

Supplementary Information

Materials:

Titanium (IV) Isopropoxide (97+ %) was purchased from Alfa Aesar. Benzaldehyde (98 %) was purchased from Baker and Adamson. Ammonium Metatungstate Hydrate (≥ 99.0 %) and Acetophenone (≥ 99.0 %) were purchased from Fluka. Methyl Alcohol Anhydrous (98.8 %) was purchased from Acros. Phenylacetaldehyde (≥ 90 %) and Phenylacetaldehyde Dimethyl Acetal (98+ %) were purchased from SACF. Zirconium (IV) Butoxide (80% wt in 1-butanol), Hafnium (IV) Chloride (98 %), Poly (ethylene glycol)- block- Poly(propylene glycol)-block-Poly(ethylene glycol) PEO₂₀-PPO₇₀-PEO₂₀ (Pluronic P123), Cyclohexanone (≥ 99.5 %), (1,1-Dimethoxy-ethyl) Benzene (97 %), Benzaldehyde Dimethyl Acetal (99 %), Cyclohexanone Dimethyl Ketal (99 %), Nitric acid (70 %), and Trans-Cinnamonaldehyde (≥ 99 %) were purchased from Sigma-Aldrich. Commercial catalysts P-25 was purchased from Degussa Inc., ZSM-5 was purchased from Zeolyst Inc., and Amberlyst 15 was purchased from Sigma-Aldrich. All chemicals were used directly as received and without further purification.

Table S1. Ti 2p_{3/2}, O 1s, and W 4f_{7/2} XPS binding energies (BE) of X% W-Ti (X=0, 5, 10, 20, 30) and WO₃.

	Ti 2p_{3/2}	O 1s	W 4f_{7/2}
Catalyst	BE (eV)	BE (eV)	BE (eV)
WO₃	-	530.79	35.84
0%W-Ti	459.07	530.72	-
5%W-Ti	458.44	530.23	35.71
10%W-Ti	458.44	529.85	35.64
20%W-Ti	458.61	529.93	35.58
30%W-Ti	458.67	529.91	35.40

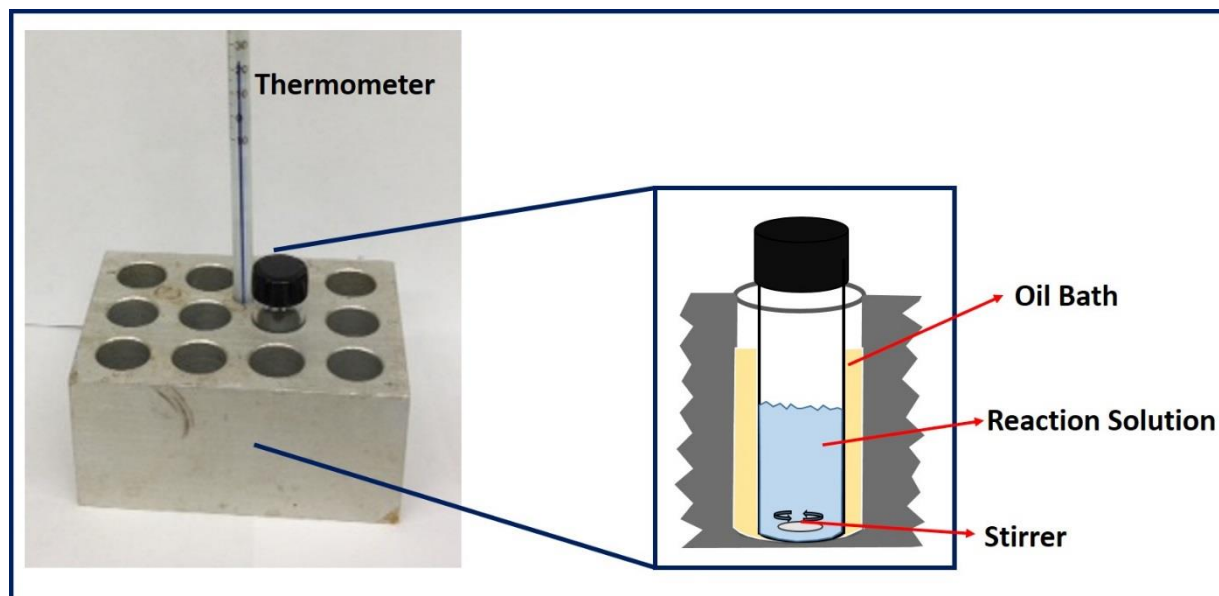


Figure 1S. Picture and schematic description of catalytic study set up (Dimensions of set up: 5x5x10 cm.).

