

Supplementary material

Experimental:

All reagents and solvents employed were commercially available and used as supplied without further purification: 3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid), (99% Sigma-Aldrich); Scandium Chloride, ScCl_3 , (99% Strem Chemicals). For the synthesis of $\text{Sc}_2(\text{C}_4\text{O}_4)$, compound **I**, Typically, 0.227 g (1.5 mmol) of ScCl_3 and 0.257 g (2.25 mmol) of squaric acid are solved in 24 ml of water. The solution is placed into a Teflon lined stainless steel autoclave, and heated at 160 °C for 60 hours. After cooling to room temperature, the product is filtered and washed with distilled water and acetone. The purity of the bulk was checked by the comparison of the experimental X-ray powder pattern with that calculated from the single crystal data.

Thermogravimetric and differential thermal analyses (TGA-DTA) were performed using a SEIKO TG/DTA 320 apparatus in the temperature range between 25 and 800 °C in static air, with a heating rate of 5°C/min. PXRD pattern were measured with a Bruker D8 diffractometer equipped with position sensitive detector, with a step size = 0.03°, and a time of exposure of 0.2 s/step. For the variable temperature collection, the sample was heated at a rate of 5°C/min, and after 30 minutes of heating, the diffraction pattern was collected.

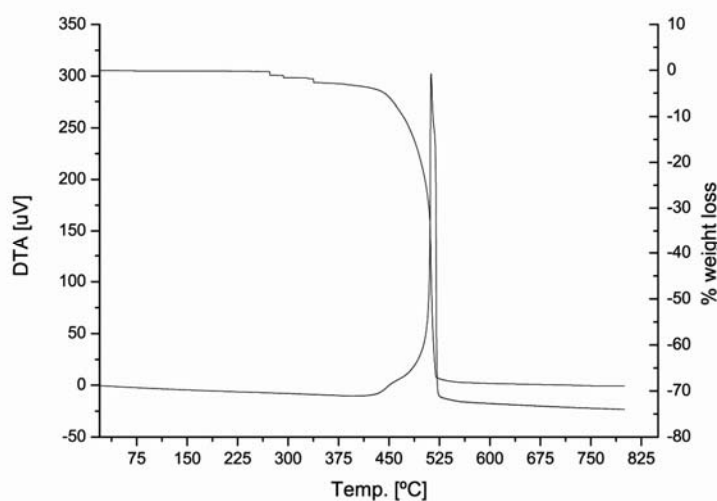


Figure S1: TG/DTA curves for compound I

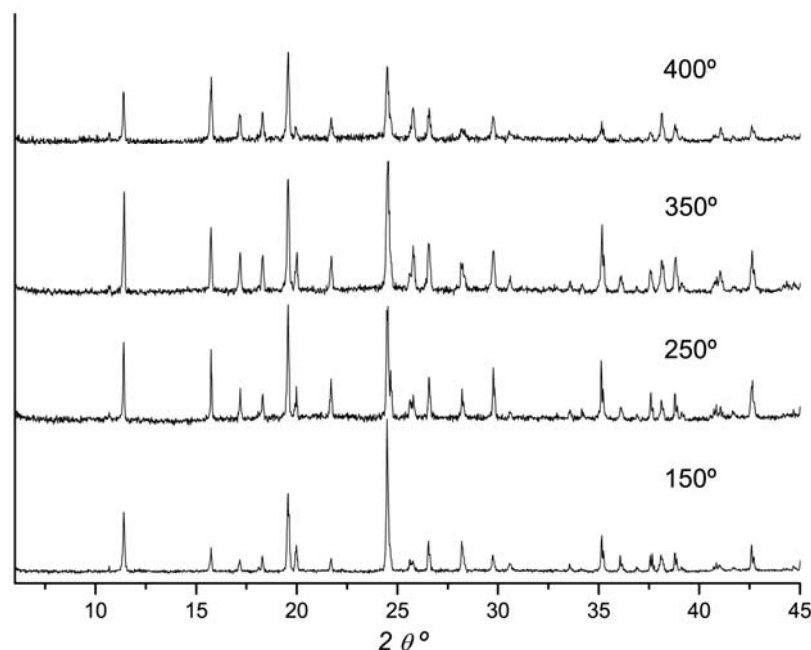


Figure S2: variable temperature X-ray powder patterns.

