Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI)

Methane decomposition to tip and base grown carbon nanotubes and COx free H_2 over mono and bimetallic 3d transition metal catalysts

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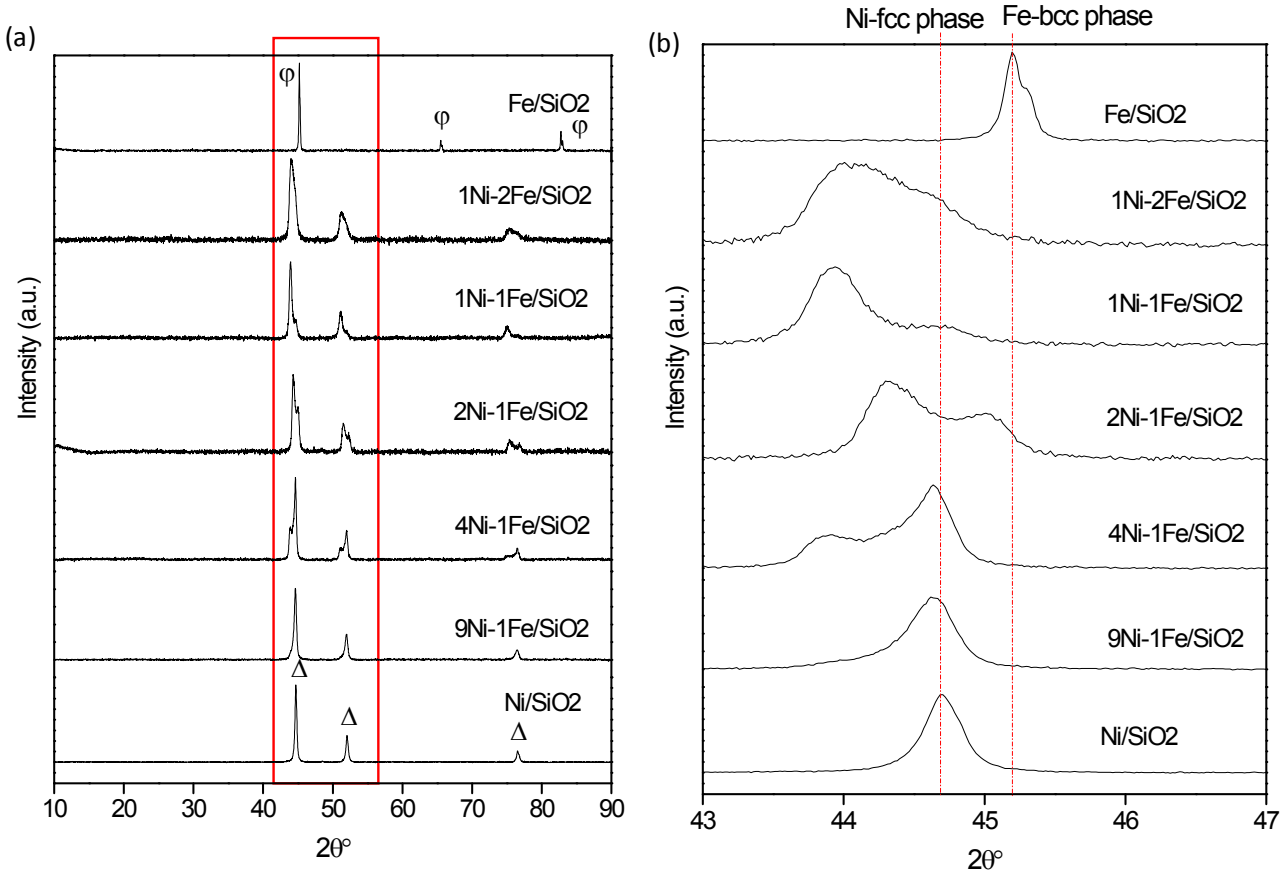
I. Figures



Figures S1(a), (b). XRD of fresh mono and bimetallic Ni-Fe catalysts.

