

# Supporting Information

## Highly recyclable fluoride for enhanced cascade hydrosilylation-cyclization of levulinates to $\gamma$ -valerolactone at low temperatures

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## Experimental section

### *Materials*

Diphenyl (silane-d<sub>2</sub>) (97 atom % D) was purchased from Sigma-Aldrich Co. LLC. Poly(methylhydrosiloxane) (PMHS), dimethyl sulfoxide (DMSO, >99.8%), and *N,N*-dimethyl formamide (DMF, 99.8%) were purchased from Shanghai Aladdin Industrial Inc. *n*-Butanol (AR), methanol (AR), THF (AR), and *n*-hexane (AR) were bought from Beijing J&K Scientific Ltd. Trimethoxysilane (>99%), triethoxysilane (98%), phenylsilane (>97%), diphenylsilane (>98%), heptamethyltrisiloxane ( $\geq$ 98%), triethylsilane (99%), tetramethyldisiloxane (>98%), KF (99%), CsF (99%), LiF (>99%), NaF (>99%), KCl (>99%), KBr (>99%) DMSO-d<sub>6</sub> (99.8 atom%D), methyl levulinate (>99%), ethyl levulinate (EL, 99%), *n*-butyl levulinate (>98%),  $\alpha$ -angelica lactone (98%), 2(5H)-furanone (98%), and  $\gamma$ -valerolactone (GVL, 99%) were purchased from Beijing Innochem Sci. & Tech. Co. Ltd.

### *Catalysts Characterization*

BET (Brunauer–Emmett–Teller) surface areas of the porous materials were determined from nitrogen physisorption measurements at liquid nitrogen temperature on a Micromeritics ASAP 2010 instrument (Tristar II 3020, Norcross, GA). XPS (X-ray photoelectron spectroscopy) measurements were recorded using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe (Physical Electronics Inc., PHI, MN) equipped with a monochromatic AlK $\alpha$  anode. EDX (Energy dispersive X-ray) spectrum was acquired with an aberration corrected FEI TECNAI G2 F30 S-TWIN (S)TEM (Hillsboro, OR) operating at 300 kV. ICP-OES (inductively coupled plasma-optical emission spectrometer) was recorded on an Optima 5300 DV instrument (PerkinElmer Inc., Waltham, MA).

### *Reaction procedures*

All the reactions were carried out in a 15 mL Ace tube. In a typical procedure, 0.5 mmol EL, 15 mg KF, 2.0 mL DMF and 2.5 equiv. PMHS were added into the tube, which was magnetically stirred at 650 rpm for a specific reaction time. The time zero was defined as the tube was placed into an oil bath that was preheated to 40, 60, 80 and 100 °C (or at room temperature). After the reaction, liquid products were quantitatively analyzed by GC (Agilent 7890B).

### *Analysis of products*

Liquid products and major by-products were identified with GC-MS (Agilent 6890N GC/5973 MS, Santa Clara, CA). The reaction mixtures were quantitatively analyzed with GC (Agilent 7890B) with a HP-5 column (30 m  $\times$  0.320 mm  $\times$  0.25  $\mu$ m) and a flame ionization detector using naphthalene as internal standard and referring to the standard curves (with  $R^2 \geq 0.996$ ) made from commercial samples.

#### ***Catalyst recycling***

After each cycle of reaction, the remaining catalyst in the mixture was recovered by centrifugation, followed by successively washing with DMF, ethanol and acetone for 3-5 times, and drying at 80 °C in N<sub>2</sub> for 5 h, which was then directly used for the next run.

#### ***Isotopic labeling experiments***

For isotopic kinetic and mechanism study, <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra of the reaction mixtures were performed in the deuterium solvent DMSO-d<sub>6</sub> on a JEOL-ECX 500 NMR spectrometer at room temperature spectrometer operating at 500 MHz.

