolein in methanol and oxidation in the presence of water.



**Fig. 2** a) Dependence of the total acrylate yield (Y) on Se-containing catalysts (compared to the PVCL microgel and reaction solvent (methanol, dioxane)). b) Viscosity of microgel solutions in methanol and dioxane (the microgel concentrations are equal to the values used in the reaction tests). c) Effect of the catalyst nature on acrylic acid (YAA) and methyl acrylate (YMA) yields. Solvent – methanol. d) Effect of the Se-unit quantity in the microgel on the acrylate yield (Y). Solvents – dioxane, methanol. Reaction time – 8 h; the Se-unit concentration in the reaction volume is constant – 0.0044 mmol ml<sup>-1</sup>. e) Effect of addition of PVCL to the Se2.0B1.5 microgel on the viscosity of the reaction mixture and the total acrylate yield (Y). Microgel concentration – 0.0044 mmol ml<sup>-1</sup>. Solvent – methanol. Reaction time – 8 h. f) Correlation between the viscosity of the reaction mixture and the total acrylate yield (Y). Microgel concentration – 0.0044 mmol ml<sup>-1</sup>. Solvent – methanol. Reaction time – 8 h.

from the hydrogen peroxide solution. Non-catalytic transformation of aldehydes into hydrates or acetals has been previously reported by several researchers.<sup>37–39</sup> A similar mechanism of reactions of oxidation and oxidative alkoxylation was proposed in ref. 22 and 24.

The diselenide crosslinker proved to be catalytically active in acrolein oxidation and oxidative alkoxylation in dioxane and methanol solutions, respectively (Fig. 2a). As a result, in dioxane, a 58.4% yield of acrylic acid was obtained; when in methanol – the yields were 9.5% acrylic acid and 57.8% methyl acrylate (Table S3<sup>†</sup>). The yield of methyl acrylate in methanol largely prevails over acrylic acid. This can be explained by the easier formation of intermediate compounds of acrolein and methanol (acetals) rather than acrolein and water (hydrates).

To ascertain the catalytic properties of Se-containing microgels with different Se contents, experiments were conducted using adjusted microgel amounts to keep the overall Se-unit concentration in the reaction mixture constant and equal to the concentration of the Se-crosslinker. All the synthesized microgels were catalytically active in the acrolein oxidation reaction both in methanol and in dioxane (Fig. 2a). The concentration of Se-units in the microgel affects its catalytic activity, and depending on the amount of Se-units, the yield of reaction products ranges from 39.3 to 91.0%. The

optimal Se-concentration is different for different solvents: in methanol solution – 2.0% (the yield of reaction products is 89.1%) while in dioxane solution – 1.0% (the acrylic acid yield is 91.0%). These results correlate well with the results of viscosity measurements of the reaction mixtures (Fig. 2b). The highest value observed for Se1.0 in methanol was 79 mPa s, while when in dioxane it was 57.1 mPa s. We can assume that the lower catalytic activity of Se1.0 in methanol was caused by diffusion limitations due to the high viscosity of the reaction mixture. As for Se2.0, the viscosities were similar in both solvents (around 30 mPa s) and judging by the high yields of reactions, there were no diffusion limitations in this case. To discern the presence of the diffusion limitations, additional reaction tests were conducted using a constant concentration of the Se2.0 microgel and by adding different amounts of non-catalytic PVCL to increase the viscosity of the reaction mixture (Fig. 2e and 3f). The results show a significant decrease in the acrylate yield when the viscosity was over ~60 mPa s, which confirms possible diffusion limitations at high microgel concentrations.

For the reactions in methanol, Se2.0 shows the best results in terms of the total yield of reaction (89.1%) and exceptional selectivity (99.1%), which is much higher than for other Se-microgels and crosslinkers, which might indicate a

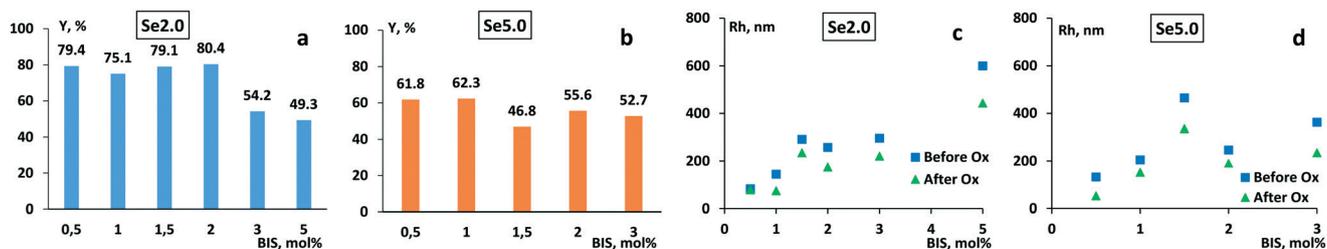


Fig. 3 Effect of BIS concentration in Se2.0 and Se5.0 microgels on: a) and b) – the acrylic acid yield ( $Y$ ), solvent – dioxane, reaction time – 8 h; (c) and d) – hydrodynamic radius of microgels in dioxane.

