Complete Dehydrogenation of Hydrazine Borane on Manganese Oxide Nanorods Supported Ni@Ir Core-Shell Nanoparticles

(Supporting Information)

Mehmet Yurderi,[†] Tuba Top,[†] Ahmet Bulut,[†] Gulsah Saydan Kanberoglu,[†] Murat Kaya,[‡] Mehmet Zahmakiran[†,]*

[†] Nanomaterials and Catalysis Research Group, Department of Chemistry, Van Yuzuncu Yil University, 65080, Campus, Van, Turkey

[‡] Department of Chemical Engineering and Applied Chemistry, Atilim University, 06836, Ankara, Turkey

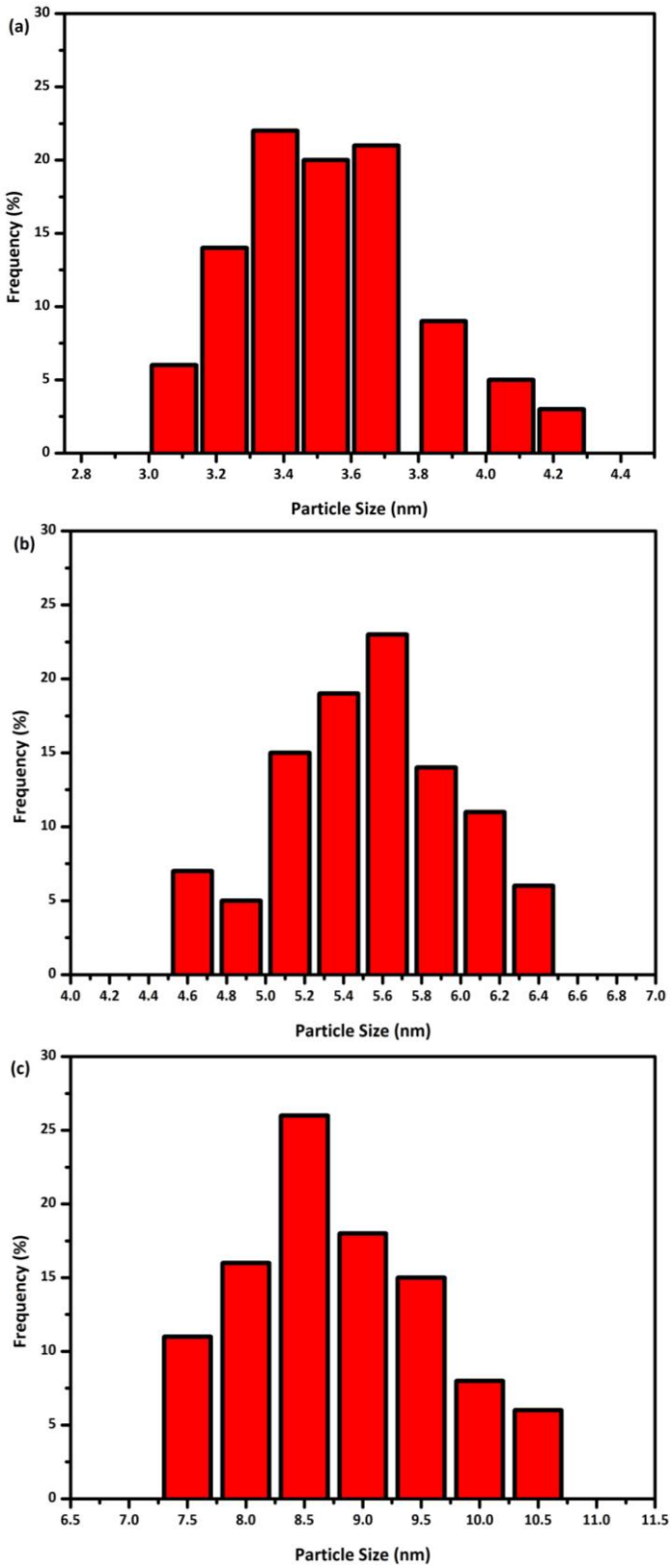

Figure S1. The particle size histograms of (a) Ni NPs, (b) Ir NPs, (c) Ni@Ir NPs.