**Table S1.** Some previously reported results of EL-to-GVL conversion with different H-donors

Entry	Catalyst	Mole of substrate	Mole/Pressure of H-donor	Temp.(°C)	Conv.(%)	Yield(%)	Sel.(%)	Ref.
1	Au-Pd/TiO <sub>2</sub>	51.7 mmol	4 MPa H <sub>2</sub>	<b>200</b>	90	87.8	97.5	S1
2	Cu/Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	0.54 mmol	3 MPa H <sub>2</sub>	<b>160</b>	99	95	96	S2
3	Ni/SiO <sub>2</sub>	0.5 mmol	3 MPa H <sub>2</sub>	<b>250</b>	99	88	0.88	S3
4	Fe <sub>3</sub> (CO) <sub>12</sub>	1 mmol	4 mmol HCOOH	<b>180</b>	100	92	92	S4
5	Ru/C	8.6 mmol	52 mmol HCOOH	<b>190</b>	87	75	86	S5
6	ZrO(OH) <sub>2</sub> ·xH <sub>2</sub> O	11.6 mmol	633 mmol 2-propanol	<b>240</b>	93.6	88.5	94.5	S6
7	Cu-Ni/Al <sub>2</sub> O <sub>3</sub>	1 mmol	21.8 mmol 2-butanol	<b>150</b>	99	97	97.9	S7
8	Hf-ATMP	1 mmol	50 mmol 2-propanol	<b>150</b>	86	85.5	86	S8

**Table S2.** The effect of different silanes on the conversion of EL to GVL

Silane name	Structure	EL conv. (%)	GVL yield (%)	GVL sel. (%)
Trimethoxysilane	(MeO) <sub>3</sub> SiH	62	26	42
Triethoxysilane	(EtO) <sub>3</sub> SiH	92	68	74
Phenylsilane	PhSiH <sub>3</sub>	95	79	83
Diphenylsilane	Ph <sub>2</sub> SiH <sub>2</sub>	90	82	91
Triethylsilane	Et <sub>3</sub> SiH	23	11	48
Heptamethyltrisiloxane	Me <sub>3</sub> Si-O-MeSiH-O-SiMe <sub>3</sub>	66	61	92
Tetramethyldisiloxane	Me <sub>2</sub> SiH-O-HSiMe <sub>2</sub>	57	53	93
Polymethylhydrosiloxane (PMHS)	Me <sub>3</sub> Si-O-(MeSiH-O) <sub>n</sub> -SiMe <sub>3</sub>	94	91	97

Reaction conditions: 0.5 mmol EL, 15 mg KF, 0.1 g silane, 2.0 mL DMF, 80 °C, 7 h.

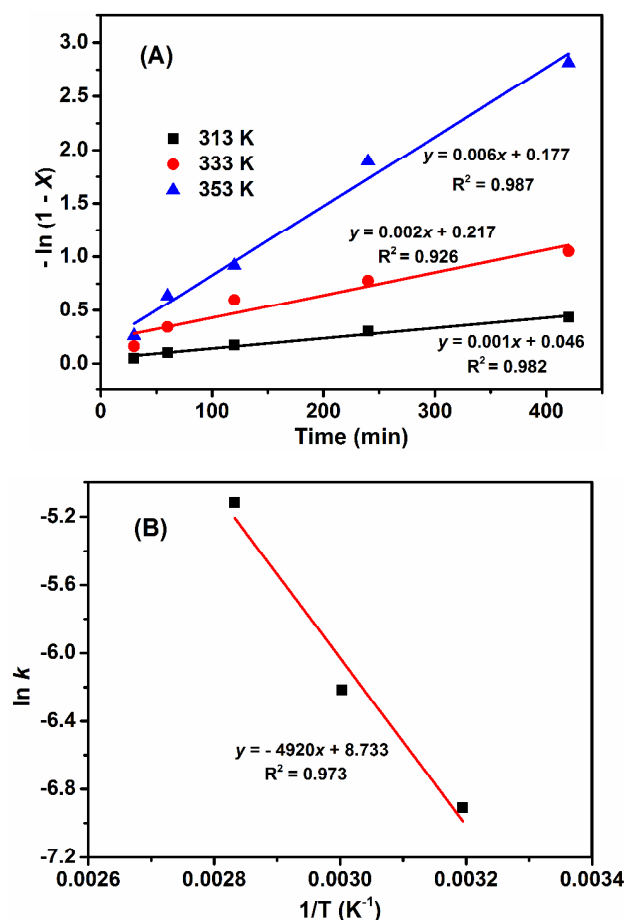
The relative activity of different silanes for the conversion of EL to GVL seems to be depended on the stabilization possibility of each silicon atom.

