SUPPORTING INFORMATION
№2

Preparation of a Microsized Cerium Chloride-Based Catalyst and its Application in Michael Addition of β-Diketones to Vinyl Ketones

Alexander O. Terent'ev,[a,b] Vera A. Vil',[a] Ivan A. Yaremenko,[a]
Oleg V. Bityukov,[a,b] Dmitri O. Levitsky,[c] Vladimir V. Chernyshev,[d,e]
Gennady I. Nikishin,[a] Fabrice Fleury.[c]

AUTHOR ADDRESSES

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prospect 47, Moscow, 119991 Russian Federation.

[b] D. Mendeleyev University of Chemical Technology of Russia, Miusskaya square 9, Moscow, 125047 Russian Federation.

[c] UFIP FRE-CNRS 3478, DNA repair team, Université de Nantes, 2 rue de la Houssinière, 44322 Nantes, France.

[d] Department of Chemistry, M.V. Lomonosov Moscow State University, 1-3 Leninskie Gory, Moscow, 119991 Russian Federation.

[e] A. N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 31 Leninsky prospect, Moscow, 119071 Russian Federation.

CORRESPONDING AUTHOR E-MAIL ADDRESS terentev@ioc.ac.ru

X-ray powder diffraction

Three powder patterns were measured for each sample – **B**, **C** and **D**, one pattern was measured immediately after the synthesis, and the next two patterns – after the incubation for 10 *min* and 50 *min*, respectively, in an open air. Since all patterns exhibited the same features, herewith we present the results observed for the sample **C** only.

The first X-ray powder diffraction pattern for the sample **C** (pattern *C1*) was measured immediately after the synthesis at Huber G670 Guinier camera (Cu $K\alpha_1$ radiation, λ = 1.54059 Å) equipped with an imaging-plate detector. To minimize the contacts with an atmosphere, the powder sample was placed between the two thin polymeric films penetrable for X-rays, and the measurements were performed during 5 *min*. All observed diffraction peaks belong to the known hexagonal crystal structure of $CeCl_3$. [1] The results of Rietveld refinement for the pattern *C1* are shown in Figure S1. In the refinement performed with the program *MRIA*, [2] the atomic coordinates were taken from the literature [1] and fixed, so variables were – background and peak shape parameters, and hexagonal unit cell dimensions *a* and *c* refined to the values 7.423(2) and 4.310(2) Å, respectively.

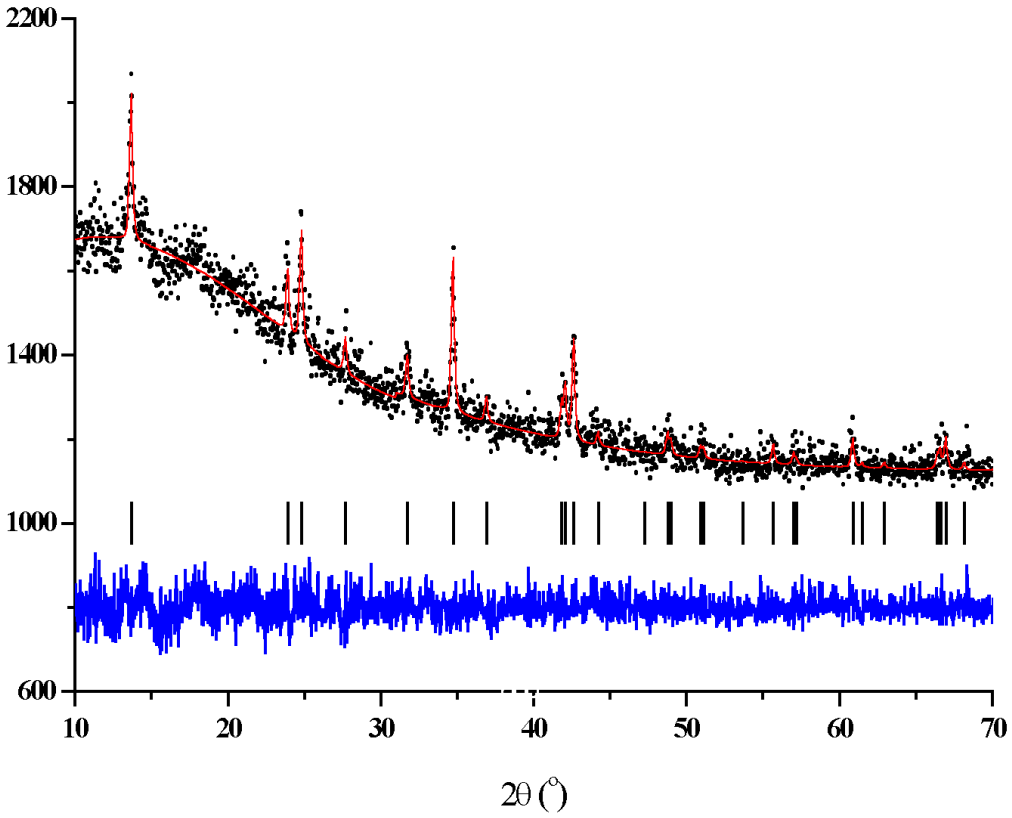


Figure S1. The Rietveld plot for the pattern *C1* showing the experimental (black dots), calculated (red) and difference (blue) curves. The vertical bars denote calculated positions of the diffraction peaks for phase $CeCl_3$.

The second X-ray powder diffraction pattern for the sample **C** (pattern *C2*) was measured at Panalytical EMPYREAN instrument with a linear X'celerator detector using Ni-filtered Cu K_α radiation. The 10 *min* measurements were started after incubation for 10 *min* in an open air. Most of the observed diffraction peaks belong to the known orthogonal crystal structure of $CeCl_3.3H_2O$. [3] The results of Rietveld refinement for the pattern *C2* are shown in Figure S2. In the refinement with the fixed atomic coordinates taken from the literature, [3] the orthogonal unit cell dimensions *a*, *b* and *c* refined to the values 12.403(2), 8.816(2) and 6.933(2) Å, respectively. We attribute the weak peaks observed on a difference (blue) curve to the hydrates of $CeCl_3$ with the unknown crystal structures, i.e. monohydrate, dihydrate etc.