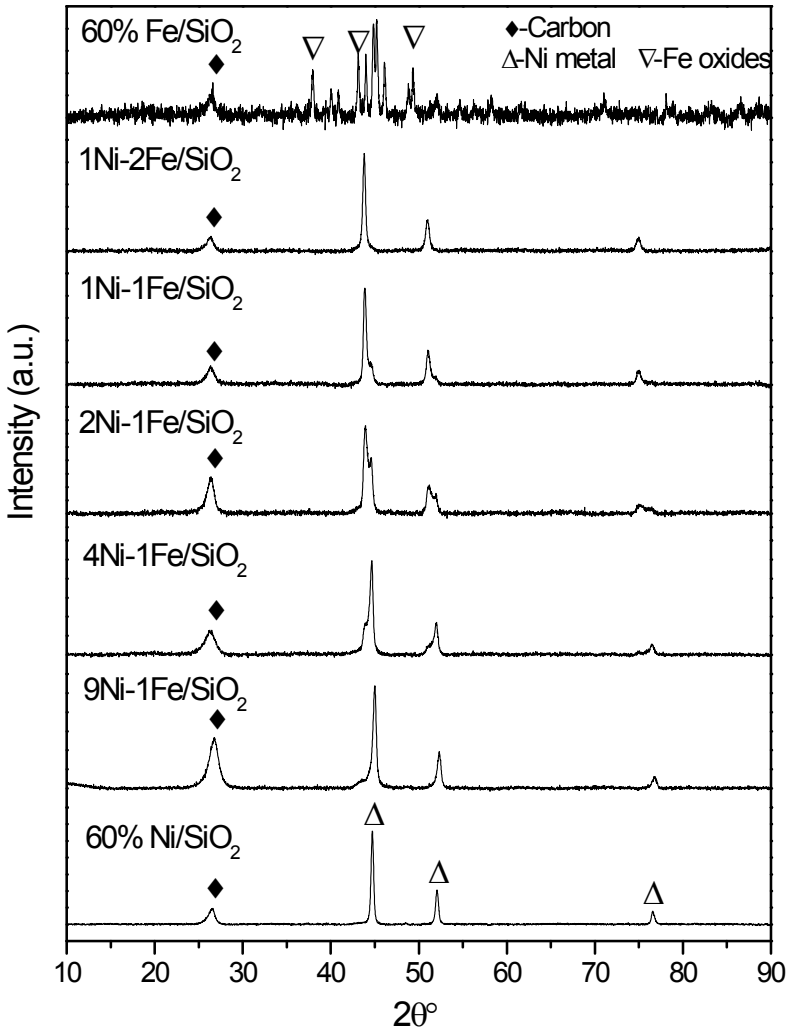
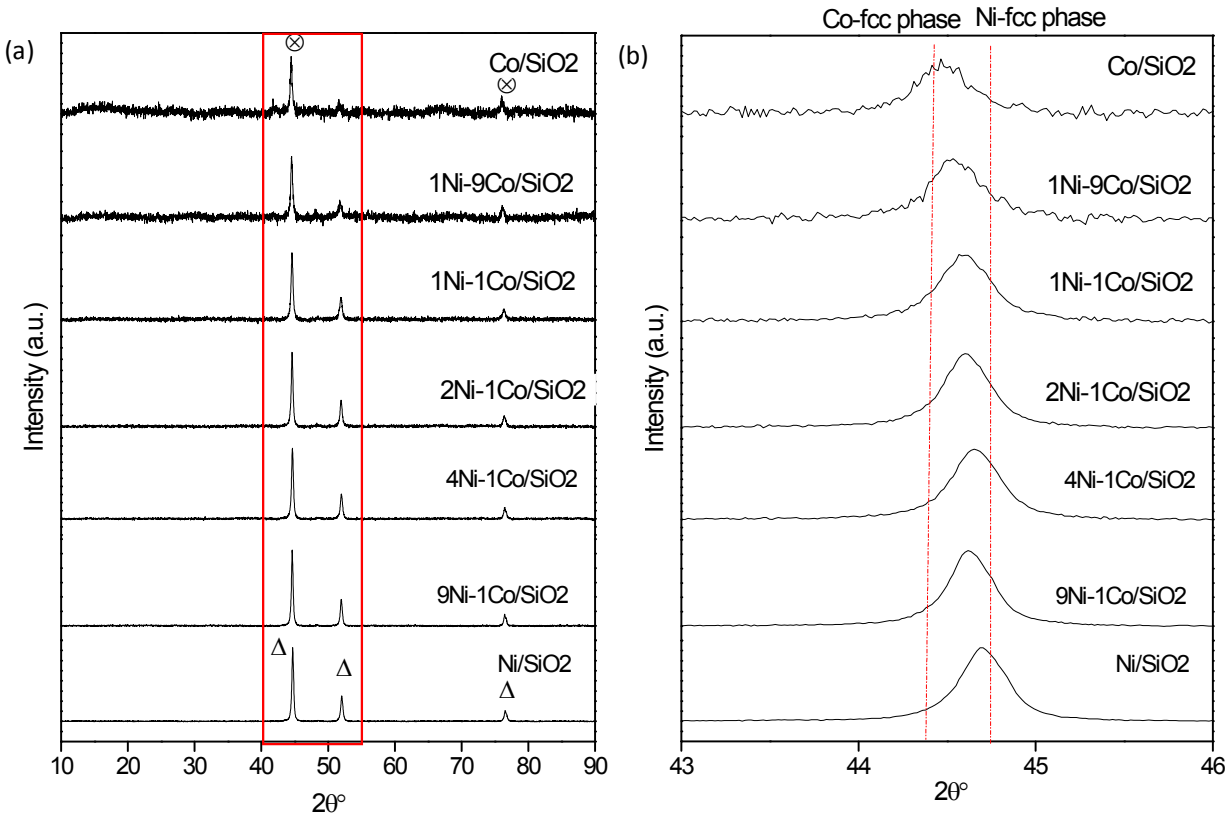


Figure S2. XRD of spent mono and bimetallic Ni-Fe catalysts.



Figures S3 (a), (b). XRD of fresh mono and bimetallic Ni-Co catalysts.

