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ESI for:

Preparation of monolithic catalysts using 3D printed templates for oxidative coupling of methane

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SI.1 Experimental Details

Characterization of monoliths

The mineralisation process was conducted according to the optimised programme for Mn, W and Na digestion. In typical procedure, the monolithic sample (ca. 0.06 g) was crashed and mineralized in Teflon vessels at 60 °C. The mineralization process was conducted in two steps. First, a mixture consists of concentrated HF (1 cm^3) and 10 % HNO_3 (5 cm^3) both suprapure was used as a mineralising solution. After this step, the samples were cooled down to ambient temperature. In the next step of the mineralization 4 cm^3 of aqua regia was added and then the mixture was heated again to 60 °C. Determination of Mn, Na and W elements ($mg_{Me}/g_{monolith}$) in the digest solutions was performed using inductively coupled plasma optical emission spectrometry (ICP-OES). The Optima 2100 DV (Perkin-Elmer, USA) ICP-OES equipped with axially viewed plasma, was used in the determination of Mn, Na and W at a wavelengths of λ_{Mn}= 257.610 nm , λ_{Na}= 589.592 nm and λ_{W}= 207.912 nm.

Powder X-ray diffraction (XRD) patterns of mesoporous materials were collected on a Panalytical X'Pert Pro instrument operated at 40 kV and 30 mA, equipped with a Cu Kα X-ray (λ = 0.154 nm) radiation source. The diffractograms (Figure 1S) were recorded in the 2θ range between 10° and 90° with a 2 θ step size 0.0167°.

Krypton adsorption-desorption isotherms were measured at -196°C (in liquid N_2) using a Micromeritcs, ASAP 2020 instrument. The samples were degassed at 250°C before measurements for 12 h in the degas port of the sorption analyzer. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure P/P_0=0.05-0.15.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a hemispherical analyzer (SES R4000, Gammadata Scienta). The AlKα X-ray source (1486.6 eV) with no charge neutralizer was applied to generate core excitation. The spectrometer was calibrated according to ISO 15472:2001. The energy resolution (for Ag line $3d_{5/2}$) of the spectrometer was 1.0 eV for the analyzer pass energy of 100 eV. The powder samples were pressed into indium foil and mounted on a holder then UHV evacuated (ca. 1×10^{-9} bar). The area of analysis was 3 mm^2. The binding energy (BE) values were charge-corrected to the carbon C 1s excitation set at 285.0 eV. The spectra (Figure 2S) were analyzed with CasaXPS 2.3.12 program. The backgrounds of spectra were approximated by the Shirley-type line and the spectra components by a symmetric Voigt profile (Gauss to Lorentz equal to 70:30).

Scanning electron microscopy (SEM) images were recorded using a JEOL JSM–5410 (with an operating voltage of 15 keV) equipped with a NORAN 679A-3SES energy dispersive spectrometer

(EDS). The sample were coated with a 15-nm carbon layer in a JEE4B evaporator (JEOL, Tokyo, Japan) to prevent charging.

Catalytic performances

The catalytic tests were carried out in the continuous flow quartz reactor with the dimensions (internal diameter)×(wall thickness)=10×1 mm. The weight of the monolithic catalyst was 4,20 g (the weights of as-prepared monolithic catalysts 4,25-4,40 g were corrected to this value). The rest (high temperatures) space of reactor was filled with quartz chips. The thermocouple was attached to the outside of the microreactor to control furnace temperature as well as to monitor the temperature in the reaction zone. Before the OCM process the monolithic catalyst placed in the reactor was preheated in dry helium for 30 min at the temperature of 820 °C. Afterwards, reactant gases consist of methane (Lindegas 99.96 %) and oxygen (Lindegas, 99.9 %) diluted with nitrogen (Lindegas 99.996 %) were co-fed into the reactor. Volumetric flow rates of gasses were controlled with mass flow controllers (Bronkhorst EL-Flow). Three different compositions of methane, oxygen and helium at a molar ratio of $CH_4/O_2/He$ = 2/1/2.1, 3.8/1/4.8 and 7/1/9.9 were applied. The total volumetric flow rate (on inlet of the reactor) was either 155 (GHSV=220 $cm^3 \cdot g^{-1}{}_{cat} \cdot h^{-1}$) or 310 $cm^3 min^{-1}$ (GHSV=4400 $cm^3 \cdot g^{-1}{}_{cat} \cdot h^{-1}$). All catalytic tests were evaluated at 820 °C under atmospheric pressure. Cold trap was placed at the outlet of reactor for separation of water produced during the OCM process. The reaction products (except water) and unreacted substrates were analyzed using the Agilent 6890N gas chromatograph equipped with two columns (molecular sieve 5A for separation of H_2, CH_4, CO and O_2 and Hayesep Q for separation of CO_2, H_2O, and hydrocarbons) and the thermal conductivity detectors.