**Table S3.** Surface area, volume and porosity of Fresh and reused KF

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g) <sup>[a]</sup>	S <sub>micro</sub> (m <sup>2</sup> /g) <sup>[b]</sup>	S <sub>meso</sub> (m <sup>2</sup> /g) <sup>[c]</sup>	V <sub>pore</sub> (cm <sup>3</sup> /g) <sup>[d]</sup>	D <sub>mean</sub> (nm) <sup>[e]</sup>
Fresh KF	37	26	11	0.05	4.7
Reused KF	125	50	75	0.29	8.4

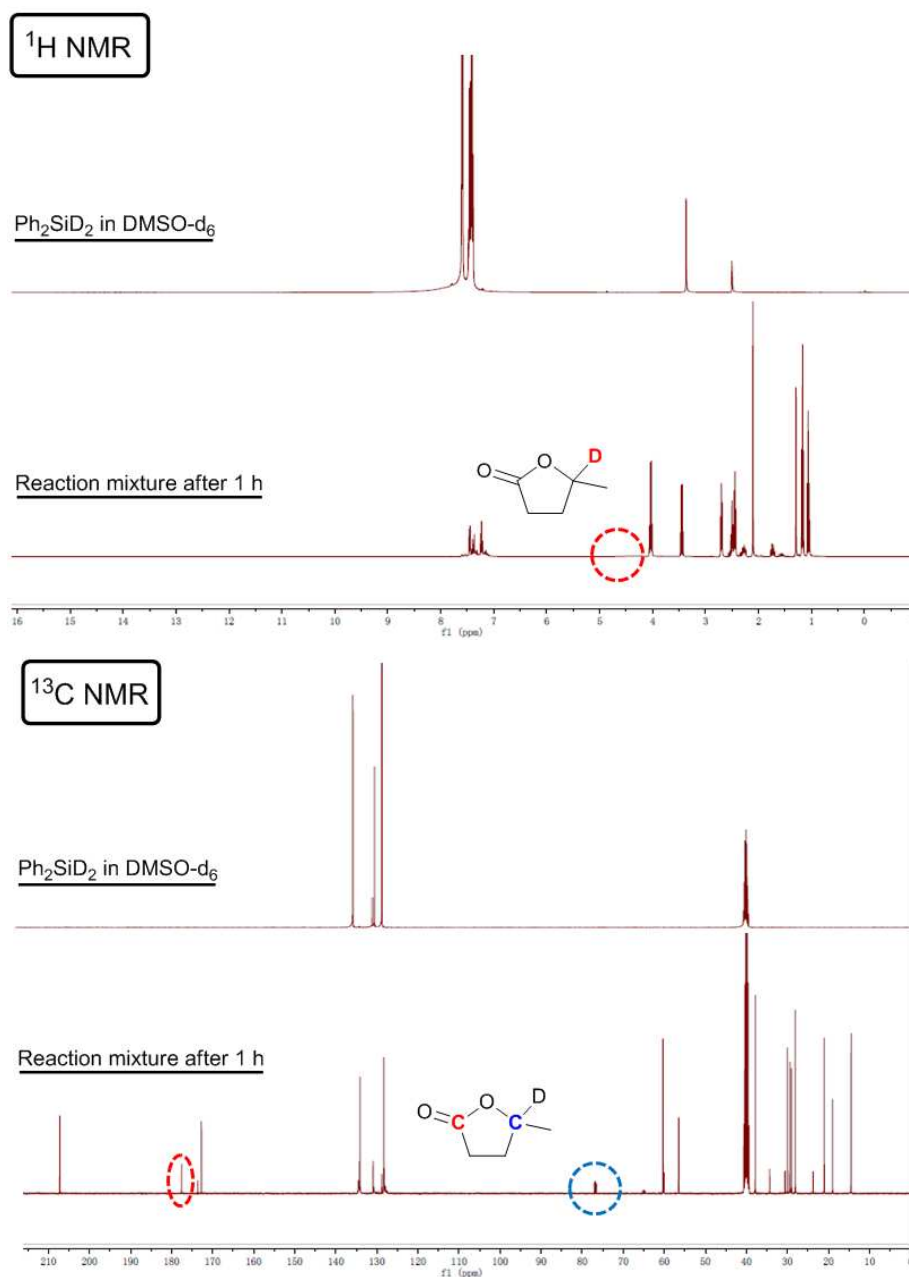
<sup>[a]</sup> BET surface area was obtained from N<sub>2</sub> adsorption isotherm. <sup>[b]</sup> Surface area of micropore was gained from the t-plot method. <sup>[c]</sup> Surface area of mesopore = (S<sub>BET</sub> - S<sub>micro</sub>). <sup>[d]</sup> Volume of pores was estimated from BJH Adsorption cumulative volume of pores. <sup>[e]</sup> Average pore size was estimated from the adsorption average pore diameter.

