Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information†

Microwave induced "egg yolk" structure in Cr/V-MIL-53

Hannes Depauw,[a] Irena Nevjestić,[b] Jonatan De Winne,[c] Guangbo Wang,[a] Katrien Haustraete,[a] Karen Leus,[a] An Verberckmoes,[c] Christophe Detavernier,[b] Freddy Callens,[b] Els De Canck,[a] Henk Vrielinck,[b] Pascal Van Der Voort[a] *

[a] Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281-S3, B-9000 Ghent, Belgium
[b] Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, B-9000 Ghent, Belgium
[c] Department of Materials, Textiles and Chemical Engineering (MaTCh), Ghent University, Valentin Vaerwyckweg 1, B-9000 Ghent, Belgium

Table of contents

Tab. S1 Overview of the amount of solvent, linker and metal ratio of the different samples synthesized via the microwave procedure.

*SAMPLE NAME	TEREPHTHALIC ACID (MMOL)	VANADIUM (MMOL)	CHROMIUM (MMOL)	THEORETICAL CHROMIUM CONCENTRATION (MOL%)	EXPERIMENTAL CHROMIUM CONCENTRATION (MOL%)
MIL-47(V)	1.66	1.66	0.00	0.00	0.00
1	1.66	1.41	0.25	0.15	0.05
2	1.66	1.16	0.50	0.30	0.10
3	1.66	0.83	0.83	0.50	0.23
4	1.66	0.50	1.16	0.70	0.50
5	1.66	0.25	1.41	0.85	0.75
MIL-53(Cr)	1.66	0.00	1.66	1.00	1.00

* For all syntheses 167 mmol of demineralized water is used.

Tab. S2 Overview of the amount of solvent, linker and metal ratio of the different samples synthesized via the solvothermal procedure.

*SAMPLE NAME	TEREPHTHALIC ACID (MMOL)	VANADIUM (MMOL)	CHROMIUM (MMOL)	THEORETICAL CHROMIUM CONCENTRATION (MOL%)	EXPERIMENTAL CHROMIUM CONCENTRATION (MOL%)
MIL-47(V)	2.21	8.73	0.00	0.00	0.00
1	2.21	7.42	1.31	0.15	0.07
2	2.21	6.11	2.62	0.30	0.13
3	2.21	4.37	4.37	0.50	0.17
4	2.21	2.62	6.11	0.70	0.37
5	2.21	1.31	7.42	0.85	0.58
MIL-53(Cr)	2.21	0.00	8.73	1.00	1.00

* For all syntheses 899 mmol of demineralized water is used.

Experimental details

All chemicals were bought from Sigma-Aldrich or TCI Europe and used without further purification. Bright-field scanning transmission electron microscopy (BF-STEM) and energy dispersive X-ray spectroscopy (EDX) was performed on a JEOL JEM-2200FS high resolution scanning transmission electron microscope equipped with an EDX spectrometer with a spatial resolution of 0.13 nm, image lens spherical aberration corrector, electron energy loss spectrometer (filter) and an emission field gun (FEG) operating at 200 KeV. Diffuse reflectance infrared spectroscopy (DRIFTS) measurements were recorded in the region of 3700-850 cm^{-1} on a Thermo Nicolet 6700 spectrometer, equipped with a nitrogen-cooled MCT-A detector and a KBr beam splitter at 393 K under vacuum. Raman spectra were obtained on an RXN1 Raman spectrometer (Kaiser Optical Systems) equipped with a 532 nm laser operating at 40mW using an optical probe at RT in air. X-ray fluorescence (XRF) spectroscopy measurements were performed using an energy-dispersive Rigaku NexCG spectrometer equipped with a silicon drift detector. Prior to the analysis, compounds were mounted in a plastic cup containing a Prolene film. Equilibrium isotherms of CO_2 were measured using the static volumetric method using an Isorb-HP1 device from Quantachrome. The measurements were performed at room temperature, the cell temperature was stabilized via an external heating bath and on board monitored. Approximately 150 mg of sample was loaded in the stainless steel sample holder. Before each measurement, the powder was degassed with a heating stage of 2 K/min to 363 K and kept at this temperature for 2 hours. X-ray powder diffraction (XRPD) were collected on a Thermo Scientific ARL X'Tra diffractometer, operated at 40 keV and 40 mA using a Cu anode (Cu-K_α, λ = 1.5406 Å). *In situ* PXRD in air was carried out on a Bruker D8 Discover XRD system equipped with a Cu-X-ray source (λ = 1.5406 Å) and a linear X-ray detector. The powder samples were mounted on a silicon wafer and placed on the heating stage. Measurements were carried out in air under atmospheric pressure. The sample was heated from RT to 450 K and finally cooled down to RT at a heating/cooling rate of 5 K min^{-1}. The temperature was analyzed with a K-type thermocouple. Data were collected in a time frame of 10 s per total scan. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449 F3 Jupiter-simultaneous thermogravimetric - differential scanning calorimetry (TG-DSC) analyzer in the temperature range of 25-800 °C under air and with a heating rate of 2 °C min^{-1}. Nitrogen sorption measurements were done on a Belsorp Mini (Bel Japan, Inc.) apparatus at 77 K. Prior to the measurements, the samples were degassed at 353 K for 2 hours.