The conversion of methane (%), selectivity to products (%) and yield of C_{2+} (ethene, ethane, propylene and propane) were calculated according to the following formulas:

Conversion of CH_4 = $(n_{(inlet)CH4} - n_{(outlet)CH4}) \times 100\% / n_{(inlet)CH4}$

Selectivity to products = $\Sigma a_i \times n_i \times 100\% / (n_{(inlet)CH4} - n_{(outlet)CH4})$

Yield to C_{2+} = (Conversion of CH_4) × (Selectivity to C_{2+})

where: $n_{(inlet)CH4}$ and $n_{(outlet)CH4}$ are numbers of methane moles in inlet and outlet of the reactor, respectively, n_i is a number of moles of the i-th product in outlet and a_i is a number of carbon atoms in "*i*" product (COx, ethane, ethene, propane and propene).

SI.2 XRD analysis

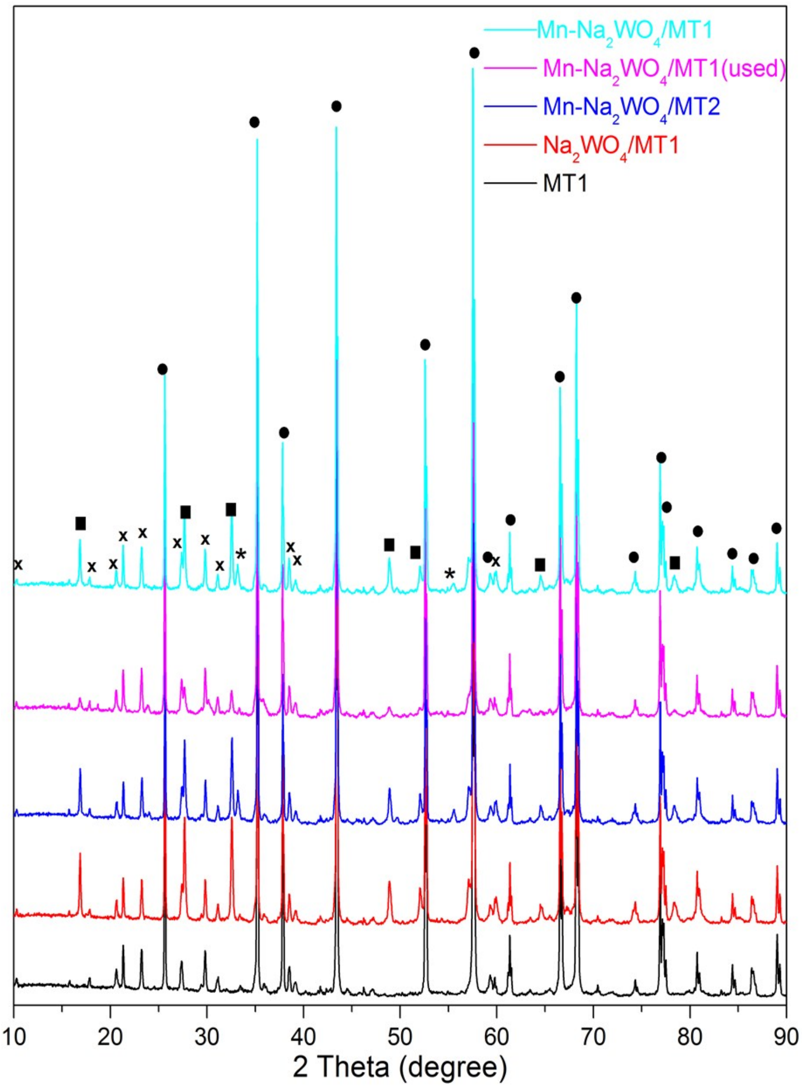

Fig.S1. XRD patterns of monoliths prepared by replication of 3-D printing hard templates.