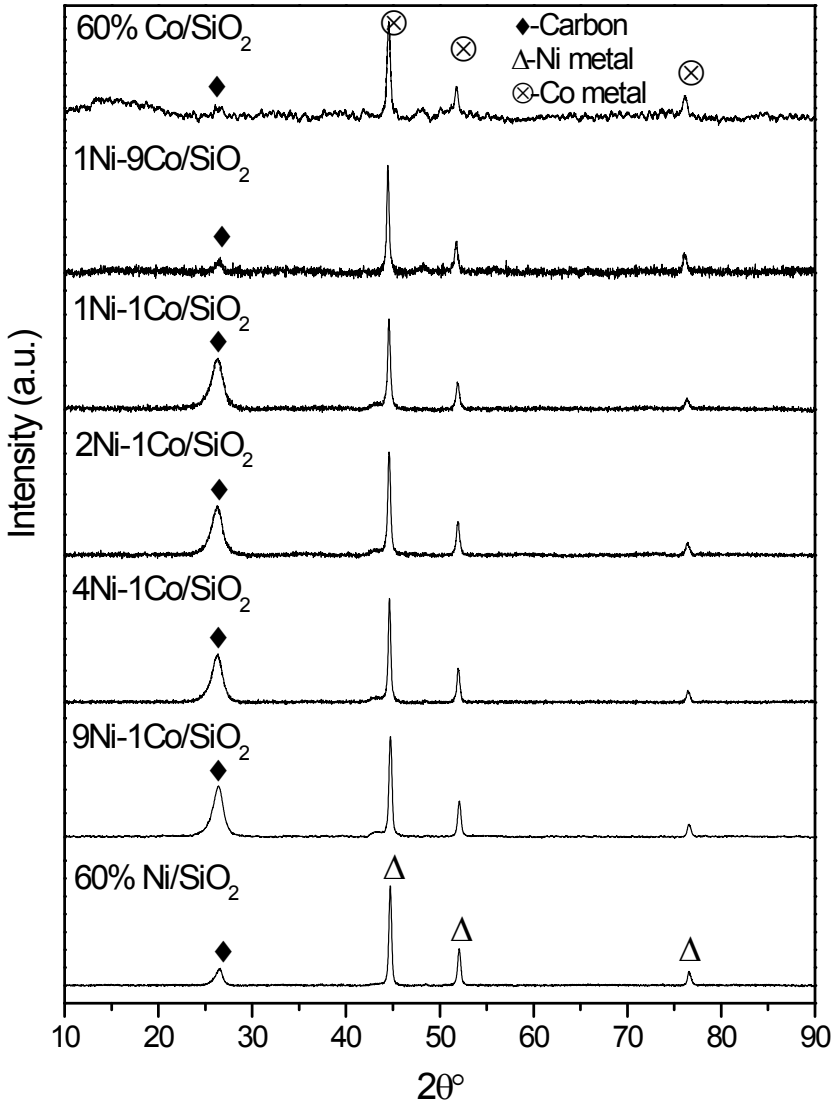
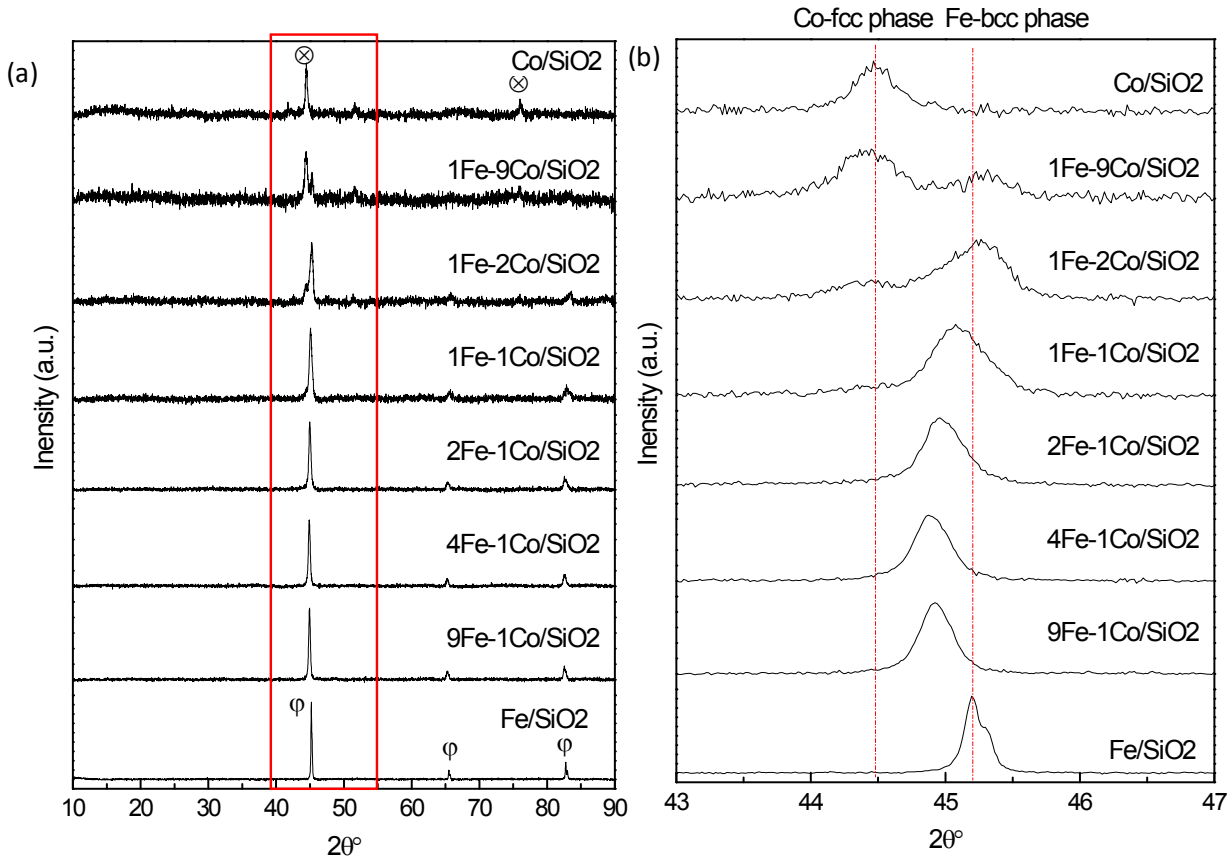


Figure S4. XRD of spent mono and bimetallic Ni-Co catalysts.



Figures S5 (a), (b). XRD of fresh mono and bimetallic Fe-Co catalysts.