N<sub>2</sub> adsorption-desorption shows that the reused KF catalyst possesses an enhanced average pore diameter (8.4 nm), surface area (125 m<sup>2</sup>/g) and pore volume (0.29 cm<sup>3</sup>/g), as compared with the fresh KF (Table S3), which can be ascribed to the formation of PMHS-based resin.

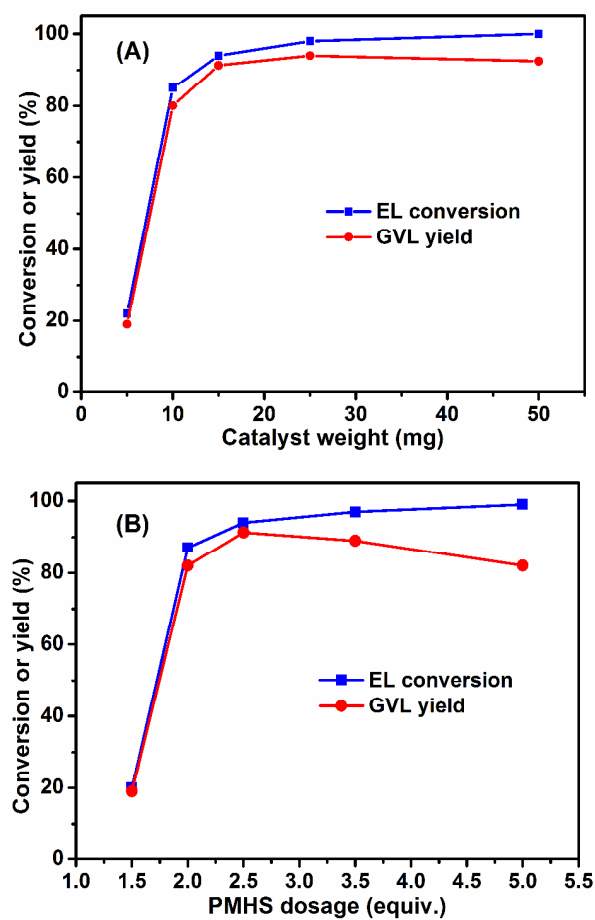


**Figure S1.** (A) Kinetic profiles and (B) Arrhenius plot of KF-catalyzed conversion of EL to GVL; Reaction conditions: 0.5 mmol EL, 2.5 equiv. PMHS, 15 mg KF, and 2.0 mL DMF