good proportion of diselenide crosslinking units and PVCL building blocks. Moreover, not only is the Se2.0 microgel more active than the crosslinker, it also shows a higher yield of the reaction product than organic and inorganic selenium catalysts (Fig. 2c). In the majority of previously published results of research on different Se-containing catalysts,<sup>18–23</sup> oxidation of benzaldehyde and its derivatives was chosen as the model reaction. Thus, it makes it difficult to compare the catalytic performance of our microgel catalyst to those of already existing ones due to the different reactivities of acrolein and benzaldehyde. Nonetheless, the amount of the catalyst used was 5 (ref. 17) to 36 (ref. 21) times higher than in our work, and in the majority of cases, the catalysts were not recyclable (except ref. 18 and 19). In addition, in most of the cases, a big excess of the oxidant ( $H_2O_2$ ), up to 5–6 times more,<sup>20,21</sup> was used, which accelerated the reaction but was not desirable from an economic point of view.

When the reactions were performed in dioxane solution, the best results were achieved with the Se1.0 microgel: acrolein conversion 94% (Table S3†) and acrylic acid yield – 91% (Fig. 2a).

The increase in the amount of Se-units in the microgel structure to over 2 mol% resulted in the decrease of the acrylic acid yield in dioxane (down to 46.8%) and methyl acrylate in methanol (down to 48.9%) when the Se-concentration was increased to 5 mol% (Fig. 2a). The decrease of the Se-unit quantity to 0.5 mol% (Fig. 2d) resulted in much lower acrylic acid and methyl acrylate yields that might be caused by lower diffusion rates of the reagents due to the high viscosity of the reaction mixture. Therefore, the optimal content of Se-units in the microgel for the reaction in dioxane is 1 mol% and in methanol – 2 mol%.

Despite the constant concentration of Se groups in the reaction volume, the yield of acrylates significantly depends on the concentration of Se groups in the microgel (Fig. 2a). Thus, the structure of the microgel has a significant effect on the course of the investigated process.

As was noted above, for the synthesis of the microgel catalysts, two types of crosslinkers – BIS (permanent) and Se-based (cleavable) – were used. As was shown in ref. 32, the internal structure and the size of the microgels are controlled during the synthesis by the total amount of both crosslinkers, and the size (swelling degree) does not significantly change after cleaving the Se-crosslinker with hydrogen peroxide. On

the one hand, the cleavage leads to the decrease of the total number of cross-links in the microgel and should result in its swelling. On the other hand, the alkyl spacers of the diselenide crosslinker are hydrophobic and get additional degrees of freedom after cleavage. They can aggregate with each other and with the hydrophobic groups of PVCL, which leads to the partial compaction of the microgel. Thus, these two effects nearly compensate each other and the microgels even weakly shrink after the cleavage (Fig. 3c and d). More detailed information on the microgel behavior including atomistic computer simulations can be found in ref. 31 and 40. The polymer volume fraction of the microgel therefore increases with a higher Se-crosslinker content, which hampers diffusion of reagents and products within the microgel. This may be the reason why an increase of the Se-crosslinker concentration in the microgel is accompanied by a decrease in the yield of acrylates (Fig. 2a and d) despite the total concentration of Se groups in the reaction volume remaining constant. Additional studies with lower and higher amounts of the permanent crosslinker (BIS) confirm the validity of such reasoning (Fig. 3a and b). In the case of Se2.0, when the BIS content was increased to 3% or higher (the total crosslinker content was 5–7%), the acrylic acid yield decreased by 30%. As for Se5.0, the acrylic acid yields were similar regardless of the value of the BIS content (total crosslinker content: 5.5–8%) and similar to the results for Se2.0 with a total crosslinker content of the same value.