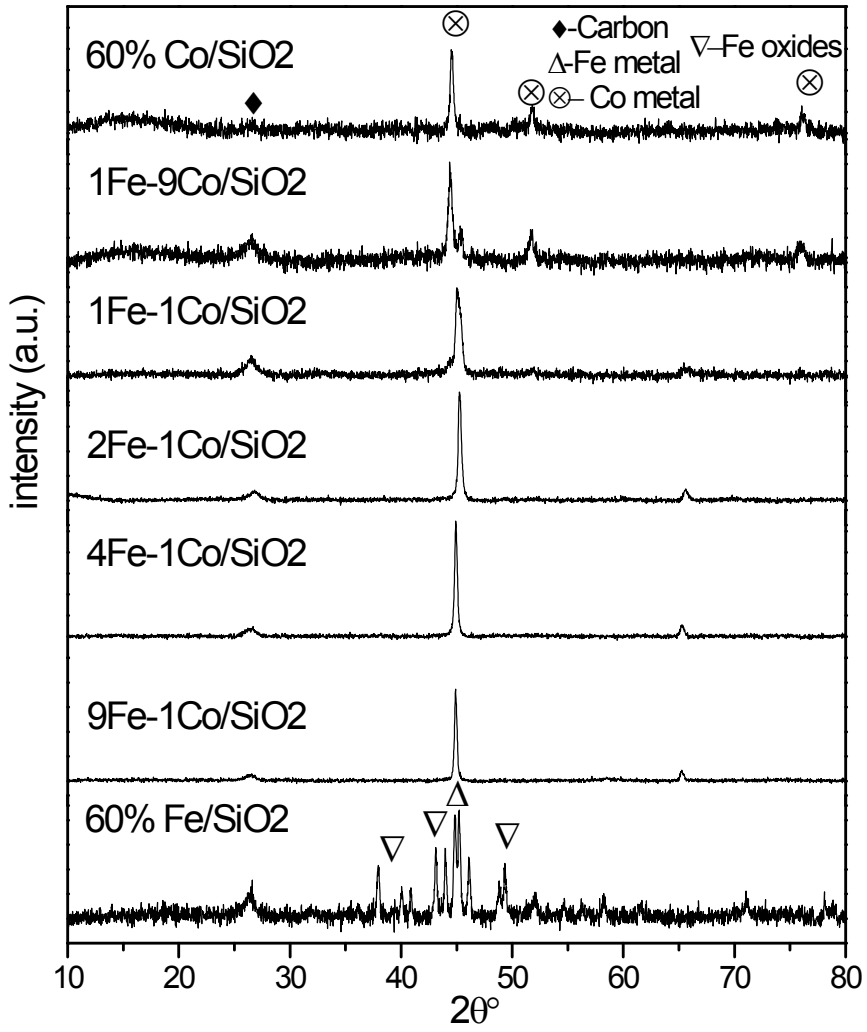


Figure S6. XRD of spent mono and bimetallic Fe-Co catalysts.

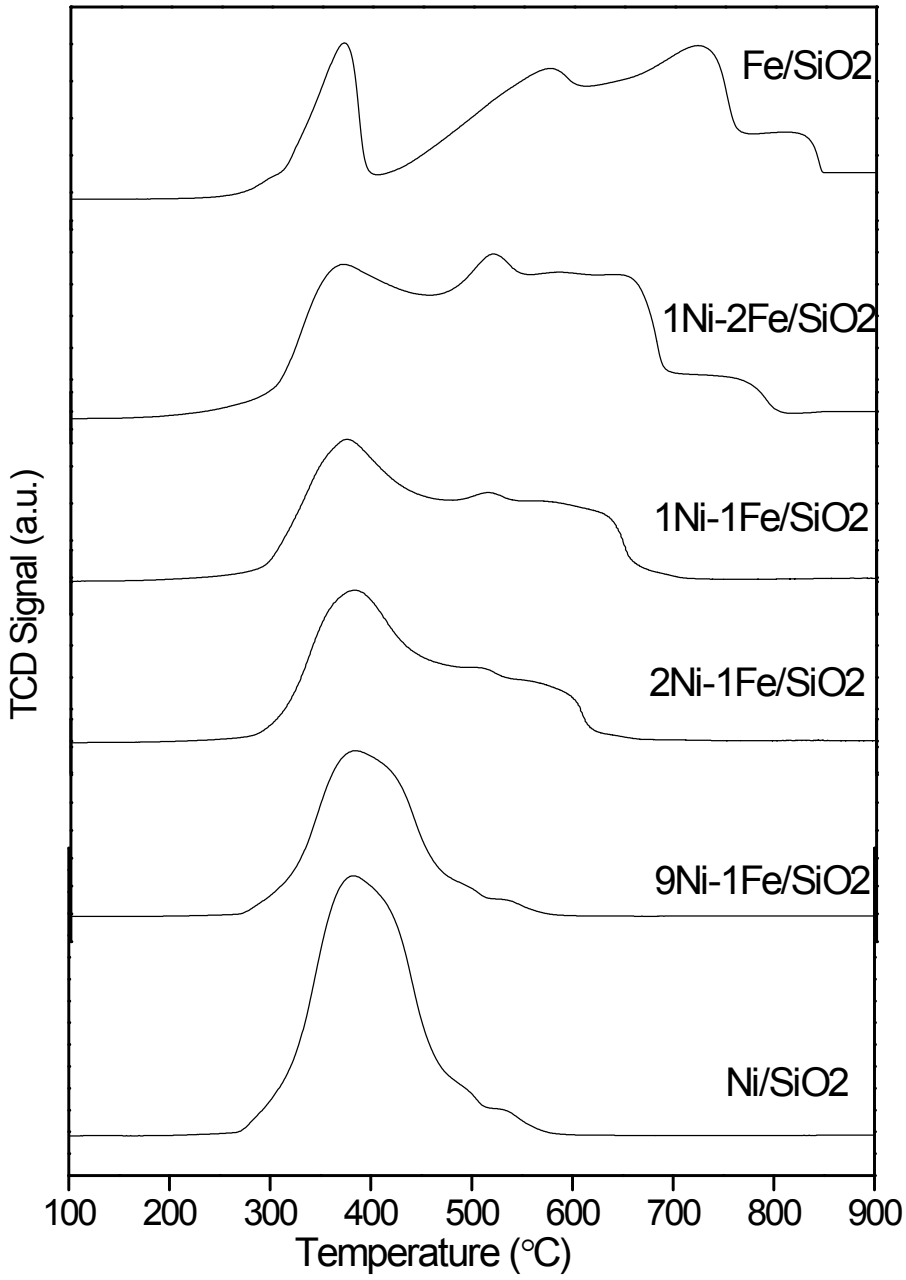


Figure S7. TPR analysis of fresh Ni-Fe catalysts.