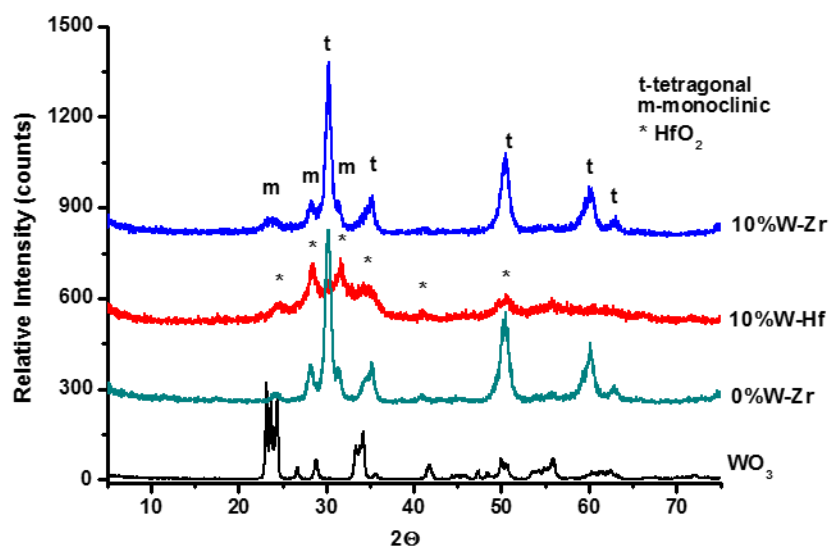


Figure 2S. Wide-angle PXRD patterns of 0% W-Zr, 10% W-Zr, 10% W-Hf, and WO₃.

