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Electronic Supplementary Information (ESI)

Lower methane combustion temperature on palladium nanoparticles anchored on TiO_x subnano-islets in stellate mesoporous silica nanospheres

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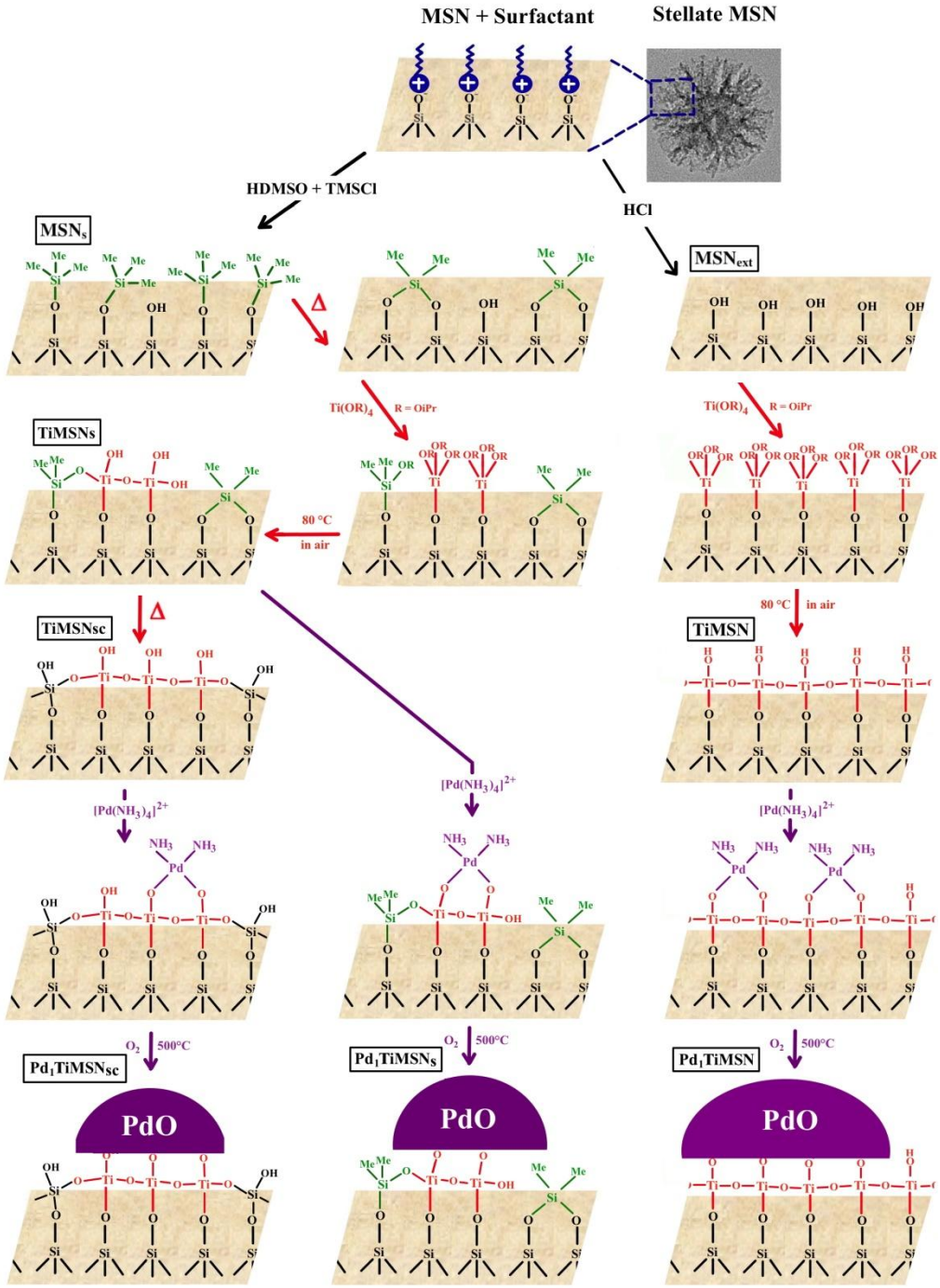

Scheme S1. Different synthesis routes followed to generate Pd_1TiMSNsc, Pd_1TiMSNs and Pd_1TiMSN catalysts.