Synthetic details

General microwave procedure: All microwave syntheses (MW) are performed in a CEM Discover SP microwave using Pyrex pressure reaction tubes of 10 mL. The tubes are equipped with a magnetic stirring bar and sealed with a silicon cap. Before the start of the synthesis, the reagents are stirred for 2 minutes to have a homogeneous distribution of the reagents. In a next step the mixture is heated under mild stirring to 473 K at 200 W and held under these conditions for 3 hours with a pressure platform set at 23 bar. Afterwards all crystals are filtered and washed three times with distilled water and twice with acetone.

(MIL-53(Cr)-AS): The synthesis of MIL-53(Cr) is based on the work of Kahn et al.[1] In this synthesis, the parameters are slightly adapted to an equimolar ratio $CrCl_3.6H_2O$:terephthalic acid of 1.66 mmol. Both components are mixed in a microwave tube, 167 mmol of deionized water (0.05 µS/cm) is added and the general MW procedure is followed as described above. Finally a grey crystalline material is obtained.

(MIL-47(V)-AS): The synthesis of MIL-47-V is based on an adapted recipe reported by Hatton.[2] Equimolar ratios, both 1.66 mmol, of anhydrous VCl_3 and terephthalic acid are combined in a microwave tube together with 167 mmol of deionized water. Afterwards a yellow solid is collected.

($MW_{Cr(x)-V(1-x)}$)-AS):. An amount of 167 mmol deionized water and 1.66 mmol terephthalic acid are added to the microwave tube. The total sum of metal salts is held fixed at 1.66 mmol and contains a mixture of anhydrous VCl_3 and $CrCl_3.6H_2O$. The experimental concentrations are listed in Tab. S1.

General solvothermal procedure: All solvothermal syntheses (SOL) are performed in a muffle furnace of Nabertherm with an operation temperature between 293 K-1673 K. All reagents are added to a teflon holder and placed in an ultrasonic bath for 5 min at room temperature. Afterwards the holder is inserted in a stainless steel autoclave and sealed. The reaction mixtures are heated 2 K min^{-1} to 473 K, kept under these conditions for 96 hours. In a final step the crystals are collected via filtration and washed three times with distilled water and twice with acetone.

(MIL-53(Cr)-AS): The synthesis of MIL-53(Cr) is based on earlier work of Serre.[3,4] In this synthesis, the parameters are slightly adapted, a molar ratio of 8.73 mmol $CrCl_3.6H_2O$ and 2.21 mmol terephthalic acid are added to the teflon liner. Afterwards 899 mmol deionized water (0.05 µS/cm) is added, finally a grey solid is obtained.

(MIL-47(V)-AS): The synthesis of MIL-47(V) is based on the recipe of Leus[5] and Barthelet.[6] The teflon liner is filled with 8.73 mmol anhydrous VCl_3 and 2.21 mmol terephthalic acid. In a next step both reagents are immersed with 899 mmol deionized water, afterwards the yellow solid is collected.