Single-crystal X-ray diffraction:

A prismatic crystal suitable for X-ray crystallography was selected under polarizing optical microscope and glued on a glass fiber for a single-crystal X-ray diffraction experiment. X-ray intensity data were collected in a Bruker SMART CCD diffractometer equipped with a normal focus, 2,4 kW sealed tube X-ray source (MoK α radiation = 0,71073 Å). Data were collected at room temperature over a hemisphere of the reciprocal space by a combination of three sets of exposures. Each exposure of 20 s covered 0.3° in ω . Unit cell dimensions were determined by a least-squares fit of 60 reflections with $I > 20\sigma(I)$. The structures were solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters for all non-hydrogen atoms. Calculations were carried out with SMART software for data collection and data reduction and SHELXTL for structure solution and refinement¹.

Table S1: Full crystallographic and refinement data table:

Identification code	compound1	
Empirical formula	C ₁₂ O ₁₂ Sc ₂	
Formula weight	426.04	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Trigonal, R-3c	
Unit cell dimensions	a = 15.2431(11) Å	α = 90°
	b = 15.2431(11) Å	β = 90°
	c = 20.579(2) Å	γ = 120°
Volume	4141.0(6) Å ³	
Z, Calculated density	12, 2.050 Mg/m ³	
Absorption coefficient	1.057 mm ⁻¹	
F(000)	2520	
Crystal size	0.30 x 0.10 x 0.10 mm	
Theta range for data collection	2.51 to 27.95 deg	
Limiting indices	-19<=h<=19	
	-18<=k<=19	
	-26<=l<=27	
Reflections collected / unique	10062 / 1086 [R(int) = 0.0427]	
Completeness to theta = 27.95°	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9017 and 0.7421	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1086 / 0 / 80	
Goodness-of-fit on F ²	1.142	
Final R indices [I>2σ(I)]	R ₁ = 0.0425, wR ₂ = 0.1178	
R indices (all data)	R ₁ = 0.0466, wR ₂ = 0.1205	
Largest diff. peak and hole	1.710 and -0.691 e·Å ⁻³	

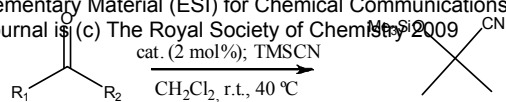
Catalytic details:

Interest in scandium has increased recently due to the successful use of its compounds in organic chemistry.² Along this line, scandium triflate has been introduced as a promising mild, powerful, and selective Lewis acid for a variety of functional group transformations.³ While most Lewis acids are decomposed or deactivated in the presence of water or protic solvents, Sc(OTf)₃, unlike other traditional Lewis acids, does not decompose or deactivate under aqueous workup conditions, and its recovery is often possible.^{3, 4} However, the most popular recycling methods for recovery of Sc(OTf)₃ are time-consuming and include the successive extraction of organic reaction mixture using deionized water.^{3,4} Therefore, there is much room for the design and preparation of new versions of scandium-based catalysts to circumvent this problem without considerable loss of its catalytic power.