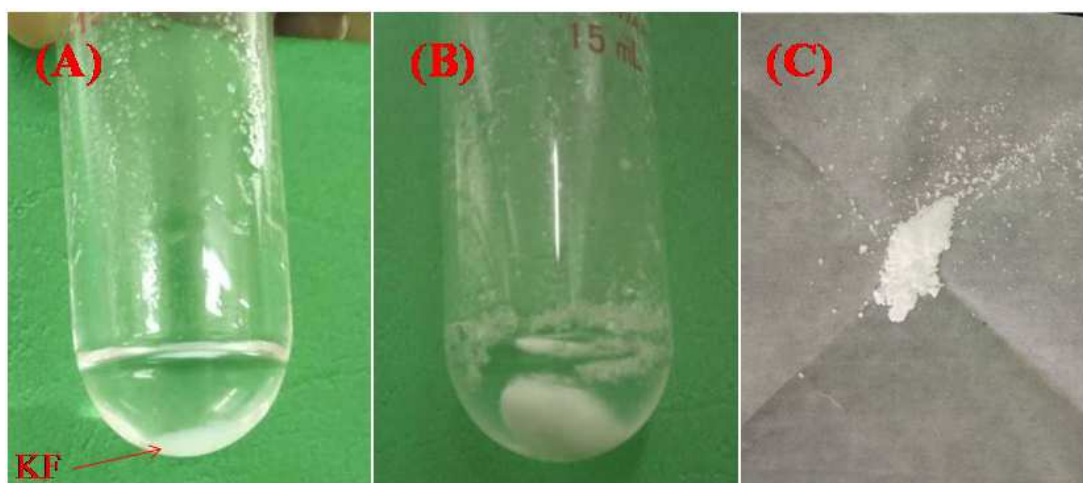
Assumed that EL-to-GVL conversion is a 1<sup>st</sup> order process, the reaction rate could be expressed as follows:  $d[\text{GVL}]/dt = k[\text{EL}] = d[\text{EL}]/dt$ ; after the subsequent integral calculation, the original equation would further become:  $-\ln(1 - X) = kt + C$ . Values of  $-\ln(1 - X)$  (where  $X$  is conversion of EL) were plotted against reaction time ( $t$ ) at different temperatures in order to obtain rate constants ( $k$ ):  $k(80\text{ }^\circ\text{C}) = 0.006\text{ min}^{-1} > k(60\text{ }^\circ\text{C}) = 0.002\text{ min}^{-1} > k(40\text{ }^\circ\text{C}) = 0.001\text{ min}^{-1}$  (FigureS2A). Then the activation energy ( $E_a$ ) was calculated from rate constants by the Arrhenius equation:  $\ln k = -E_a/RT + \ln A$  (FigureS2B), and found to be 40.9 kJ/mol.



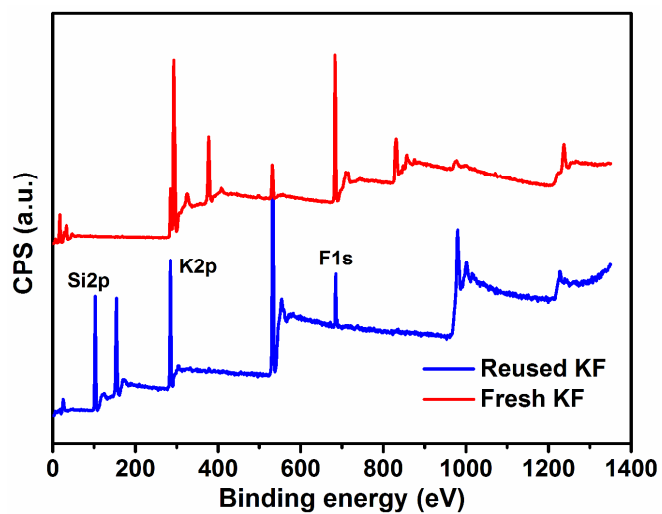
**Figure S2.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of EL-to-GVL conversion in DMSO-d<sub>6</sub>; Reaction conditions: 0.5 mmol EL, 2.5 equiv. Ph<sub>2</sub>SiD<sub>2</sub>, 15 mg KF, 2.0 mL DMSO-d<sub>6</sub>, 80 °C for 1 h