($SOL_{Cr(x)-V(1-x)}$)-AS): An amount of 899 mmol deionized water and 2.21 mmol terephthalic acid are loaded in a teflon holder. The total sum of metal salts is 8.72 mmol and contains of a mixture of VCl_3 and $CrCl_3.6H_2O$. The experimental concentrations are listed in Tab. S2.

Tab. S3 Relative reaction rates at 150 °C for the solvothermal synthesis of MIL-47(V) and MIL-53(Al) compared to MIL-53(Cr).[7,8]

Porous material (SOL)	Nucleation rate	Crystal growth rate
MIL-53(Cr)	1	1
MIL-53(Al)	31.4	18.3
MIL-47(V)	73.6	50.6

Tab. S4 Relative reaction rates calculated from experimental data at 150 °C for the microwave synthesis of MIL-47(V) and MIL-53(Al) compared to MIL-53(Cr).[8]

Porous material (MW)	Nucleation rate	Crystal growth rate
MIL-53(Cr)	1	1
MIL-53(Al)	238.6	44.6
MIL-47(V)	487.5	201.0

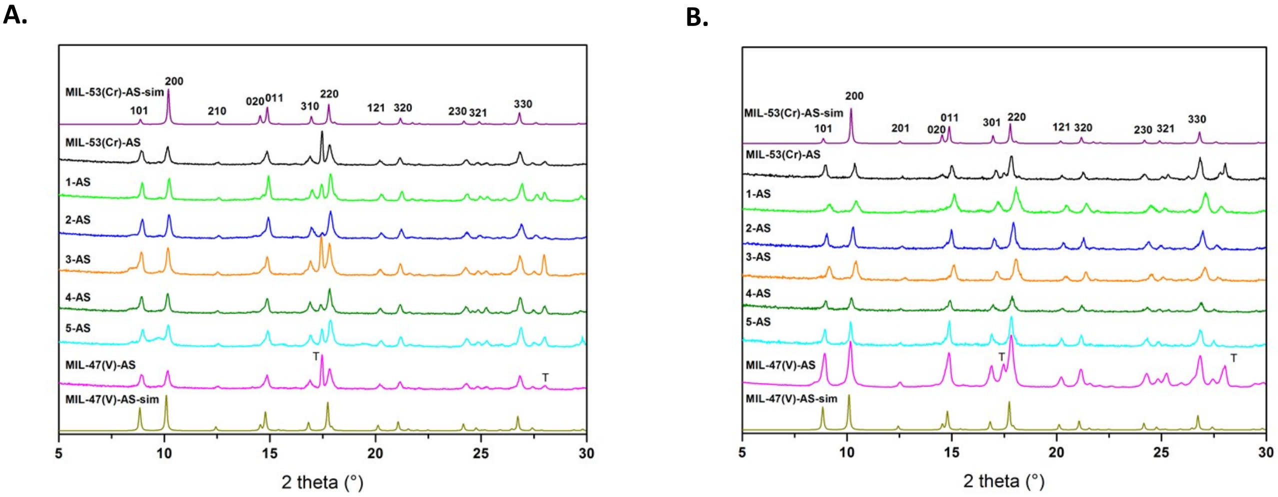

Fig. S1 XRPD data between 0-30° of A. MW synthesized mixed-metal series **1-5**, monometallic MIL-53(Cr) and MIL-47(V); B. SOL synthesized mixed-metal series 1-5 and monometallic MIL-53(Cr) and MIL-47(V). In both graphs, simulated (sim) diffraction patterns of MIL-53(Cr) and MIL-47(V) are presented. T in the spectra indicates the diffractions of terephthalic acid.

