Electronic Supplementary Information

Controlled Synthesis of High Quality Scandium-based Nanocrystals as Promising Recyclable Catalysts for Silylcyanation Reaction

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Experimental

Chemicals
Oleylamine (OM, 70%) and oleic acid (OA, 90%) were purchased from Aldrich and used without further purification. The scandium (III) oxide (Sc2O3, 99.9%), sodium trifluoroacetate (CF3COONa, 99.9%), potassium trifluoroacetate (CF3COOK, 99.9%) were purchased from Alfa Aesar and used as received. The trifluoroacetic acid (CF3COOH, >99.0%) was obtained from TCI. Aromatic aldehydes and cyanotrimethylsilane (TMSCN) were obtained from Alfa Aesar and used without further purification. Absolute ethanol, methanol, cyclohexane and acetonitrile were analytical reagent grade, and acetonitrile was distilled before use.

Synthesis of Sc(CF3COO)3
3 g of Sc2O3 was added into 10 mL of DI water in a flask (50 mL) at room temperature. 6 mL of CF3COOH was added into the slurry with magnetic stirring and the mixture was heated to 80 °C. Then, around every 6 hours later, 1 mL of CF3COOH was added, till the solution was totally transparent. After filtration, the mixture was transferred into a crucible and dried in air at 100 °C overnight.

Synthesis of NaScF4 and KSc2F7 nanocrystals
The synthesis of NaScF4 and KSc2F7 nanocrystals was established via the modified thermal decomposition method. A given amount of CF3COONa (or CF3COOK) and Sc(CF3COO)3 (0.3 mmol) were added into 10 mmol of OA/OM (the ratio of OA:OM was changed from 1:1 to 4:1) in a three-necked flask (50 mL). The mixture was heated to 120 °C to remove dissolved gas, water and organic impurities with low boiling points, with vigorous magnetic stirring under vacuum for 30 min, and thus forming a transparent liquid. Then the mixture was heated to a certain temperature within the range of 270-330 °C rapidly, and kept at the temperature for 30-120 min under a N2 atmosphere. After the reaction was completed and cooled to room temperature, a proper amount of ethanol was added into the mixture. The consequent mixture was separated by centrifugation at 9000 r/min and the products were collected. The products were washed ~3 times with the mixture of ethanol and a small amount of cyclohexane, and dried in a vacuum drying oven at 60 °C overnight.

General experimental of catalysis
All manipulations with air-sensitive reagents were carried out under a dry nitrogen atmosphere. Commercial reagents were used as received without further purification unless otherwise stated. All solvents used were dried using standard, published methods and were distilled before use. NaScF4 and KSc2F7 nanocrystals were used after surface modification.

As for the synthesis of 1b, to a suspension of NaScF4/KSc2F7 (3.6 mg/6.6 mg,
0.025 mmol) in freshly distilled acetonitrile (1 mL) was added cyanotrimethylsilane (TMSCN) (131.2 μL, 1.2 mmol) and Anisic aldehyde (59.0 μL, 0.5 mmol). The reaction was stirred at room temperature until the reaction was complete, as indicated by ¹H-NMR analysis. The reaction mixture was centrifuged, and the upper supernatant was evaporated to get the product of 1b (the conversion ratio is ~99%).

**Instrumentation**

Powder X-ray diffraction (XRD) patterns were recorded on D/MAX-RB SMARTLAB(3) diffractometer (Rigaku, Japan) at the scanning rate of 10 °min⁻¹ with a slit of (1/2)°, using Cu-Kα radiation (λ = 1.5418 Å), and the operating voltage was 40 kV with operating current of 30 mA. X-ray photoelectron spectroscopy (XPS) spectra were acquired with K-Alpha+ X-ray photoelectron spectrometer (Thermo Fisher, the USA). Transmission electron microscopy (TEM) images were acquired with a Hitachi HT-7700 transmission electron microscope (Japan) operated at 100 kV. High-resolution TEM (HRTEM) micrographs were obtained with a Philips Tecnai F20 FEG-TEM (The USA) operated at 200 kV. Samples for TEM analysis were prepared on amorphous carbon coated copper grids by drying a drop of dispersion liquid of nanocrystals in cyclohexane. Infrared spectra were recorded on a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer (Thermo Fisher, the USA). Thermogravimetry (TG) curves were recorded on TGA 4000 thermogravimetric analyzer (PerkinElmer, the USA). Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance-400 spectrometer (the USA) and chemical shifts (δ) were reported in parts per million (ppm). ¹H-NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ¹³C-NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. The specific surface areas and pore sizes were estimated with Autosorb-iQ-C automated physisorption and chemisorption analyzer (Quantachrome, the USA) and the assistance of Brunauer-Emmett-Teller (BET) method, by nitrogen adsorption at 77 K. Before the adsorption desorption measurements, the samples (after thermal treatment) were degassed at 453 K for 10 h. Atomic emission spectra (AES) data were tested on Plasma 1000 inductively coupled plasma atomic emission spectrometer (ICP-AES, NCS, China).
Controlled synthesis of high quality NaScF₄ nanocrystals