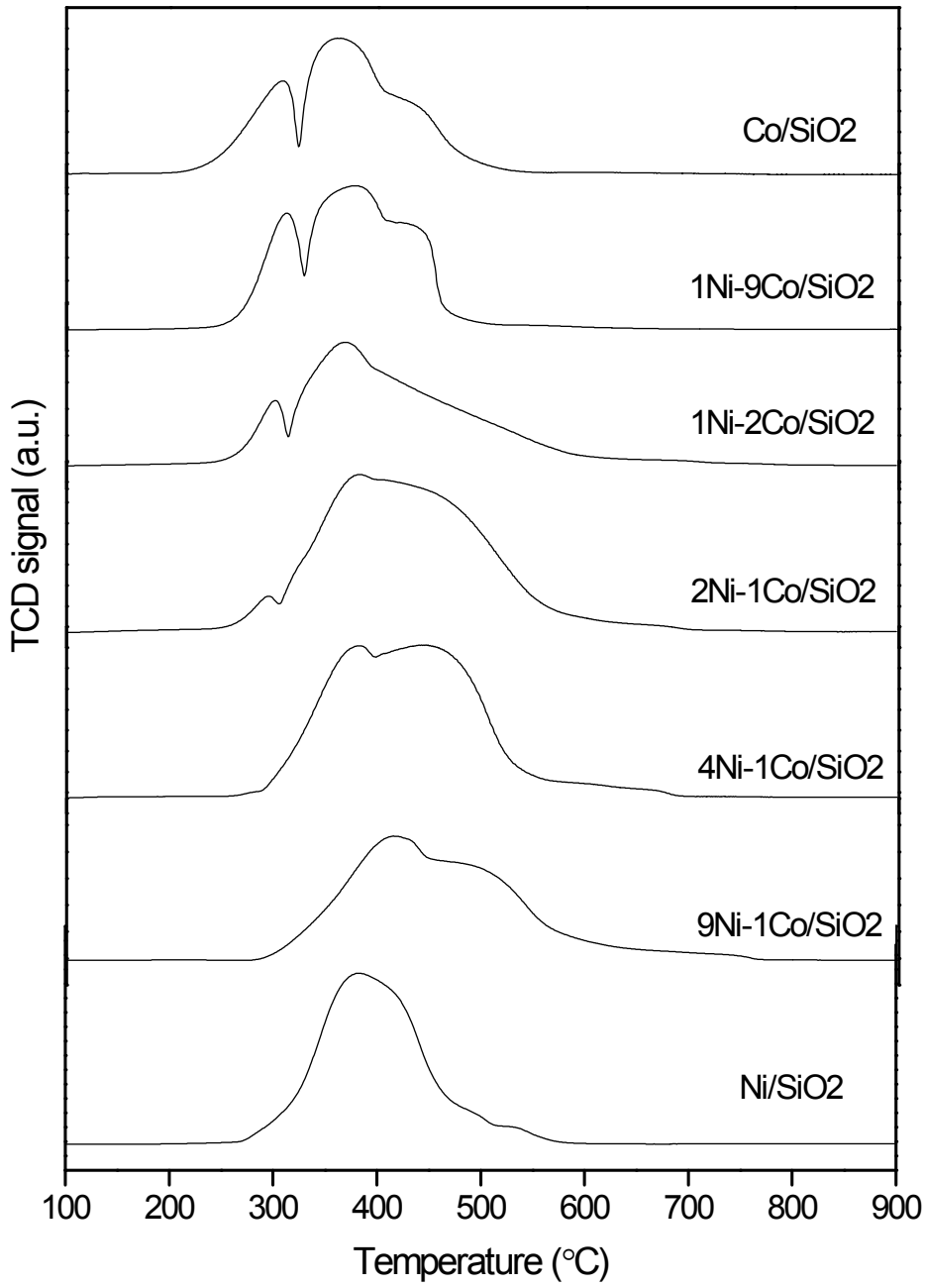


Figure S8. TPR analysis of fresh Ni-Co catalysts.

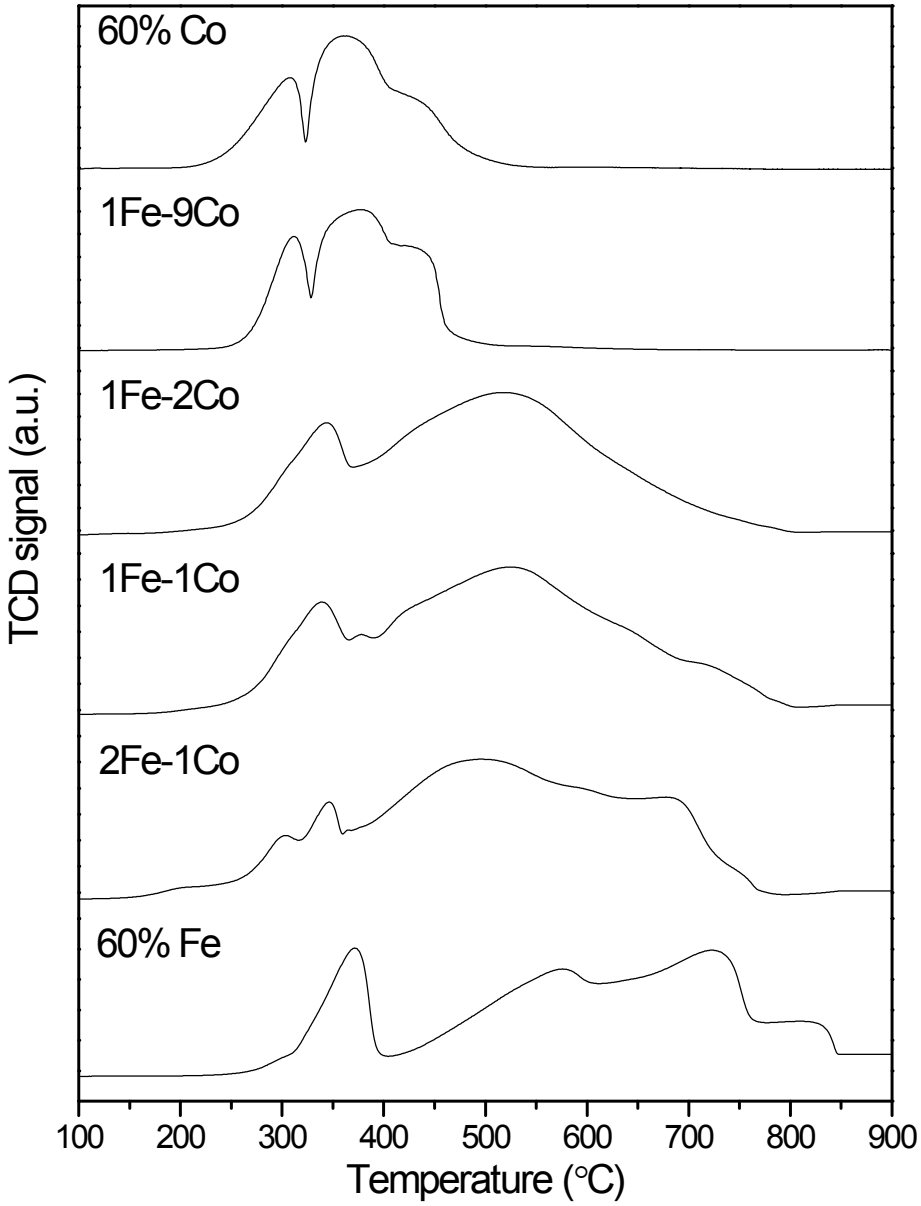


Figure S9. TPR analysis of fresh Fe-Co catalysts.