**Figure S3.** (A) The effect of catalyst weight and (B) PMHS dosage on the conversion of EL to GVL; Reaction conditions: 0.5 mmol EL, 2.5 equiv. (or variable) PMHS, 15 mg (or variable) KF, 2.0 mL DMF, 80 °C for 7 h

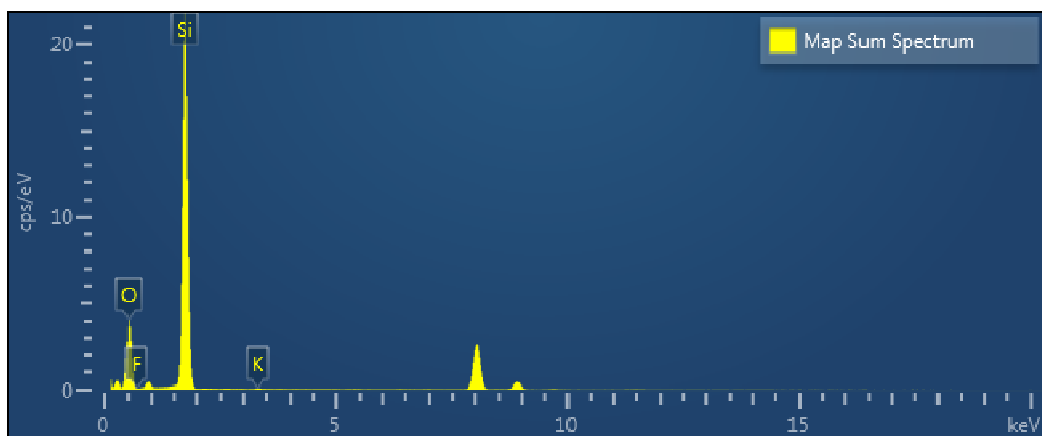


**Figure S4.** Photos of the KF-catalyzed reaction: (A) initial reaction solution, (B) after the reaction, and (C) the recovered silicone resin containing F species