Fig. S1 TEM images of NaScF₄ nanocrystals obtained under different solvent ratio: (a) OA:OM = 1:1; (b) OA:OM = 2:1; (c) OA:OM = 3:1; (d) OA:OM = 4:1. The reactions are conducted of 0.3 mmol CF₃COONa and 0.3 mmol Sc(CF₃COO)₃ in the solvent of OA and OM (10 mmol in total) at 310 °C for 1 h.

The ratio of OA and OM. With the increase of the proportion of OA, from OA:OM = 1:1 to 4:1, the morphology became uniform gradually (Fig. S1a, b and c) and then disordered (Fig. S1d). It can be easily noticed that the optimum ratio of OA and OM for synthesis is 3:1.
Fig. S2 TEM images of NaScF₄ nanocrystals obtained at different reaction temperature: (a) 270 °C; (b) 290 °C; (c) 310 °C; (d) 330 °C; The reactions are conducted of 0.3 mmol CF₃COONa and 0.3 mmol Sc(CF₃COO)₃ in the solvent of OA:OM = 3:1 (10 mmol in total) for 1 h.

**Reaction temperature.** As showed in Fig. S2, nanocrystals obtained at lower temperatures were with smaller sizes (Fig. S2a and b). When synthesized at 310 °C, the nanocrystals had uniform morphologies and larger sizes (Fig. S2c). Further elevating the temperature, the nanocrystals became non-uniform (Fig. S2d). Therefore, the temperature which is not higher than 310 °C is the optimum temperature for synthesis.
Fig. S3 TEM images of NaScF$_4$ nanocrystals obtained at different reaction time: (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min. The reactions are conducted of 0.3 mmol CF$_3$COONa and 0.3 mmol Sc(CF$_3$COO)$_3$ in the solvent of OA:OM = 3:1 (10 mmol in total) at 310 °C.

**Reaction time.** TEM images of nanocrystals obtained at different reaction time demonstrate the growing process of NaScF$_4$ nanocrystals, as shown in Fig. S3. With
the synthesis continued from the beginning to 60 min (Fig. S3a to c), the square-like nanocrystals formed gradually. Further prolonging the reaction time, the nanocrystals were getting non-uniform (Fig. S3d) and even aggregation (Fig. S3e). Therefore, 60 min is the optimum reaction time for synthesis.
Fig. S4 TEM images of KSc$_2$F$_7$ nanocrystals obtained under different solvent ratio: (a) OA = 10 mmol; (b) OA:OM = 1:1; (c) OA:OM = 2:1; (d) OA:OM = 3:1; (e) OA:OM = 4:1. The reactions are conducted of 0.3 mmol CF$_3$COOK and 0.3 mmol Sc(CF$_3$COO)$_3$, in 10 mmol OA and OM in total, at 310 °C for 1 h.
The ratio of OA and OM. The nanocrystals synthesized in pure OA were messy (Fig. S4a). With the increase of the proportion of OA from 1:1 to 3:1, the size and morphology was getting monodisperse (Fig. S4b, c and d). Further increasing the amount of OA, the as-obtained products were severely aggregated and non-shaped (Fig. S4e). Hence, the optimum ratio of OA and OM for synthesis is 3:1.