- Stability of bimetallic catalysts is higher than that of monometallic ones due to the alloy formation as shown in Figures S7, S8 and S9.

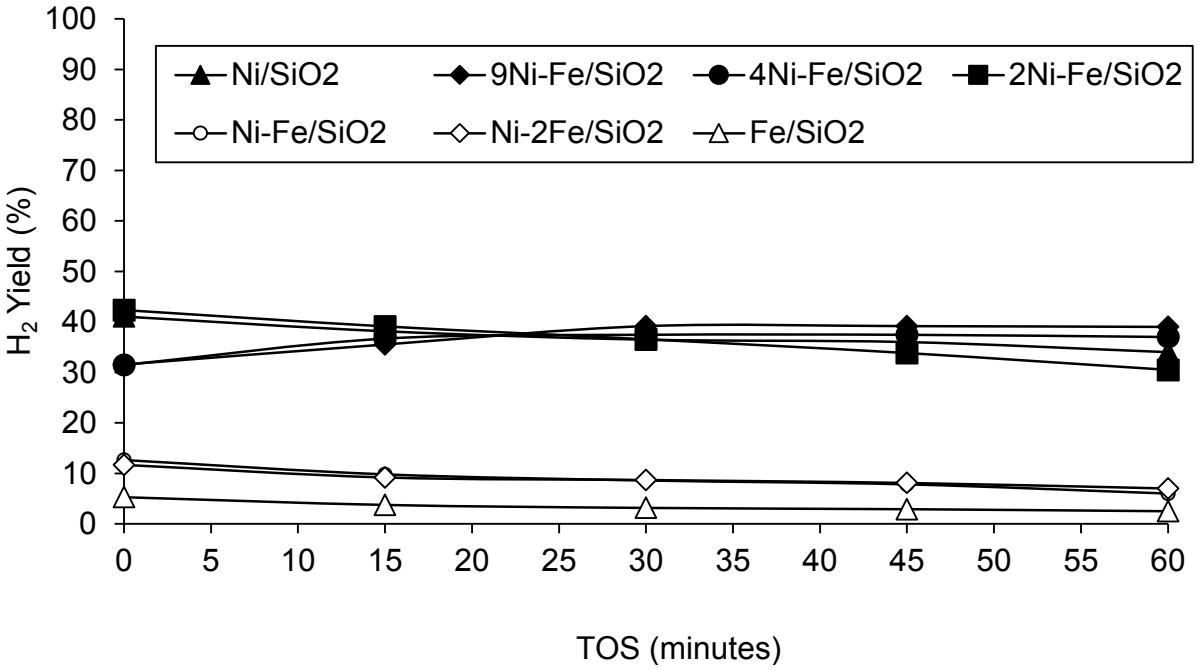


Figure S10. H_2 yield over Ni-Fe/SiO_2 catalysts with various mole ratios at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

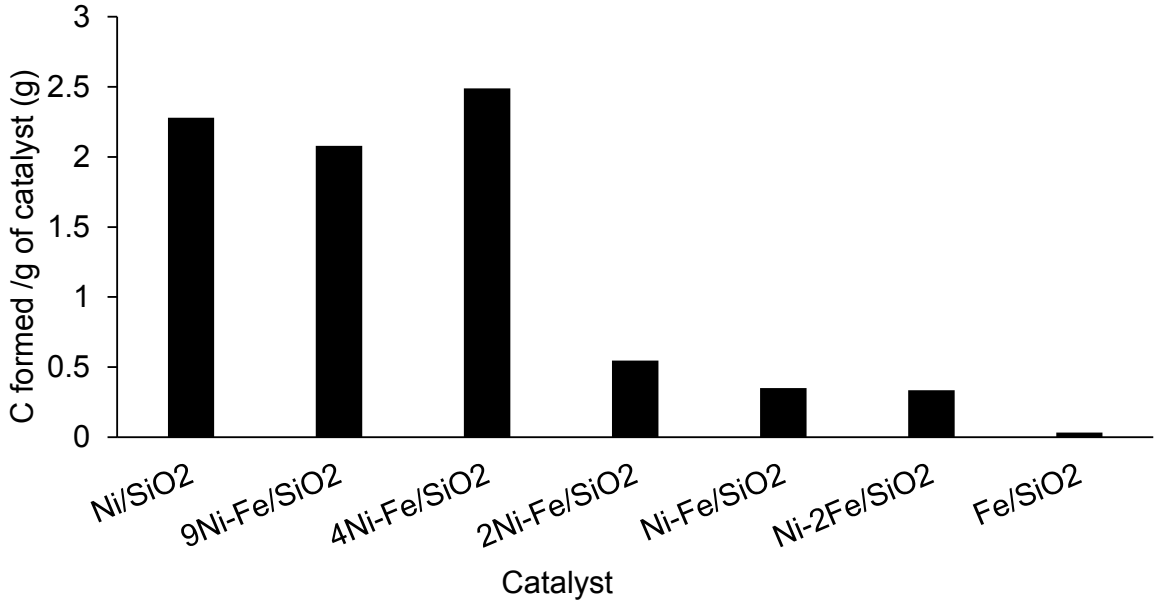


Figure S11. Amount of carbon formed over Ni-Fe/SiO_2 catalysts with various mole ratios at T = 650 °C, TOS = 0-60 minutes, GHSV = 42000h^{-1}.