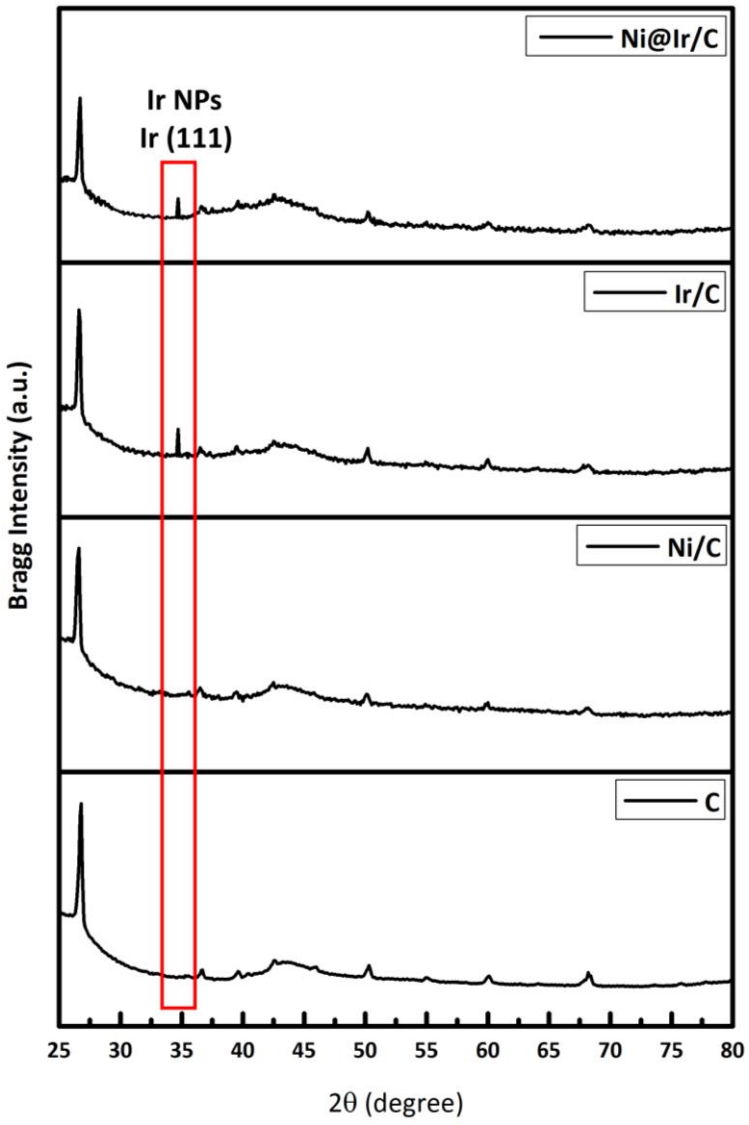

Figure S2. P-XRD patterns of C, Ni/C, Ir/C and Ni@Ir/C samples in the range of 2θ = 25-80°.

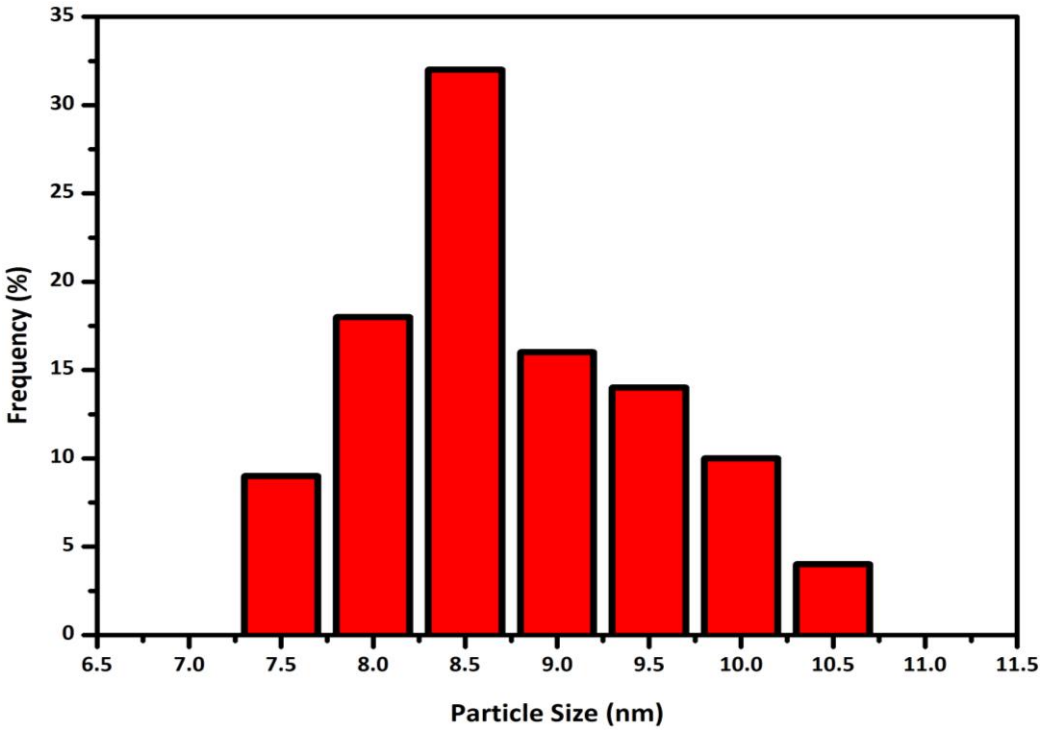

Figure S3. The particle size histograms of $Ni_{0.78}@Ir_{0.22}$/OMS-2 catalyst.

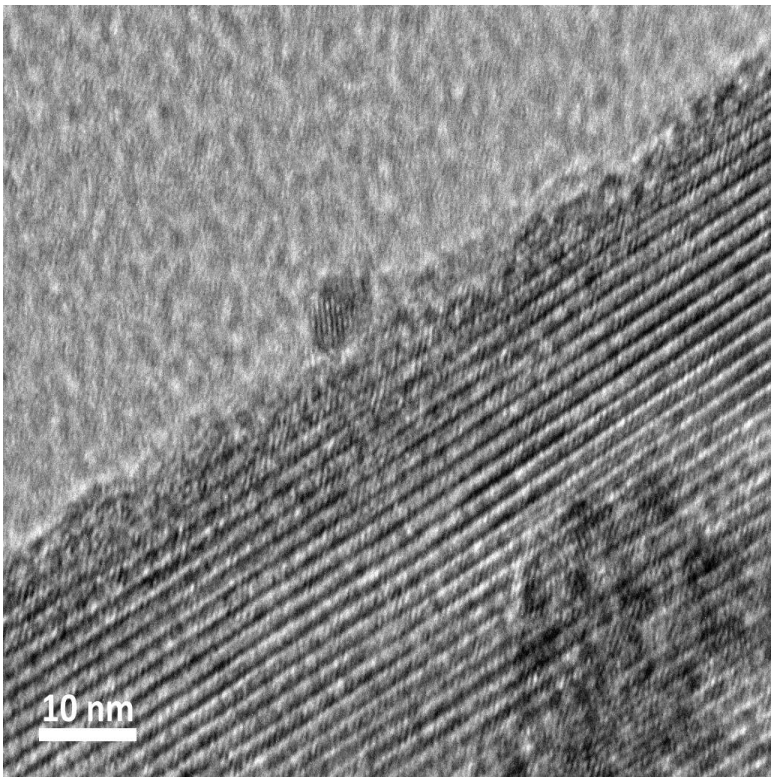

Figure S4. HRTEM image of $Ni_{0.78}@Ir_{0.22}$/OMS-2 catalyst.