![TEM images of KSc2F7 nanorods obtained at different reaction temperature: (a) 270 °C; (b) 290 °C; (c) 310 °C; (d) 330 °C; The reactions are conducted of 0.3 mmol CF3COOK and 0.3 mmol Sc(CF3COO)3 in the solvent of OA:OM = 3:1 (10 mmol in total) for 1 h.]](image)

Reaction temperature. As showed in Fig. S5, when the temperatures were low, nanocrystals were non-uniform in sizes and morphologies (Fig. S5a and b). Nanocrystals obtained at 310 °C had relatively uniform morphologies and sizes (Fig. S5c), which was the optimum temperature for synthesis. Further increasing the reaction temperature will result in nonuniform nanocrystals with low yields (Fig. S5d).
**Fig. S6** TEM images of KSc$_2$F$_7$ nanocrystals obtained at different reaction time: (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min; (f) 150 min. The reactions are conducted of 0.3 mmol CF$_3$COOK and 0.3 mmol Sc(CF$_3$COO)$_3$ in the solvent of OA:OM = 3:1 (10 mmol in total) at 310 °C.
**Reaction time.** TEM images of nanocrystals obtained at different reaction time demonstrate the growing process of KSc$_2$F$_7$ nanocrystals, as shown in Fig. S6. From the beginning to 60 min (Fig. S6a to c), nanocrystals became uniform gradually. With the reaction continuing, the nano-products were non-uniform (Fig. S6d) and accompanied with the aggregations (Fig. S6e), even occurred the Ostwald ripening process (Fig. S6f). Therefore, the optimum reaction time is 60 min for the synthesis.

**XPS spectra of NaScF$_4$ nanocrystals**

![XPS spectra of NaScF$_4$ nanocrystals](image)

**Fig. S7** XPS spectra of NaScF$_4$ nanocrystals: (a) survey, (b) Na 1s, (c) F 1s, (d) O 1s.

The binding energy of Na, Sc and F element are noted in the XPS survey spectrum (Fig. S7a). In Fig. S7b, the peak located at 1072.0 eV attributed to the Na 1s spin orbital. And the peak located at 685.6 eV (Fig. S7c) represents the F 1s spin orbital. The peak located at 530.0 eV (Fig. S7f) indicates that a very small part of the sample is oxidized, and peaks located at 532.4 eV and 534.4 eV are the O 1s signals of adsorbed oxygen. XPS signals of the sample indicate that the sample is nearly pure NaScF$_4$, with a little oxidation.
Size distribution histogram of NaScF₄ nanocrystals.

Fig. S8 Size distribution histograms of NaScF₄ nanocrystals obtained at different reaction temperature: (a) 270 °C, (b) 290 °C and (c) 310 °C; As the histograms showed, the size is ~22 nm, ~29 nm and ~38 nm for the nanocrystals synthesized at 270 °C, 290 °C and 310 °C, respectively. The reactions are conducted of 0.3 mmol CF₃COONa and 0.3 mmol Sc(CF₃COO)₃, in the solvent of OA:OM = 3:1 (10 mmol in total) for 1 h.
Fig. S9 (a) XRD pattern of KSc$_2$F$_7$ nanocrystals; (b-f) XPS spectra of KSc$_2$F$_7$ nanocrystals: (b) survey, (c) K 2p, (d) Sc 2p, (e) F 1s, (f) O 1s.

X-ray diffraction (XRD) pattern of NaScF$_4$ nanocrystals (Fig. S9a) shows that all
diffraction peaks can be well matched with the orthorhombic phase KSc$_2$F$_7$ (JCPDS No. 34-0394) with calculated $a=10.643$ Å, $b=6.540$ Å, $c=4.030$ Å. The binding energy of K, Sc and F element is noted in the XPS survey spectrum (Fig. S9b). In Fig. S9c, the peaks located at 293.2 eV and 296.0 eV represent the K 2p$_{3/2}$ and K 2p$_{1/2}$ spin orbital, respectively. XPS spectrum of Sc in KSc$_2$F$_7$ (Fig. S9d) includes four peaks because of the appearance of satellite peaks, which arising from the high Sc content of the sample, and the usage of electron floodgun (Ref: A. D. Hamer, D. G. Tisley and R. A. Walton, *J. Inorg. Nucl. Chem.*, 1974, 36, 1771.). The state of Sc is still inferred from Sc 2p$_{3/2}$ and Sc 2p$_{1/2}$ signals of the sample, which are 402.2 eV and 405.0 eV and confirm the Sc in the sample is Sc$^{3+}$ state. The peak located at 685.3 eV (Fig. S9e) represents the F 1s spin orbital. The peak located at 529.7 eV (Fig. S9f) indicates that there is a very small part of the sample is oxidized, and peaks located at 532.0 eV and 534.8 eV are the O 1s signals of adsorbed oxygen. XPS signals of the sample indicate that the sample is nearly pure KSc$_2$F$_7$, with a little oxidation. (Ref: J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation: Eden Prairie, MN, 1992.).
As shown in above, the average size of KSc₂F₇ nanocrystals is of ~17 nm in width and ~240 nm in length.
Surface modification of NaScF₄ and KSc₂F₇ nanocrystals

