Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material

Catalysis effect on the CO_2 methanation using MgH_2 as hydrogen portable medium

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Calculation procedure S1: Methane yield calculation procedure and numerical examples

Trough GC experiments the molar amount of gaseous CH_4 was quantified using a calibration curve which relate the obtained experimental area with the corresponding molar percentage of CH_4 in the sample. After the reaction occurs, the total pressure (P_{total}) inside the reactor can be measured. As the CH_4 molar fraction (x_{CH4}) was determined, its partial pressure (P_{CH4}) can be obtained. Considering the volume of the reactor, the moles of CH_4 (n_{CH4}) in the mixture at ambient temperature (T_{amb}) can be calculated as follows: $n_{CH4} = x_{CH4}.\ P_{total}\ .\ V_{reactor}\ /\ R.\ T_{amb}$

Methane yield (%) was considered to be the ratio between the produced CH_4 moles (n_{CH4}) and the total CO_2 moles at the beginning of the reaction (n_{CO2}) . 100.

The total CO_2 moles at the beginning of the reaction (n_{CO2}) are determined at the starting of the experiment based on chosen H_2:CO_2 ratio. The amount of solid sample remained constant (100 mg) for all the experiments and provided the required H_2. To obtain a 2:1 ratio 1.9 $.10^{-3}$ moles of CO_2 are required, whereas for a 4:1 ratio 9.5 $.10^{-4}$ moles of CO_2 are initially introduced in the reactor.

$V_{reactor}$= 0.00982 l

T_{amb}= 298 K

R= 0.082 lt.atm/mol.K

	Temperature MgH_2:CO_2 Reaction time	Molar percentage of CH_4 (%)	x_{CH4}	P_{total} (atm)	P_{CH4} (atm)	n_{CH4}	n_{CO2}	CH_4 yield (%)
Example 1	400 4:1 24 h	17.8	0.178	5.63	1.002	$4.028.10^{-3}$	$9.5\ .10^{-4}$	42.4
Example 2	400 2:1 5 h	6.8	0.068	2.99	0.203	$8.17.10^{-5}$	$1.9\ .10^{-3}$	4.3

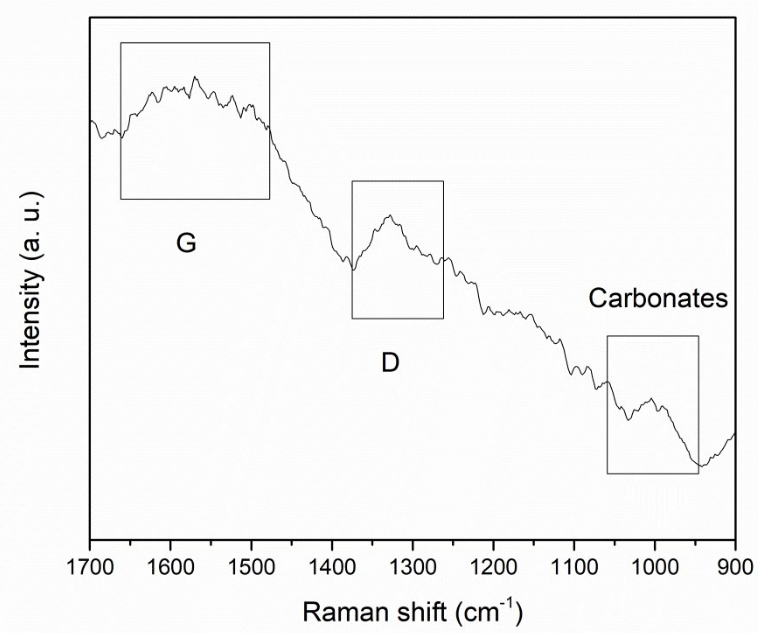

Figure S1: Raman spectrum of MgH_2 after thermal treatment with CO_2 at 400°C for 24 h (molar ratio of 2:1).

