Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Conversion of greenhouse gas CO_2 to methanol over supported intermetallic Ga-Ni catalyst at atmospheric pressure: Thermodynamic modelling and Experimental study

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Supplementary information

Fig. S1. shows the schematic procedure for the synthesis of Ga_3Ni_5 catalyst through three different preparation methods.

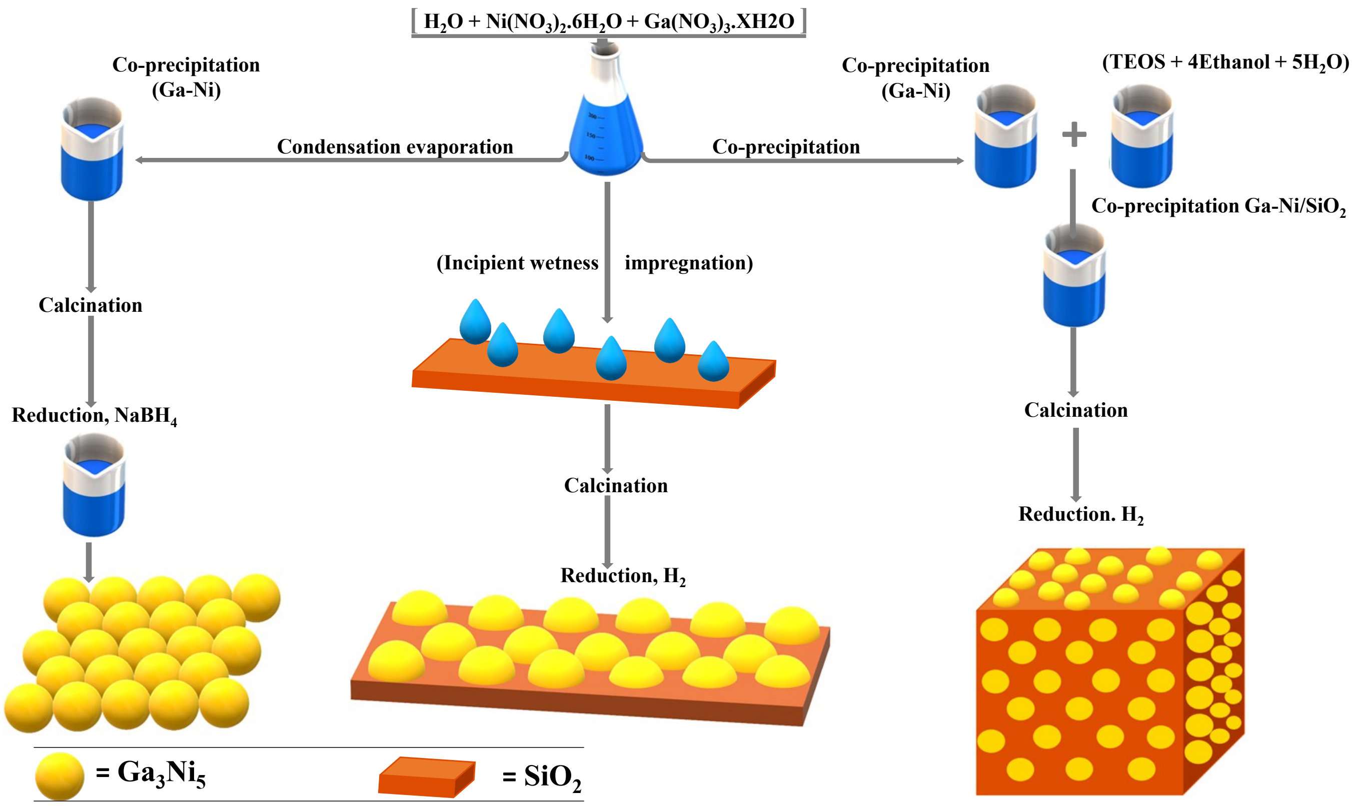

Fig. S1. Schematic Ga_3Ni_5 catalyst synthesis by three preparation methods.

From **Fig. S2,** the XRD pattern of calcined sample exhibits peak corresponding to NiO phase only, as the SiO_2 and Ga_2O_3 being amorphous in nature do not appear in anthe alysis. The peaks in the reduced sample at ~45^o, 50^o, 55^o, 76^o, and 87^o confirmed the formation of δ-Ga_3Ni_5 phase. The absence of any peak other than that of δ-Ga_3Ni_5 phase implies the phase purity and accuracy of catalyst preparation. The similarity in XRD patterns of spent and reduced catalysts indicates negligible change in phases during reaction and rules out sintering or dealloying of the catalyst.