![Fig. S11 TG curve of (a) NaScF₄ and (b) KSc₂F₇ nanocrystals; FT-IR spectrum of KSc₂F₇ nanocrystals (c) before and (d) after thermal treatment.]

The TG curve suggests that the weight of NaScF₄ nanocrystals is decreased fast around 330 ºC (Fig. S11a), whereas, KSc₂F₇ nanocrystals is around 310 ºC (Fig. S11b). The thermal treatment of hydrophobic nanocrystals is conducted at 500 ºC under the protection of Ar/H₂ for 1 h. The peaks located at 2922 cm⁻¹, 2852 cm⁻¹, 1548 cm⁻¹ and 1465 cm⁻¹ in FT-IR spectra of KSc₂F₇ nanocrystals before thermal treatment (Fig. S11c) indicate that there are also alkyl (2922 cm⁻¹ and 2852 cm⁻¹) and carboxyl (1548 cm⁻¹ and 1465 cm⁻¹) groups on the surface. After thermal treatment, the characteristic peaks (2922 cm⁻¹ and 2852 cm⁻¹) disappear (Fig. S11d), indicating that the alkyl and carboxyl groups on the surface are removed.
$^1$H-NMR spectra and $^{13}$C-NMR spectra of the products

![1H-NMR and 13C-NMR spectra of the products](image)

Fig. S12 $^1$H-NMR of 1b in CDCl$_3$. Ref: S. T. Kadam and S. Kim, B. Korean Chem. Soc., 2008, 29, 1320.

Fig. S13 $^{13}$C-NMR of 1b in CDCl$_3$. Ref: A. Baeza, C. Najera, M. de Gracia Retamosa and J. M. Sansano, Synthesis, 2005, 16, 2787.
Fig. S14 $^1$H-NMR of 2b in CDCl₃.

Fig. S15 $^{13}$C-NMR of 2b in CDCl₃.
**Fig. S16** $^1$H-NMR of 3b in CDCl$_3$.

**Fig. S17** $^{13}$C-NMR of 3b in CDCl$_3$. 

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Fig. S18 $^1$H-NMR of 4b in CDCl$_3$. Ref: H. Härle and J. C. Jochims, Chemische Berichte, 1986, 119, 1400.

Fig. S19 $^{13}$C-NMR of 4b in CDCl$_3$. Ref: A. Baeza, C. Najera, M. de Gracia Retamosa and J. M. Sansano, Synthesis, 2005, 16, 2787.
Fig. S20 $^1$H-NMR of 5b in CDCl$_3$. Ref: H. Härle and J. C. Jochims, Chemische Berichte, 1986, 119, 1400.

**Fig. S21** $^1$H-NMR of 6b in CDCl$_3$.

**Fig. S22** $^{13}$C-NMR of 6b in CDCl$_3$. 
**Fig. S23** $^1$H-NMR of $7b$ in CDCl$_3$. Ref: L. Mei, K. Yu Ping, L. Xiao Xuan, Y. Hao, H. Ke Liang and J. Ying, *Synthetic Commun.*, 2006, **36**, 2483.

$^{13}$C-NMR data of $7b$ is in Ref: L. Mei, K. Yu Ping, L. Xiao Xuan, Y. Hao, H. Ke Liang and J. Ying, *Synthetic Commun.*, 2006, **36**, 2483.

Fig. S26 $^1$H-NMR of 9b in CDCl$_3$. Ref: S. C. Georgea and S. Kim, B. Korean Chem. Soc., 2007, 28, 1167.