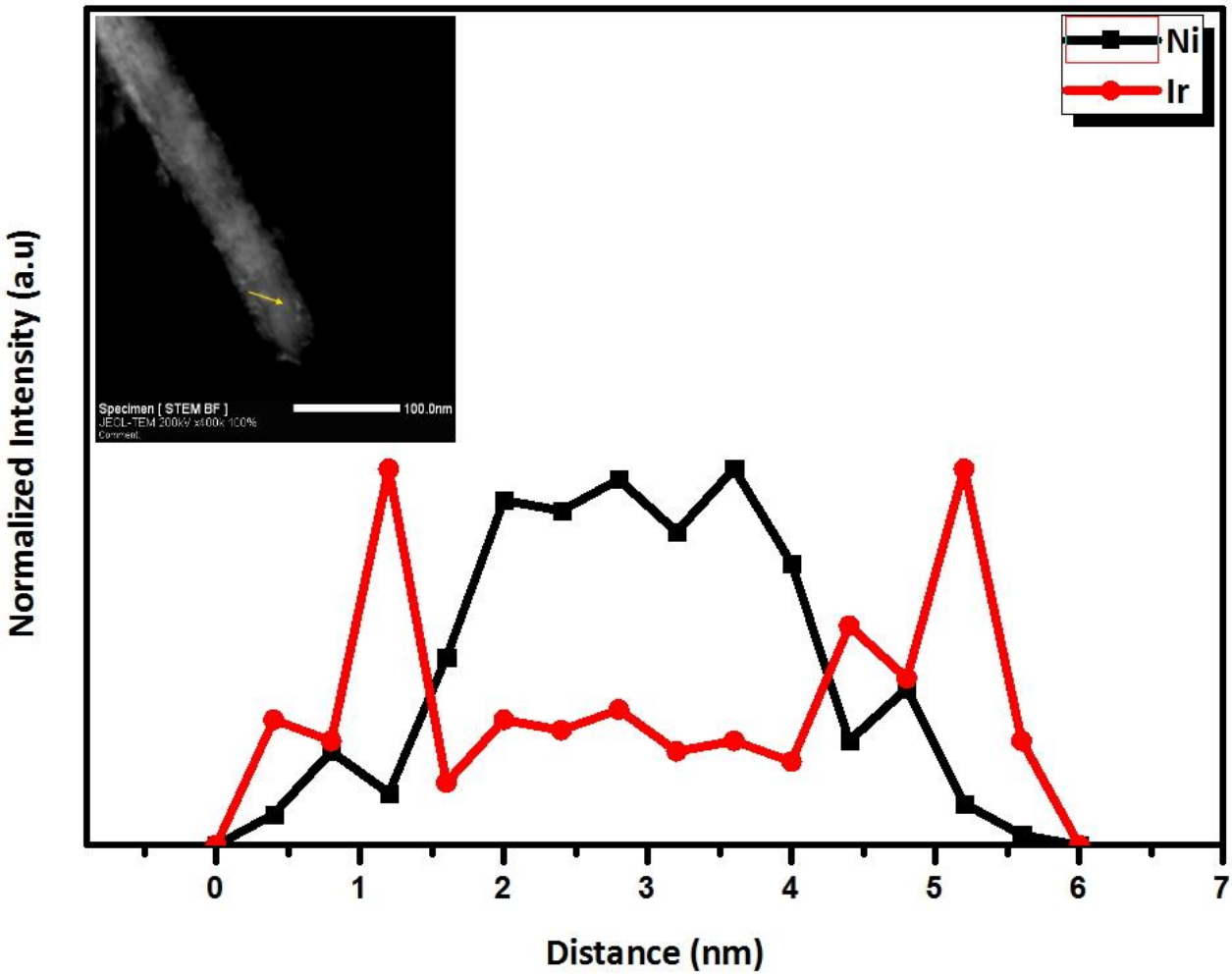

Figure S5. HAADF-STEM line analysis of $Ni_{0.78}@Ir_{0.22}$/OMS-2 catalyst.

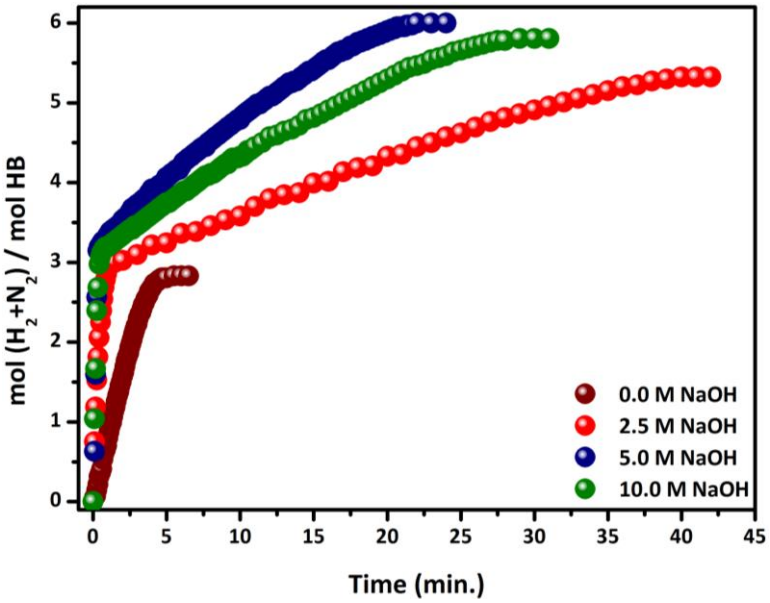

Figure S6. Mole ratio of generated gas (H_2 + N_2)/HB versus time graph for $Ni_{0.22}$@$Ir_{0.78}$/OMS-2 catalyzed dehydrogenation of aqueous HB (in all [Ni + Ir] = 1.264 mM, [HB] = 0.2 M, V_{water} = 5.0 mL) starting with various NaOH concentrations (0.0, 2.5, 5.0 and 10.0 M) at 323 K.