The heterogenization of inorganic reagents and catalysts useful in organic reactions is a very important area in so-called “Green” or sustainable chemistry.⁵ One of the major goals is to facilitate easy separation of the final reaction mixture.⁶ This feature can lead to improved processing steps, better process economics, and finally, environmentally friendly industrial manufacturing. However, traditional heterogeneous and supported catalysts are rather limited in the nature of their active sites and, thus, the scope and reproducibility of reactions that they can accomplish.⁷ One way to overcome this uncertainty of the heterogeneous catalysts is to covalently incorporate an organic entity (flexible spacer) onto inorganic solids to create organic-inorganic hybrid (interphase) catalysts.⁸ In these types of solid catalysts the reactive center is highly mobile similar to homogeneous catalysts, and at the same time it has the advantage of recyclability. Recently, Kobayashi et al. have prepared a new polymer-supported scandium triflate which shows high activity in water.⁹ While this is the first example of polymer supported scandium, its preparation suffers from the drawbacks of the use of expensive starting organic polymers and reagents. One example of silica-based scandium(III) interphase catalysts has also been reported.¹⁰

Cyanosilylation of carbonyl compounds

In the course of preliminary studies of catalytic properties of Sc₂(C₄O₄)₃, we found that a small amount of Sc-catalyst (10 mg, 2 mol %) catalyzes efficient cyanosilylation of various types of carbonyl compounds (Table 1, Scheme 2).



Scheme S1: scheme reaction of cyanosilylation of carbonyls with TMSCN.

Cyanohydrin trimethylsilyl ethers are industrially valuable and important intermediates in the synthesis of cyanohydrins, β -amino alcohols, α -hydroxy acids, and other biologically active compounds.¹¹ They generally have been prepared by the reaction of a carbonyl with TMSCN in the presence of Lewis acids,¹² lanthanide salts,¹³ base catalysts,¹⁴ and solid base catalysts.¹⁵ However, many of the existing methods for this transformation have disadvantages such as prolonged reaction time,¹⁴ the use of non-recoverable catalysts,¹¹ and poor yields of the corresponding cyano trimethylsilyl ether especially in the case of ketones. Carbonyl compounds that were cyanosilylated in this way are benzaldehyde, acetophenone. Representative results are shown in Table S2.

Table S2. Cyanosilylation of Carbonyl Compounds Using TMSCN in the Presence of Scandium Catalyst^a

Entry	Substrate	t (h)	Conv. (%)
1		12	90
2	benzaldehyde	24	0 ^b
3		5 ^c	45 ^c
4		12	55
5	acetophenone	24	80

^aThe molar ratio of substrate/TMSCN/cat is 1:2:0.02. ^bThe reaction was performed in the absence of catalyst. ^cThe reaction was carried out in the presence of the solid catalyst for 5 h, and at that point the catalyst was filtered off and further stirring was done in the absence of catalyst for 3 h.

To show the catalyst's activity we have also performed cyanosilylation reaction of benzaldehyde using TMSCN in the absence of catalyst under other similar reaction parameters. The reaction did not progress even after 24 h (Table S1, entry 2).

When using a heterogeneous catalyst two points become increasingly crucial issues. The first is the possibility that some active metal migrates from the solid to liquid phase and that the leached Sc^{3+} would become responsible for a significant extent of the catalytic activity. To rule out the contribution of homogeneous catalysis in the results shown in Table S2, the reaction was carried out in the presence of the solid catalyst for 5 h, and at that point the catalyst was filtered off. The liquid filtrate was then allowed to react, but no significant conversion was observed after 3 h under the presented reaction

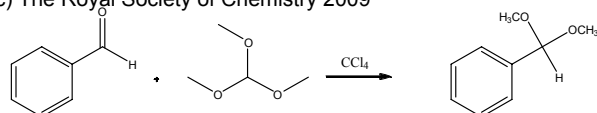
conditions (Table S2, entry 2). This clearly indicates that no active species were present in the supernatant. The second point is the deactivation and reusability of the new Sc-MOF as heterogeneous catalyst. It should be noticed that while most Lewis acids are decomposed or deactivated in the presence of protic solvents, the new heterogenized scandium catalyst is stable both in water and organic solvents and could be easily recovered and reused for at least 3 cycles without loss of yields of products. Recycling experiments were examined for the cyanosilylation of benzaldehyde. Thus, after the first run, which gave the corresponding cyanosilyl ether in 95% yield, after recovery the catalyst was subjected to a second cyanosilylation reaction from which it gave the cyanosilyl ether in 98% yield; the average chemical yield for 3 consecutive runs was 96%, which clearly demonstrates the practical recyclability of this catalyst.

