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Supporting information

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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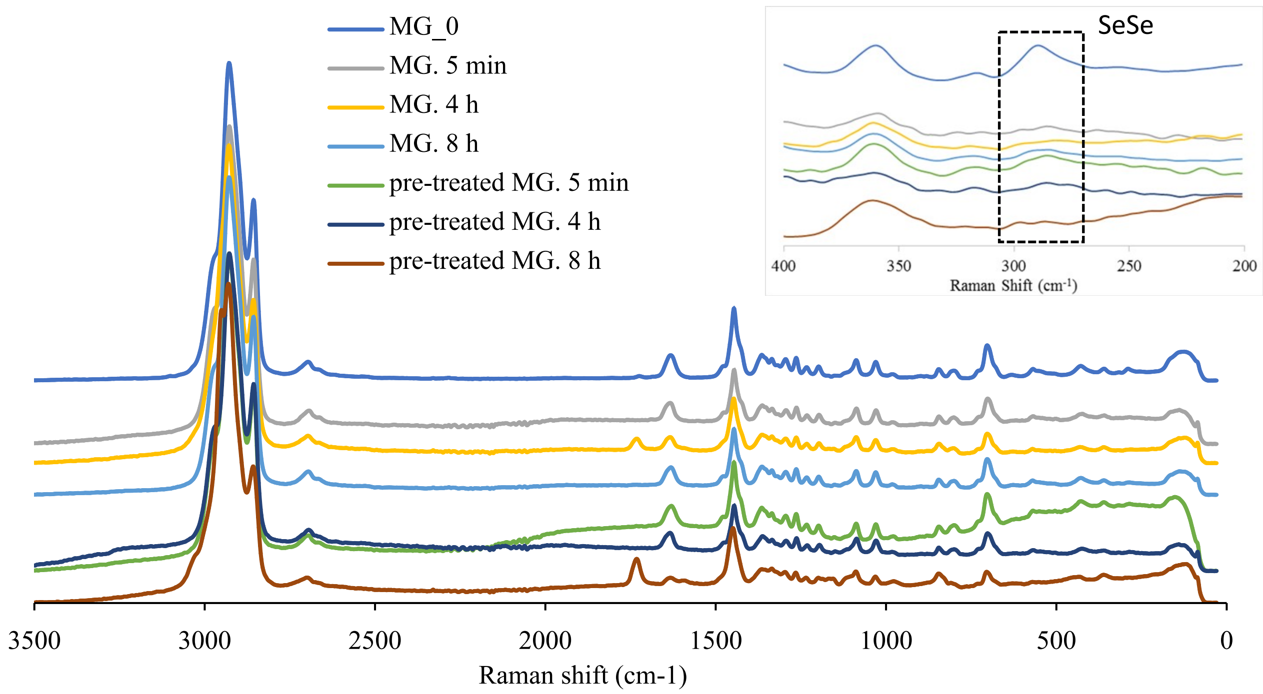

Fig. S1. Raman spectrums of MG_0 – microgel before reaction; MG – samples of microgel from reaction mixture after 5 min, 4 h and 8 h of the reaction; pre-treated MG – samples of microgel (previously dissolved in hydrogen peroxide solution overnight, and then used in oxidation reaction) from reaction mixture after 5 min, 4 h and 8 h of the reaction.

