

## Supporting Information

### Raw biogas as feedstock for the OCM process

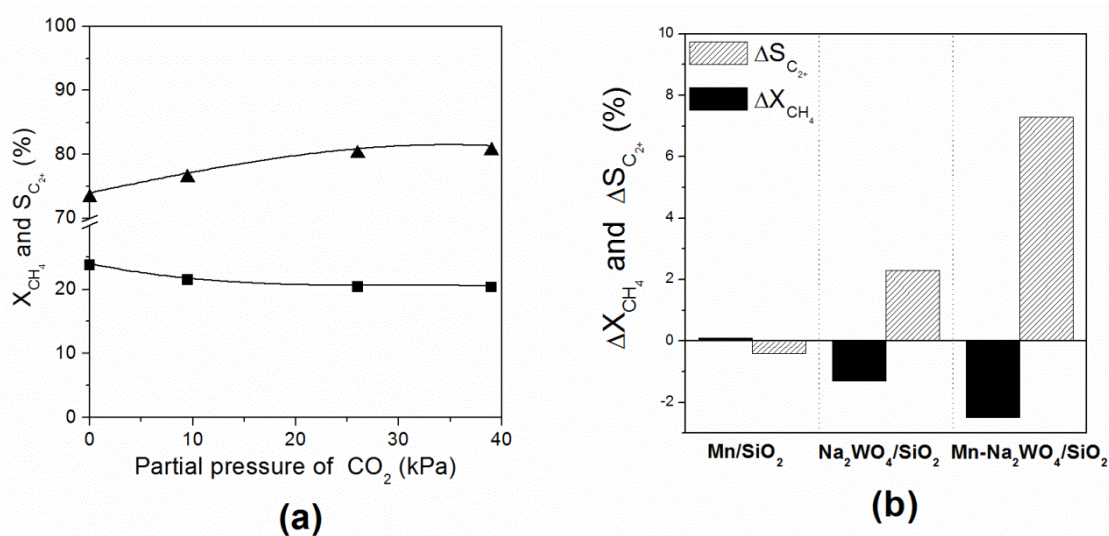
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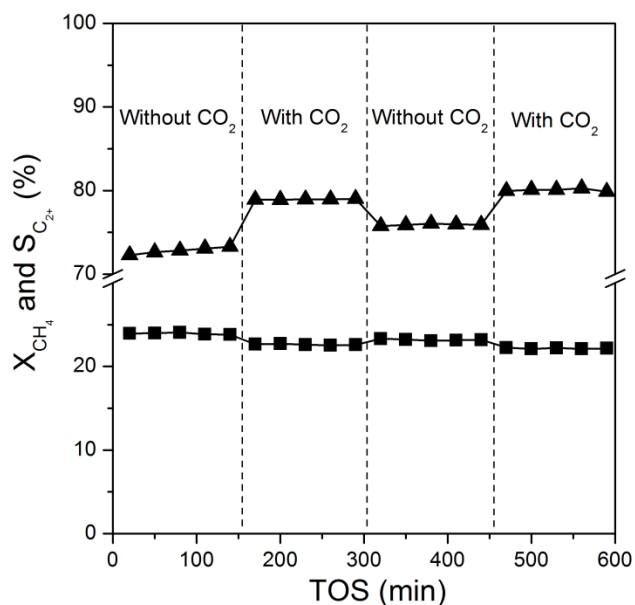
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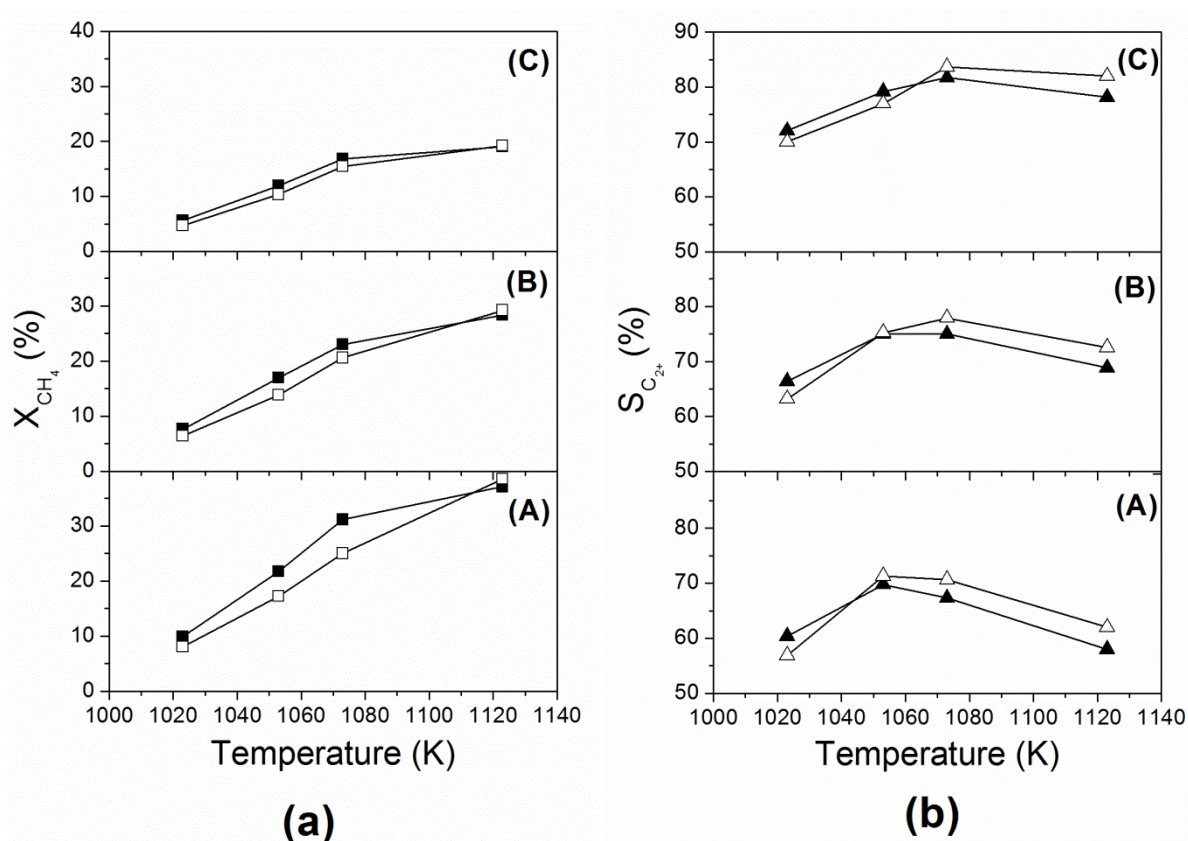
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**Figure S1.** (a) Variation of (■) methane conversion and (▲) selectivity to  $C_{2+}$  with partial pressure of  $CO_2$  over  $Mn-Na_2WO_4/SiO_2$  catalyst. (b) Calculated differences between methane conversion ( $\Delta X_{CH_4}$ ) and selectivity to  $C_{2+}$  ( $\Delta S_{C_{2+}}$ ) for OCM reaction carried out in presence and in absence of  $CO_2$  over  $Mn/SiO_2$ ,  $Na_2WO_4/SiO_2$ , and  $Mn-Na_2WO_4/SiO_2$  catalysts. Reaction conditions:  $T = 1073$  K;  $GHSV = 23400$   $cm^3 \cdot g^{-1} \cdot h^{-1}$ ;  $m_{cat} = 400$  mg; molar ratio of  $CH_4 : O_2 : He : CO_2 = 3.8 : 1 : X : (4.8 - X)$ , where:  $X = 4.8, 3.9, 2.3, 1.1$ ; total flow rate  $156$   $cm^3 \cdot min^{-1}$ .