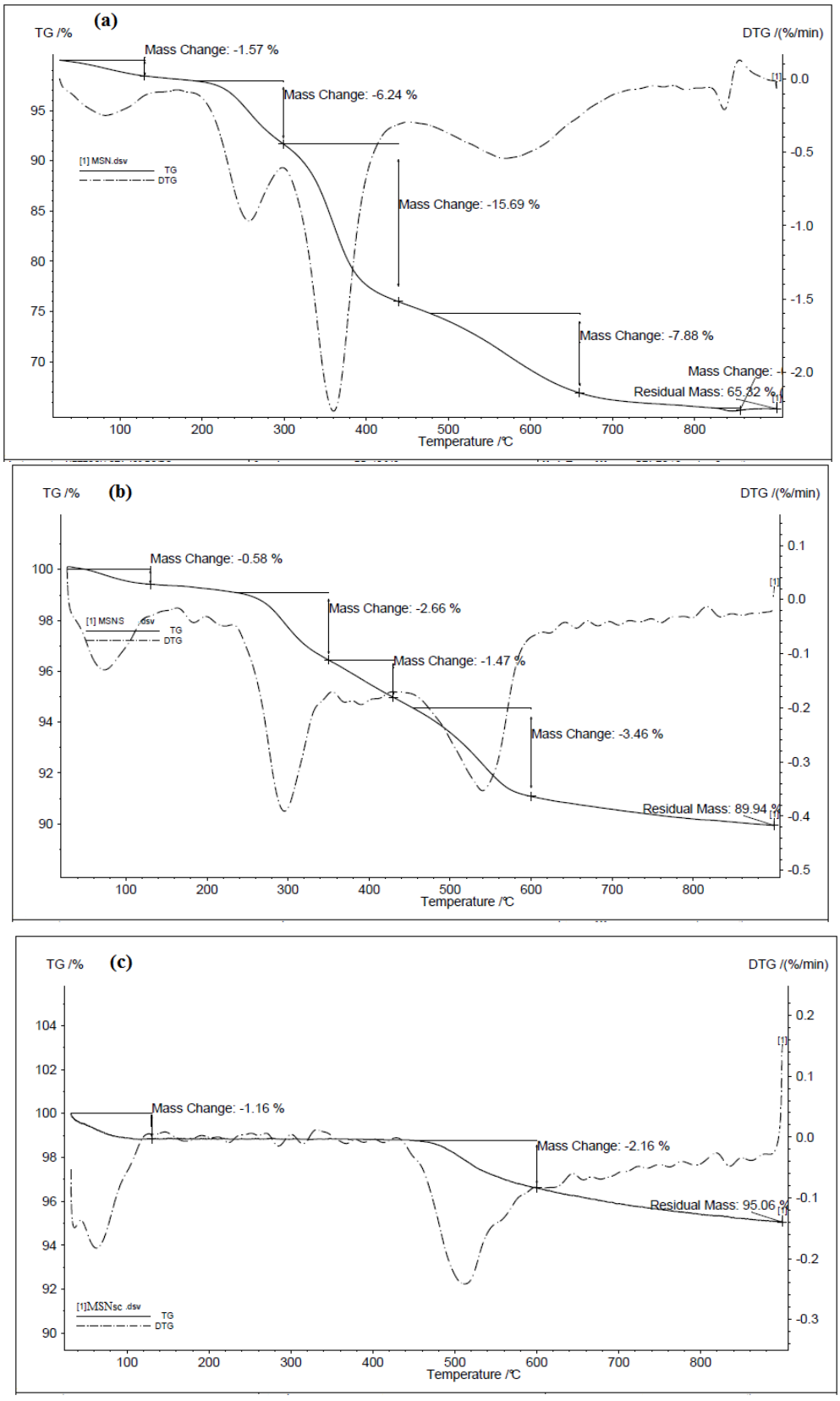

Fig. S1: Thermogravimetric analysis (TG) of (a) MSN, (b) MSN_S and (c) $MSN_{S'}$.