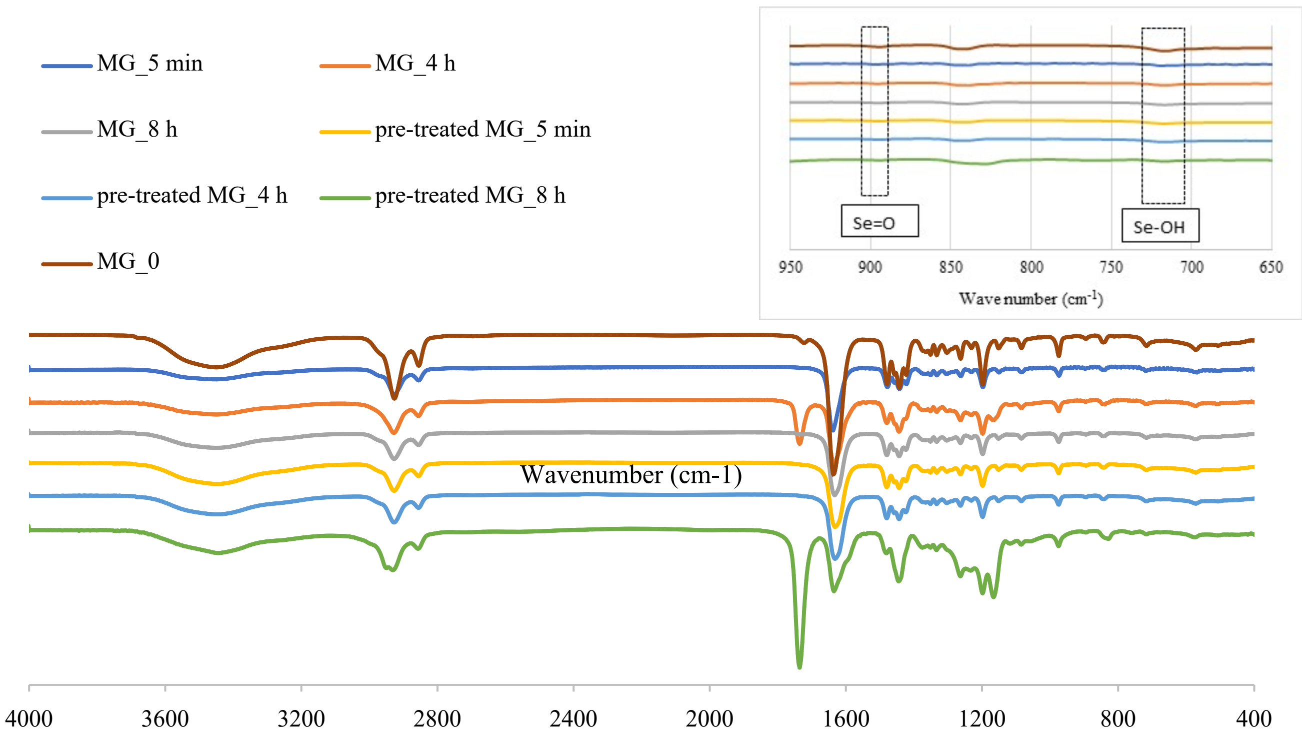

Fig. S2. FT-IR spectrums of MG_0 – microgel before reaction; MG – samples of microgel from reaction mixture after 5 min, 4 h and 8 h of the reaction; pre-treated MG – samples of microgel (previously dissolved in hydrogen peroxide solution overnight, and then used in oxidation reaction) from reaction mixture after 5 min, 4 h and 8 h of the reaction.