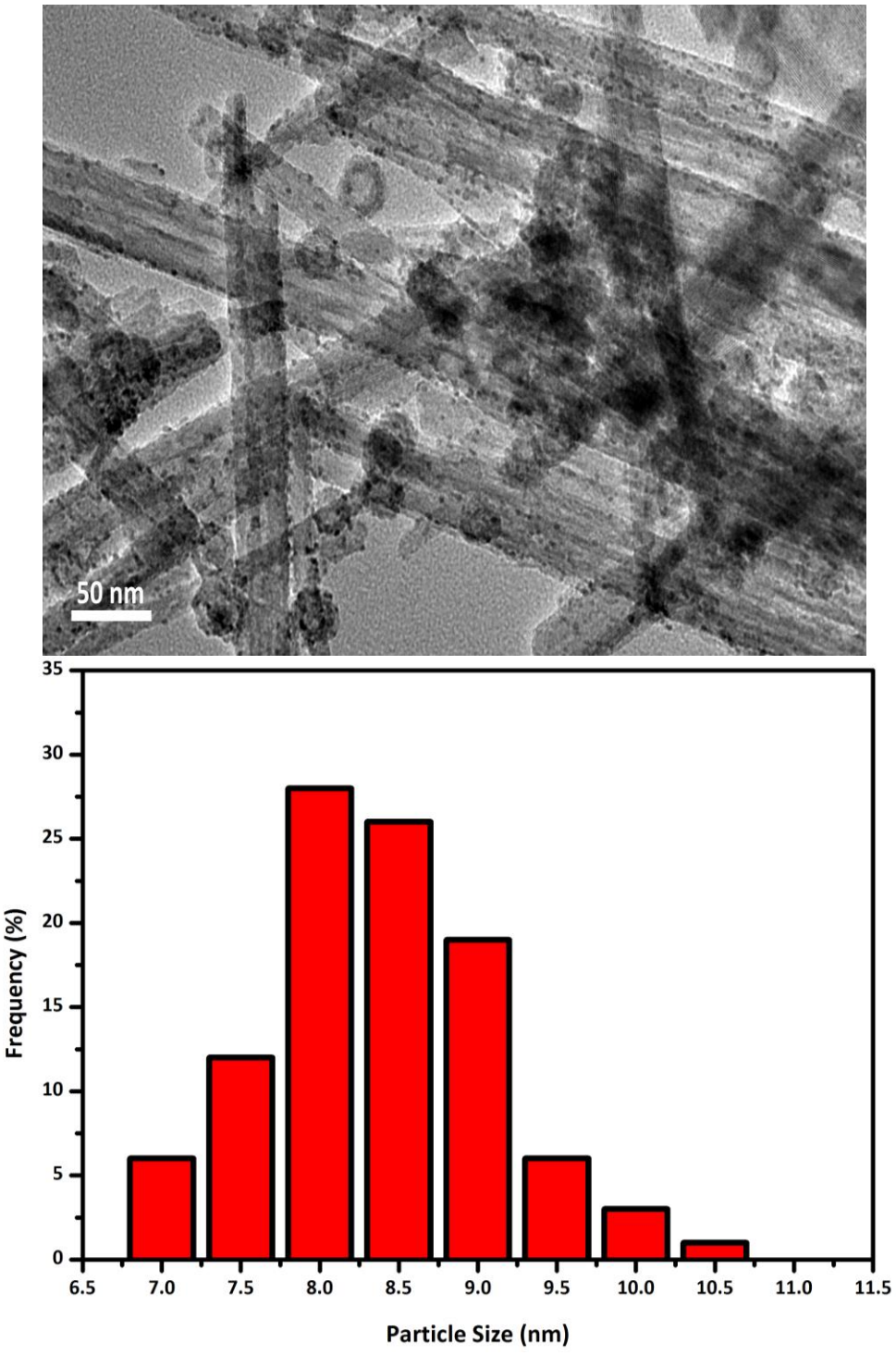

Figure S7. BFTEM image and corresponding particle size histogram of $Ni_{0.76}@Ir_{0.24}$/OMS-2 catalyst.