The first mass loss occurring at 130 °C was attributed to physically adsorbed water. The weight loss centered at 350 °C was attributed to CTA^+ adsorbed onto its tosylate counterion and the peak located at 250 °C was associated to CTA^+ interacting directly with silanolate groups (SiO^-). The last mass loss at 600 °C was assigned to water evolution from silanol condensation. Fig. S1b shows TGA profiles of silylated MSN particles (MSN_S) which displays weight loss at 100 °C due to the adsorbed water of the external surface of MSN and it was approximately less than 0.5% which confirm the hydrophobicity enhancement obtained by the replacement of the surface silanol groups by trimethylsilyl groups. A small

weight loss was observed at 300 °C probably due to the remaining surfactant. The decomposition of TMS groups occurs at higher temperature, between 450° and 600 °C. The TGA decomposition curve of silylated MSN particles (MSN_s) after calcination at 450ºC ($MSN_{S'}$) shows the appearance of a small weight loss about 550 °C attributed to the decomposition of methyl groups to form siloxane bridge.

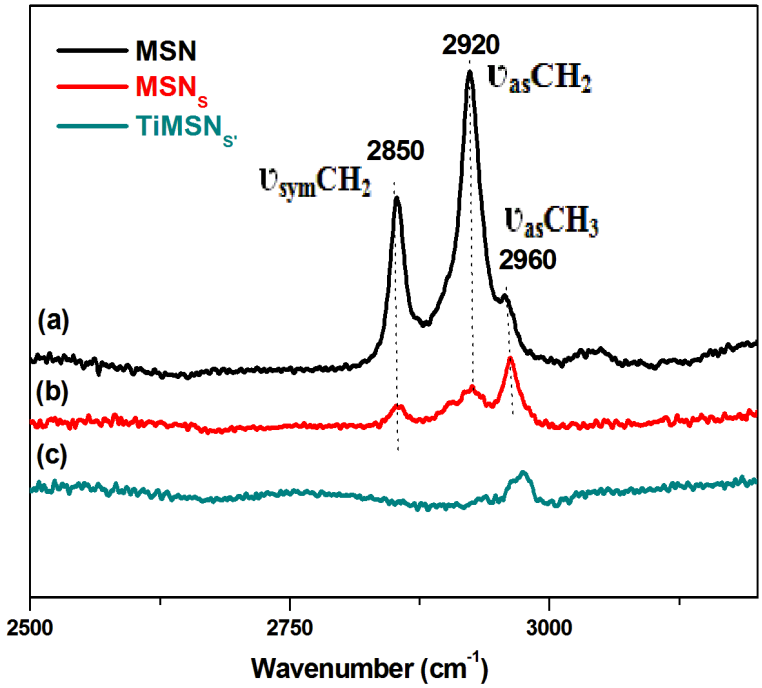

Fig. S2: FT-IR spectra of (a) as-made MSN, (b) MSNs and (c)$TiMSN_{S'}$.