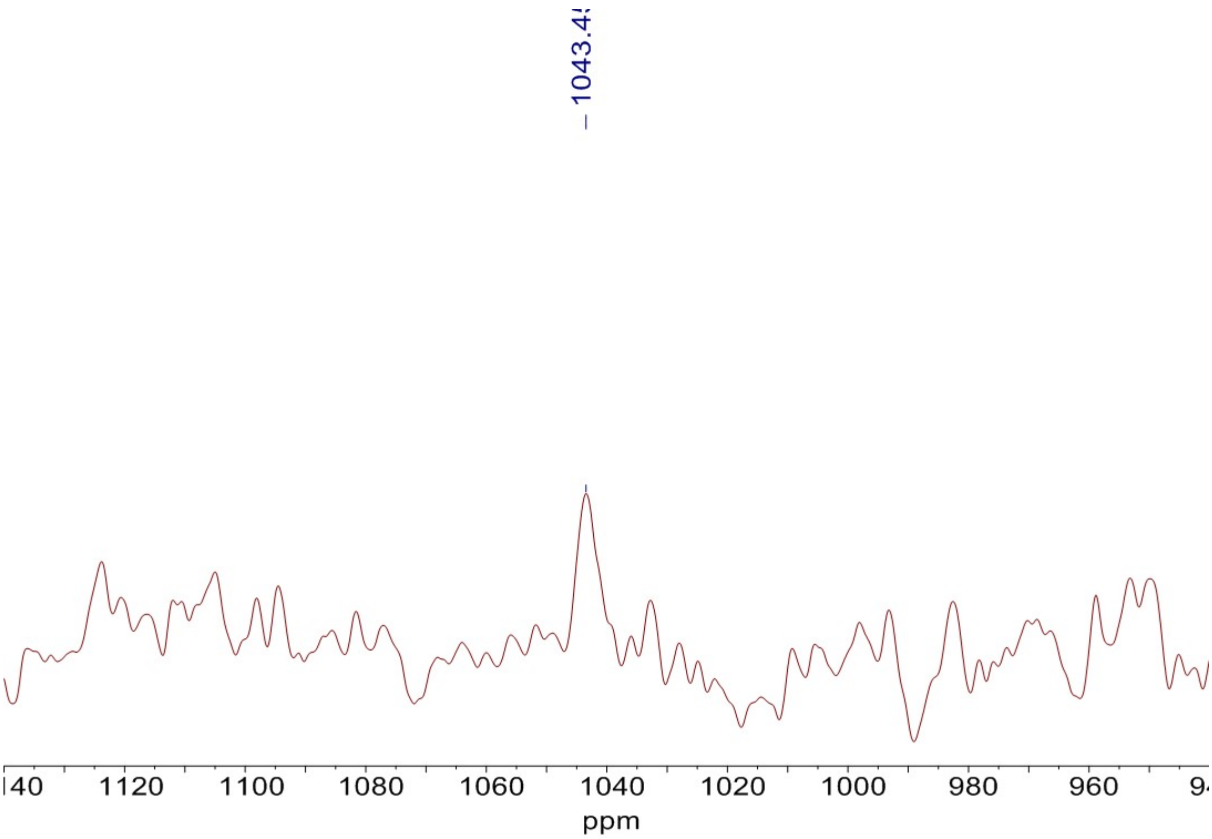

Fig. S3. ^{77}Se NMR spectra of B1.5Se2.0 microgel.

Table S1. FT-IR peaks intensity of PVCL and PVCL-Se microgels

Microgel sample	Peak intensity		
	890 cm^{-1} (Se=O)	1637 cm^{-1} (PVCL)	Se=O/PVCL ratio
PVCL	0.040	1.471	0.027
MG_0	0.046	1.614	0.028
MG_0 Oxidized	0.051	0.973	0.052
MG_5min	0.011	0.388	0.028
MG_4h	0.025	0.484	0.052
MG_8h	0.118	1.742	0.068
Pre-treated_MG_5min	0.088	1.565	0.056
Pre-treated_MG_4h	0.054	1.048	0.052
Pre-treated_MG_8h	0.060	0.577	0.104

Table S2. Oxidation and oxidative alkoxylation of acrolein by Se-modified microgel catalysts (C=0.0044 mmol/ml) on 8th hour of synthesis

Catalyst	Acrolein conversion, %	Selectivity (MA+AA), %	Methyl acrylate yield, %	Acrylic acid yield, %	Solvent
-	82	18.3	15	-	methanol
-	9	32.2	-	2.9	dioxane
PVCL	70	17.3	11.8	0.3	methanol
PVCL	7	15.7	-	1.1	dioxane
Crosslinker	90	74.7	57.8	9.5	methanol
Crosslinker	60	97.3	-	58.4	dioxane
Se0.5	72	50.2	35.8	0.5	methanol
Se0.5	59	96.4	-	57.0	dioxane
Se 1.0	63	62.4	37.3	2	methanol
Se 1.0	94	96.8	-	91.0	dioxane
Se 2.0	90	99.1	82.6	6.5	methanol
Se 2.0	80	99.0	-	79.1	dioxane
Se 3.0	93	64.2	51.5	8.2	methanol
Se 3.0	61	98.7	-	60.1	dioxane
Se 5.0	78	66.3	48.9	2.9	methanol
Se 5.0	67	70.2	-	46.8	dioxane

Table S3. Kinetic data (time dependence of concentrations) for Fig. 4a.

Solvent – dioxane, catalyst – Se 2.0 microgel, temperature – 50 °C

Catalyst concentration, mmol/ml	Acrolein concentration, mmol/ml					
	0 h	0.5 h	1 h	2 h	3 h	8 h
0,0022	2.000	1.925	1.854	1.718	1.592	1.380
0,0033	2.000	1.869	1.747	1.526	1.333	0.940
0,0044	2.000	1.801	1.622	1.315	1.066	0.418
0,0088	2.000	1.785	1.593	1.269	1.011	0.332

Table S4. Kinetic data (time dependence of concentrations) for Fig. 4b.

Solvent – methanol, catalyst – Se 2.0 microgel (C=0.0044 mmol/ml)

Temperature, °C	Acrolein concentration, mmol/ml					
	0 h	0.5 h	1 h	2 h	3 h	8 h
20	2.000	1.908	1.821	1.658	1.509	1.234
30	2.000	1.880	1.767	1.561	1.379	1.028
40	2.000	1.805	1.630	1.328	1.082	0.454
50	2.000	1.771	1.569	1.231	0.965	0.218

Table S5. Kinetic data (time dependence of concentrations) for Fig. 5a.

Solvent – dioxane, catalyst – Se 2.0 microgel, temperature – 50 °C

Catalyst concentration, mmol/ml	Acrolein concentration, mmol/ml						
	0 h	0.5 h	1 h	2 h	3 h	8 h	24 h
1st cycle	2.000	1,801	1,622	1,315	1,066	0,374	0,204
2nd cycle	2.000	1,805	1,629	1,327	1,081	0,387	0,252
3rd cycle	2.000	1,808	1,635	1,336	1,092	0,399	0,286