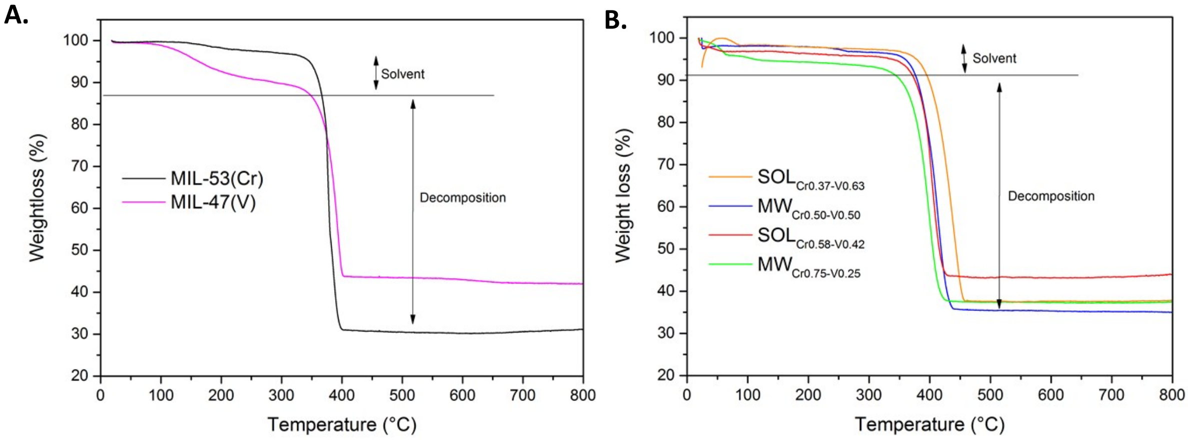

Fig. S2 A. TGA analysis between 25-800°C in air; A. compounds MIL-47(V), MIL-53(Cr); B. mixed-metal frameworks **SOLCr$_{0.37}$-V$_{0.63}$**, **MWCr$_{0.50}$-V$_{0.50}$**, **SOLCr$_{0.58\text{-}V0.42}$** and **MWCr$_{0.75}$-V$_{0.25}$**.

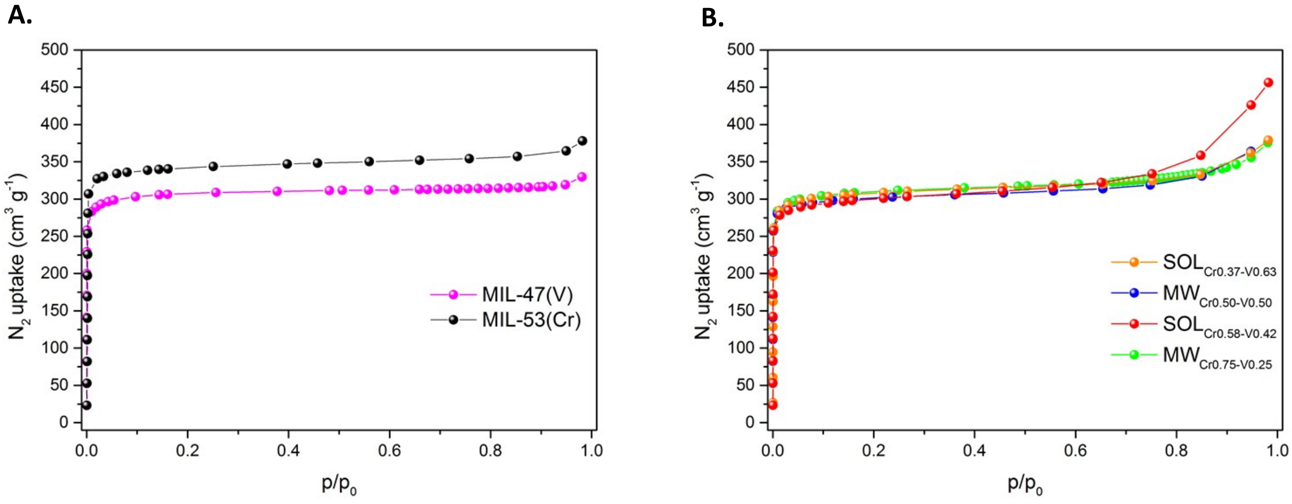

Fig. S3 N$_2$ adsorption isotherms from 0-1 bar at 77 K; A. compounds MIL-47(V), MIL-53(Cr); B. mixed-metal frameworks **SOL$_{Cr0.37-V0.63}$**, **MW$_{Cr0.50-V0.50}$**, **SOL$_{Cr0.58-V0.42}$** and **MW$_{Cr0.75-V0.25}$.**

Tab. S5 Overview of the EDX data via line analysis of Cr and V at the edge and in center of the crystal. In the final right column the surface area of the compounds after activation is presented.