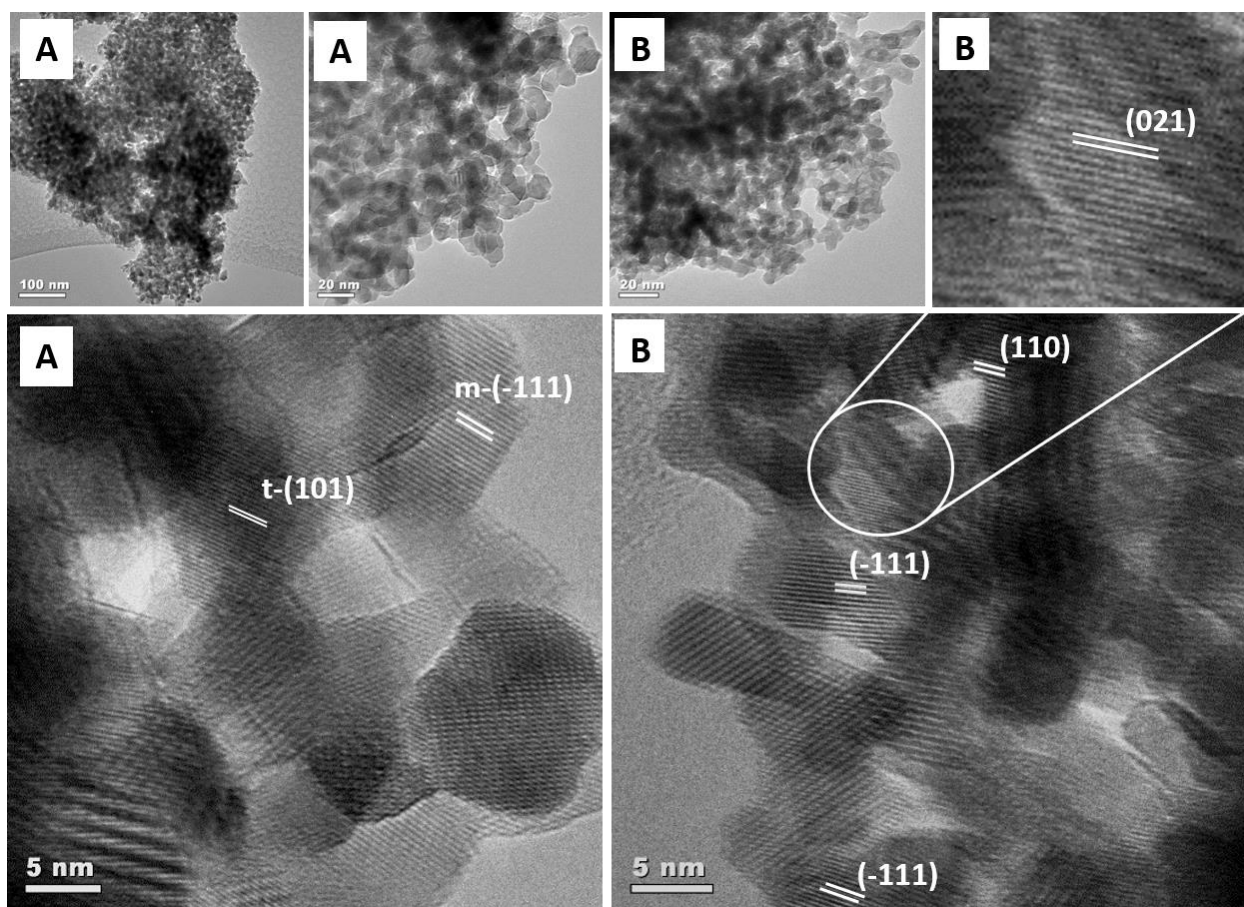


Figure S3. HR-TEM images of (A) 10% W-Zr (m stands for monoclinic phase and t stands for tetragonal phase) and (B) 10% W-Hf.

