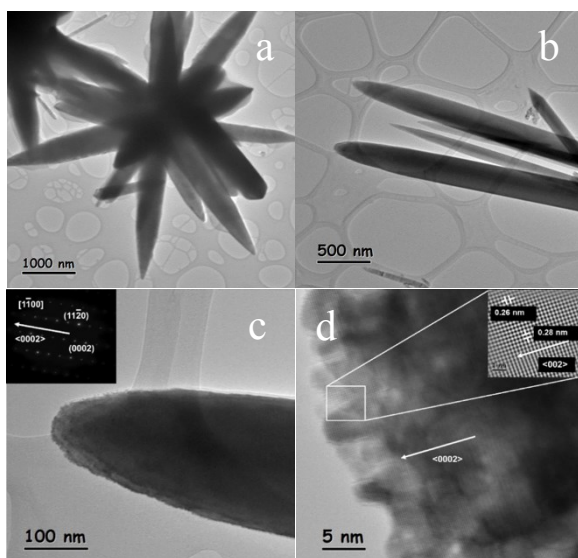


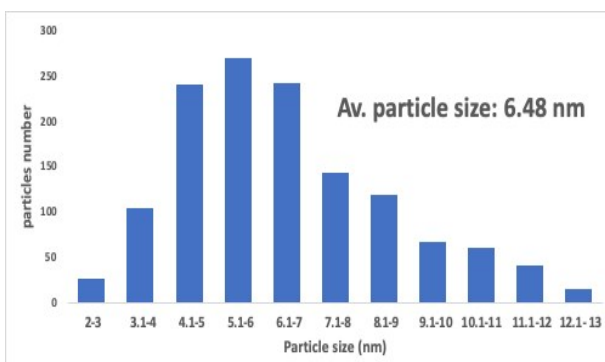
(SI-c and SI-d). This behavior was attributed to the presence of a higher Ni content versus the Pt content in the samples. Since the support has a low surface area, NiO agglomeration becomes more evident. Inset image (SI-c) shows that the Ni particles are distributed along the ZnO-rod.

SI. 1. A representative SEM image of the synthesized ZnO-rods and Ni, Pt and NiPt-supported ZnO-rod catalysts. All these samples possess a regular one-dimensional rod-like morphology<sup>1</sup>. SEM image of raw ZnO rod (SI-a). Pt/ZnO-rod shows Pt nanoparticles (inset image SI-b) distributed over the surface of the ZnO-rods support. SEM images of the monometallic Ni/ZnO-rod and bimetallic PtNi/ZnO-rod catalysts, showed a rough surface along the ZnO-rods can be identified in both samples

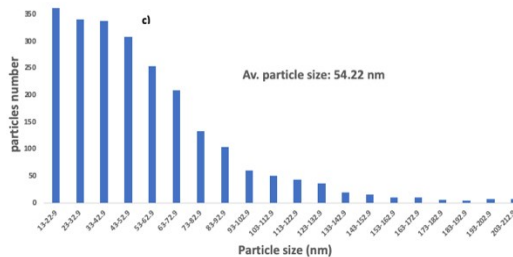
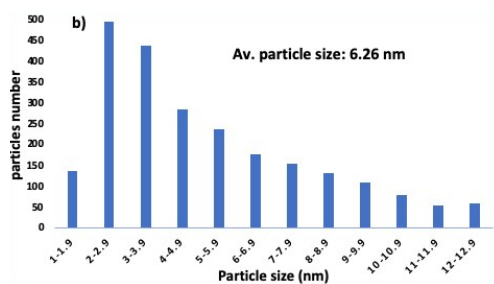


SI2. TEM and HRTEM images of raw ZnO-rod.