Fig. S27 $^{13}$C-NMR of 9b in CDCl$_3$. Ref: S. C. Georgea and S. Kim, B. Korean Chem. Soc., 2007, 28, 1167.


Fig. S32 $^1$H-NMR of 12b in CDCl$_3$.

Fig. S33 $^{13}$C-NMR of 12b in CDCl$_3$. 

Me – O – CN
                  OTMS

Me – O – CN
                  OTMS
Fig. S34 $^1$H-NMR of 13b in CDCl$_3$.

Fig. S35 $^{13}$C-NMR of 12b in CDCl$_3$. 
The comparison of catalytic reactivity

**Fig. S36** $^1$H-NMR of the conversion of p-anisaldehyde in CDCl$_3$, the experiment was carried out with 1% NaScF$_4$ loaded for 24 h, and the conversion is 58.8%.

**Fig. S37** $^1$H-NMR of the conversion of p-anisaldehyde in CDCl$_3$, the experiment was carried out with 1% KSc$_2$F$_7$ loaded for 24 h, and the conversion is 68.6%.
Fig. S38 ¹H-NMR of the conversion of p-anisaldehyde in CDCl₃, the experiment was carried out with 5% NaScF₄ (with the size of ~ 22 nm) loaded for 3 h, and the conversion is 52.4%.

Fig. S39 ¹H-NMR of the conversion of p-anisaldehyde in CDCl₃, the experiment was carried out with 5% NaScF₄ (with the size of ~ 29 nm) loaded for 3 h, and the conversion is 51.7%.
**Fig. S40** $^1$H-NMR of the conversion of p-anisaldehyde in CDCl₃, the experiment was carried out with 5% NaScF₄ (with the size of ~38 nm) loaded for 3 h, and the conversion is 66.6%.

**Fig. S41** $^1$H-NMR of the conversion of p-anisaldehyde in CDCl₃, the experiment was carried out with 5% bulk NaScF₄ loaded for 10 h, and the conversion is 6.5%.
Fig. S42 $^1$H-NMR of the conversion of p-anisaldehyde in CDCl$_3$, the experiment was carried out with 5% bulk KSc$_2$F$_7$ loaded for 10 h, and the conversion is 33.3%.

Fig. S43 $^1$H-NMR of the conversion of p-anisaldehyde in CDCl$_3$, the experiment was carried out with 5% bulk Sc$_2$O$_3$ (99.9%, purchased from Alfa Aesar and used as received) loaded for 10 h, and the conversion is 11.5%.
As shown in $^1$H-NMR spectra of Fig. S36 and Fig. S37, the two adjacent peaks are the shifts of H in MeO- group of p-anisaldehyde and 1b, respectively. The calculated conversion (from the integral of these two peaks) is 58.8% and 68.6% respectively, for 1% loading of NaScF$_4$ and KSc$_2$F$_7$. In Fig. S38, Fig. S39 and Fig. S40, the conversion is 52.4%, 51.7% and 66.6% for 3 h reaction and 5% loading of NaScF$_4$ nanocrystals with the size of ~22 nm, ~29 nm and ~ 38 nm, respectively. As for bulk fluorides, the catalytic reactivity is much lower: when experiments carried out with 5% bulk catalysts loaded for 10 h, the conversion of p-anisaldehyde is 6.5% for bulk NaScF$_4$ and 33.3% for bulk KSc$_2$F$_7$, which are much lower than nanocatalysts, as shown in Fig. S41 and Fig. S42. And the catalytic reactivity of bulk Sc$_2$O$_3$ is much lower than fluorides, as shown in Fig. S43. The conversions are also summarized in Table S1, in which we can easily notice the advantages of nano-sized catalysts, and the similar catalytic reactivity of NaScF$_4$ nanocrystals with different sizes. It’s worth to mention that the bulk Sc$_2$O$_3$ has very low catalytic reactivity, so we can ignore the tiny oxidation on the surface of the fluoride nanocrystals.