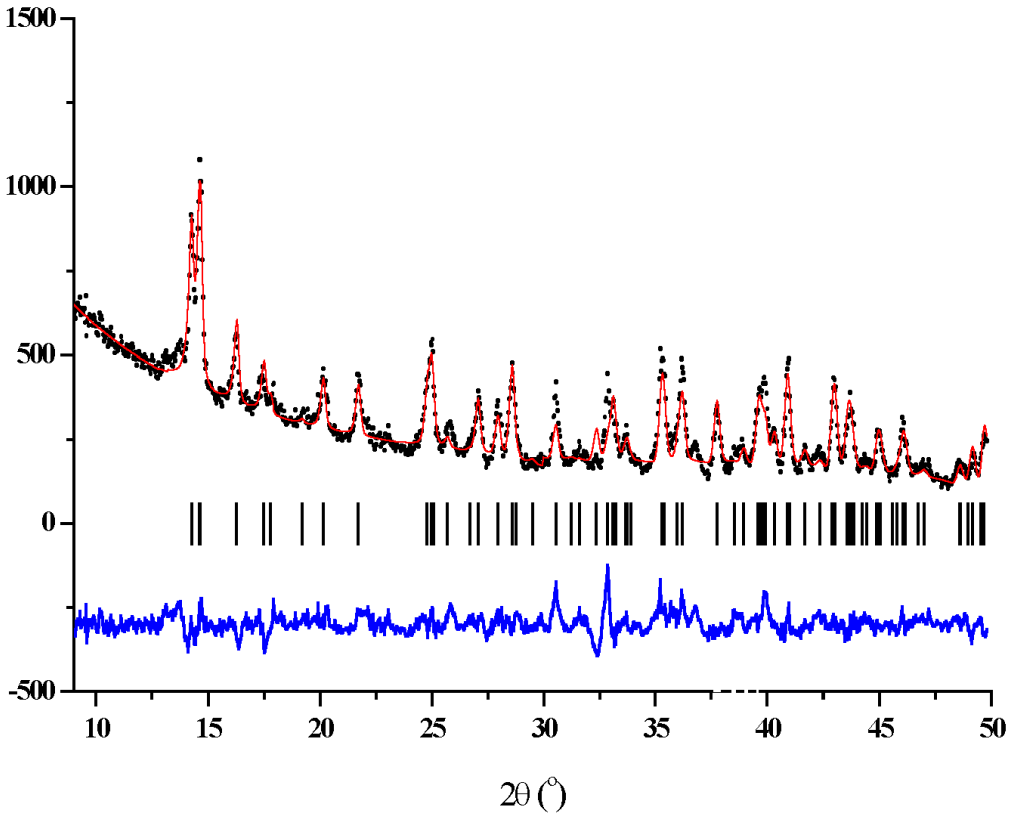


Figure S2. The Rietveld plot for the pattern *C2* showing the experimental (black dots), calculated (red) and difference (blue) curves. The vertical bars denote calculated positions of the diffraction peaks for phase $CeCl_3 \bullet 3H_2O$.

The third X-ray powder diffraction pattern for the sample **C** (pattern *C3*) was measured at Panalytical EMPYREAN instrument. The 10 *min* measurements were started after incubation for 50 *min* in an open air. All observed diffraction peaks belong to the known triclinic crystal structure of $CeCl_3.7H_2O$. [4] The results of Rietveld refinement for the pattern *C3* are shown in Figure S3. In the refinement with the fixed atomic coordinates taken from the literature, [4] the triclinic unit cell parameters were refined to the following values - a = 8.011(1) Å, b = 8.255(1) Å, c = 9.202(1) Å, α = 71.48(2)°, β = 72.44(2)°, γ = 81.58(3)°.

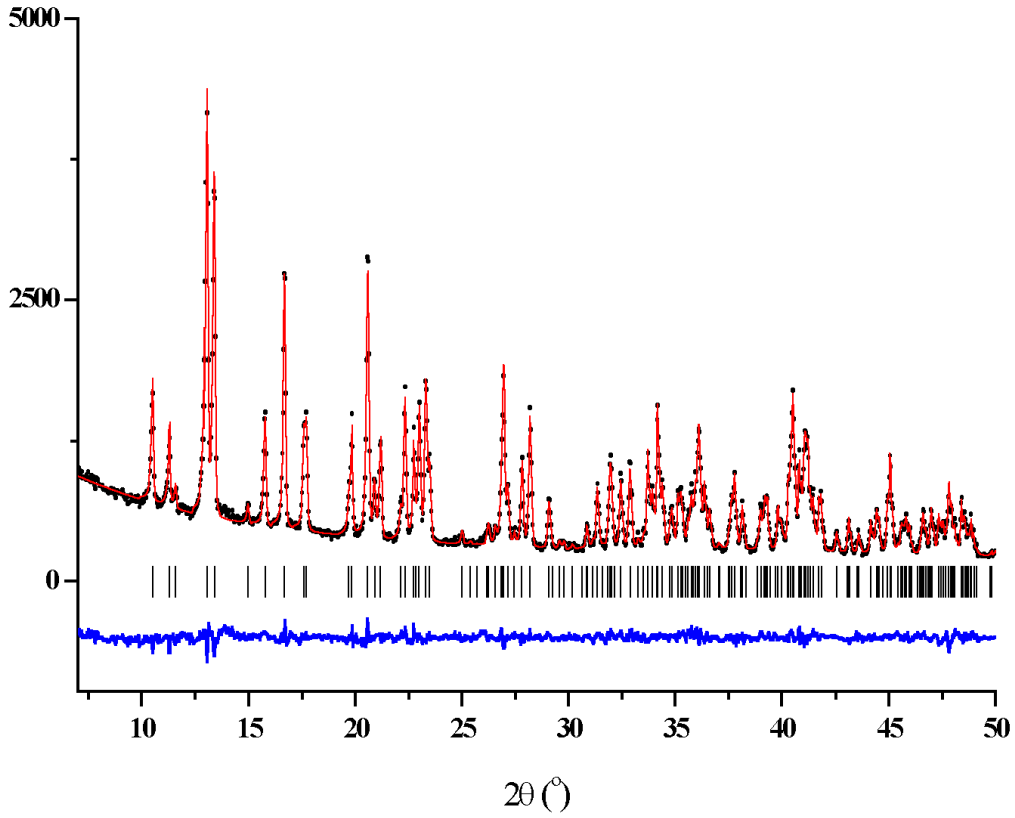


Figure S3. The Rietveld plot for the pattern *C3* showing the experimental (black dots), calculated (red) and difference (blue) curves. The vertical bars denote calculated positions of the diffraction peaks for phase $CeCl_3 \bullet 7H_2O$.

References.

(1) Zachariasen, W.H. *Acta Crystallogr.* **1948**, *1*, 265-268.