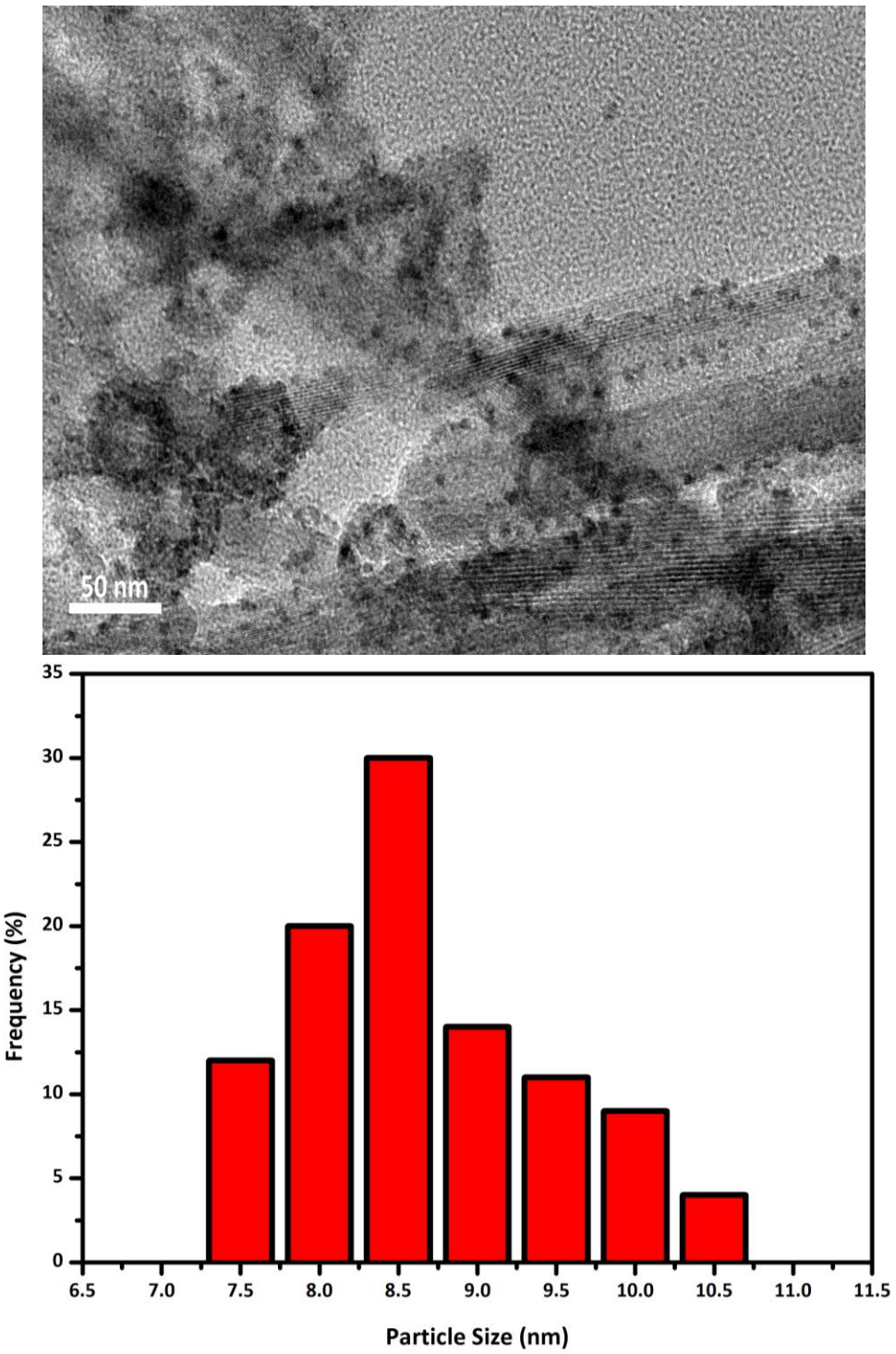

Figure S8. BFTEM image and corresponding particle size histogram of $Ni_{0.48}@Ir_{0.52}$/OMS-2 catalyst.

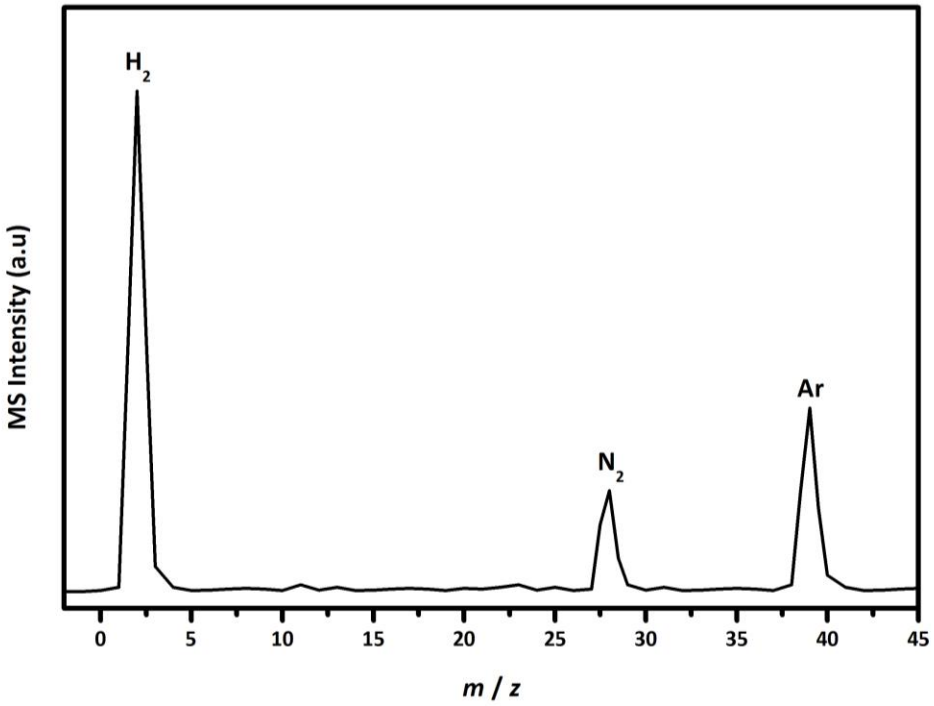

Figure S9. MS analysis result of the gas generated from $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyzed dehydrogenation of HB.