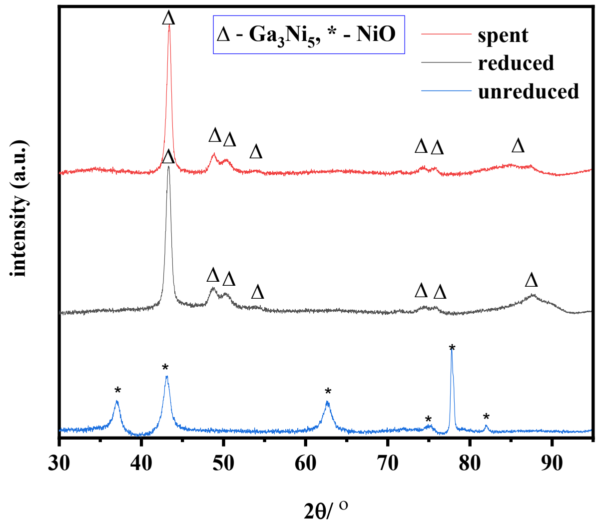

Fig. S2: XRD pattern of unreduced, reduced, and spent Ga_3Ni_5-CP catalyst compared with Ga_3Ni_5 (JCPDS: 00-043-1376) and NiO (JCPDS: 71-117).

Thermodynamic analysis:

The thermodynamic modelling in the main article was done based on the experimental outcome. Following are the possible reactions in addition to methanol synthesis which can occur in CO_2 hydrogenation process.

Table S1. Various reactions in direct hydrogenation CO_2.

Reaction	Reaction
1) Methanol synthesis	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$
2) Reverse water gas shift reaction	$CO_2 + H_2 \leftrightarrow CO + H_2O$
3) Dimethyl ether synthesis	$CO_2 + 4H_2 \leftrightarrow H_3COCH_3 + H_2O$
4) Methane formation	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$
5) Coke formation	$CO_2 + 2H_2 \rightarrow C(s) + 2H_2O$

The broader thermodynamic analysis involving the influence of temperature and CO_2/H_2 on CO_2 conversion and selectivity to various products considering all reactions (**Table**

S1) occurring simultaneously is depicted in **Fig. S3**. From the Fig. S3, the presence of reaction (1) and (5) has shifted the selectivity towards CH_4 and coke. Again, the CO_2 conversion has reached to its maximum and the process is least selective for methanol, DME, and CO. This behaviour can be attributed to the minimum Gibbs free energy change (ΔG) reaction (4) and reaction (5) among the reactions mention in Table S1. The ΔG calculated from the standard values of formation enthalpies and entropies [1] of all the reactions is plotted in **Fig. S4**.

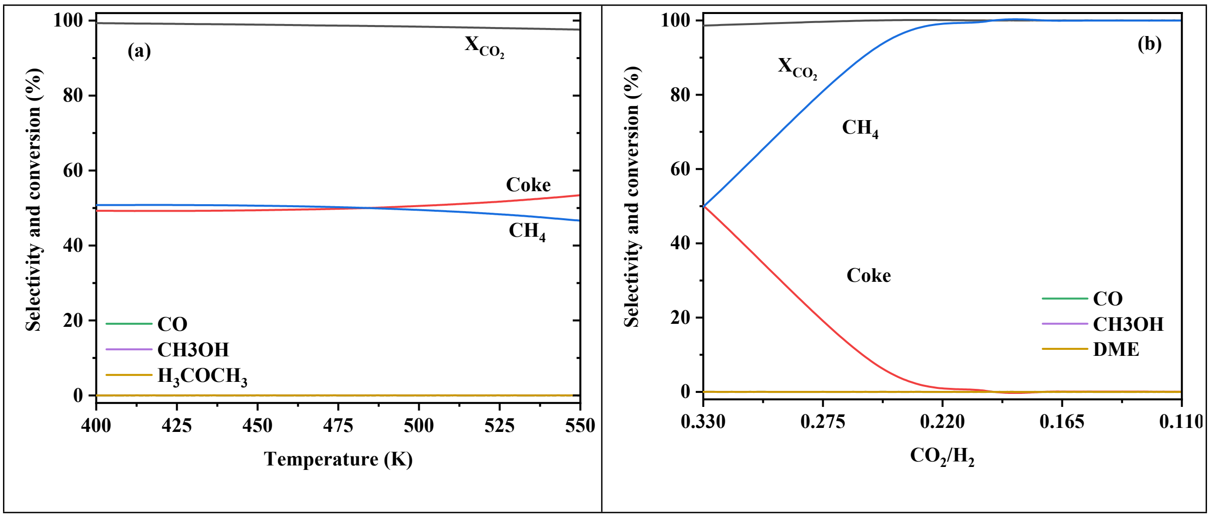

Fig. S3. Effect of temperature and CO_2/H_2 ration on CO_2 conversion and selectivity to CH_4, Gibbs free energy change for all considered reactions