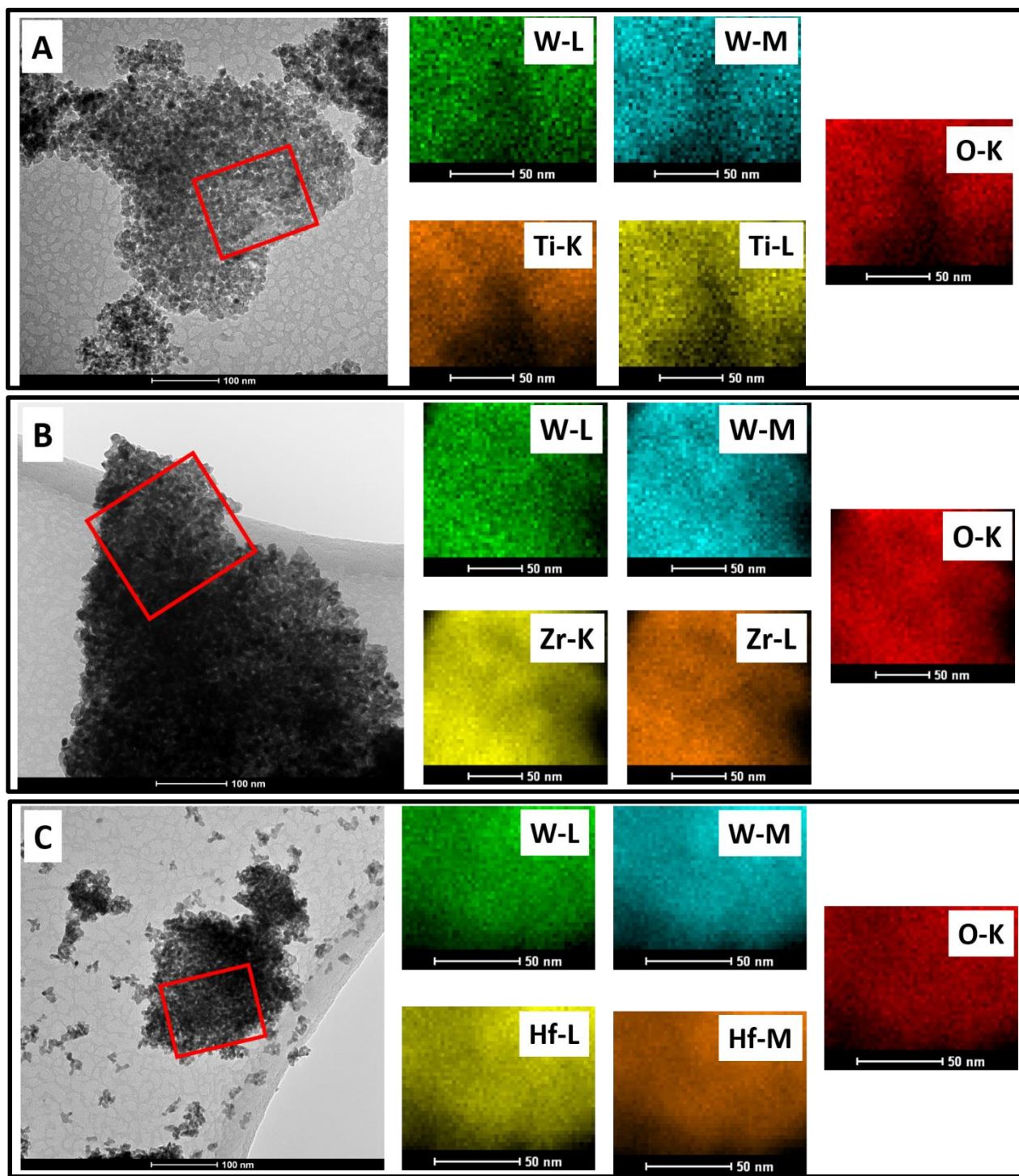


Figure S4. TEM images and EDAX mapping at selected area (red box in TEM images) of (A) 10% W-Ti (B) 10% W-Zr, and (C) W-Hf samples.

