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Electronic Supplementary Information for

**A novel route for preparation of Mn-containing hollow framework TS-
1, and its selective allylic oxidation of cyclohexene**

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1. Experimental

1.1. Synthesis of the catalytic materials

First, solid titanium-containing MFI-Type zeolite (TS-1) was prepared hydrothermally through following the procedure reported in the literatures.¹ Tetraethyl orthosilicate (TEOS), titanium butoxide (TBOT) and tetrapropylammonium hydroxide (TPAOH, 10%) were used as silica source, titanium source and the template, respectively. The preparation procedure was as follows. 0.8 mol of TEOS was added dropwise into a pre-prepared basic solution composed of TPAOH (0.2 mol) and distilled water (12.5 mol) under vigorous stirring. The solution was kept for stirring for 1 h after the addition of TEOS. A solution composed of 0.03 mol of TBOT and 0.9 mol of anhydrous isopropyl alcohol was then slowly added into the above solution under vigorous stirring. The obtained mixture was heated to 80 °C and kept for stirring for 2 h to remove the alcohol. After having cooled to room temperature, the synthesis solution was transferred to a Teflon-lined stainless steel autoclave and crystallized at 170 °C for 3 days. The product obtained was filtered, washed with distilled water, dried at 120 °C and finally calcined at 500 °C for 10 h. Second, the hollow-structured titanium-containing MFI-type zeolite (HTS-1) was obtained according to a literature method.² The previously obtained traditional TS-1 was treated with H₂SO₄ solution with a weight ratio of the TS-1:H₂SO₄:water = 10:1.0:140 for 3 h at room temperature, and the acid-treated solid TS-1 dispersed in TPAOH solution in a weight ratio of 10 TS-1:1.5 TPAOH:125 H₂O under vigorous stirring for 6 h. The well-mixed mixture was then recrystallized at 170 °C for 3 days under static conditions. The solid product was filtered, washed, dried and finally calcined at 500 °C for 10 h.

The manganese-containing hollow TS-1 catalyst was prepared by a novel method, desired mass of manganese(III)-acetylacetonate (1-7 wt.% of manganese in the final product) was fully dissolved in 20 ml ethanol. This solution was added dropwise into half of the aforementioned acid-treated mixture containing TPAOH before being placed into the autoclave and stirred for 6 h to obtain a well-dissolved manganese-containing mixture. The same hydrothermal treatment was then performed as aforementioned. The obtained catalysts were denoted as xMTS-1, where x as the metal wt.%.

1.2. Catalyst characterization

XRD data were collected on a Bruker Advanced D8 diffractometer using Cu K α radiation ($\lambda=1.542 \text{ \AA}$) at a beam

voltage of 40 kV and a 45 mA beam current. FT-IR spectra were taken from pressed pellets with KBr diluted samples on a PerkinElmer Spectrum 100 spectrometer. CaF₂ windows were used; dry N₂ was purged into the cell and passed through to eliminate all the moisture and CO₂ absorbed on the samples before each test. The UV-visible diffuse reflectance spectra of the samples were recorded from 190 to 800 nm on a Varian-Cary 5000 spectrometer using BaSO₄ as a reference. The Raman spectra were taken on a Renishaw 2000 Raman microscope, which includes an optical microscope and a CCD camera for multichannel detection. A high-resolution transmission electron microscope (HRTEM) was used to characterize the crystallized structure and the morphology of the samples by using a JEOL-JEM-2100 instrument with an accelerating voltage of 200 kV. X-ray Photoelectron Spectra (XPS) of samples were collected on an Imaging Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.) using Al Ka radiation (1486.7 eV). The energy was calibrated with a C 1s peak (BE = 284.8 eV). XPS Advantage software was used for curve fitting. The adsorption and desorption isotherms were measured on a Tristar 3000 sorptometer instrument. Samples were degassed at 500 °C for 6 h prior to each measurement in order to remove water and other adsorbed species. The isotherms of adsorption and desorption were measured at relative pressures (P/P₀) from 0.001 to 0.995 and from 0.995 to 0.001, respectively. The surface area was determined by Brunauer-Emmett-Teller (BET) equation, while total pore volume was measured at P/P₀ = 0.99. The pore size distributions were determined from the adsorption branch of the isotherms using BET method.

1.3. Catalytic Test

Selective allylic oxidation of cyclohexene was used as a probe reaction to detect the oxidation active sites of the MTS-1. The reaction was carried out in a Teflon-lined stainless steel autoclave of 100 ml capacity, equipped with a magnetic stirrer. In a typical experiment, cyclohexene (9.8 g) was mixed with certain quality catalyst and then raised to specified temperature. Oxygen was then charged into the reactor to the desired pressure and reaction was started by adjusting stirrer speed to 800 rpm. After reaction, the mixture was cooled down, dissolved in acetone and filtered. The reaction products were carried out by a gas chromatography using chlorobenzene as the internal standard.