SAMPLE NAME	CHROMIUM EDGE (MOL%)	VANADIUM EDGE (MOL%)	CHROMIUM CENTER (MOL%)	VANADIUM CENTER (MOL%)	LANGMUIR SURFACE AREA (m^2 g^{-1})
MIL-47(V)	n.a.*	n.a.*	n.a.*	n.a.*	1368
SOL$_{Cr0.37-V0. 63}$	0.50	0.50	0.50	0.50	1415
MW$_{Cr0.50-V0.50}$	0.85	0.15	0.60	0.40	1418
SOL$_{Cr0.58-V0.42}$	0.82	0.18	0.82	0.18	1405
MW$_{Cr0.75-V0.25}$	0.93	0.07	0.88	0.12	1345
MIL-53(Cr)	n.a.*	n.a.*	n.a.*	n.a.*	1550

* n.a.: not analyzed, theoretical values of single metal compounds are expected.

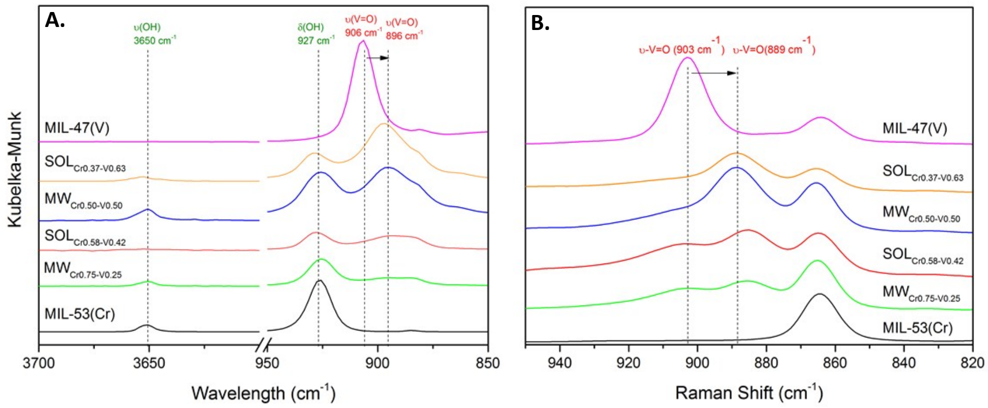

Fig. S4 A. DRIFTS spectra in the region between 3700-3600 and 950-850 cm^{-1}; B. Raman spectra in the region between 950-820 cm^{-1} of both compounds MIL-47(V), **SOL$_{Cr0.37\text{-}V0.63}$**, **MW$_{Cr0.50\text{-}V0.50}$**, **SOL$_{Cr0.58\text{-}V0.42}$**, **MW$_{Cr0.75\text{-}V0.25}$** and MIL-53(Cr).