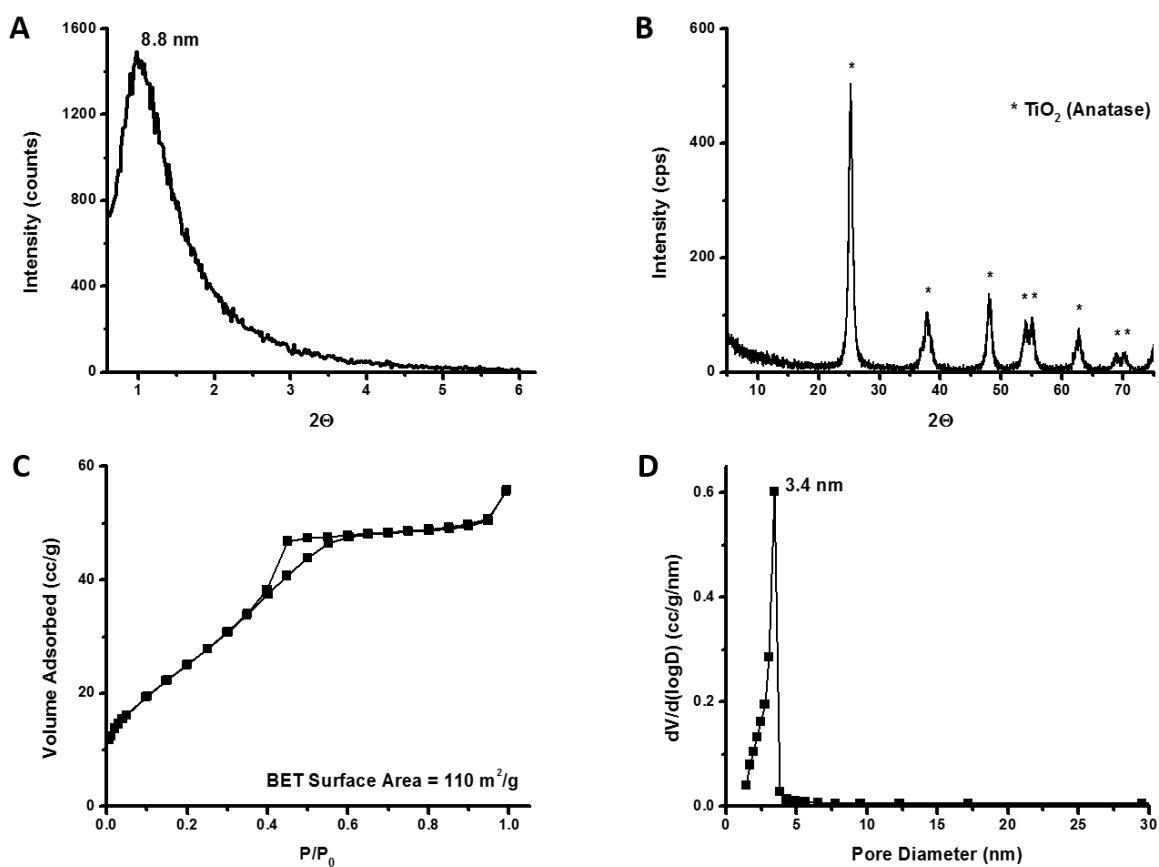


Figure S5. (A) Low-angle PXRD, (B) Wide-angle PXRD, (C) N_2 sorption isotherm, and (D) BJH Desorption pore size distribution