Supporting information

Design of a Functionalized Lacunary Polyoxometalate Catalyst for Efficient Epoxide Ring-Opening and Biodiesel Production

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Materials and instrumentation

Polyoxometalate and Sodium bicarbonate were purchased from Sigma-Aldrich. 3-aminopropyltrimethoxysilane, 1,3-propanesultone, hydrochloric acid, sulfuric acid, methanol, ethanol, propanol, toluene, styrene oxide, oleic acid, were purchased from Merck.

Fourier transform infrared (FT-IR) spectra of solid samples were recorded on a Perkin-Elmer RXI FT-IR spectrometer using KBr disks. Powder X-ray diffraction (XRD) analyses were conducted by a Rigaku D-max CIII X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). The XPS was done on XPS-Thermofisher + scientific K-ALPHA. Analyses of the morphology and EDX spectrum of samples were conducted by a TSCAN-Mira III field emission scanning electron microscope (FE-SEM). The Micro Active for TriStar II plus 2.03 device was used for nitrogen adsorption-desorption analysis and to determine the specific surface area. Micromeritics TPD/TPR2900 was used for NH_3-TPD, and monitoring of desorbing molecules from the sample was performed using a quadrupole mass spectrometer (QMG220, Prisma Plus). Agilent GC 7890A MSD 5975 gas chromatography (GC) was used to identify the products of catalytic reactions with the FID detector. Identifications were made based on comparisons with the proposed structures available at the library of the device.

General procedure for the TPD analysis

The determination of catalyst acidity, in terms of concentration and strength of acidic sites, was accomplished through ammonia temperature programmed desorption (NH_3-TPD) within a temperature range of 100–800°C. Before NH_3-TPD experiments, a sample (0.1g) was outgassed with pure helium (30 $mL.min^{-1}$) at 600°C for 1 hour. Subsequently, the sample was cooled to 100°C and saturated with NH_3 (5% molar base) diluted in helium. Desorption was carried out with a linear heating rate of 10°C min^{-1} in a flow of pure helium (30 $mL.min^{-1}$).

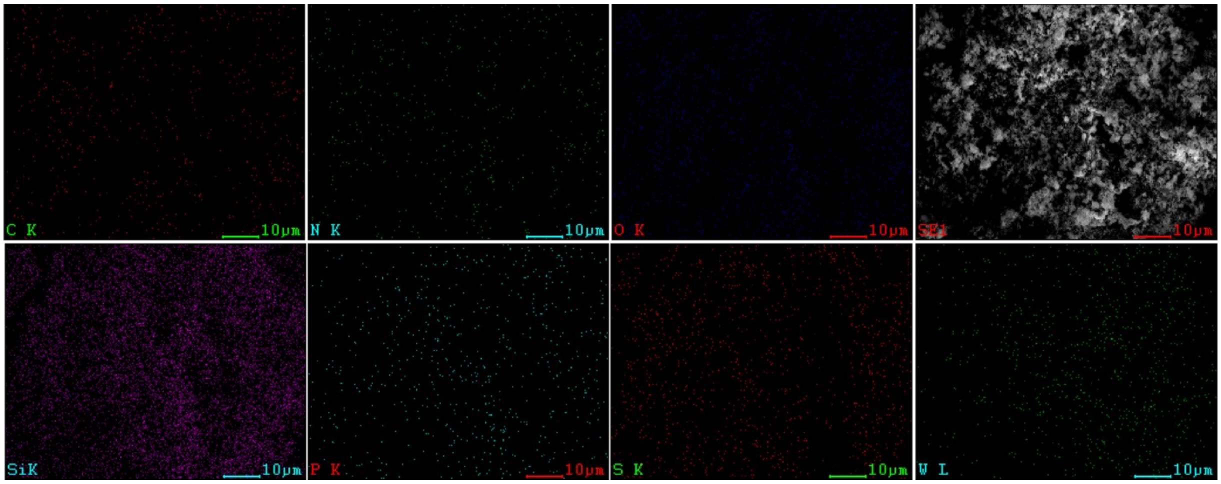

Fig. S1. Elemental mapping of the LPOM/APTMS/1,3-PS.

Elements	**Fresh LPOM/APTMS/1,3-PS Content (wt.%)**	**Recovered LPOM/APTMS/1,3-PS Content (wt.%)**
C	2.37	2.33
H	1.23	1.25
N	0.5	0.48
S	0.2	0.19

Table S1. The CHNS elemental analysis of the fresh and recovered LPOM/APTMS/1,3-PS.

Table S2. The yield of the esterification of the oleic acid in the presence of substrates lacking –SO_3H groups.

Entry	Time (h)	Yield (%)
1[a]	2	0
2[b]	2	0
3[c]	2	0

Reaction conditions: Catalyst amount (40 mg), Methanol (50 mmol), Oleic acid (2.5 mmol), temperature (80 °C).

[a] without catalyst, [b] LPOM, [c] LPOM/APTMS.