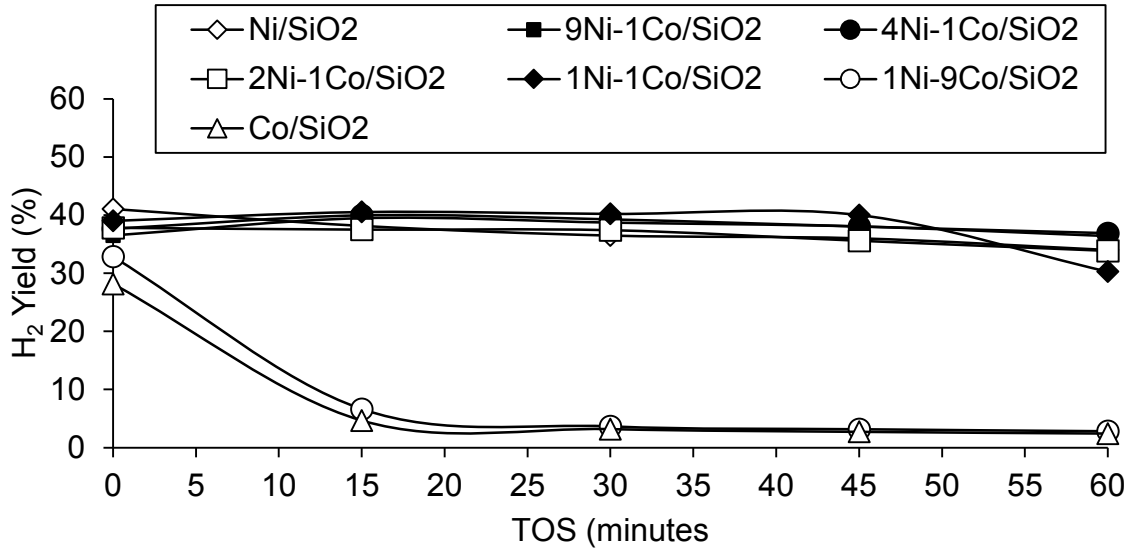


Figure S12. H_2 yield over Ni-Co/SiO_2 catalysts with various mole ratios at T = 650 °C, TOS = 0-60 minutes, GHSV = 42000h^{-1}.

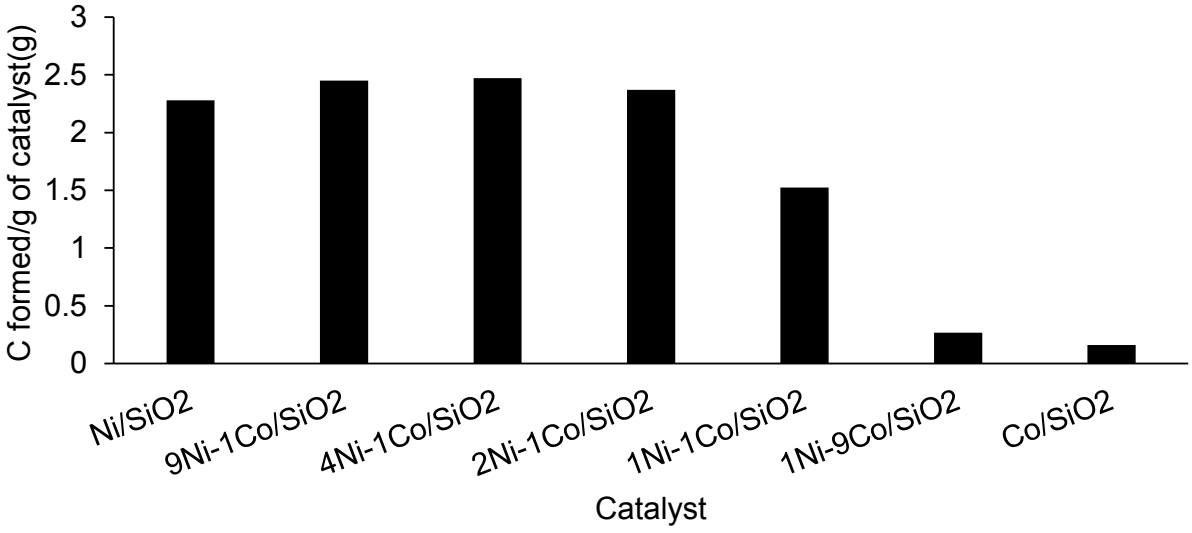


Figure S13. Amount of carbon formed over Ni-Co/SiO_2 catalysts with various mole ratios at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

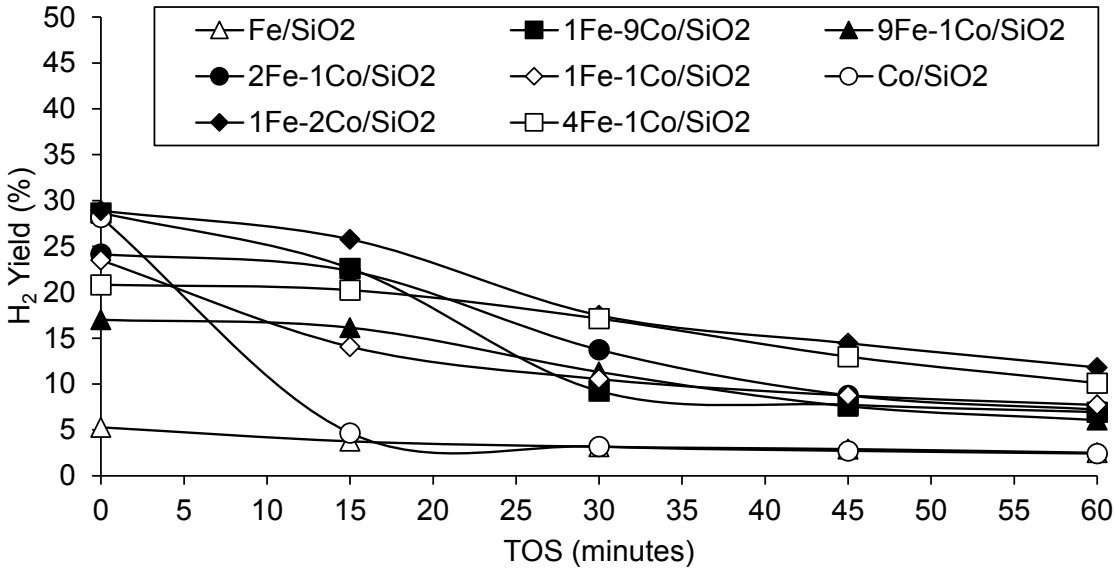


Figure S14. H_2 yield over Fe-Co/SiO_2 catalysts with various mole ratios at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