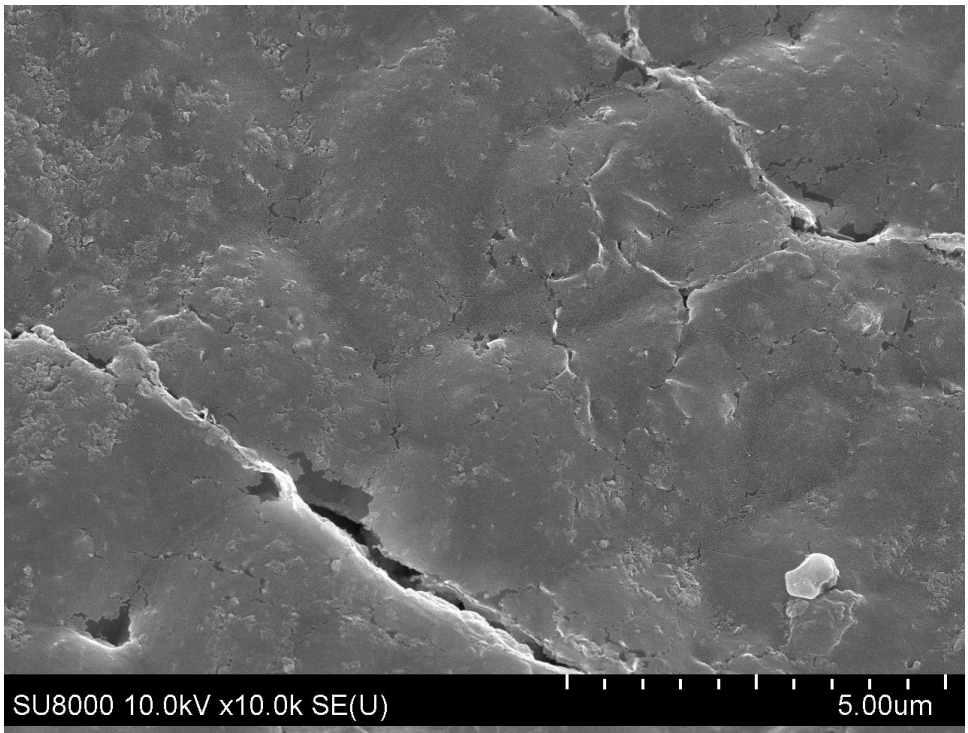
(2) Zlokazov, V. B.; Chernyshev, V. V. *J. Appl. Crystallogr.* **1992**, *25*, 447–451.

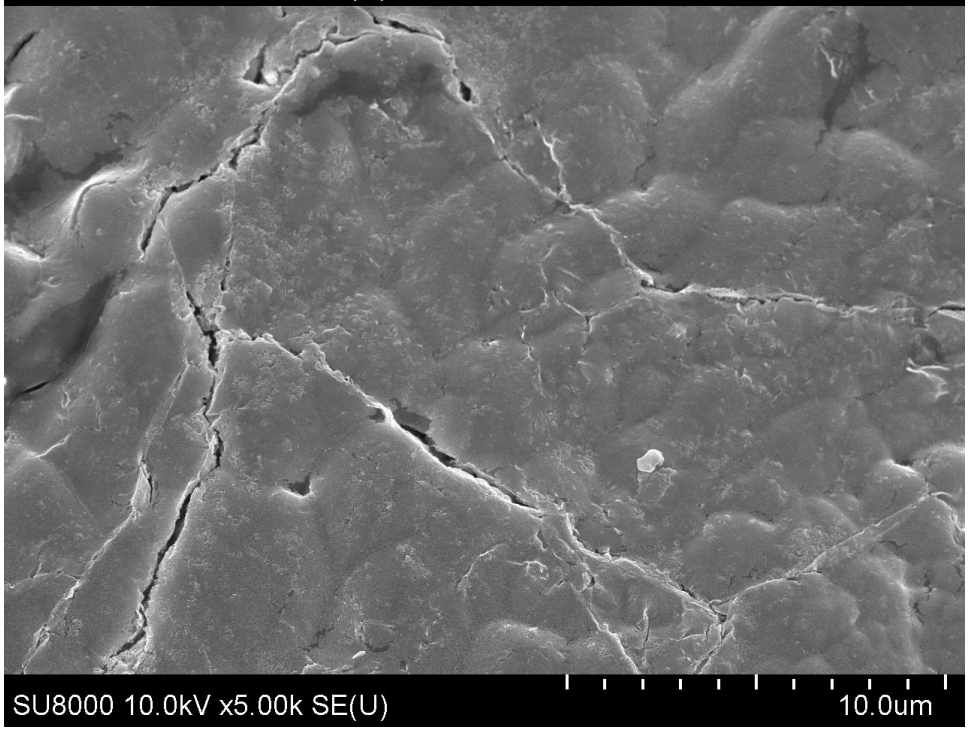
(3) Reuter, G.; Fink, H.; Seifert, H.J. *Z. Anorg. Allgem. Chemie*, **1994**, *620*, 665-671.

(4) Levason, W.; Webster, M. *Acta Crystallogr., Section E*, **2002**, *E58*, i76-i78.

Micrographs of catalysts A, C, D, F

Catalyst A





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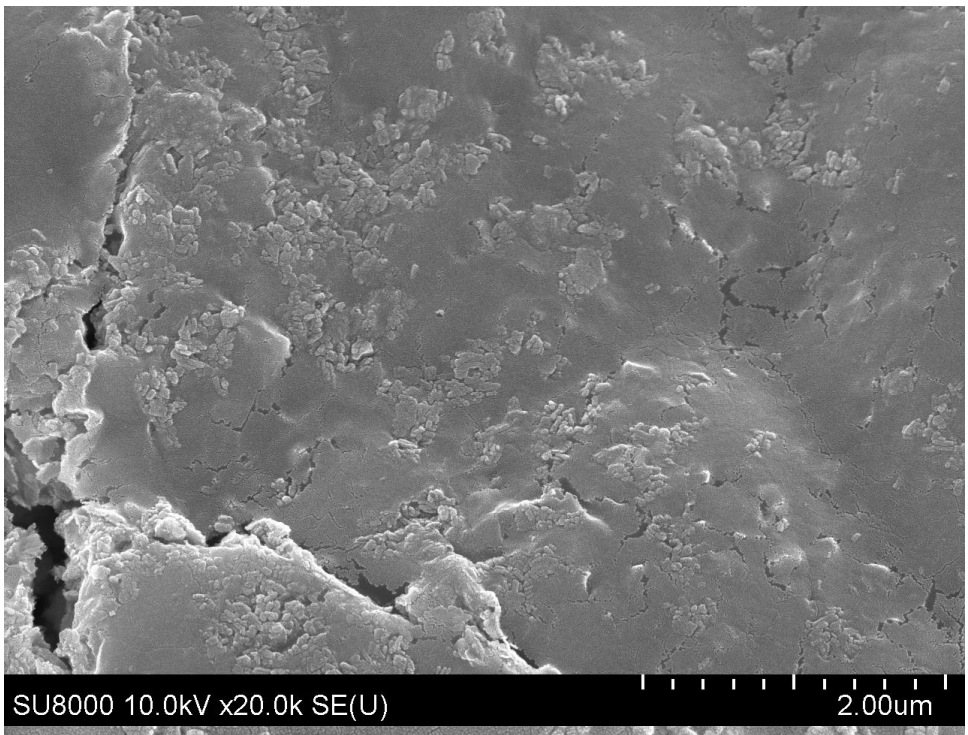