**Figure S5.** XPS spectra of fresh and recovered KF after six cycles





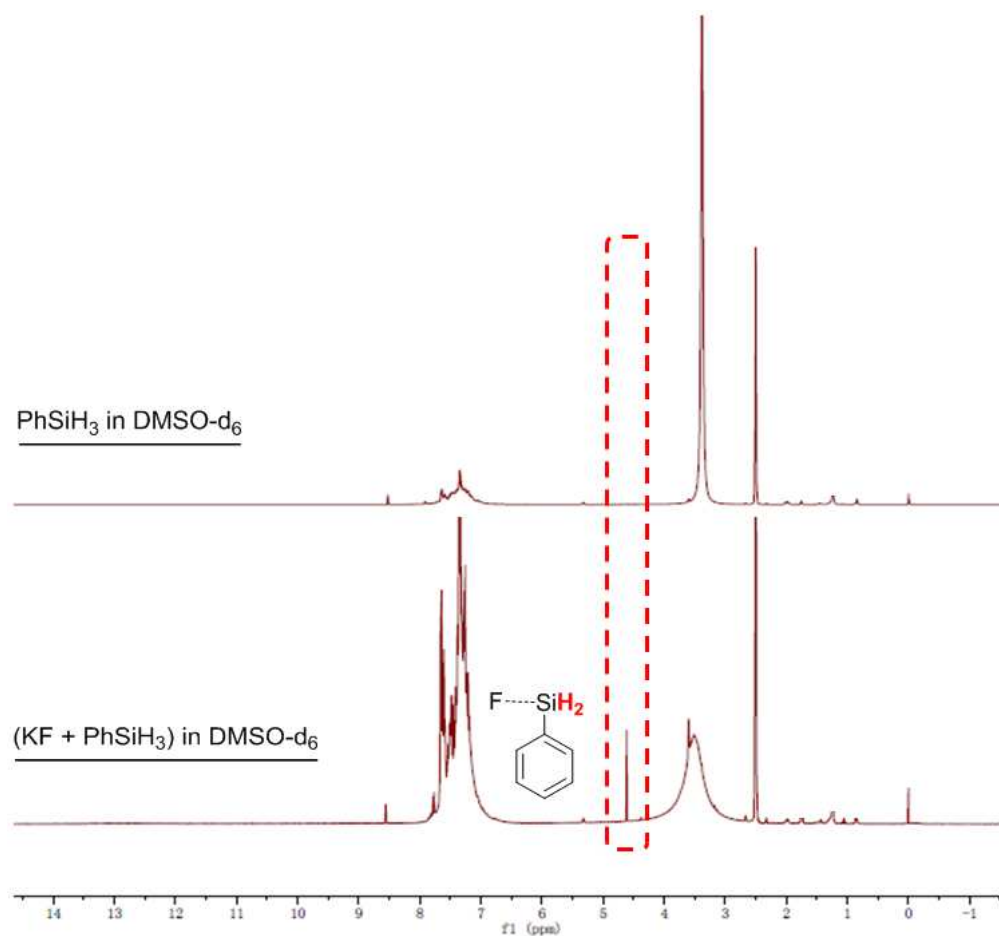
Element	Line Type	k factor	Absorption Correction	Wt%
O	K series	1.86867	1.00	<b>17.87</b>
F	K series	1.75182	1.00	<b>5.06</b>
Si	K series	1.00000	1.00	<b>75.40</b>
K	K series	0.96973	1.00	<b>1.67</b>
Total:				<b>100.00</b>

**Figure S6.** EDX spectrum and results of recovered KF after six cycles

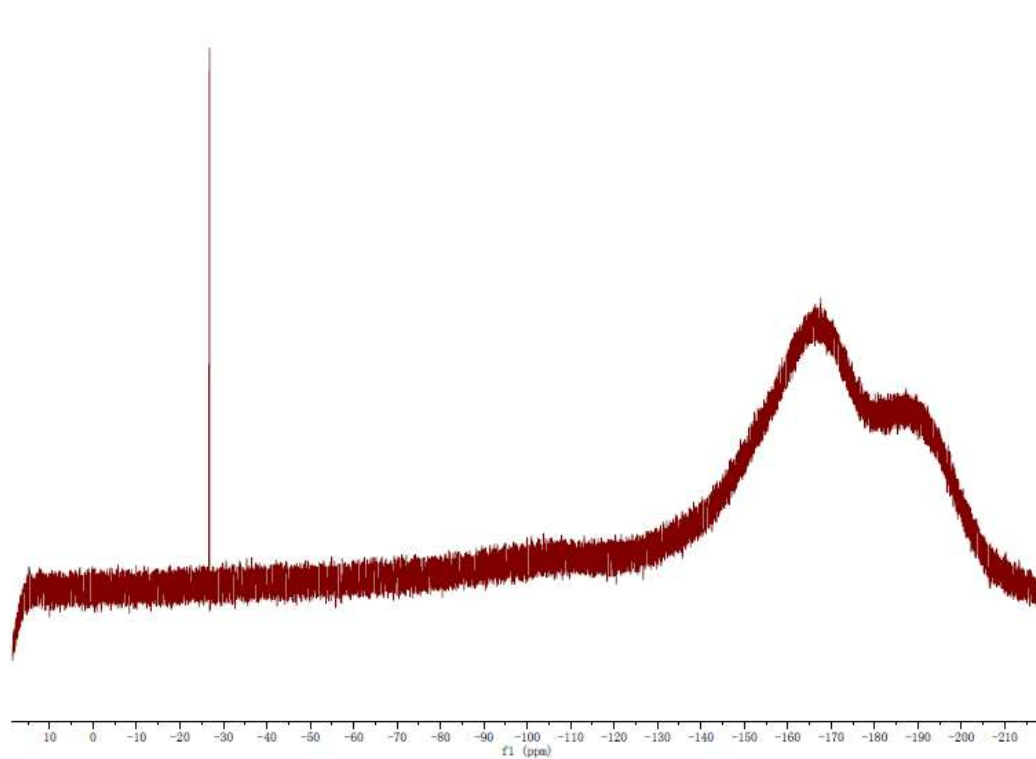
**Weight of F in the fresh catalyst** =  $15 \text{ mg} \times 19/58 = 4.91 \text{ mg}$