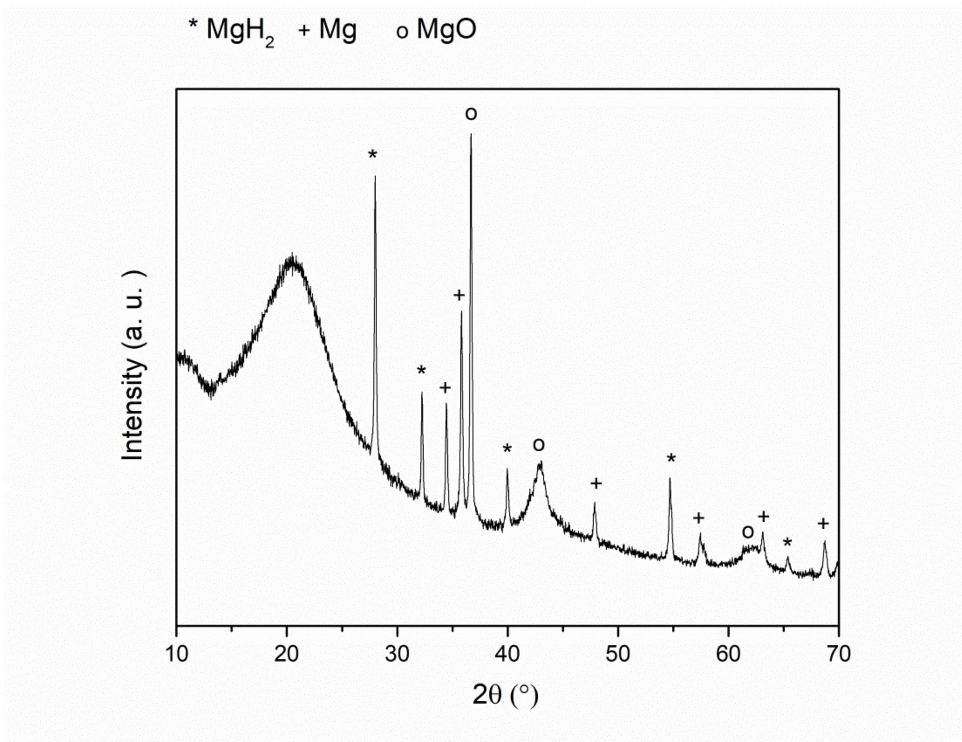

Figure S2: XRPD pattern of MgH_2 after thermal treatment with CO_2 at 350°C for 24 h (molar relation of 2:1).

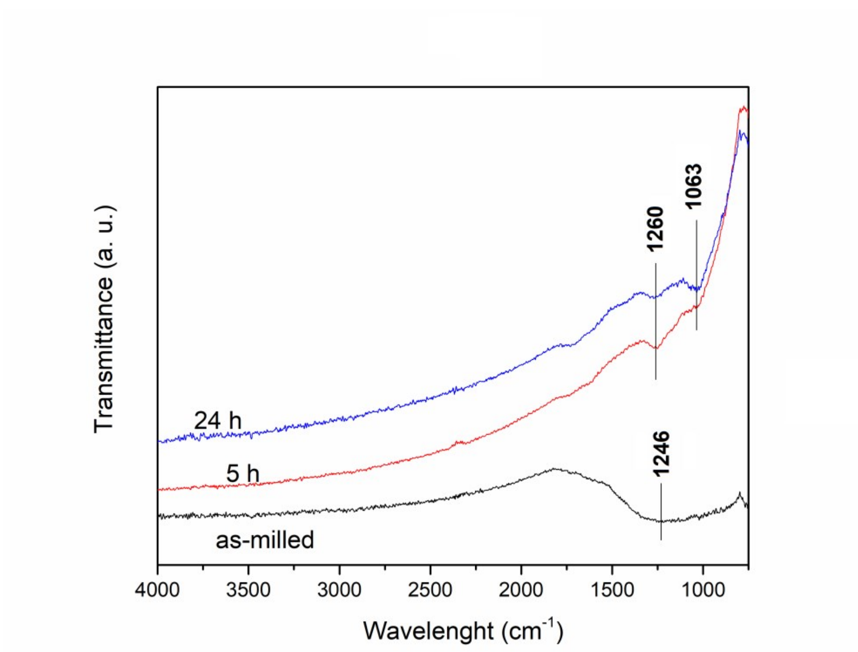

Figure S3: Solid-state FTIR profiles for the as milled MgH_2-10%Co and after thermal treatment (400°C, 5 and 24h) under CO_2 (molar relation of 4:1).