On the other hand, reducing the content of Se-crosslinkers in the catalyst while keeping the concentration of Se groups in the reaction volume constant requires a larger amount of microgel leading to an increase in the viscosity of the reaction medium, which, in turn, also affects the yield of products. Thus, we have the maximum acrylate yield at some Se-crosslinker content because of these two opposing factors.

The matching values of the acrylic acid yields for BIS0.5Se2.0 and BIS1.5Se2.0 (Fig. 3a) suggests that with a total crosslinker content of at least up to 3.5% there are no diffusion limitations. To confirm this assumption, an additional study on the effect of the size of the colloidal particles of the microgel on the acrylic acid yield was performed (Table 2). The results (79.1% acrylic acid yield for the 235 nm B1.5Se2.0 microgel and 89.6% yield for the 65 nm B1.5Se2.0 microgel) match quite well, which suggests that there are no diffusion difficulties when using the catalytic system BIS1.5 Se2.0 for the oxidation of acrolein.

However, in the case of B0.5Se5.0, when the total crosslinker content was 5.5%, a decrease of the microgel size resulted in a 30% higher yield of acrylic acid, which additionally proves our point.

In summary, increasing the Se-crosslinker content in the microgel allows the use of a lower microgel concentration in the reaction medium, but this can lead to microgel compacting due to aggregation of its cleaved chains, thus negatively affecting the accessibility of Se-moieties for reagents and decreasing catalytic activity. This can be partially offset by adjusting the BIS content, thus keeping the overall crosslinker content under 3.5%. The optimum crosslinker ratios are BIS1.5 Se1.0 for the acrolein oxidation and BIS1.5 Se2.0 for the acrolein oxidative alkoxylation, based on the maximum product yield.

### 3.3. Reaction conditions

**Catalyst concentration.** In order to determine the most effective conditions for the acrolein oxidation process, the optimal concentration of the catalyst had to be determined. For that, we performed a set of reactions with variable concentrations of Se-units in the microgel in the range 0.0022–0.0088 mmol ml<sup>-1</sup> (Fig. 4a, Table S3†). Based on the results, an increase of the catalyst concentration leads to an increase of the acrylic acid yield and the initial reaction rate. However, the increase of the catalyst concentration to higher than 0.0044 mmol ml<sup>-1</sup> does not result in a significant increase of the initial reaction rate and acrylic acid yield (the acrylic acid initial formation rate increases by ~8% with doubling of the catalyst concentration to 0.0088 mmol ml<sup>-1</sup>). Therefore, we can consider 0.0044 mmol ml<sup>-1</sup> as the optimal catalyst concentration.

**Reaction temperature.** To study the effect of the reaction temperature on the catalytic performance of the Se-microgel catalyst, oxidation reactions were performed at the temperature range of 20–50 °C (Fig. 4b, Table S4†) with the B1.5Se2.0 microgel, which proved to be the most effective among the Se-microgels tested. The maximum temperature of 50 °C was chosen in consideration of the acrolein boiling point of 53 °C.

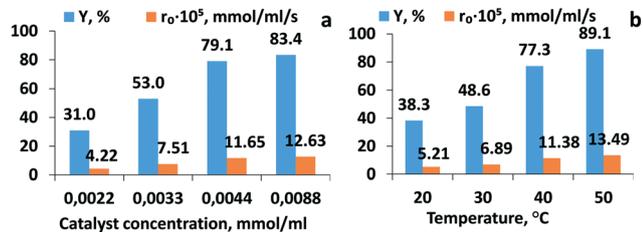


Fig. 4 a) Effect of the B1.5Se2.0 microgel concentration (mmol ml<sup>-1</sup>) on the acrylic acid yield (Y) and acrylic acid initial formation rate (r<sub>0</sub>), solvent – dioxane. b) Effect of the reaction temperature (°C) on the total acrylate yield (Y) and total acrylate initial formation rate (r<sub>0</sub>), solvent – methanol, catalyst – Se 2.0 microgel (C = 0.0044 mmol ml<sup>-1</sup>). Reaction time – 8 h.

As should be expected, with increasing temperature the yield of acrylates increases. This is indicative that the reaction occurs even at room temperature – the yield of methyl acrylate in this case is 38.3%. It is also important that in the temperature range of 20–30 °C the only product of the reaction is methyl acrylate, and acrylic acid is formed at the temperature of 40 °C and above. The apparent activation energy of the global reaction – 26.4 kJ mol<sup>-1</sup> – was calculated from the initial reaction rates.

