Supporting Information for

Enhanced catalytic performance of Mn_xO_y-Na_2WO_4/SiO_2 for the oxidative coupling of methane using an ordered mesoporous silica support

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Preparation of the Catalyst

The silica materials were impregnated with an aqueous solution containing appropriate concentration of manganese (II) acetate (Fluka, >99 %) at room temperature, followed by drying in air at 75 °C overnight. Afterwards, the obtained materials were impregnated with an aqueous solution containing the appropriate concentration of sodium tungstate (Sigma-Aldrich, min. 99 %) at room temperature. Samples were then dried in air overnight at 75 °C. The calcination process was performed in air, heating the samples in 4 h from room temperature up to 750 °C with a heating rate of approximately 1 K/min and holding the temperature for 1 h at 750 °C. The loading of the Na_2WO_4 and was calculated according to the Equation 1 and the Mn-loading was calculated according to the Equations 2, respectively.

$$\text{Na2WO4 [wt\%]} = \frac{\text{Na2WO4 [g]}}{\text{Mn [g]} + \text{Na2WO4 [g]} + \text{Support [g]}} \times 100\% \qquad (1)$$

$$\text{Mn [wt\%]} = \frac{\text{Mn [g]}}{\text{Mn [g]} + \text{Na2WO4 [g]} + \text{Support [g]}} \times 100\% \qquad (2)$$

Preparation of ordered mesoporous silica support material (SBA-15)[1,2]

4 g of P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800) was dissolved in a mixture of distilled water (30 g) and 2 M hydrochloric acid solution (120 g), with continuous stirring and the temperature was controlled at ~35°C; after the P123 was fully dissolved, 8.5 g of TEOS was added and the resulting mixture was kept at ~35 °C for 24 h, subsequently aged at 80 °C for another 20 h without stirring. Finally, the sample was filtered, dried at 100 °C overnight and calcined at 550 °C for 4 h to remove the P123.

Ref:

1. Zhao, D. Y., Feng, J. L., Huo, Q. S., Melosh, N., Fredrickson, G. H., Chmelka, B. F., Stucky, G. D., *Science,* **1998**, 279, 548.
2. Junjiang Zhu, Kamalakannan Kailasam, Xiao Xie, Reinhard Schomaecker, and Arne Thomas, *Chem. Mater.*, **2011**, *23*, 2062.

Methods

BET

The specific surface area was determined by Micromeritics Gemini III 2375 Surface Area Analyzer, using N_2 adsorption at -196 °C. Before measuring, the samples were degassed at 300 °C at least for 30 minutes. The surface areas were calculated by the method of Brunauer, Emmett and Teller.

XRD

Powder X-Ray diffractograms (XRD) were obtained ($CuK\alpha_1$ radiation wavelength 0.154 nm) using Bruker AXS D8 ADVANCE X-ray diffractometer. The angle variation was performed from 2 to 90°, with a step size of 0.008°. The diffractograms were analyzed with the program STOE WinXPOW.

TEM

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai 20 microscope, using carbon-coated copper grids (the specimens were loaded directly onto the copper grids; no solvent dispersion was used).

SEM-EDX

The surface microstructure (morphology and particle size) and chemical composition of the samples were studied by scanning electron microscopy (SEM) at the Department of Electron Microscopy ZELMI, TU Berlin. A small amount of the sample powder was placed on a conducting carbon pad (Plano GmbH, Germany) and sputtered with a thin carbon layer. The investigations were performed by means of a JXA-8530F microprobe (JEOL GmbH, Germany) equipped with a field emission source. Qualitative chemical analysis and beam scan mapping were carried out by 20kV acceleration voltage with integrated energy dispersive X-ray spectroscopy using a SDD detector.

Catalytic Testing

A 6-fold parallel reactor was used to determine the catalytic activity. This device was purchased from Integrated Lab Solutions Berlin. It has 6 parallel, packed-bed, linear, tubular reactors made of quartz glass. The outer diameter is 6 mm and the inner diameter 4 mm. For each catalytic run, 50 mg catalyst were diluted with approximately 1.5 ml quartz sand (quartz sand: purchased from Merck, it has already been washed with HCl and calcined, ca. 60 % of the particles have the size 0.2 - 0.8 mm) for proper heat transfer. The reactors behave like a plug flow tubular reactor (PFTR). Below and above the catalyst bed, a small amount of pure quartz sand was put to ensure proper heat transfer. The particle size of the catalyst was below 200 µm in each experiment to exclude internal mass transfer effects.

The gas was feed via calibrated mass flow controllers from Bronkhorst. Methane and synthetic air, as oxygen source, were fed into the reactor with a flow rate of 60 ml/min and a feed gas composition of $CH_4:O_2:N_2 = 4:1:4$.

Each reactor was heated within its own electric furnace; isothermal conditions were insured. Under reactant gas flow, the reactor was heated to 750°C with a heating rate of 20 K/min. Afterwards, the composition of the outlet gas is determined for each reactor for the given time on stream. The same test protocol was applied for every experiment.