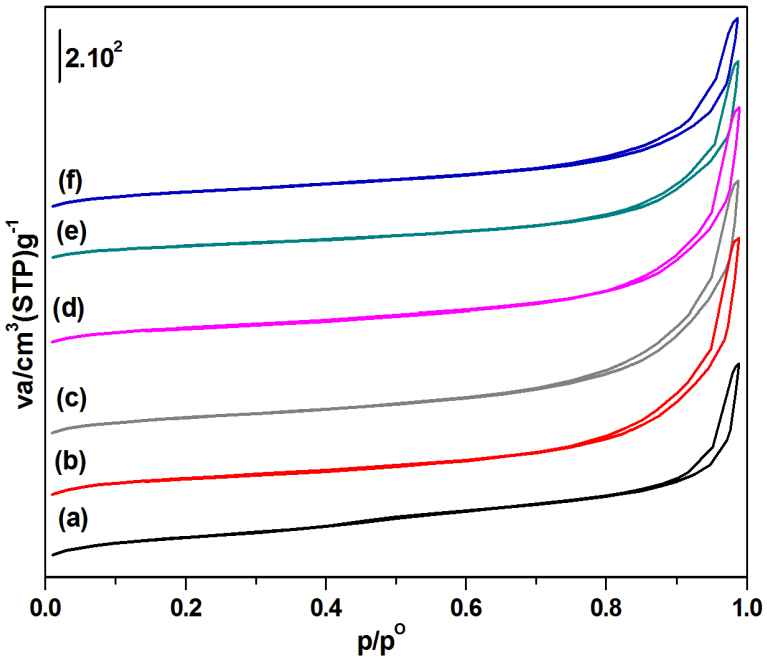

Fig. S3: N_2 adsorption-desorption isotherms at 77K of calcined materials (a) Pd_1MSN, (b) $Pd_{0.2}MSN$, (c) $Pd_{0.2}TiMSN$, (d) Pd_1TiMSN, (e) Pd_1TiMSN_S, and (f) $Pd_1TiMSNsc$.

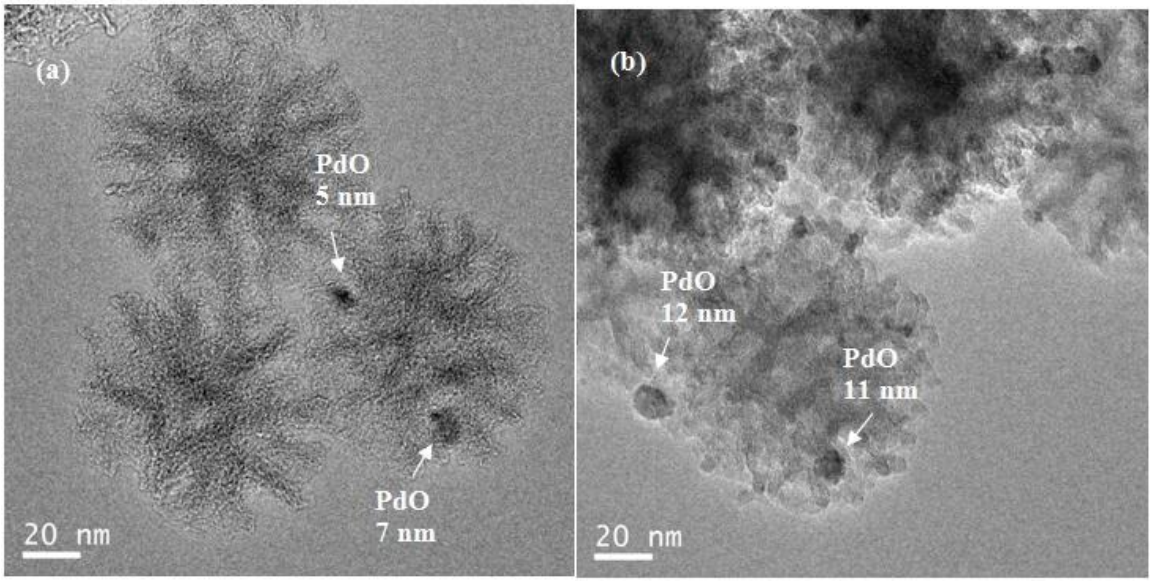

Fig. S4: TEM images of (a) $Pd_{0.2}TiMSN$ and (b) Pd_1TiMSN catalysts.