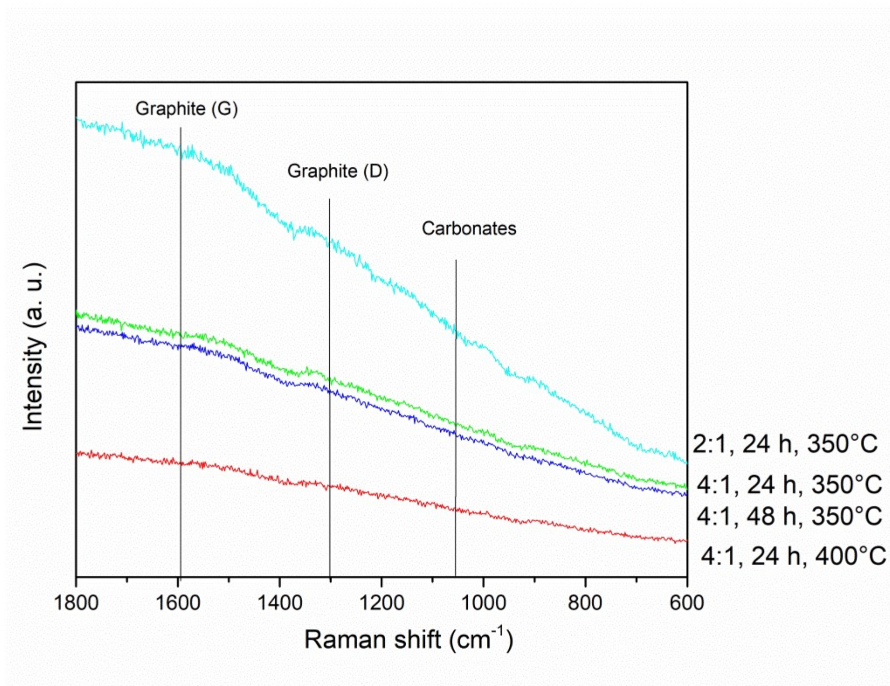

Figure S4: Raman spectra of MgH_2-10%Co after reaction with CO_2considering different experimental conditions.

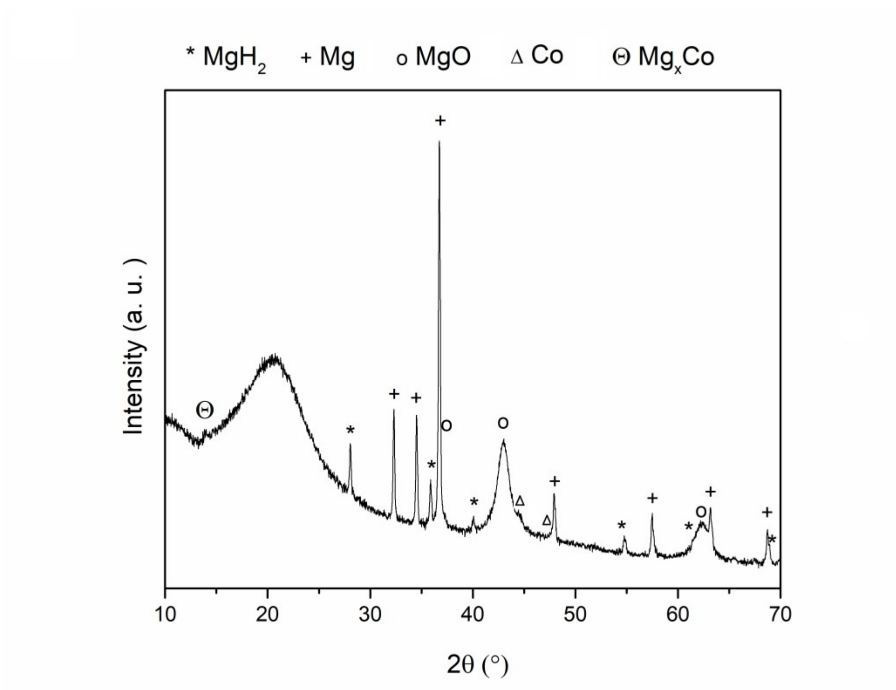

Figure S5: XRPD pattern of the sample MgH_2-10%wt Co with a molar ratio MgH_2:CO_2 of 4:1 (Co milled during the last 10 minutes).