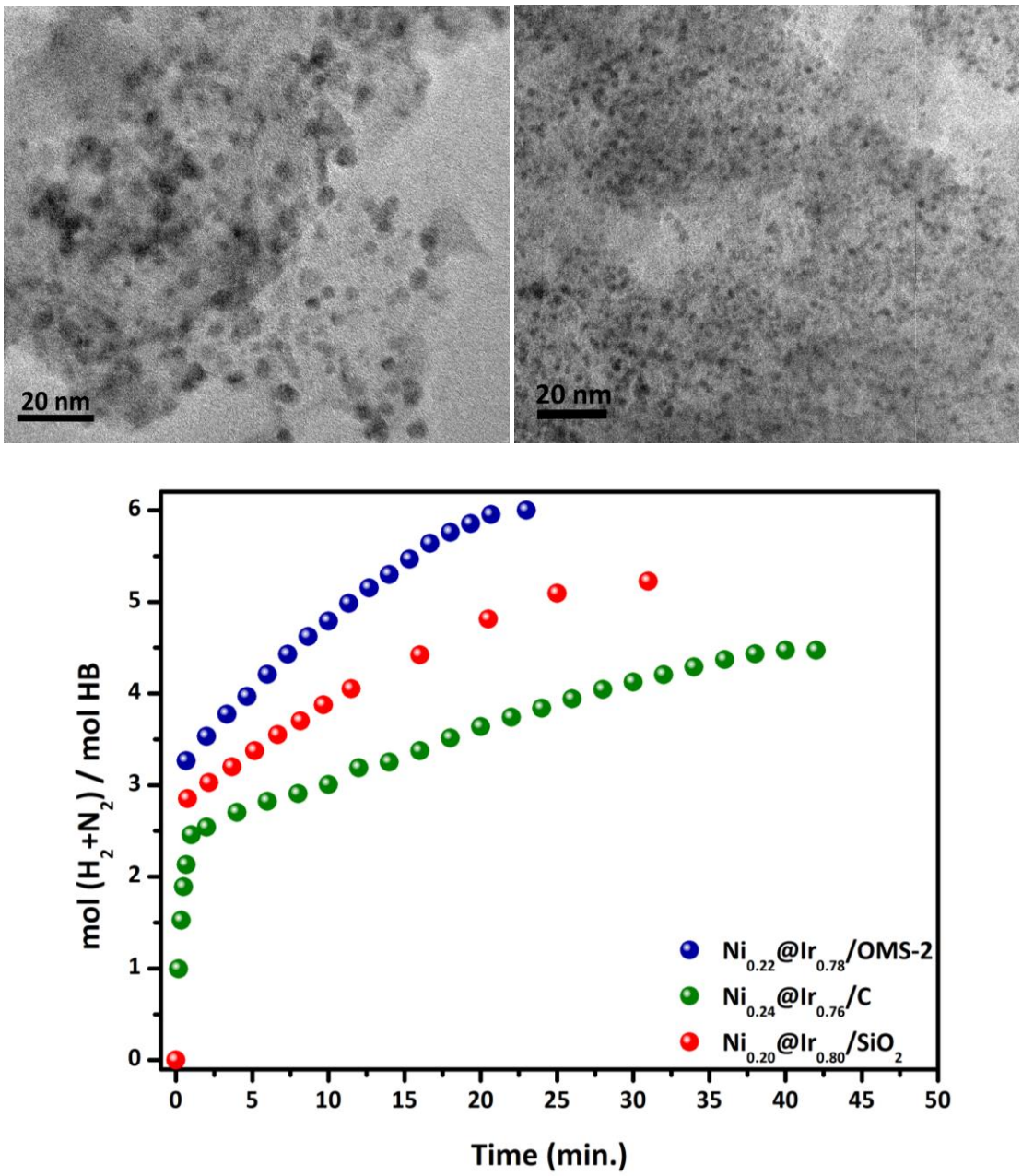

Figure S10. BFTEM images of $Ni_{0.24}@Ir_{0.76}/C$ (left) and $Ni_{0.20}@Ir_{0.80}/SiO_2$ (right) catalysts and the mole ratio of generated gas (H_2 + N_2)/HB versus time graph for $Ni_{0.24}@Ir_{0.76}/C$, $Ni_{0.20}@Ir_{0.80}/SiO_2$ and $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyzed dehydrogenation of aqueous HB (in all [Ni + Ir] = 1.264 mM, [HB] = 0.2 M, [NaOH] = 5.0 M, V_{water} = 5.0 mL) at 323 K.

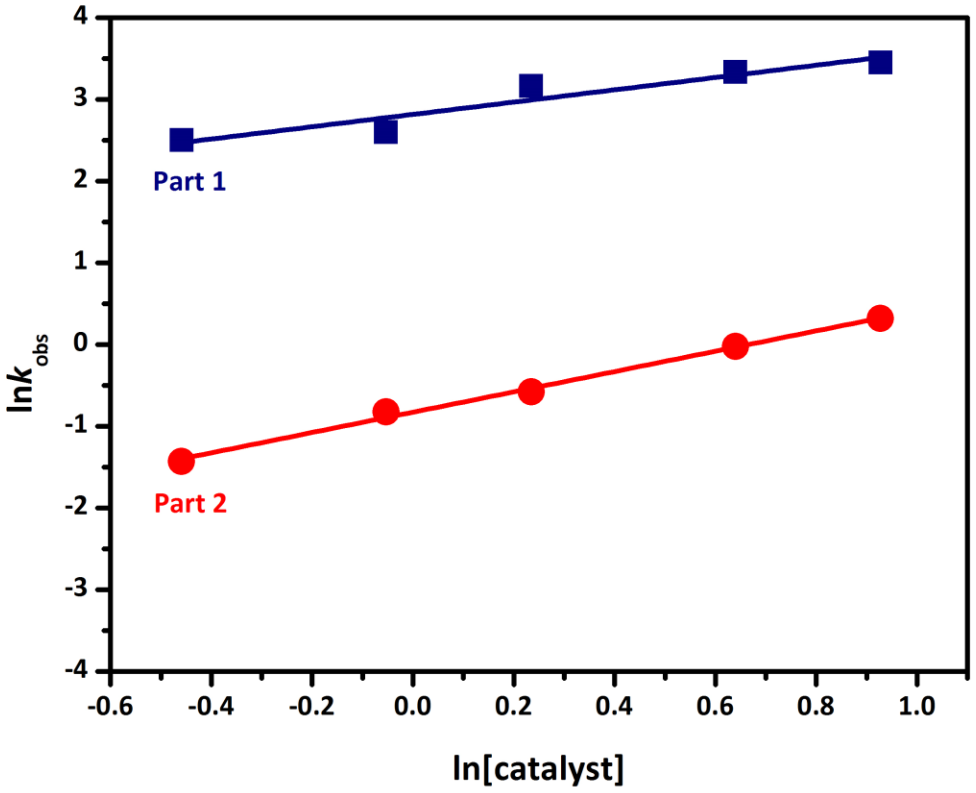

Figure S11. The logarithmic plots of the observed rate constants (k_{obs}) versus catalyst concentrations for $Ni_{0.22}$@$Ir_{0.78}$/OMS-2, catalyzed dehydrogenation of aqueous HB ([HB] = 0.2 M, [NaOH] = 5.0 M, V_{water} = 5.0 mL) at 343 K starting with various catalyst concentrations.