Table S1 The Ti and Mn contents, BET surface area, pore volume and pore size samples.

Sample	Ti ^a (wt%)	Mn ^a (wt%)	S _{BET} ^b (m ² /g)	V _p (cm ³ /g)	Pore size(nm)
TS-1	1.65	-	323	0.233	0.53
HTS-1	1.63	-	341	0.258	3.13
1% MTS-1	1.58	0.91	355	0.270	3.12
5% MTS-1	1.54	4.12	335	0.259	3.10

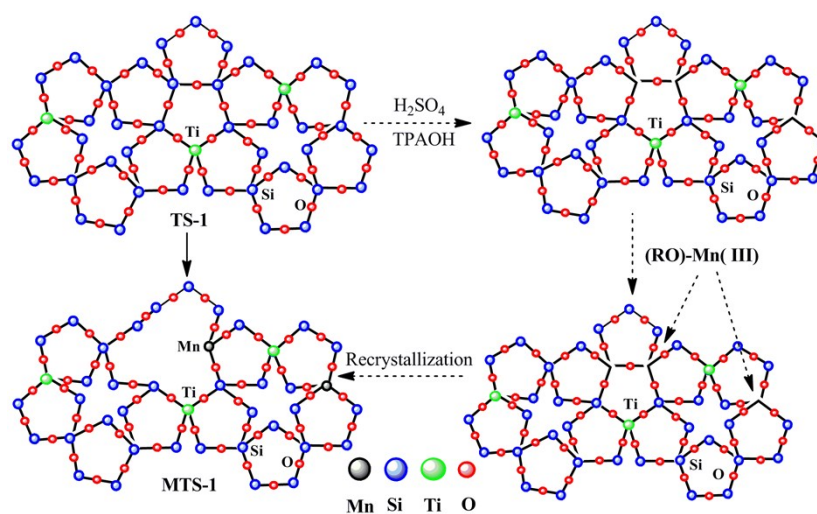
^aVanadium and sulfur contents of the samples measured by ICP-AES.

^b BET surface area.

Table S2

Comparison between the novel catalytic system and the others reported previously

Entry	Catalytic system	Solvent	Conv. (%)	A+B Sele. (%)	Oxidant	Temp. (°C)	Time (h)	Reference
1	MTS-1	No	25.4	96.6	O ₂	70	6	This work
2	MTS-1	No	45.5	93.1	O ₂	70	15	This work
3	Au-TUD/ ^t Buty-OOH	No	52	36.0	O ₂	70	8	[3]
4	Cr-MIL-101/ ^t Buty-OOH	No	12	83	O ₂	60	16	[4]
5	Fe-MIL-100/ ^t Buty-OOH	No	10	57	O ₂	50	16	[4]
6	CuNi-ELD/Co-3	No	39.3	39.7	O ₂	75	6	[5]
7	MSS-SH-Au ⁰	Toluene	61.0	67.0	O ₂	100	8	[6]
8	(Cr)MCM-41	Chlorobenzene	51.1	91.6	TBHP	120	12	[7]
9	FePcS-SiO ₂	CH ₃ CN	65.0	95.3	TBHP	40	24	[8]
10	Ru/Ti-PILC	heptane	59.0	90.0	TBHP	70	6	[9]
11	Cr-APTSSal	THF	80.1	94.8	H ₂ O ₂	80	24	[10]



Scheme S1 Design idea of the catalyst

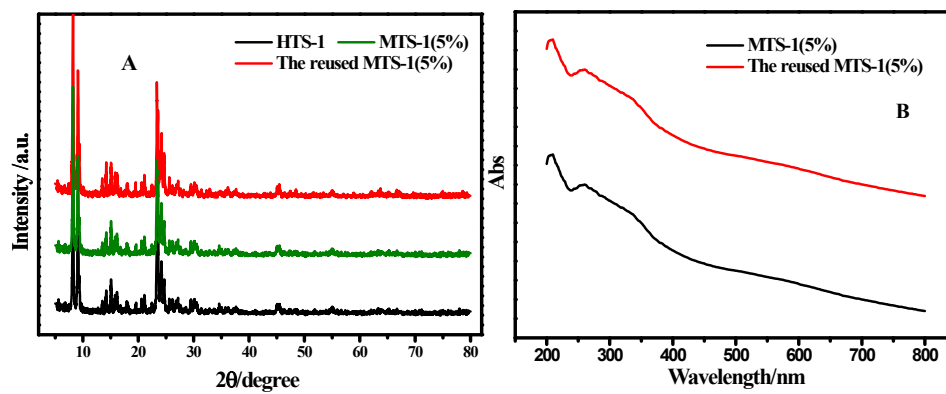


Fig. S2 XRD image (A) and UV-vis spectra (B) of samples parent HTS-1, the MTS-1(5%), the reused MTS-1(5%)

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