**Figure S2.** Variation of (■) conversion of CH<sub>4</sub> and (▲) selectivity to C<sub>2+</sub> with time-on-stream during repeatable switching on CO<sub>2</sub> during OCM process over the Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst. Reaction conditions: T = 1073 K; GHSV = 23400 cm<sup>3</sup>·g<sup>-1</sup>·cat·h<sup>-1</sup>; m<sub>cat</sub> = 400 mg; molar ratio of CH<sub>4</sub> : O<sub>2</sub> : He : CO<sub>2</sub> = 3.8 : 1 : 4.8 : 0 (without CO<sub>2</sub>) and CH<sub>4</sub> : O<sub>2</sub> : He : CO<sub>2</sub> = 3.7 : 1 : 1.1 : 3.7 (with CO<sub>2</sub>); total flow rate 156 cm<sup>3</sup>·min<sup>-1</sup>.



**Figure S3.** (a) Variation of methane conversion and (b) selectivity to C<sub>2+</sub> with temperature in the OCM process carried out with (open symbols) and without (solid symbols) CO<sub>2</sub> over Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst. Reaction conditions: GHSV = 23400 cm<sup>3</sup>·g<sup>-1</sup>·cat·h<sup>-1</sup>; m<sub>cat</sub> = 400 mg; molar ratio of CH<sub>4</sub> : O<sub>2</sub> : He : CO<sub>2</sub> (A) 3.8 : 1.5 : 0.6 : 3.7, (B) 3.8 : 1 : 1.1 : 3.7, and (C) 3.8 : 0.6 : 1.5 : 3.7; total flow rate 156 cm<sup>3</sup>·min<sup>-1</sup>.