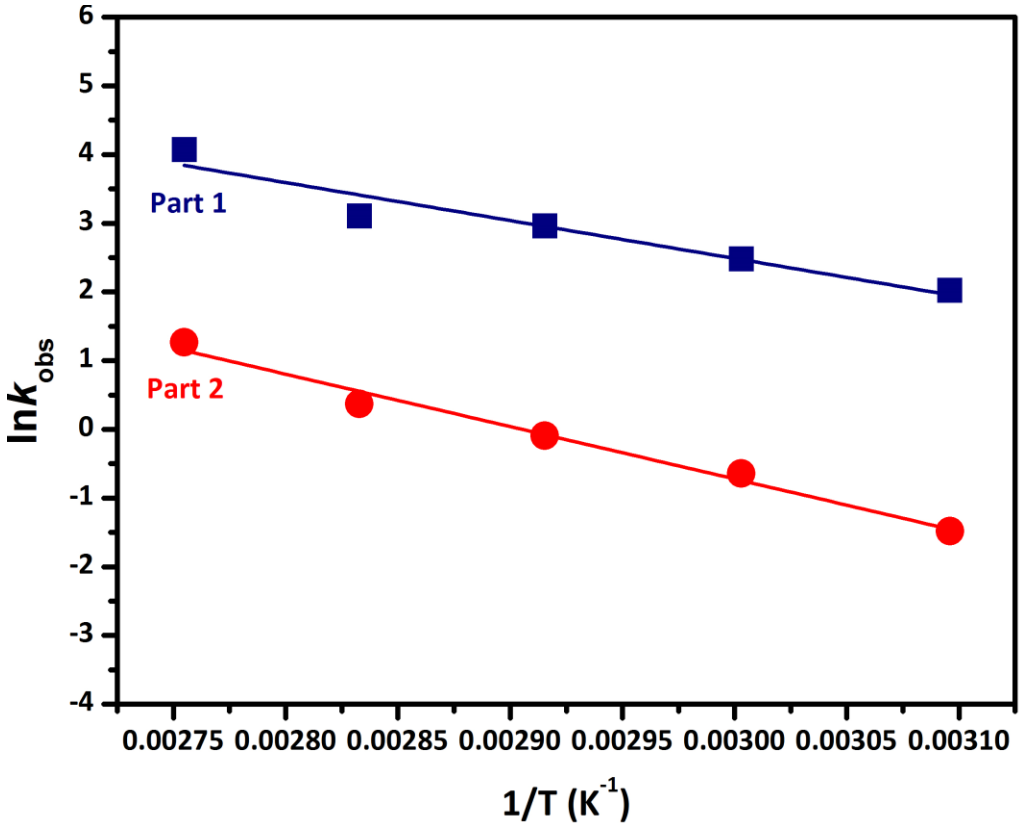

Figure S12. Arrhenius plot for $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyzed dehydrogenation of aqueous HB (in all [Ni + Ir] = 1.264 mM, [HB] = 0.2 M, [NaOH] = 5.0 M, V_{water} = 5.0 mL) at different temperatures.

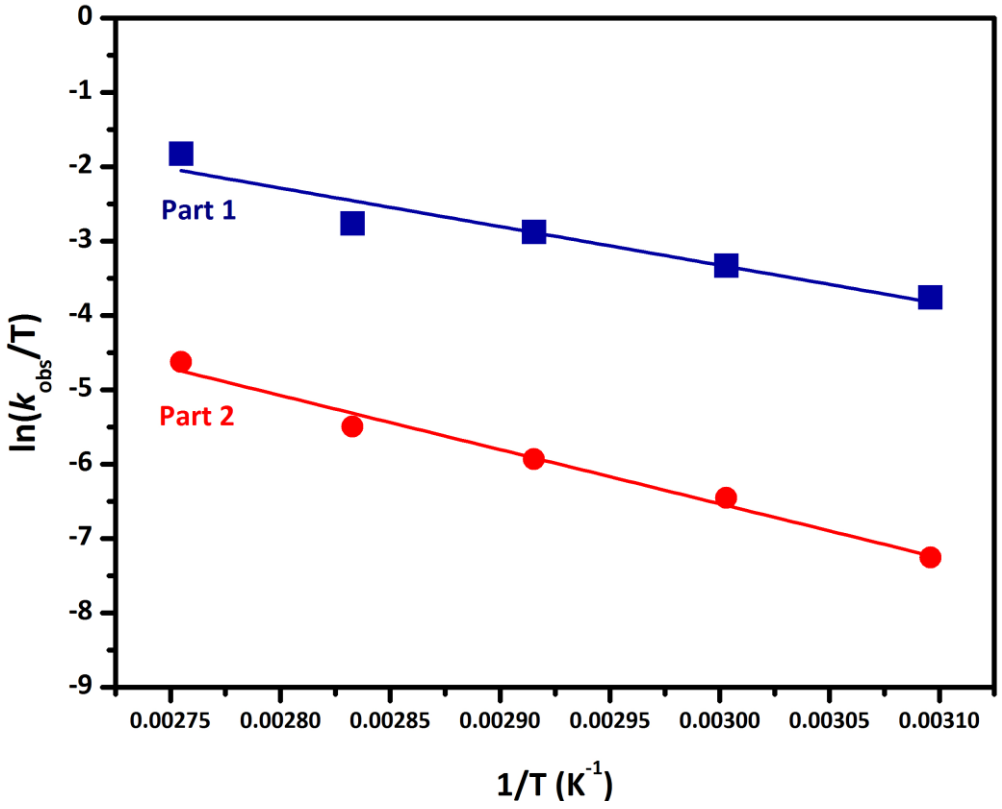

Figure S13. Eyring plot for $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyzed dehydrogenation of aqueous HB (in all [Ni + Ir] = 1.264 mM, [HB] = 0.2 M, [NaOH] = 5.0 M, V_{water} = 5.0 mL) at different temperatures.

Determination of *Average* Turnover Frequency (TOF) Values

The activity values in this report are not corrected for the number of exposed surface atoms; that is, the values given are lower limits. For $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyst; mol (Ir) = 1.36 μmol, mol (Ni) = 4.96 μmol, mol (Ir + Ni) = 6.32 μmol, mol (HB) = 1 mmol and from Figure 5(a) $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyst provides 6 moles equiv. gas generation at t = 22 min.