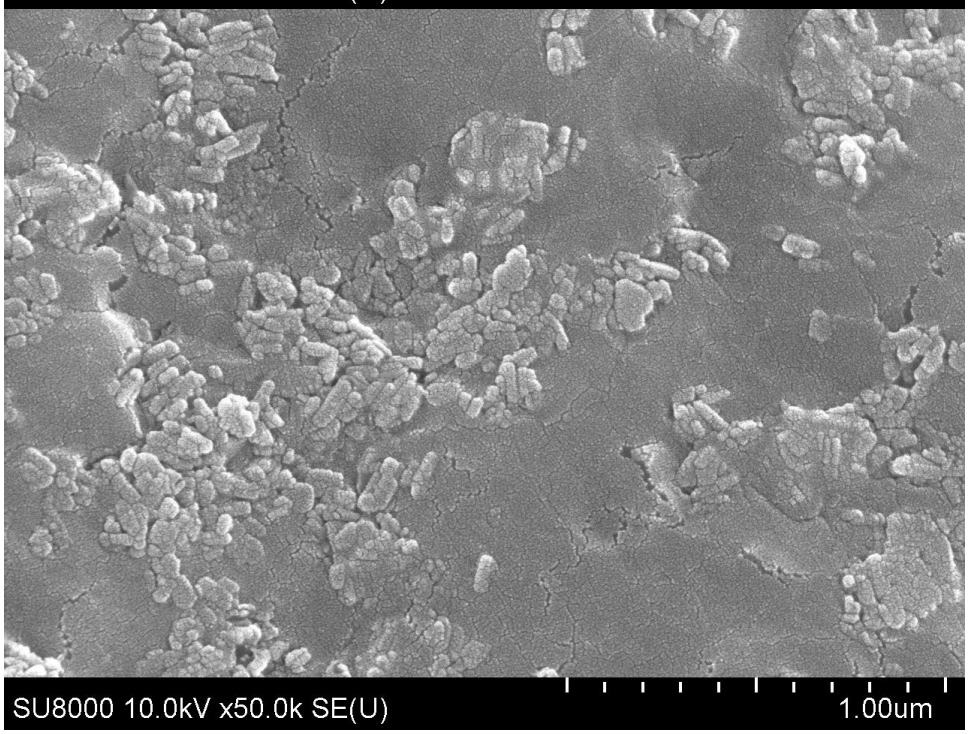

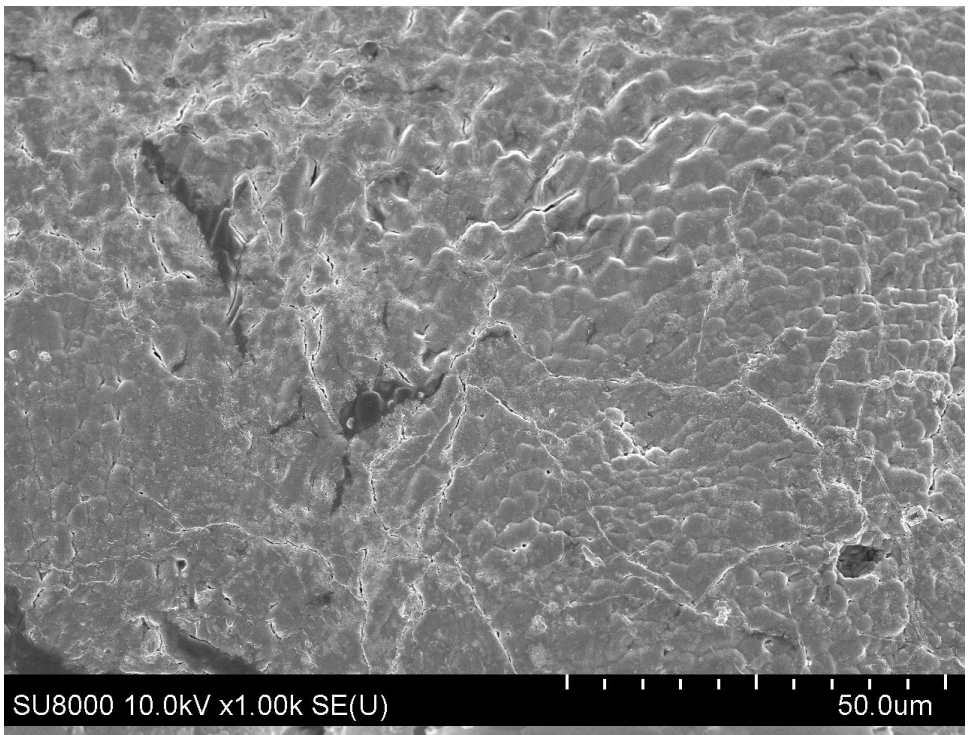

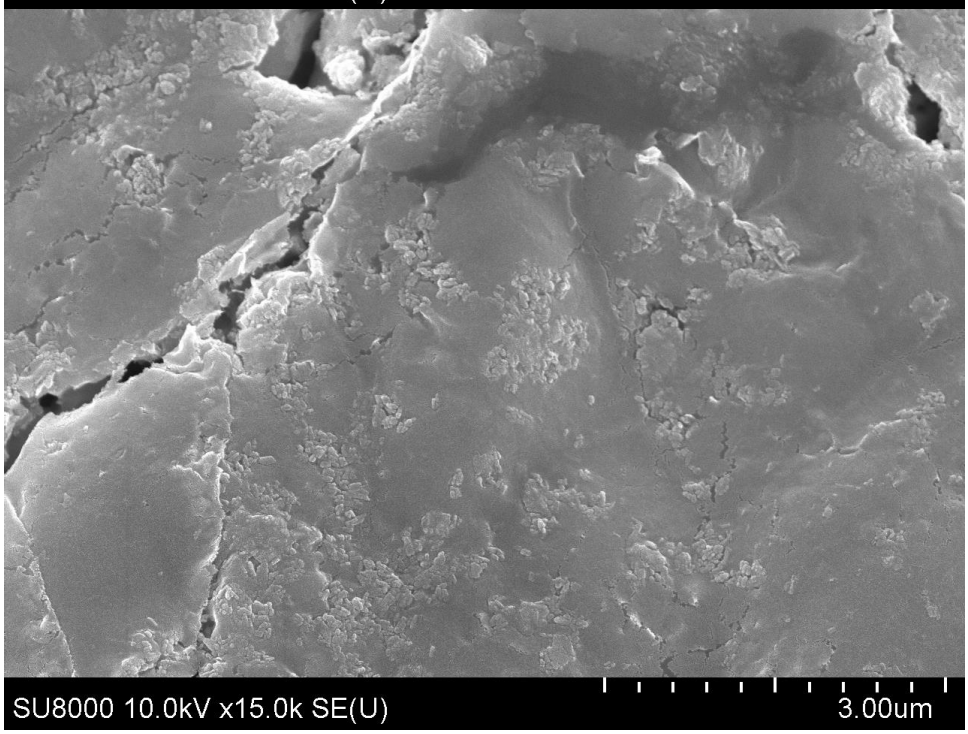