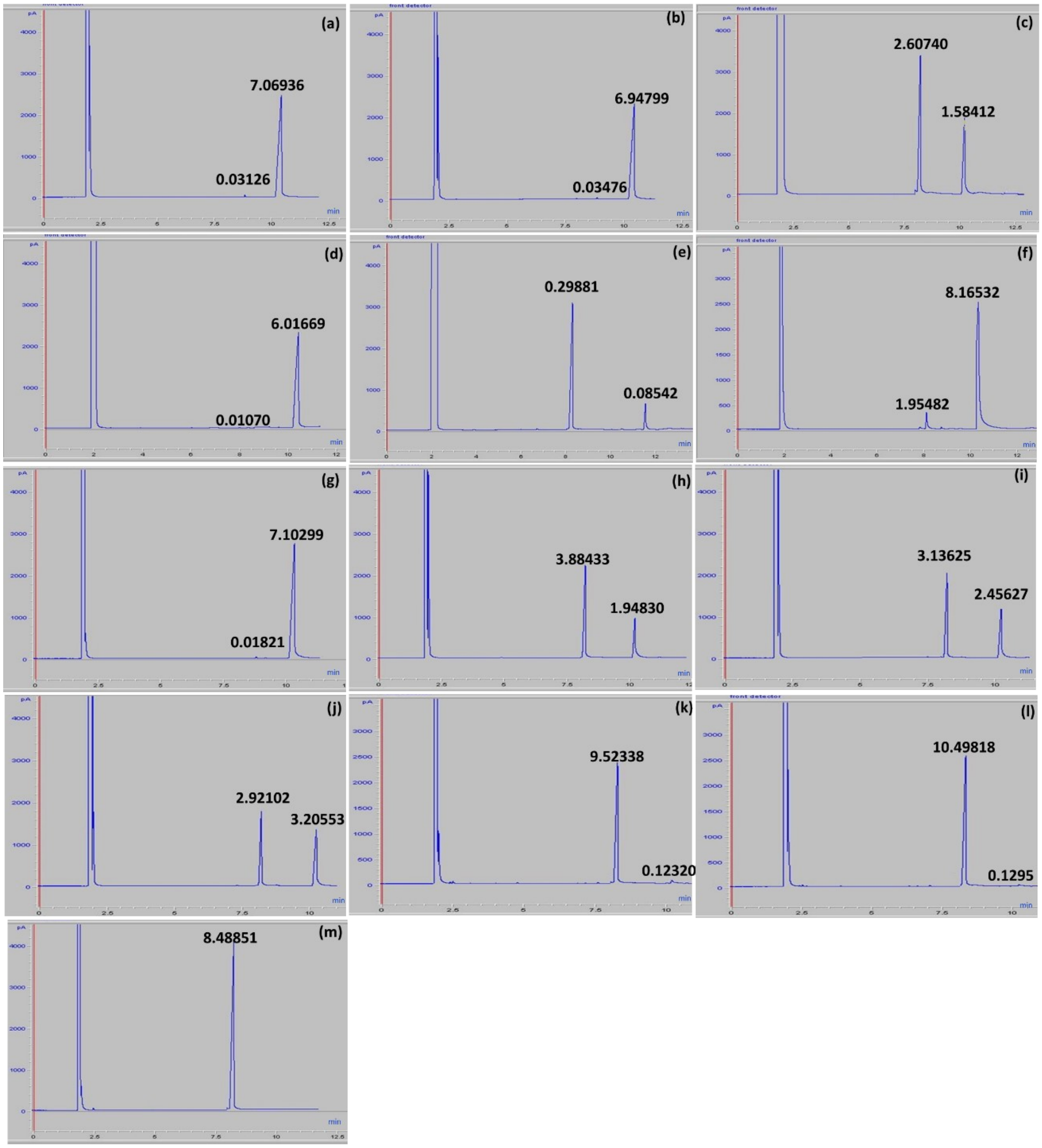
(a)
7.06936
0.03126
(b)
6.94799
0.03476
(c)
2.60740
1.58412
(d)
6.01669
0.01070
(e)
0.29881
0.08542
(f)
8.16532
1.95482
(g)
7.10299
0.01821
(h)
3.88433
1.94830
(i)
3.13625
2.45627
(j)
2.92102
3.20553
(k)
9.52338
0.12320
(l)
10.49818
0.1295
(m)
8.48851
pA
min
front detector

Fig. S2. GC graph of ring-opening of styrene oxide catalyzed by LPOM/APTMS/1,3-PS calculated in Table 1 (a) entry 1, (b) entry 2, (c) entry 3-1, (d) entry 3-2, (e) entry 4, (f) entry 5, (g) entry 6, (h) entry 7, (i) entry 8, (j) entry 9, (k) entry 10, (l) entry 11, (m) entry 12 (Reaction conditions: styrene oxide (1 mmol), alcohol (5 mL), temperature (25 °C)).

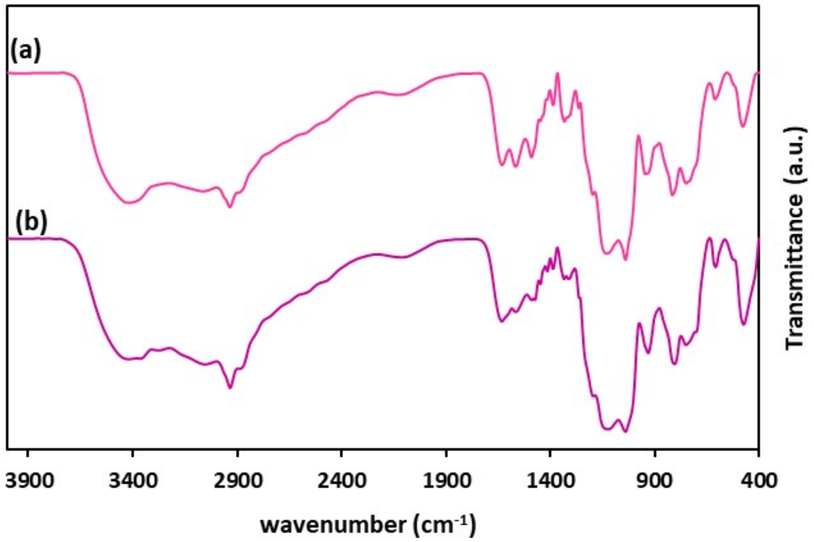

Fig. S3. FT-IR spectra of (a) fresh and (b) recovered LPOM/APTMS/1,3-PS.