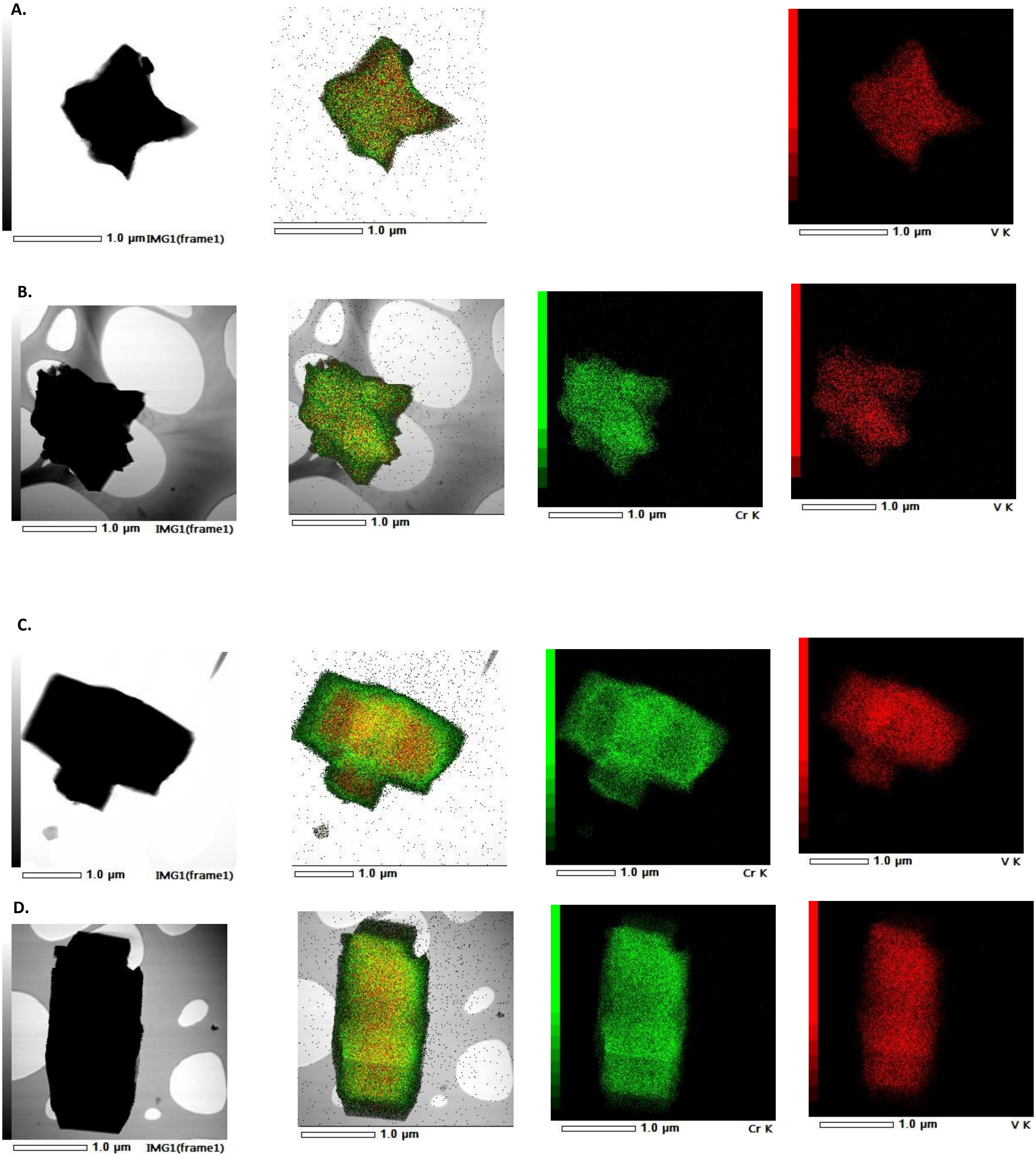

Fig. S5 Bright-field scanning transmission electron microscopy (BF-STEM) energy dispersive X-ray (EDX) mapping of chromium (green) and vanadium (red) on a mixed-metal particles: A. **SOL**$_{\mathbf{Cr0.37\text{-}V0.63}}$; B. **SOL**$_{\mathbf{Cr0.58\text{-}V0.42}}$; C. **MW**$_{\mathbf{Cr0.50\text{-}V0.50}}$ and D. **MW**$_{\mathbf{Cr0.75\text{-}V0.25}}$.

References

1. N. A. Khan, J. W. Jun and S. H. Jhung, *European Journal of Inorganic Chemistry*, 2010, **2010**, 1043-1048.
2. A. Centrone, T. Harada, S. Speakman and T. A. Hatton, *Small*, 2010, **6**, 1598-1602.
3. F. Millange, C. Serre and G. Férey, *Chemical Communications*, 2002, 822-823.
4. C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *Journal of the American Chemical Society*, 2002, **124**, 13519-13526.
5. K. Leus, M. Vandichel, Y.-Y. Liu, I. Muylaert, J. Musschoot, S. Pyl, H. Vrielinck, F. Callens, G. B. Marin and C. Detavernier, *Journal of catalysis*, 2012, **285**, 196-207.
6. K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angewandte Chemie*, 2002, **114**, 291-294.
7. E. Haque, J. H. Jeong and S. H. Jhung, CrystEngComm, 2010, **12**, 2749-2754.
8. E. Haque, N. A. Khan, C. M. Kim and S. H. Jhung, Crystal Growth & Design, 2011, 11, 4413-4421.