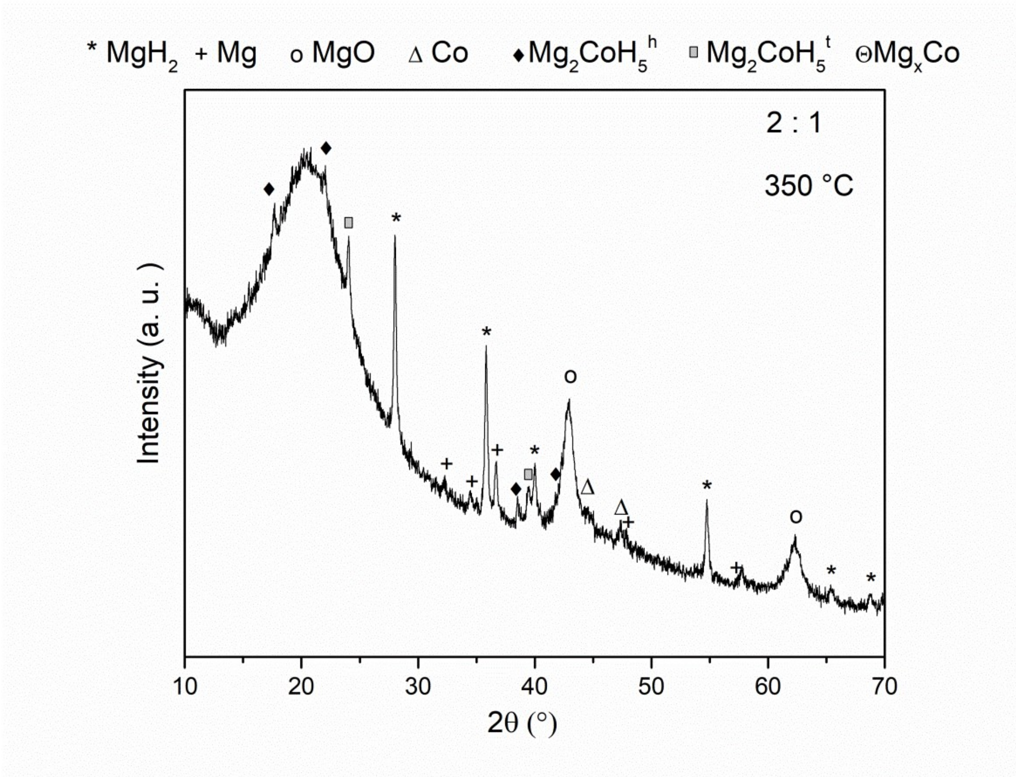

Figure S6: XRPD profile of the sample MgH_2-10%wt Co after thermal treatment under CO2 at 350°C, 24 h (molar ratio MgH_2:CO_2 of 2:1).

Table S1: Gas-phase composition determined by gas chromatography analyses of the MgH_2-10wt % Co sample at 300°C.

Reaction time (h)	Molar percentage of CH_4 (%)	Molar percentage of CO_2 (%)	Molar percentage of CO (%)	Molar percentage of H_2 (%)	CH_4 yield (%)
24 h	0,8	70.1	28	1.1	0.7

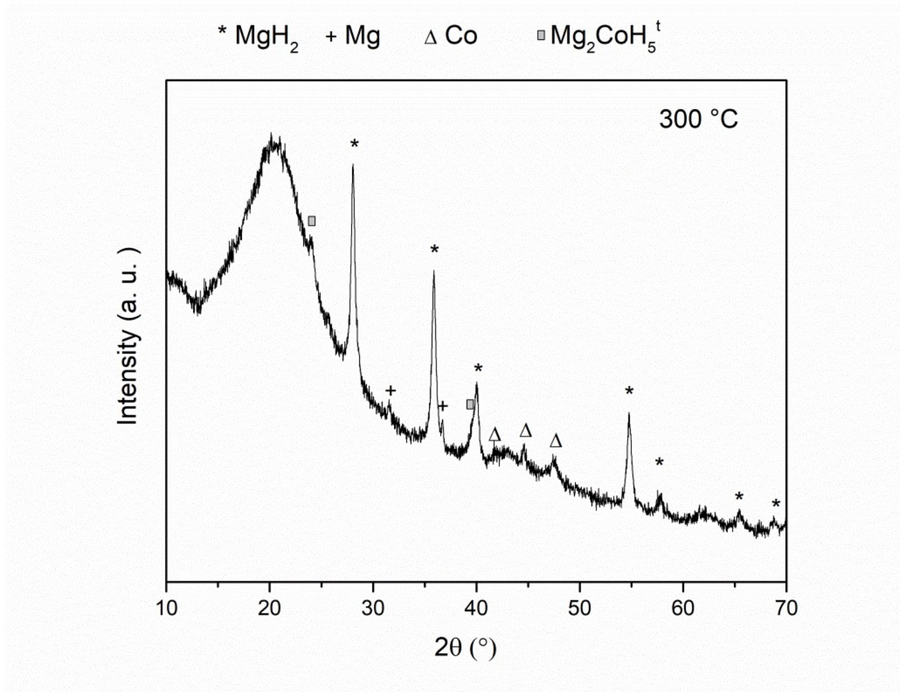

Figure S7: XRPD profile of the sample MgH_2-10%wt Co at 300°C with a molar ratio MgH_2:CO_2 of 4:1.