The analysis was performed with a gas chromatograph Agilent 7890 A, equipped with a flame ionization detector (FID), a thermal conductivity detector (TCD), a HP-PLOT/Q and a HP Molsieve column. He (Air Liquide) was used as carrier gas. The analyzed compounds were O_2, N_2 and CO_2 via TCD, CH_4, C_2H_4 and C_2H_6 via FID. N_2 was used as internal standard. Higher reaction products, such as C_3H_8 and C_3H_6, were not detected for similar experiments,[1] therefore a method was applied which is not suitable for their detection. The reproducibility of conversion (X) and selectivity (S) is sufficient. The conversion and selectivity was calculated with a mass balance based on the inlet and outlet concentration of reactants and products, see Equations 3 and 4, taking into account the different numbers of C-atoms in the different molecules. The carbon balance was always well above 95 %.

$$X = \frac{\sum(Reaction\ Products)}{\sum(Reaction\ Products) + \ (Unconverted\ Reactants)} \qquad (3)$$

$$SA = \frac{Product\ A}{\sum(Reaction\ Products)} \qquad (4)$$

No visible formation of deposited carbon were found. The carbon content was not measured, because in a previous study[2], we did not find any carbon deposition after catalysis.

The desired reaction products of the oxidative coupling of methane are C_2H_4 and C_2H_6. The selectivity of these two products is discussed as a sum, the C_2 selectivity.

In order to determine the degree of thermal conversion of CH_4, blank experiments with pure quartz sand, with quartz spherules, with a particle size of 0.4 mm ± 0.1 mm (Quarzglas QCS, Maintal, Germany), and with an empty reactor, were conducted under the above described reaction conditions. The importance of the homogeneous gas phase reaction in the OCM is significant,[3] therefore, the obtained results for CH_4 conversions and the according selectivities are shown in detail in Table S1. At 700°C and below the contribution of the thermal reaction was negligible in the applied experimental set-up. At 750°C, a contribution of the thermal reaction was observed. However, since the CH_4 conversion was rather small the influence of the thermal reaction was neglected. The degree of contribution of the gas phase reaction strongly depends on several different factors, such as partial pressures of all compounds, temperature, residence time, free reactor volume et cetera.[3] Therefore, it is not surprising that different CH_4 conversions were observed in a reactor which is empty, filled with quartz sand or quartz spherules.

Table S1: Contribution of the homogeneous gas phase reaction to the oxidative coupling of methane, in reactors with different inert fillings. The error of these values is relatively large due to the small conversions. Moreover, no CO_x was observed, which is probably due to the lower sensitivity of the TCD detector.

Reaction Conditions		Quartz Balls			Quartz Sand			Empty Reactor		
Temperature [°C]	Flow [ml/min]	$X(O_2)$ [%]	$X(CH_4)$ [%]	$S(C_2)$ [%]	$X(O_2)$ [%]	$X(CH_4)$ [%]	$S(C_2)$ [%]	$X(O_2)$ [%]	$X(CH_4)$ [%]	$S(C_2)$ [%]
700	30	1.1	0.3	97.2	2.5	0.3	93.2	2.9	0.6	100.0
700	60	-	-	-	0.7	0.1	100.0	0.3	0.1	100.0
700	90	-	-	-	-	-	-	-	-	-
700	120	-	-	-	-	-	-	-	-	-
750	30	1.7	0.2	92.4	2.8	0.3	90.1	6.2	1.1	100.0
750	60	0.2	0.1	100.0	1.2	0.2	93.8	1.7	0.4	100.0
750	90	-	-	-	0.3	0.1	100.0	0.3	0.2	100.0
750	120	-	-	-	-	-	-	-	-	-

Sample Preparation for Structural Analysis

For a structural analysis after the reaction, it is necessary to retrieve the catalysts. With the applied quartz sand this is not possible, because its particle size distribution is too large and it overlaps with the particle size of the catalysts. Thus, quartz spherules with a particle size of 0.4 mm ± 0.1 mm (Quarzglas QCS, Maintal, Germany) and a very narrow particle size distribution were used instead of quartz sand as inert diluent, enabling a separation of catalysts and inert material after the reaction by sieving. The reaction conditions and the time on stream for the sample preparation were identical to those described above. For the separation of catalyst and diluent, a 200 µm sieve was used.

The contribution of the gas phase reaction is different when quartz sand or quartz spherules are used, as shown in Table 1. Therefore, it could be that the catalytic behavior and the deactivation process of the reaction with quartz sand and quartz spherules are not absolutely identical. However, the general trends should still be observable in a reliable manner.

Ref:

1. Arndt, S.; Simon, U.; Heitz, S.; Berthold, A.; Beck, B.; Görke, O.; Epping, J.D.; Otremba, T.; Aksu, Y.; Irran, E.; Laugel, G.; Driess, M.; Schubert, H.; Schomäcker, R. Topics Catal **2011**, 54, 1266.
2. Simon, U.; Arndt, S.; Otremba, T.; Schlingmann, T.; Dinse, K.P.; Schomäcker, R.; Schubert, H. Catal. Commun. **2012**, 18, 132.
3. Kalenik, Z.; Wolf, E.E. in Methane Conversion by Oxidative Processes, Chapter 2. The Role of Gas-Phase Reactions during Methane Oxidative Coupling, Van Nostrand Reinhold, **1992**.

Table S2: The intended and determined loadings for fresh samples of Cat-1, Cat-2 and Cat-3 determined by ICP measurements.

Active Components	Intended Loading	Determined Loading		
		Cat-1	Cat-2	Cat-3
Mn [wt %]	2.00	2.36	2.22	2.48
Na [wt %]	0.78	0.72	0.85	0.69
W [wt %]	3.13	3.36	3.31	3.42