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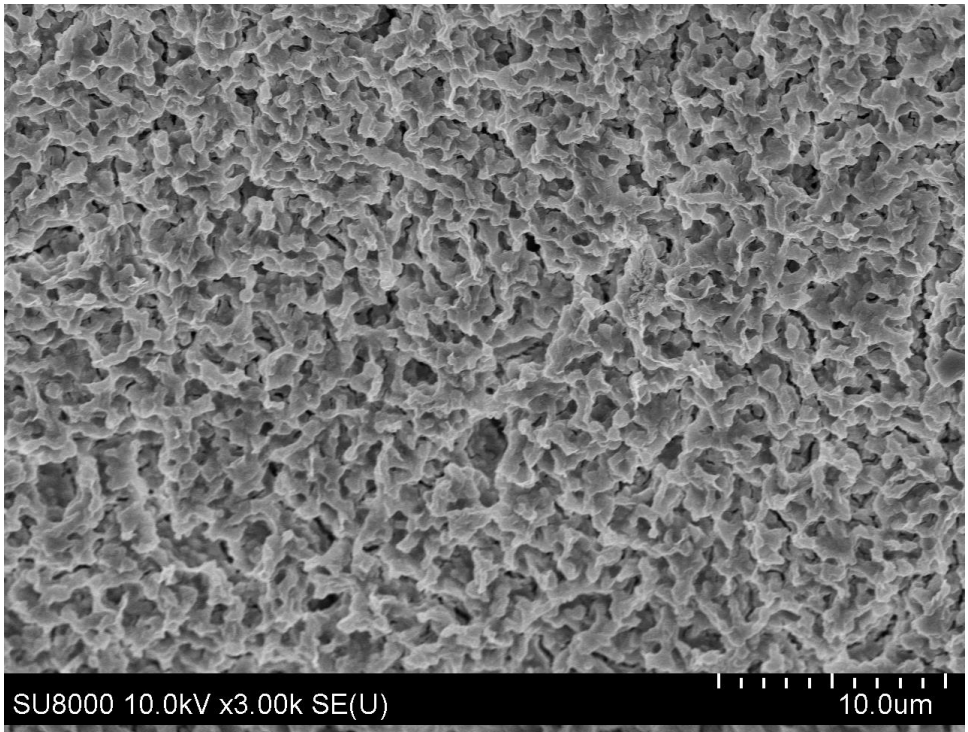
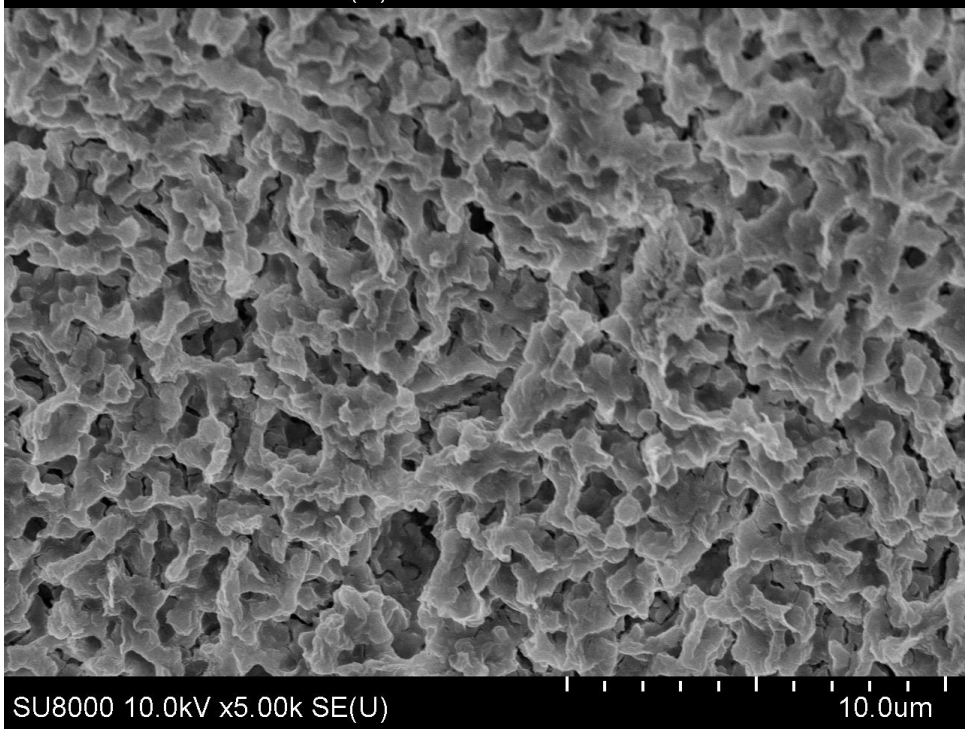