**Weight of F in the recovered catalyst after six cycles** =  $90 \text{ mg} \times 5.06 \% = 4.55 \text{ mg}$

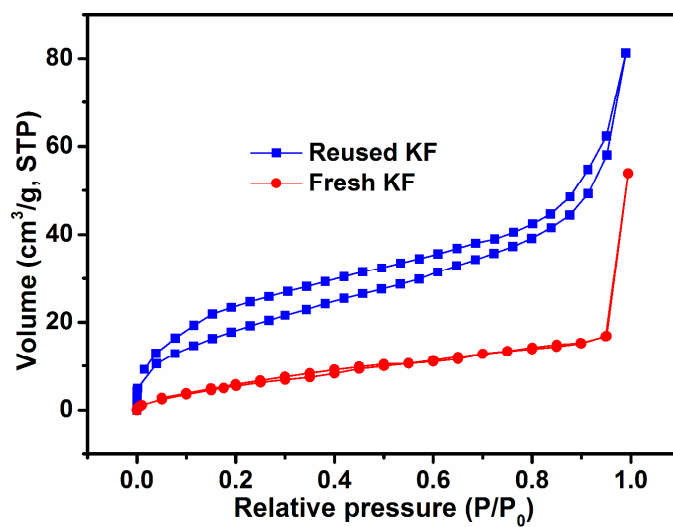
These results showed the little leaching of fluoride into solution during six consecutive cycles, which was consistent with the results of ICP-OES.



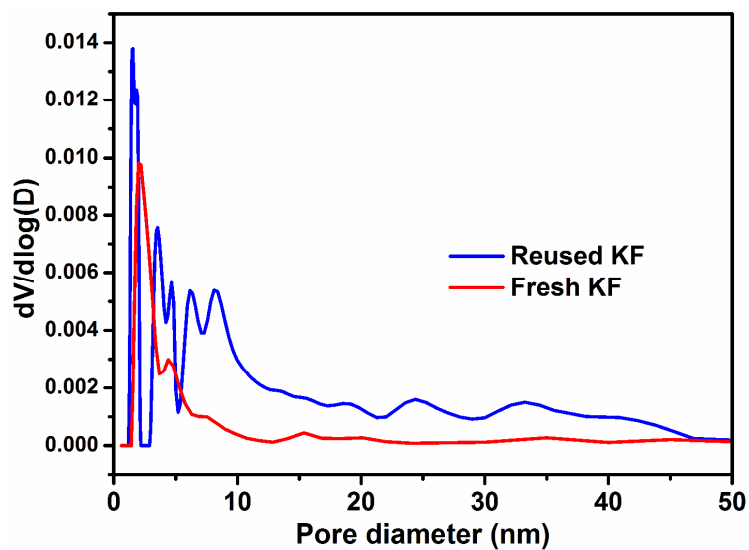
**Figure S7.**  $^1\text{H}$  NMR spectra of PhSiH<sub>3</sub> in DMSO-d<sub>6</sub> without or with KF stirring for 10 min



**Figure S8.**  $^{19}\text{F}$  NMR spectrum of  $\text{PhSiH}_3$  in  $\text{DMSO-d}_6$  with KF stirring for 10 min



**Figure S9.** N<sub>2</sub> adsorption-desorption isotherms of fresh and recovered KF after six cycles



**Figure S10.** Pore size distribution of fresh and recovered KF after six cycles

## References:

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