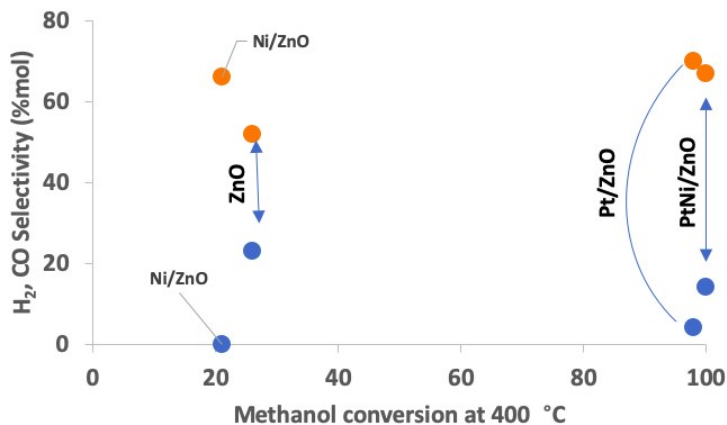
TEM characterization of raw ZnO-rods, showed that ZnO grows with star-like morphologies ca. 3  $\mu\text{m}$  long (SI2-a,b). Inset in SI2-c, shows the electron diffraction pattern of a ZnO-rod in the zone axes [1-100] which corresponds to Zincite (ZnO), with a hexagonal structure ( $a = 0.325 \text{ nm}$  and  $c = 0.520 \text{ nm}$ ), indicating that the rod grows in the <0002> direction. This is confirmed with the HRTEM image of the ZnO-rod shown in SI2-d. It was reported that ZnO-rods, like those in SI2-d are formed by the assembly of nanocrystals with a particle size ca. 5 nm<sup>2</sup>.



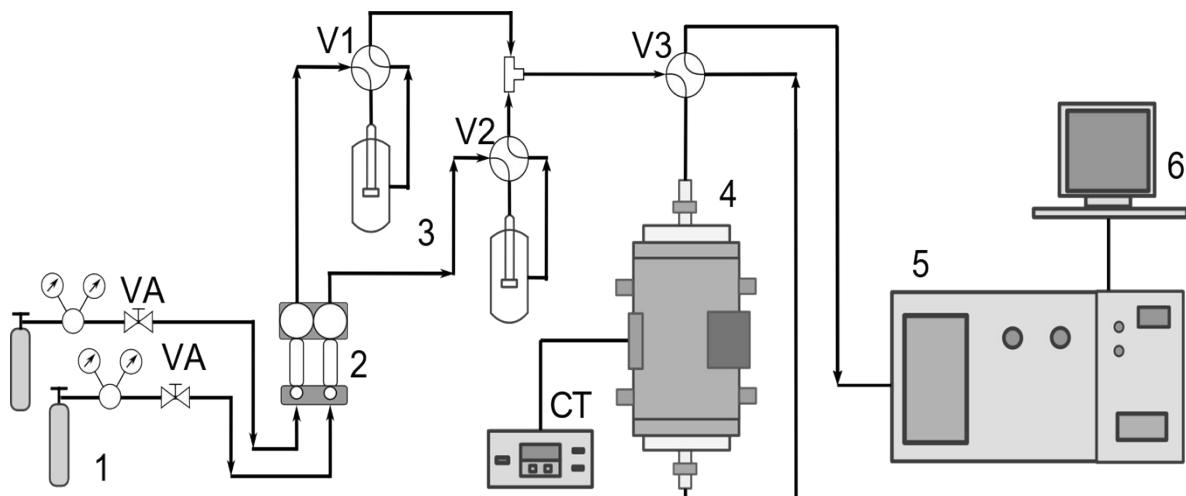
SI3a. Particle size distribution of the PtZn alloy, the analysis was based on the measurement of more than 1300 particles.



SI3. The particle size distribution of the PtZn alloy (b) and NiZn particles respectively on PtNi/ZnO catalyst (c).



SI4. Comparison of H<sub>2</sub> (orange) and CO (blue) selectivity as a function of methanol conversion on ZnO, Pt/ZnO, Ni/ZnO and PtNi/ZnO rod-catalysts at 350 °C. It is clear that the ZnO support is better to produce low CO selectivity and high selectivity for H<sub>2</sub> production.



SI5. Schematic design of experimental setup for ASRM measurements. VA-valve, (V1, V2, V3)-4-way valves, 1-gas supply, 2-mass flow controller, 3-Methanol-saturator and H<sub>2</sub>O-saturator, 4-Furnace and reactor, CT-Temperature Controller, 5-gas chromatography and 6-Workstation. Credits to Jorge Altamirano Cortes.

1. Pérez-Hernández, R. *et al.* Hydrogen Production by Steam Reforming of Methanol over a Ag/ZnO One Dimensional Catalyst. *Adv. Mater. Res.* **132**, 205–219 (2010).
2. Mondragón-Galicia, G., Gutiérrez-Wing, C., Eufemia Fernández-García, M., Mendoza-Anaya, D. & Pérez-Hernández, R. Ag nanowires as precursors to synthesize Ag–ZnO nanostructured brushes. *RSC Adv.* **5**, 42568–42571 (2015).