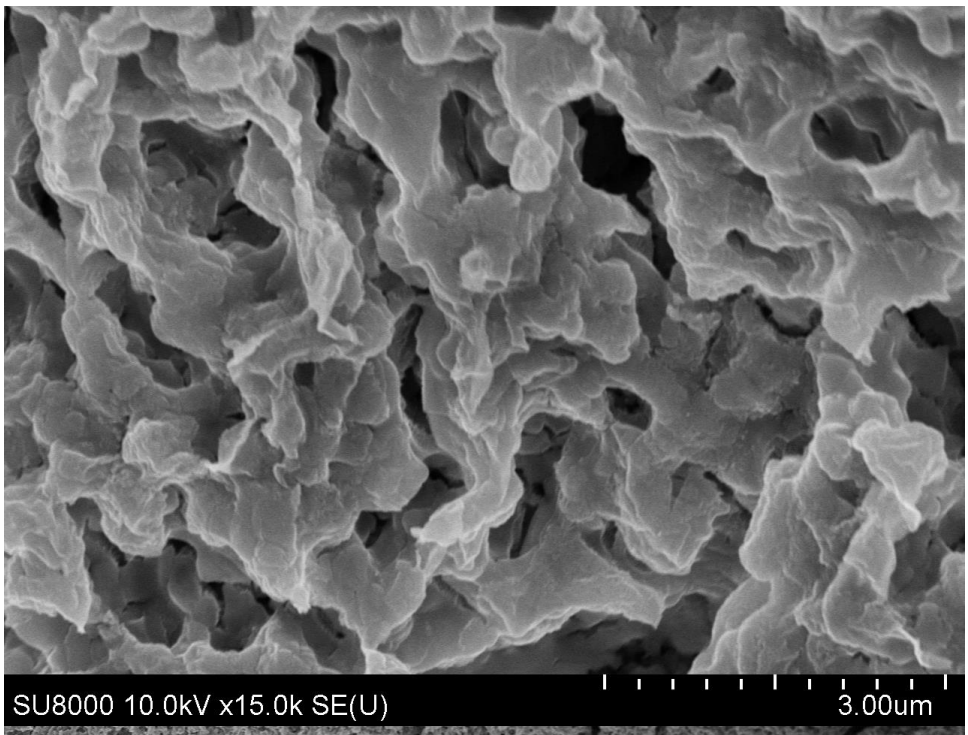
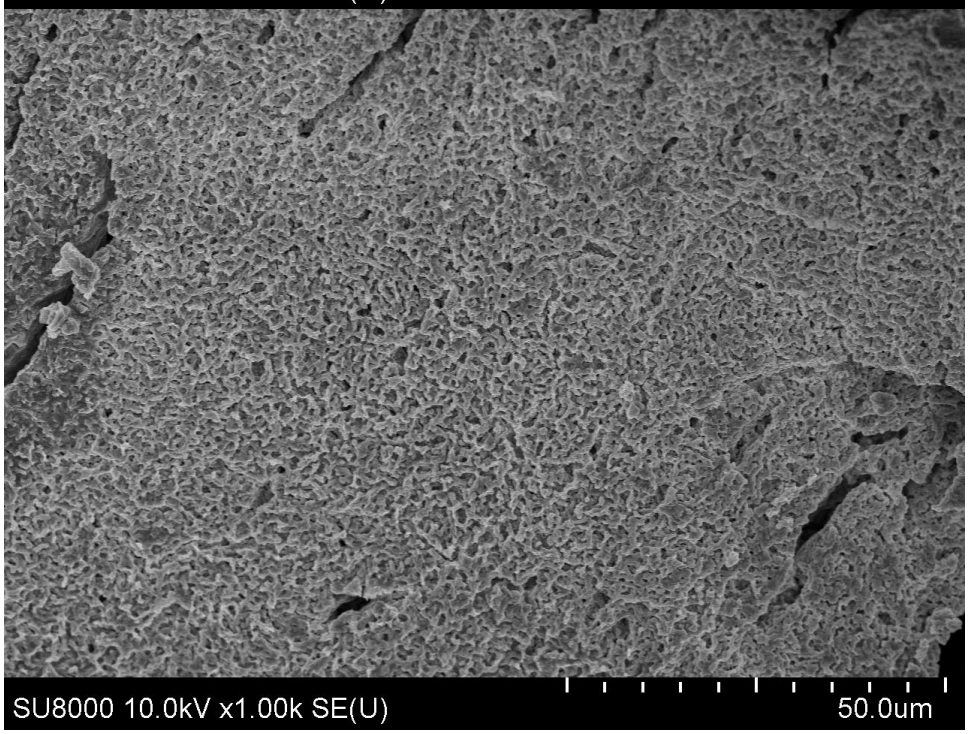
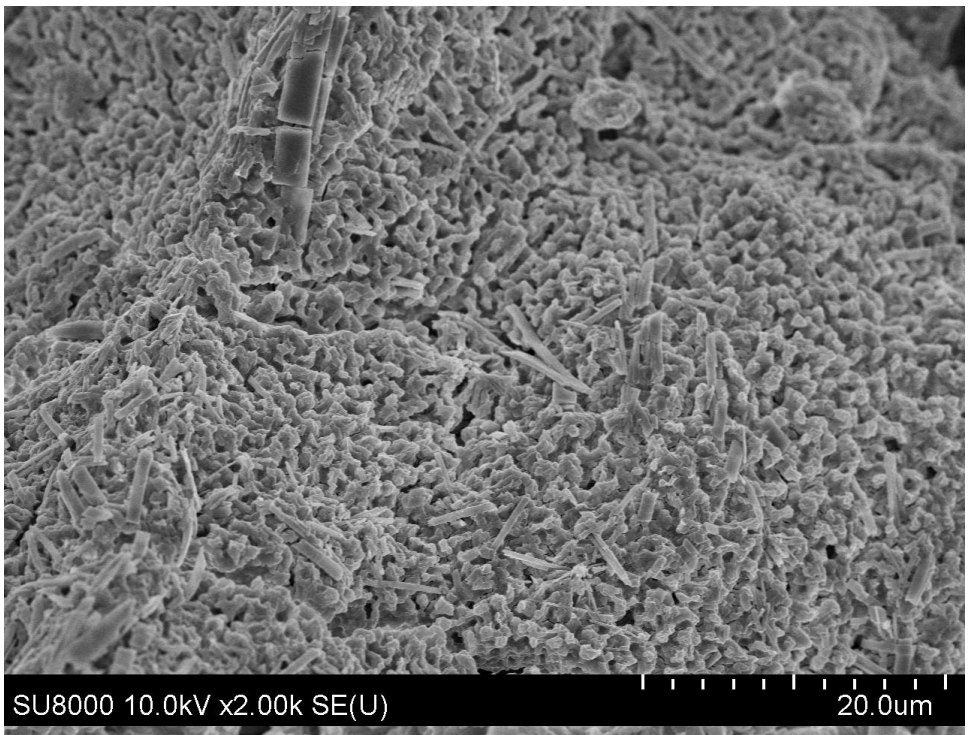
Catalyst C