of 0% W-Ti sample calcined at 450°C for 4 h.

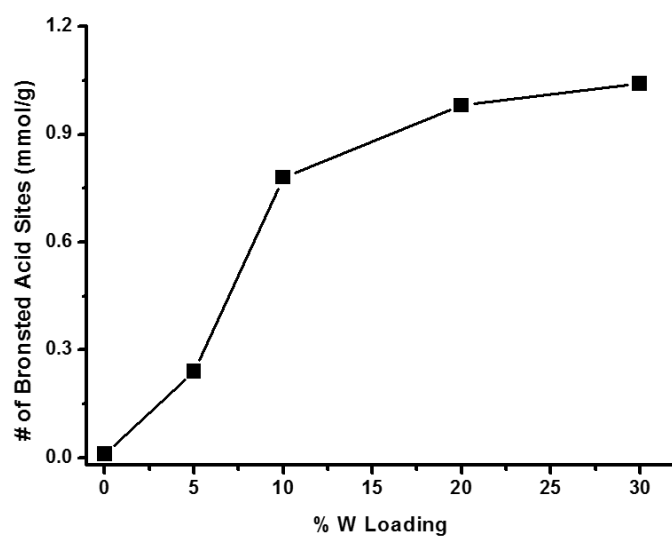
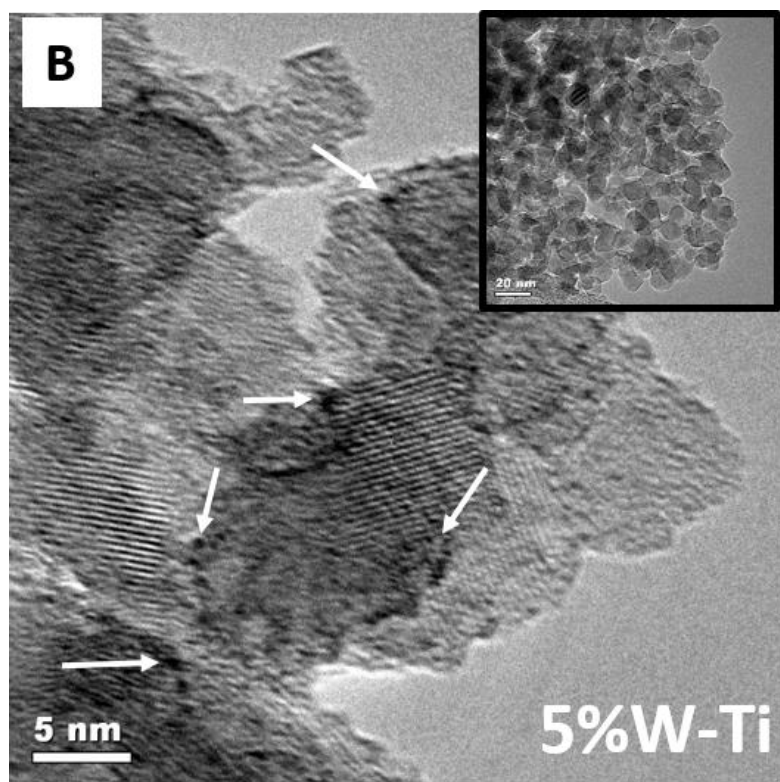
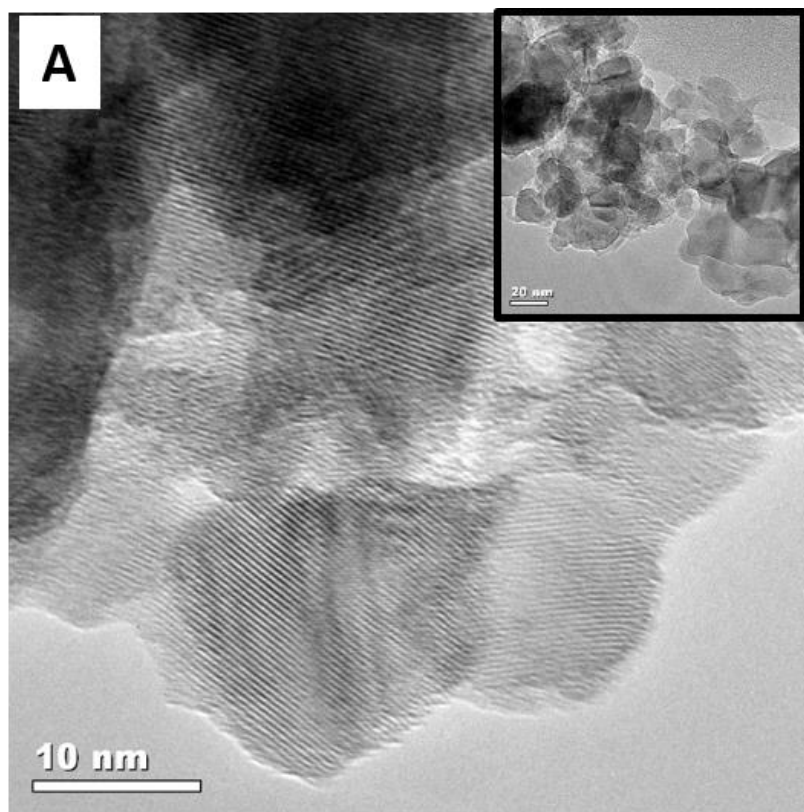