$TOF_{(average)}$ = moles of product / moles of catalyst × time (where 100 % conversion was achieved)

$TOF_{(average)} = (6\times10^{-3}\ mol) / (6.32\times10^{-6}\ mol) \times (22/60\ h)$

$TOF_{(average)} = 2590\ h^{-1}$ (The lower limit TOF value if we consider not only Ir atoms but also Ni atoms [Ni + Ir])

$TOF_{(average)} = (6\times10^{-3}\ mol) / (4.96\times10^{-6}\ mol) \times (22/60\ h)$

$TOF_{(average)} = 3300\ h^{-1}$ (The upper limit TOF value if we assume active sites are only provided by Ir ([Ir])

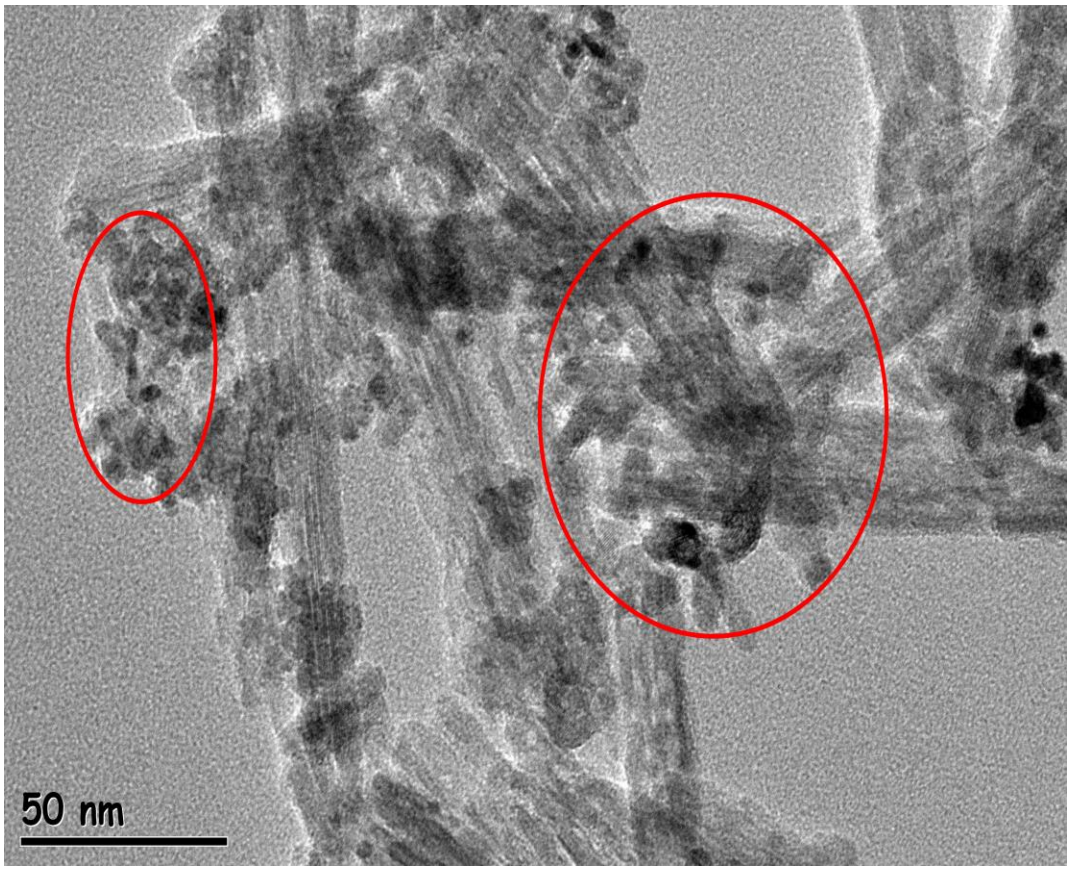

Figure S14. BFTEM image of $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyst recovered from 5th catalytic recycle, the regions of the clumped particles are labeled with red circle.

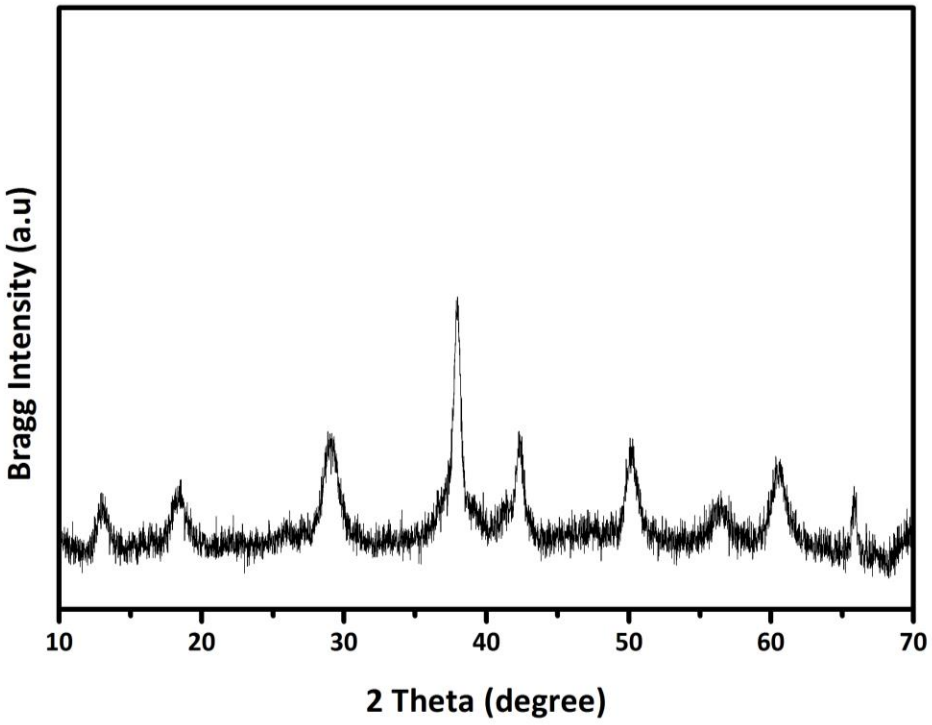

Figure S15. P-XRD pattern of $Ni_{0.22}@Ir_{0.78}$/OMS-2 catalyst recovered from 5th catalytic reuse in the range of 2θ = 10-70°.