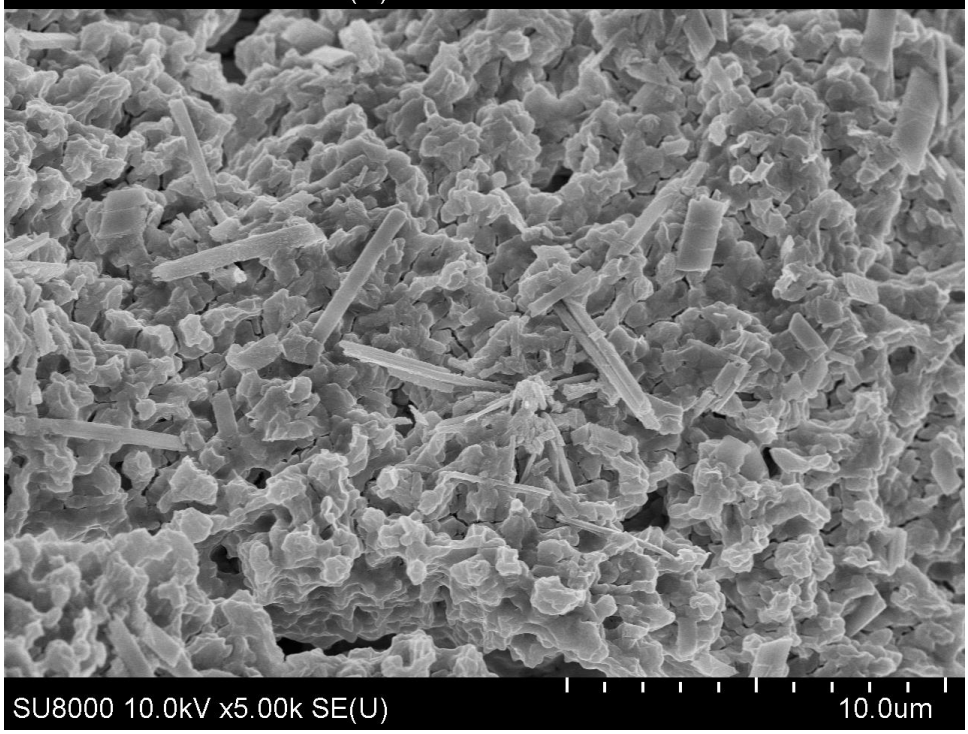


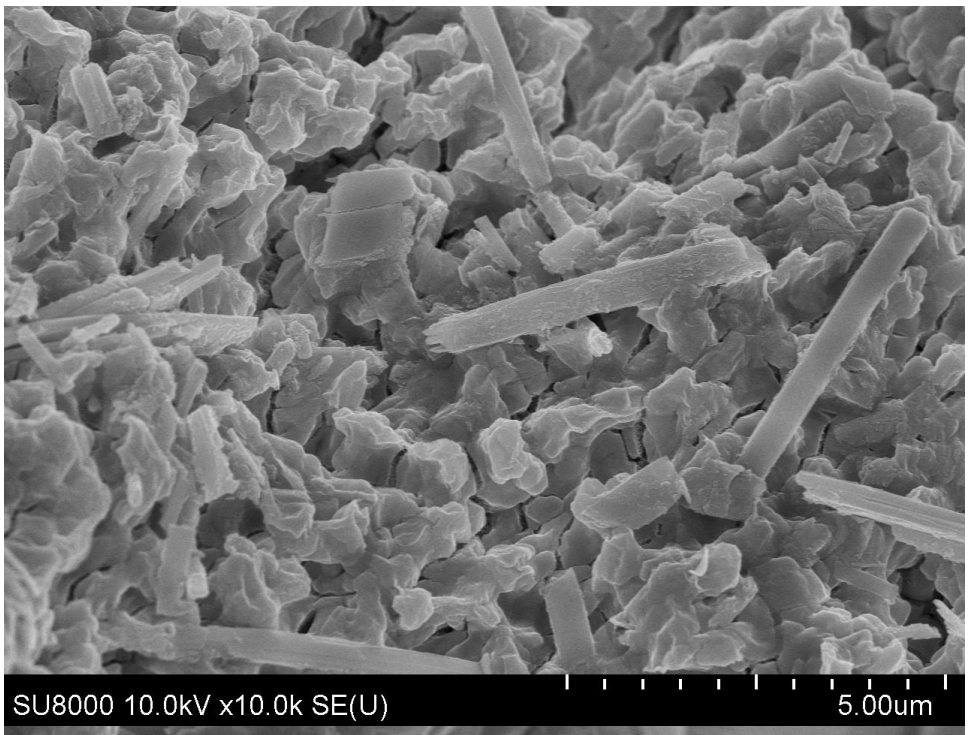


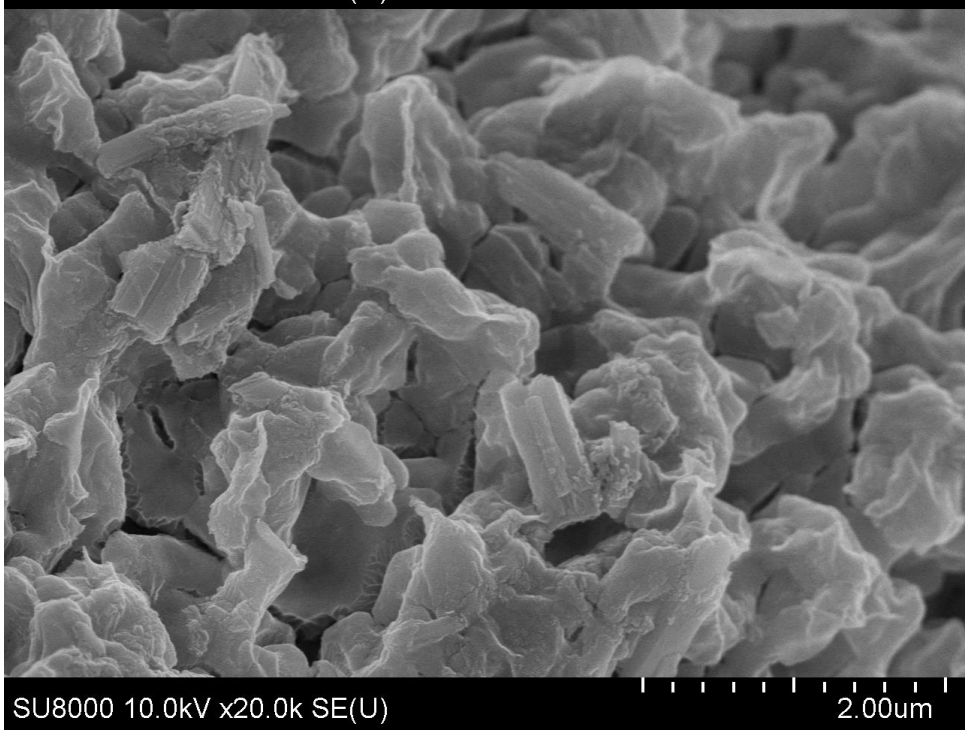


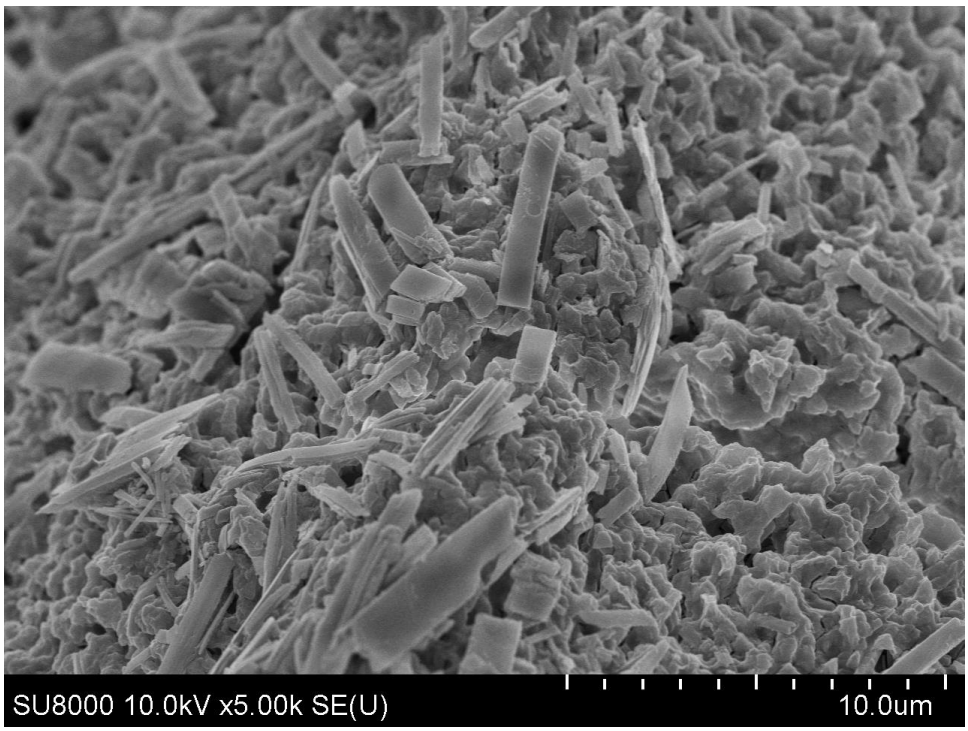