Designations:

● α-Al_2O_3; Corundum; References code 04-010-6477

■ Na_2WO_4; Disodium tungstate; References code 04-008-8508

★ Mn_2O_3; References code: 01-071-3820

✗ $Na_{7.15}(Al_{7.2}Si_{8.8}O_{32})$; Nepheline (Si-rich); References code: 01-079-0993

SI.3 XPS analysis

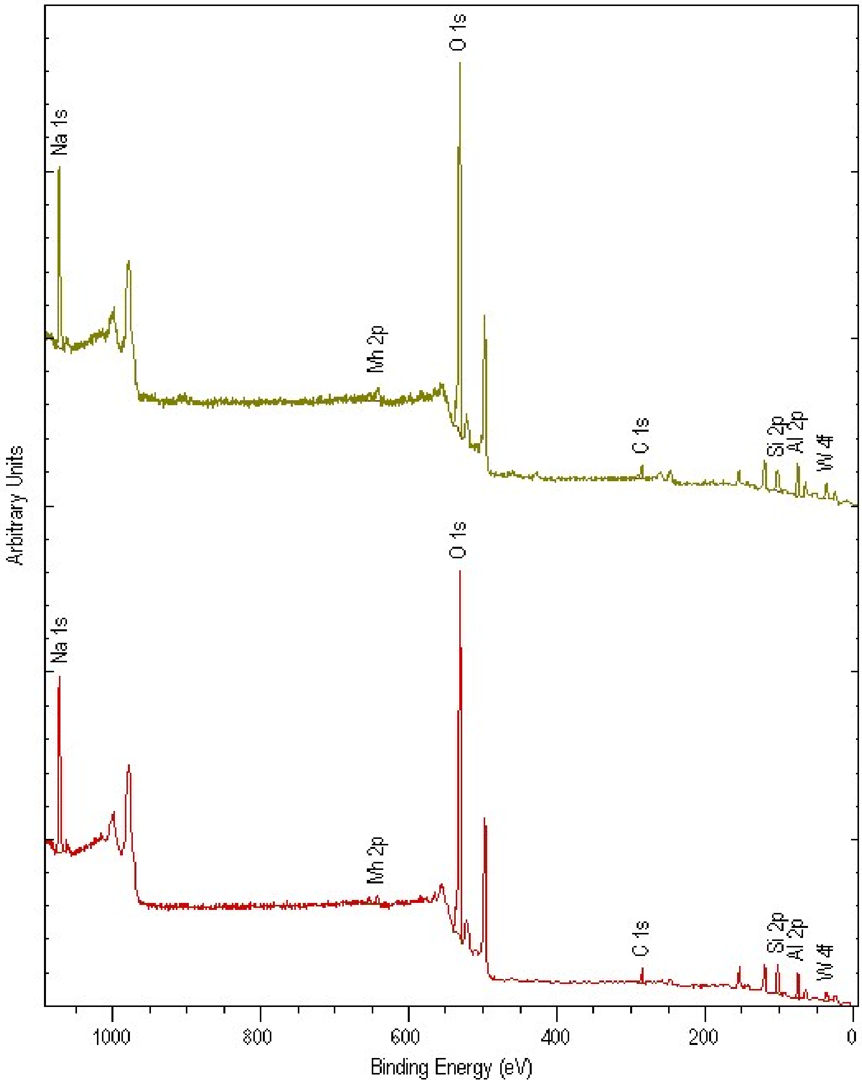

Fig.S2. XPS spectra of fresh (green line) and used (red line) Mn-Na_2WO_4/MT1 sample.

Table S1. Observed XPS binding energies (eV) and near-surface compositions (at %) of fresh and used Mn-Na_2WO_4/MT1 sample

Sample	Na (1s)		W (4f)		Mn (2p)		Si (2p)		Al (2p)		O (1s)	
	BE (eV)	In (at. %)	BE (eV)	In (at. %)	BE (eV)	In (at. %)	BE (eV)	In (at. %)	BE (eV)	In (at. %)	BE (eV)	In (at. %)
Fresh	1071.97	8.6	35.4	0.8	641.92	1.2	102.42	12.7	74.92	20.65	531.97	50.5
Used	1071.54	8.2	35.3	0.6	641.54	0.8	102.29	15.2	74.54	15.9	531.29	53.4