Considering that the yields of methyl acrylate and acrylic acid increase significantly throughout the temperature range, it is expedient to carry out the process at a temperature of 50 °C, which allows achieving the highest yield of the target products.

**Solvent nature.** The solvent nature affects the formation of the reaction products and their ratio (Table 3). In an inert solvent (like dioxane), the main product is acrylic acid. In alcohol solvents (methanol, ethanol, butanol), ester is also produced *via* oxidative alkoxylation of aldehyde. All the tested alcohol solvents themselves were not oxidized by hydrogen peroxide under reaction conditions, which was confirmed by conducting blank tests without acrolein.

Table 3 Oxidation and oxidative alkoxylation of aldehydes

Substrate	Solvent	Product	Yield, %
<chem>C=CC=O</chem>	Methanol	<chem>C=CC(=O)OC</chem>	82.6
<chem>C=CC=O</chem>		<chem>C=CC(=O)O</chem>	6.5
<chem>C=CC=O</chem>	Ethanol	<chem>C=CC(=O)OCC</chem>	48.4
<chem>C=CC=O</chem>		<chem>C=CC(=O)O</chem>	11.6
<chem>C=CC=O</chem>	<i>n</i> -Butanol	<chem>C=CC(=O)OCCCC</chem>	36.3
<chem>C=CC=O</chem>		<chem>C=CC(=O)O</chem>	13.5
<chem>C=CC=O</chem>	Dioxane	<chem>C=CC(=O)O</chem>	79.1
<chem>C=CC=O</chem>	Dioxane	<chem>C=CC(=O)O</chem>	63.1
<chem>C=CC=O</chem>	Dioxane	<chem>C=CC(=O)O</chem>	44.9
<chem>CC(C)=CC=O</chem>	Dioxane	<chem>CC(C)=CC(=O)O</chem>	29
<chem>CC(C)=CC=O</chem>	Dioxane	<chem>CC(C)=CC(=O)O</chem>	45.8
<chem>CCCC=O</chem>	Dioxane	<chem>CCCC(=O)O</chem>	63.1
<chem>CCCC=O</chem>	Dioxane	<chem>CCCC(=O)O</chem>	80.7
<chem>CCCCC=O</chem>	Dioxane	<chem>CCCCC(=O)O</chem>	58.6

Reaction time 8 h, temperature – 50 °C, catalyst – B1.5Se2.0, 0.0044 mmol ml<sup>-1</sup> (for all substrates).

The developed catalysts proved to be effective for the synthesis of other esters of acrylic acid – ethyl acrylate and butyl acrylate, which are of great industrial importance (Table 3). With the increase of the carbon chain in alcohol, the ester/acid ratio shifts from 0.95 in methanol to 0.81 in ethanol and 0.73 in butanol with a decrease of the total yield from 89.1% in methanol to 60% in ethanol and 49.8% in butanol, respectively. This can be explained by the lower reactivity of alcohols with a longer carbon chain. A similar pattern was observed for the Se-crosslinker: the ester/acid ratio shifts from 0.86 in methanol to 0.49 in ethanol and 0.29 in butanol, but the total yield was much lower – 67.3% in methanol and 29.8% in butanol.

### 3.4. Oxidation of other aldehydes with Se-MG

The developed Se-containing microgel catalysts were tested in the oxidation of a series of aldehydes (acrolein, methacrolein, 2-ethylacrolein, croton-, propion-, butyr-, hexan-, nonan-aldehyde) with C<sub>3</sub>–C<sub>9</sub> length (Table 3). Se-Microgel catalysts proved to be active in oxidation of selected aldehydes. However, the yield of the resulting carboxylic acid varies depending on the structure of the alkyl group of the aldehyde. When we compare C<sub>3</sub> aldehydes (acrolein and propionaldehyde), unsaturated aldehydes have higher reactivity (79.1% yield compared to 45.8%). In the case of C<sub>4</sub> aldehydes, the reactivity is similar for linear aldehydes (croton- and butyraldehyde – 63.1%) but lower for aldehydes with a CH<sub>2</sub>=CH-group in the iso-position (44.9% yield). A further increase of the alkyl chain results in an even more prominent decrease of reactivity (29% yield for 2-ethylacrolein) due to steric hindrance. Thus, for aliphatic aldehydes, other methodologies need to be considered.

Thus, Se-containing microgel catalysts allow the oxidation of a wide range of aldehydes, yielding valuable products – carboxylic acids.