Typical Procedure for Acetophenone Cyanosilylation: A 10-mL double wall Schlenk flask was charged with the catalyst (ca. 10 mg, 0.016 mmol, 2.0 mol% vs. acetophenone), THF (1 mL), and acetophenone (94 μ L, 0.81 mmol). A solution of trimethylsilyl cyanide (TMSCN) (216 μ L, 1.62 mmol), in THF was then added dropwise. The reaction mixture was heated to 40 °C. After 12 h, the reaction was quenched.

Acetalization of aldehydes

It was also shown that **I** is an active and selective catalyst for acetalization of aldehydes (Scheme S2, figure S3, table S3). The reaction of benzaldehyde with trimethyl orthoformate (TMOF) proceeds efficiently, and the total conversion to dimethyl acetal is obtained in a short reaction time (1 h) and under mild conditions (60°C), using the new Sc-MOF (5 mol%) as catalyst. When a more hindered substrate is employed, as it is of α -methyl benzeneacetaldehyde, longer reaction times are required, and a conversion of ca 80 % is reached after 12 hours.

It is noticed that while most Lewis acids are decomposed or deactivated in the presence of water, the new heterogeneous Lewis catalyst is stable both in water and organic solvents and could be easily recovered by filtration and reused at least in four cycles without loss of yield or selectivity. Geometrical constraints do not allow the reactants to diffuse inside the pores of the catalyst and only the external surface area of this material becomes available to the reactants.



Scheme S2: Scheme reaction of acetalization of aldehydes using TMOF

Table S3. Acetalization of Carbonyl Compounds in the Presence of Scandium Catalysts.^a

Catalyst	benzaldehyde		α -methyl benzeneacetaldehyde	
	t (h)	Conv. (%)	t (h)	Conv. (%)
$\text{Sc}_2(\text{C}_4\text{O}_4)$ (compound I)	1	100	12	78
$\text{Sc}_2(\text{OOCCH}_2\text{H}_4\text{COO})_{2.5}(\text{OH})^{16}$	4	70	12	65

^a T = 60 °C, 5 mol% catalyst

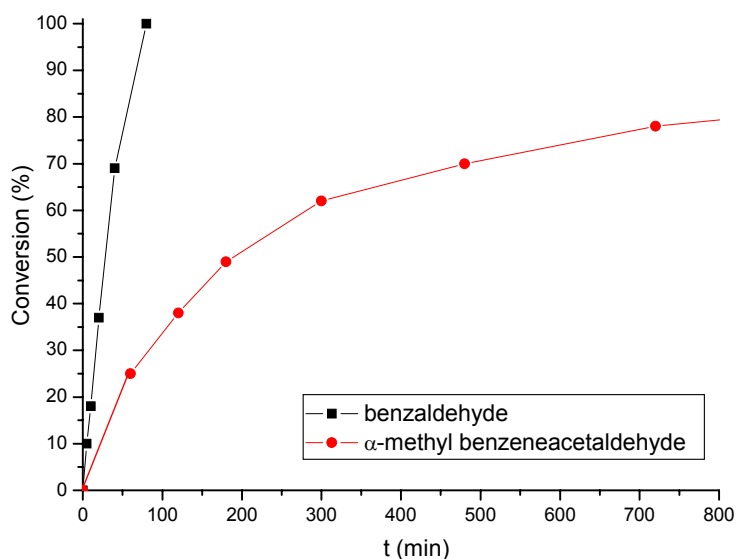


Figure S3: acetalization of aldehydes employing the $\text{Sc}_2(\text{C}_4\text{O}_4)_3$ compound as heterogeneous catalyst.

¹ Software for the SMART System V5.04 and SHELXTL V 5.1, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1998.

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