Figure S6. Number of Brønsted acid sites of X% W-Ti samples (X= 0, 5, 10, 20, 20) determined by titration experiments.



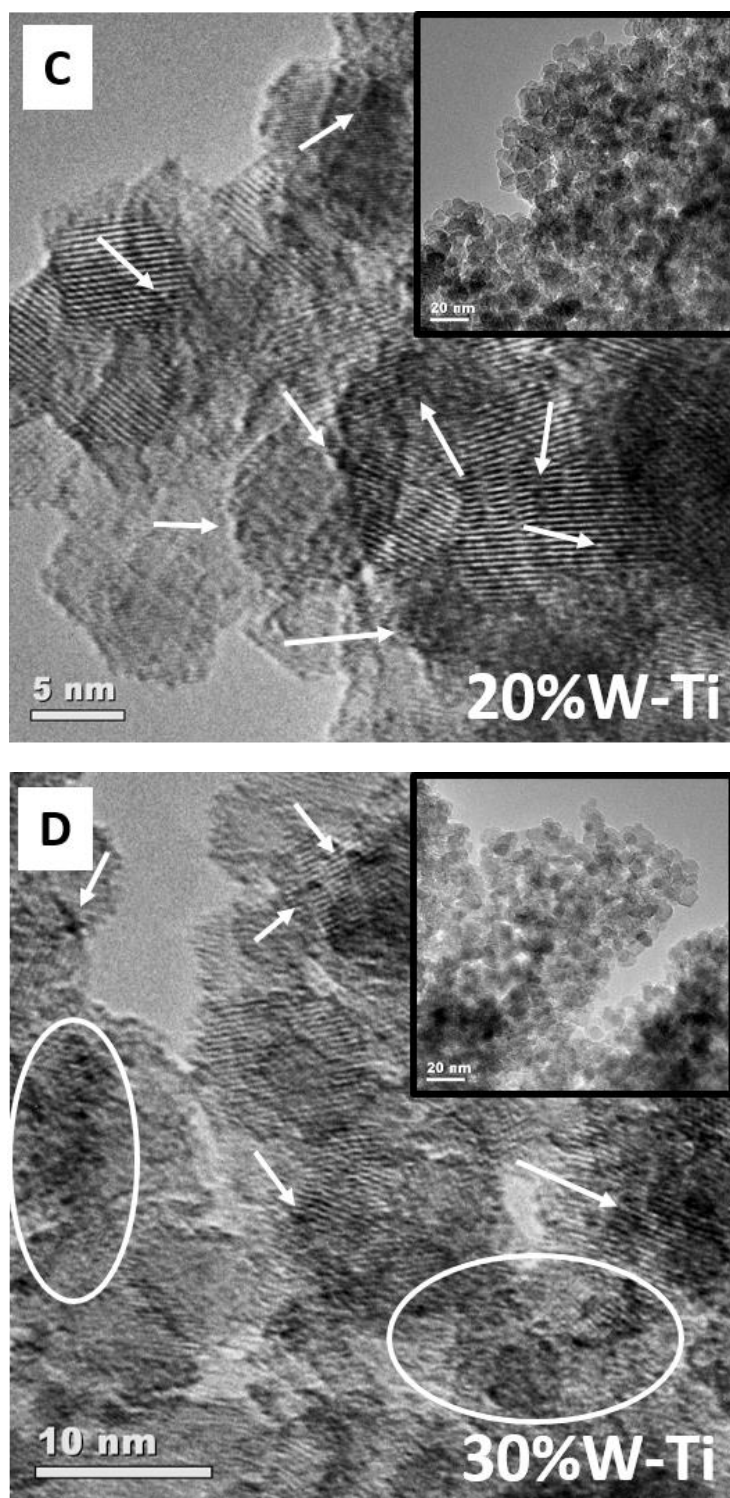


Figure S7. HR-TEM images of (A) 0% W-Ti, (B) 5% W-Ti, (C) 20% W-Ti, and (D) 30% W-Ti. White arrows point some of the nano-WO_x clusters and white circles highlight the regions with high number of nano-WO_x clusters.

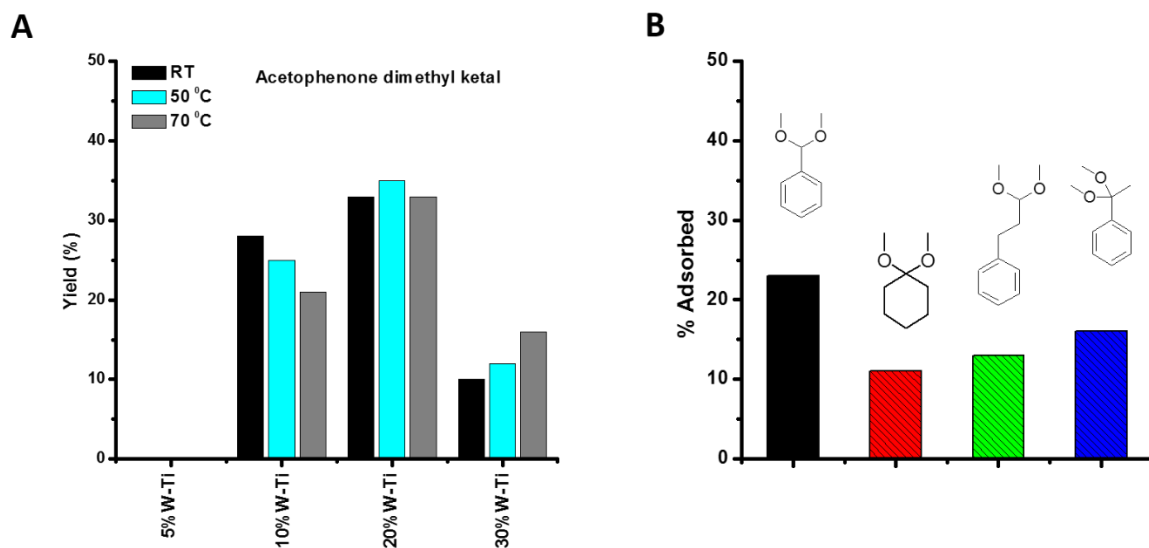


Figure S8. (A) Effect of temperature on acetophenone ketalization with X% W-Ti catalyst, where X = 5, 10, 20, 30 (0.5 mmol substrate in 5 mL MeOH (0.1 M), 25 mg of catalysts, RT-70°C, 4 h). (B) Adsorption of acetals and ketals on 10% W-Ti (1 mmol product in 5 mL MeOH (0.1 M), 25 mg of catalysts, RT, 2 h).