Table S1: Conversions of aromatic aldehydes substrates when using different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (%)</th>
<th>Reaction time (h)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaScF$_4$ (~38 nm)</td>
<td>1</td>
<td>24</td>
<td>58.8</td>
</tr>
<tr>
<td>KSc$_2$F$_7$</td>
<td>1</td>
<td>24</td>
<td>68.6</td>
</tr>
<tr>
<td>NaScF$_4$ (~22 nm)</td>
<td>5</td>
<td>3</td>
<td>52.4</td>
</tr>
<tr>
<td>NaScF$_4$ (~29 nm)</td>
<td>5</td>
<td>3</td>
<td>51.7</td>
</tr>
<tr>
<td>NaScF$_4$ (~38 nm)</td>
<td>5</td>
<td>3</td>
<td>66.6</td>
</tr>
<tr>
<td>NaScF$_4$ (~38 nm)</td>
<td>5</td>
<td>10</td>
<td>99</td>
</tr>
<tr>
<td>NaScF$_4$ (bulk)</td>
<td>5</td>
<td>10</td>
<td>6.5</td>
</tr>
<tr>
<td>KSc$_2$F$_7$ (bulk)</td>
<td>5</td>
<td>10</td>
<td>33.3</td>
</tr>
<tr>
<td>Sc$_2$O$_3$ (bulk)</td>
<td>5</td>
<td>10</td>
<td>11.5</td>
</tr>
</tbody>
</table>
The bulk catalysts (bulk NaScF$_4$ and KSc$_2$F$_7$) are prepared by direct thermal decomposition: 0.3 mmol NaCF$_3$COO and 0.3 mmol Sc(CF$_3$COO)$_3$, or 0.3 mmol KCF$_3$COO and 0.3 mmol Sc(CF$_3$COO)$_3$, are mixed by grinding, and then transferred into tube furnace, without any other reagent addition; the decomposition is conducted at 500 °C in N$_2$ atmosphere for 1h. After cooling down, the product powder is collected. The obtained bulk NaScF$_4$ and KSc$_2$F$_7$ are of irregular micro-sized bulks, with impurities in XRD patterns, as shown in Fig. S44.
**BET isotherms of NaScF₄ and KSc₂F₇ nanocatalysts**

**Fig. S45** BET isotherms of NaScF₄ nanocatalysts with the size of (a) ~22 nm, (b) ~29 nm and (c) ~38 nm; (d) BET isotherms of KSc₂F₇ nanocatalysts.

The N₂ adsorption-desorption isotherms of NaScF₄ nanocrystals (Fig. S45a, b and c) are of IV type, suggesting the sample is mesoporous and the adsorption can happen inside the catalyst. The N₂ adsorption-desorption isotherm of KSc₂F₇ nanocrystals (Fig. S45d) is almost of II type, and the inflection point in low P/P₀ area of the curve represents that the saturated adsorption capacity of monomolecular layer is small, and the convexity of the curve in this area indicates that the adsorption is relatively weak.
Table S2 BET surface area, pore volume and pore size of NaScF₄ and KSc₂F₇ nanocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaScF₄ (~22 nm)</td>
<td>14.5</td>
<td>0.03</td>
<td>7.66</td>
</tr>
<tr>
<td>NaScF₄ (~29 nm)</td>
<td>12.6</td>
<td>0.03</td>
<td>11.1</td>
</tr>
<tr>
<td>NaScF₄ (~38 nm)</td>
<td>20.5</td>
<td>0.04</td>
<td>8.8</td>
</tr>
<tr>
<td>KSc₂F₇</td>
<td>21.7</td>
<td>0.11</td>
<td>20.6</td>
</tr>
</tbody>
</table>

The BET analysis results (Table S2) show that for NaScF₄, the BET surface area, pore volume and pore size are all smaller than KSc₂F₇, maybe indicating that the property of NaScF₄ is the worse. However, the mesoporous structure of NaScF₄ nanocatalysts is more remarkable than KSc₂F₇ (shown in Fig. S45), meaning the adsorption can happen inside the NaScF₄ nanocatalysts more easily, which can improve the catalysis. So finally the catalyzing activities of NaScF₄ and KSc₂F₇ are similar.

Recyclability experiments

![Fig. S46 XRD patterns of (a) NaScF₄ and (b) KSc₂F₇ after catalysis.](image)

XRD patterns of NaScF₄ and KSc₂F₇ nanocrystals after catalysis (Fig. S46a, b) indicate that the crystalline structures of them are not changed after reaction.