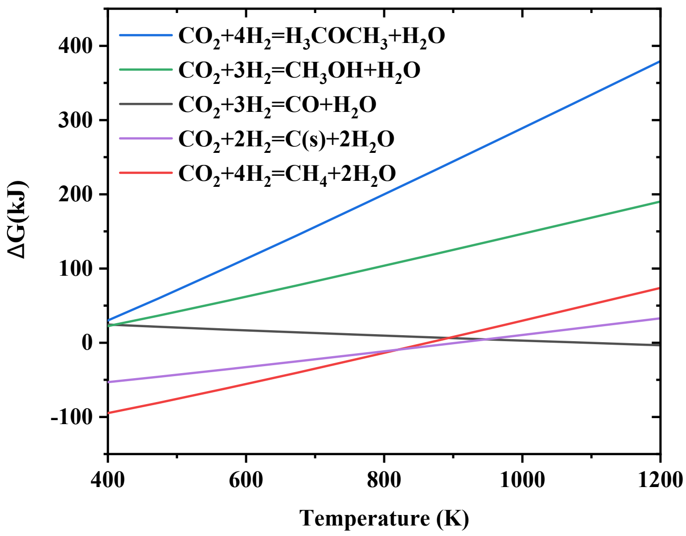

Fig. S4. Gibbs free energy change for all the reactions vs temperature.

XPS analysis was performed to further confirm the chemical nature of Ga_3Ni_5 nanoparticles in Ga_3Ni_5/SiO_2. The wide scan XPS spectra of Ni 2p and Ga 3p are shown in Fig. S5.

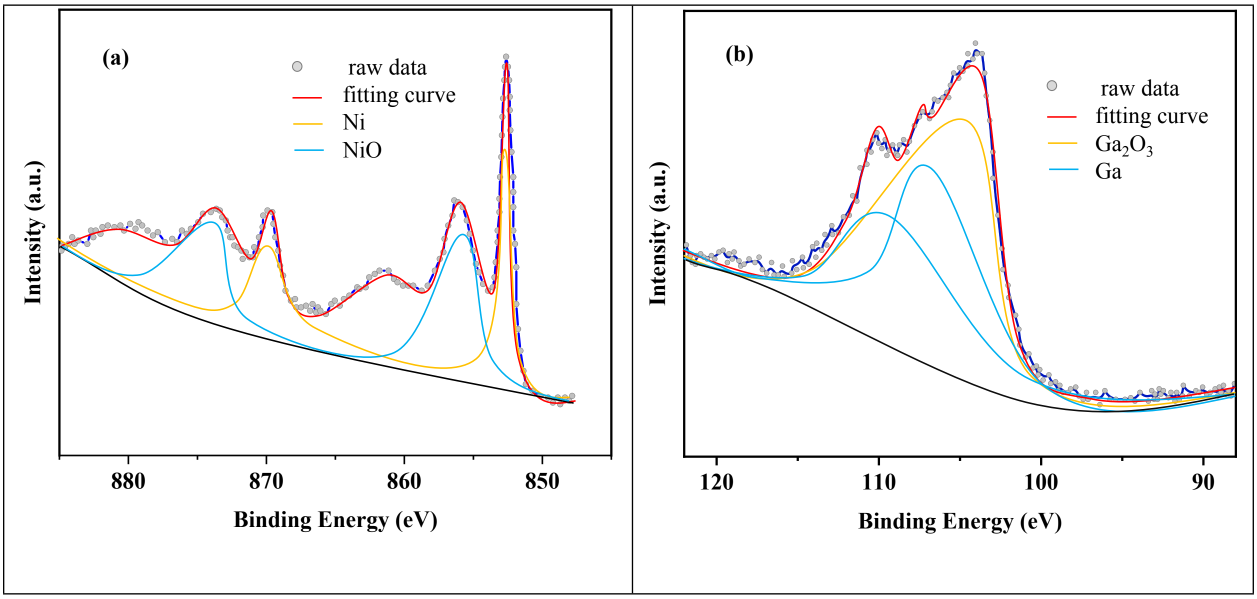

Fig. S5 XP spectra showing (a) the Ni 2p and (b) Ga 3p regions.

In the Ni spectra the peaks at ~852 eV and ~870 eV correspond to Ni in the nickel-gallium films, while the peaks at ~856 eV and ~874 eV correspond to oxidized Ni. Other peaks in the

Ni spectra are satellite peaks. In the Ga 3p region the peaks at ~106 eV and ~109 eV correspond to oxidized Ga while the small peak at ~104 eV corresponds to metallic Ga.

Reference

[1] M.M.A. J.M. Smith, H. C Van Ness, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill Chemical Engineering Series, McHGraw-Hill Education, 2005.