### 3.5. Catalyst reuse

Reusability is one of the key parameters of a catalyst from environmental and economic points of view. Preliminarily, we tested the reusability of the B1.5Se2.0 microgel without separation from the reaction volume and confirmed that it works across multiple catalytic cycles without considerable loss of activity.<sup>32</sup> Here, we studied the possibility of reusing this microgel after its separation from the reaction volume in the reaction of acrolein oxidation in dioxane (Fig. 5a, Table S5†). The catalyst was separated from the reaction mixture by precipitation. Hexane was used as a precipitant. Precipitation was carried out in several cycles in order to completely isolate the reaction products from the microgel. The reaction volume and reagent amounts in each cycle were tuned to the amount of the recovered Se-microgel catalyst, so that the initial concentrations remained the same through all cycles. Each cycle was 24 h long.

The catalytic performance of the B1.5Se2.0 microgel didn't significantly change – the catalyst remained active and

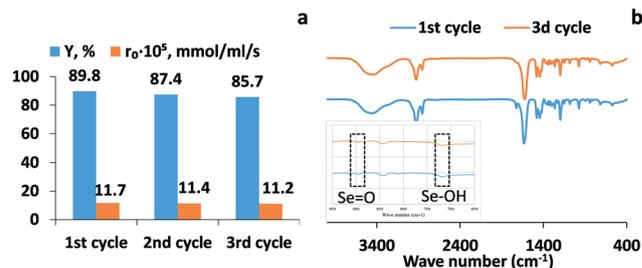


Fig. 5 a) Dependence of the acrylic acid yield (Y) and acrylic acid initial formation rate ( $r_0$ ) on the reusability of the catalyst, solvent – dioxane, catalyst – Se 2.0 microgel, reaction time – 24 h. b) FT-IR spectra of the Se 2.0 microgel after first and third use of the catalyst in the oxidation reaction.

showed a high acrylic acid yield, with less than 5% decrease even after the 3rd cycle in the oxidation reaction. The initial reaction rates also remained pretty stable over 3 cycles. The FT-IR spectra (Fig. 5b) of the used microgel show that the microgel structure didn't change after using the catalyst three times, and Se=O, Se-OH bonds are still present in the microgel, which confirms the chemical stability of the microgel over 72 h use.

## Conclusions

Highly active colloidal Se-containing microgel catalysts have been developed for the oxidation and oxidative alkoxylation of acrolein to acrylic acid and its esters by precipitation polymerization of PVCL using cleavable (diselenide) and permanent (BIS) crosslinkers. It has been shown that the Se-unit content and cleavable/permanent crosslinker ratio have significant effects on the hydrodynamic radius and polymer density of the microgel's particles and subsequently on its catalytic efficiency.

Microgel catalysts containing 1–2 mol% Se and 1.5 mol% BIS exhibit excellent catalytic activity and selectivity under mild reaction conditions at 20–50 °C and atmospheric pressure using hydrogen peroxide as “green” oxidant. Using dioxane as solvent, acrylic acid was synthesized in 91.0% yield and with 96.8% selectivity. Performing the process in methanol solution provides a route for effective one-step methyl acrylate synthesis (methyl acrylate and acrylic acid total yield of 89.1% and total selectivity of 99.1% with a methyl acrylate ratio of 0.95). The catalysts were also active for ethyl acrylate and butyl acrylate synthesis using the respective alcohols as solvents.

Importantly, incorporation of Se-containing catalytically active units into the microgel polymer support allows for the microgel catalyst's easy separation and reuse in subsequent catalytic cycles without loss of activity, which is a significant advantage over known Se-containing inorganic and low molecular weight organic catalysts.

The high efficiency, ease of separation, and mild working conditions of acrolein oxidation and oxidative alkoxylation using Se-containing microgel catalysts allow us to consider it

as an alternative to the industrial method of acrylic acid synthesis by oxidation of propylene for small-scale production.

## Author contributions

K. H. Tan performed the experiments, designed the synthesis procedure of the diselenide crosslinker and Se-microgels, and performed  $^{77}\text{Se}$  NMR, Raman, FT-IR, and DLS-measurements, T. Kharandiuk performed catalytic experiments and wrote the manuscript, I. Kubitska performed catalytic experiments, M. A. Al Enezy-Ulbrich performed rheological measurements, and V. Ivasiv performed kinetic calculations and wrote the manuscript. R. Nebesnyi, I. I. Potemkin, and A. Pich conceived the project, discussed the results, and wrote the manuscript. All the authors provided input and feedback for manuscript preparation and approved the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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