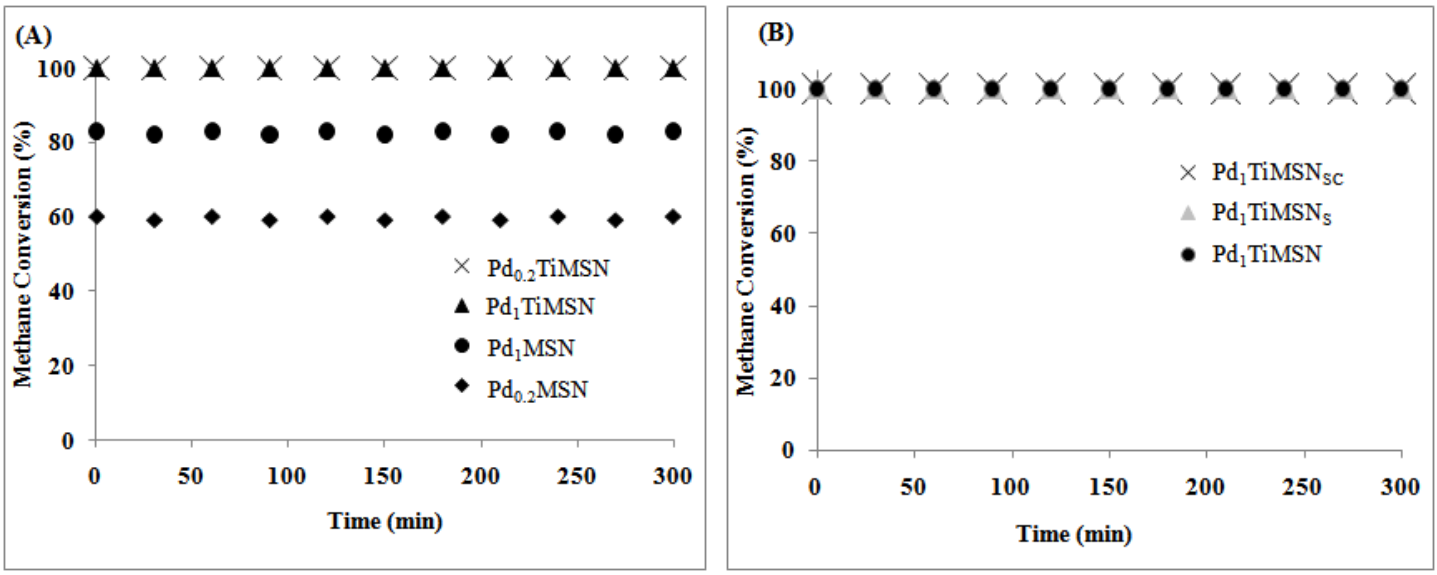

Fig. S5: Stability test at 500°C of catalysts (A) Pd_1TiMSN, $Pd_{0.2}TiMSN$, Pd_1MSN and $Pd_{0.2}MSN$ and (B) Pd_1TiMSN, Pd_1TiMSN_S and Pd_1TiMSN_{SC}.

Table S1: H/Pd molar ratio of hydrogen consumed by reduction or by formation of hydride between 25 and 80 °C from Temperature programmed reduction (TPR) and tentative distribution of PdH_2, Si-H and Ti^{3+}.

catalysts	Pd[a] (mmol g^{-1})	H_2 consumption[b] (mmol g^{-1})	H/Pd[c]	molar distribution per Pd of H spill over / PdH_2 / Ti^{3+} [d]
$Pd_{0.2}$MSN	0.019	0.042	4.4	2.4 / 1 / 0
$Pd_{0.2}$TiMSN	0.019	0.055	5.8	2.4 / 1 / 2.4
Pd_1MSN	0.103	0.383	7.4	5.4 / 1 / 0
Pd_1TiMSN	0.103	0.307	5.6	2.4 / 1 / 2.2
Pd_1TiMSN_S	0.094	0.239	5.1	2.4 / 1 / 1.7

a) Pd content from chemical analysis

b) H_2 consumption from the area integration of TCD signal mesured between 50 to 75°C;

c) molar ratio of hydrogen atoms consumed per palladium atoms

d) molar ratio of Si-H, Ti^{3+} ions species calculated assuming that, i) at 25°C PdO particles are totally reduced into metallic Pd^0 particles, ii) yielding first hydride PdH_2 above 25°C followed by reduction of the support consumption of the hydride forming Si-H from surface silanol groups, Si-OH and Ti^{3+} ions in the presence of TiO_x anchoring sub-nano islands.