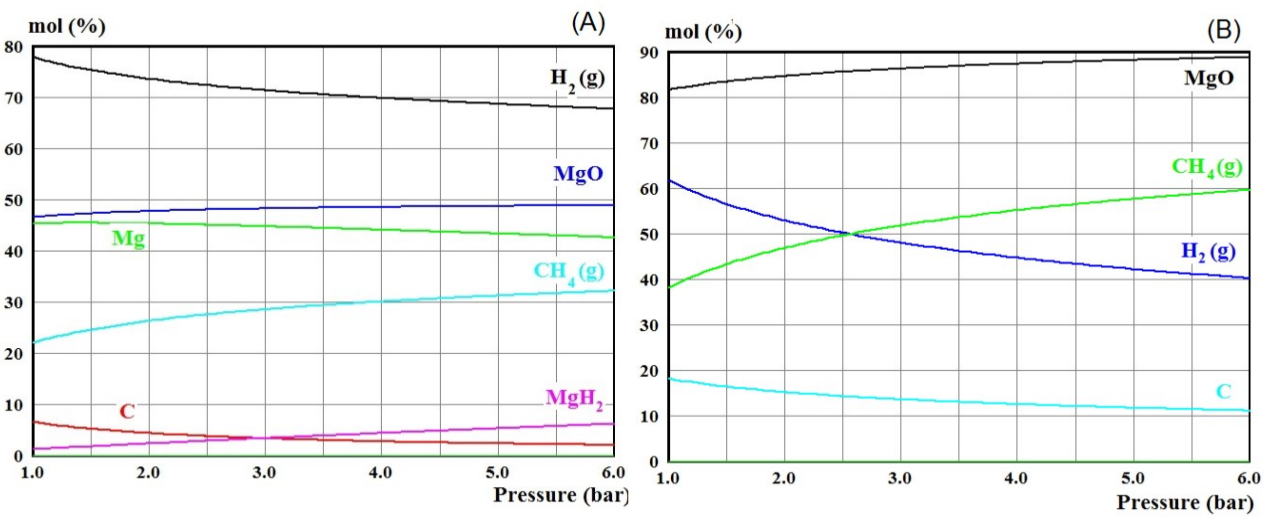

Figure S8: Equilibrium composition (mol%) as a function of pressure at 450 °C for a molar ratio MgH_2:CO_2 of 4:1 (A) and 2:1 (B).

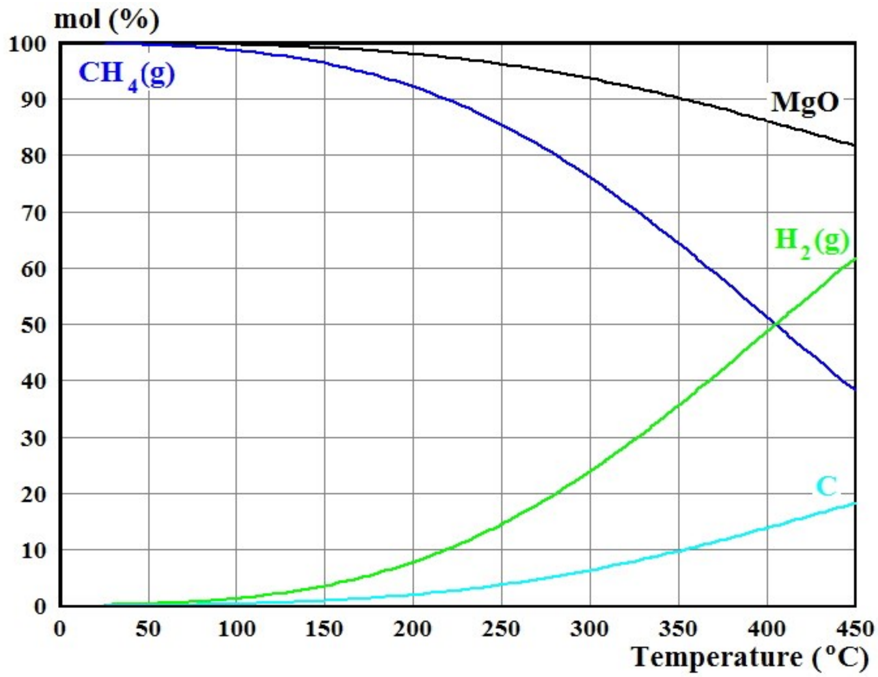

Figure S9: Equilibrium composition (mol %) as a function of temperature at 1bar for molar ratio MgH_2:CO_2 of 2:1.