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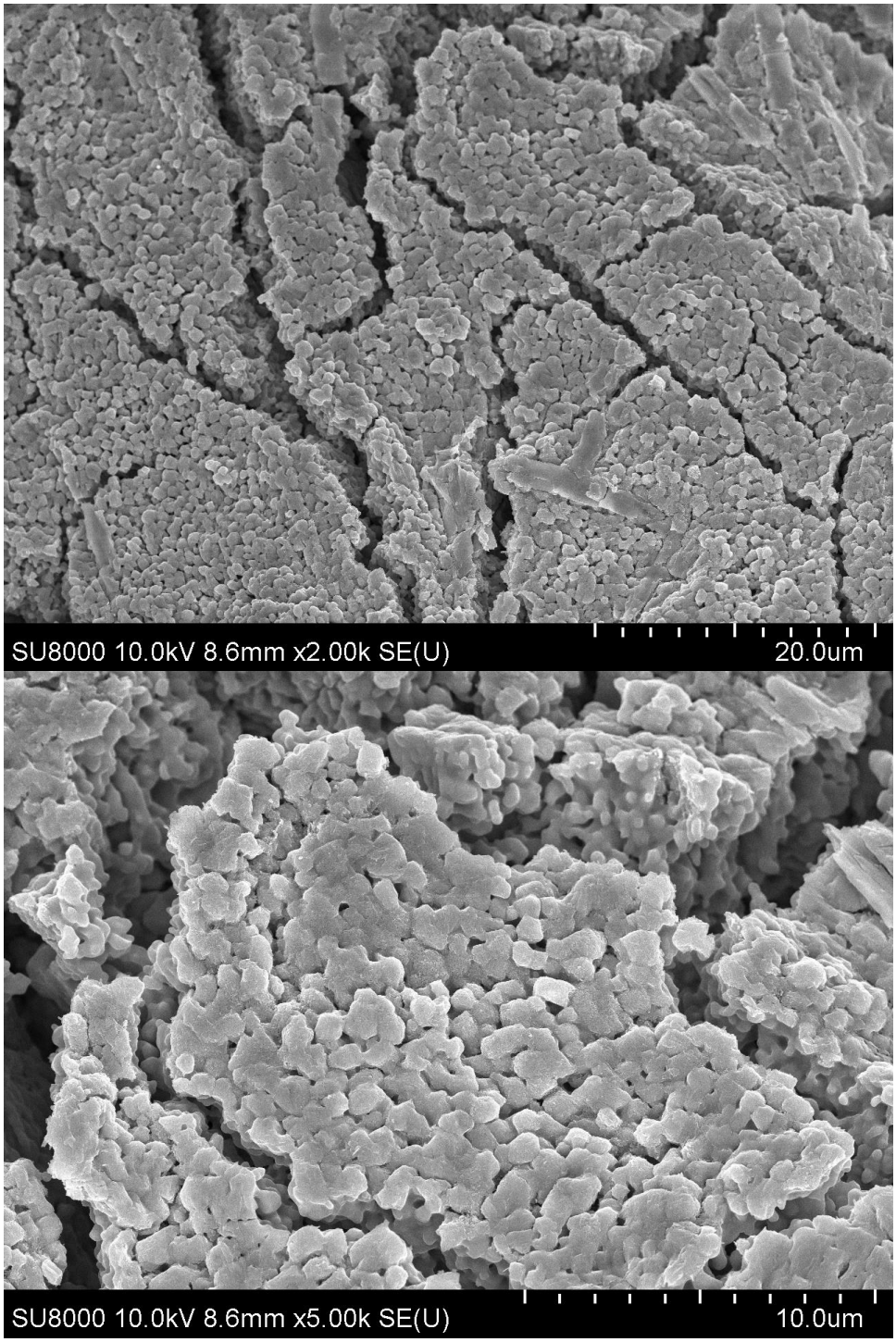
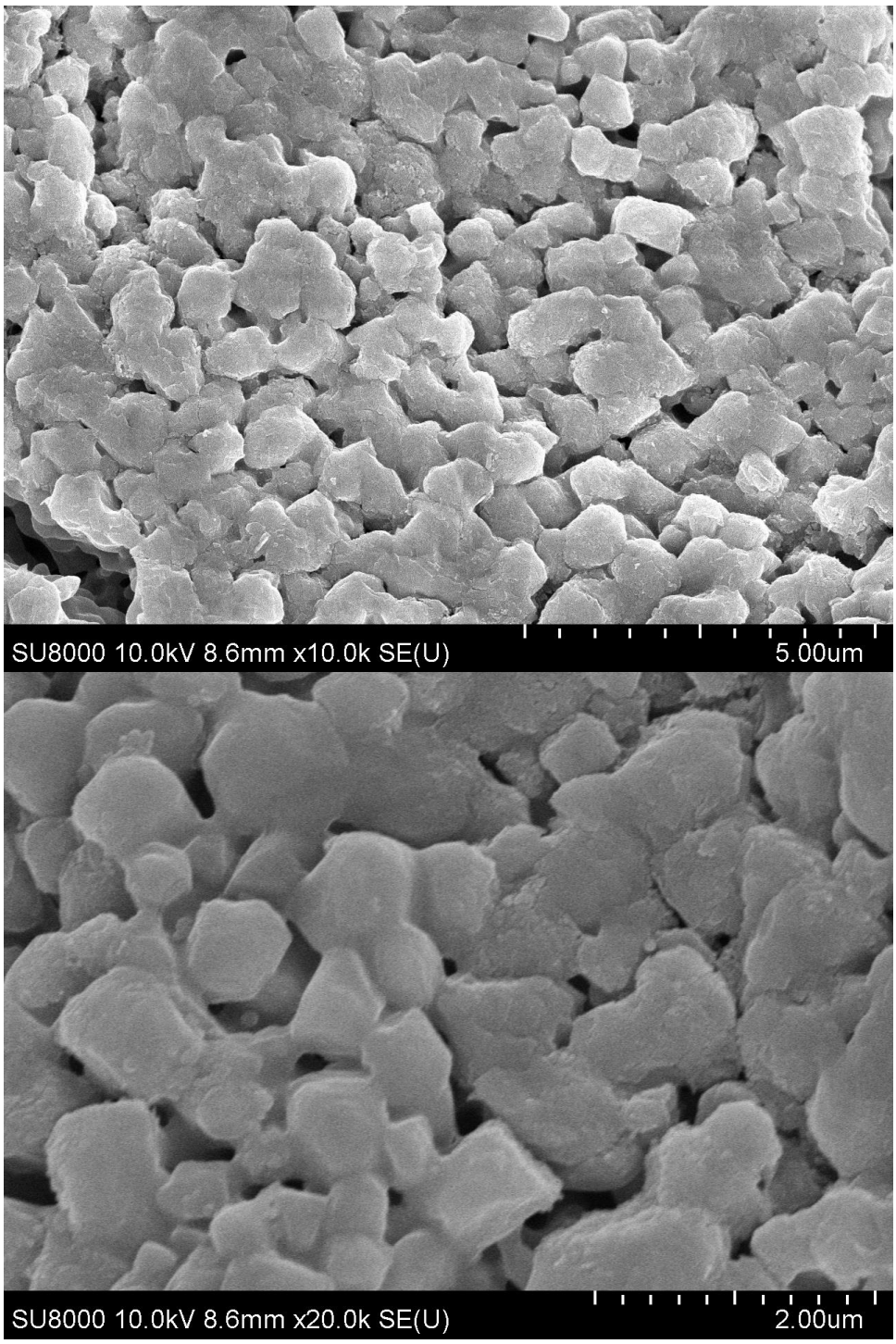
Catalyst D





Catalyst F