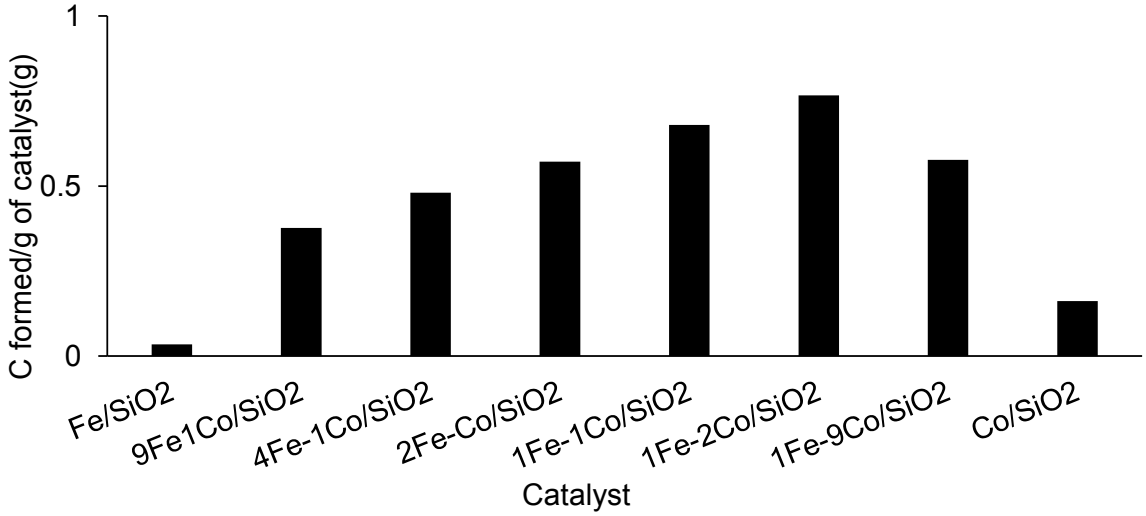


Figure S15. Amount of carbon formed over Fe-Co/SiO_2 catalysts with various mole ratios at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

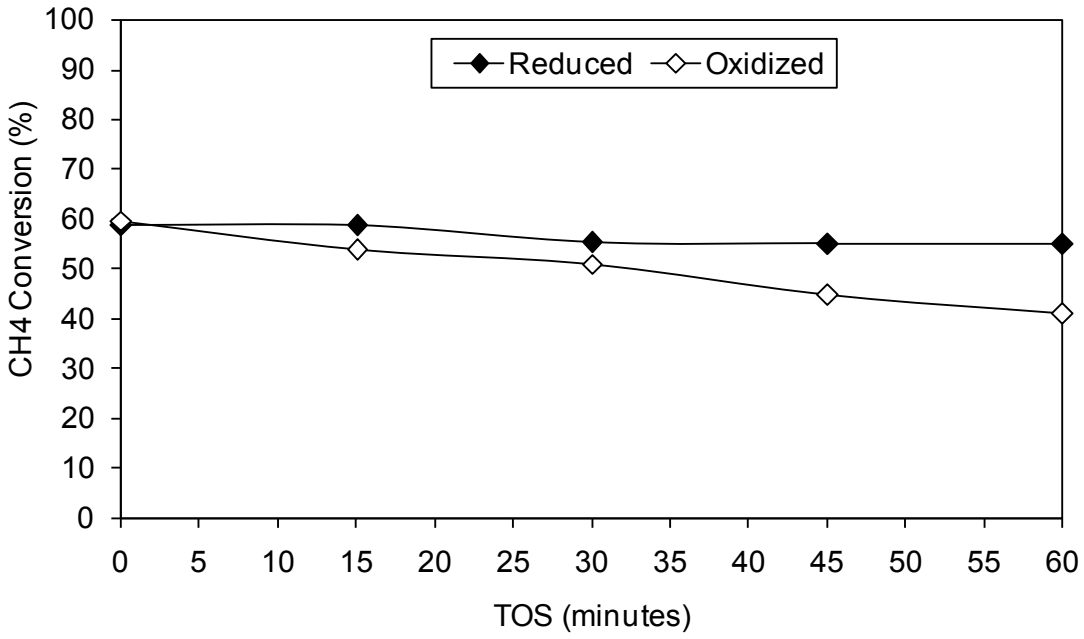


Figure S16. Methane decomposition over reduced and oxidised forms of 9Ni-1Fe/SiO_2 catalysts at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

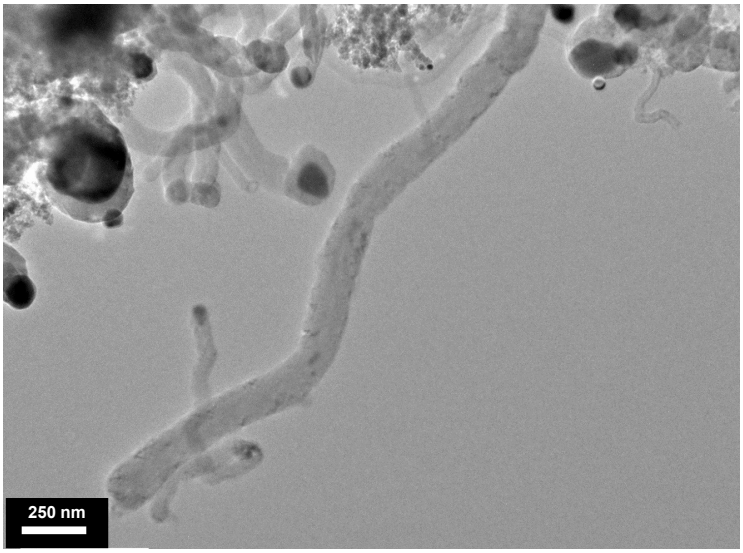


Figure S17. Tip and base grown CNT's over 9Ni-1Co/SiO_2 catalysts at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

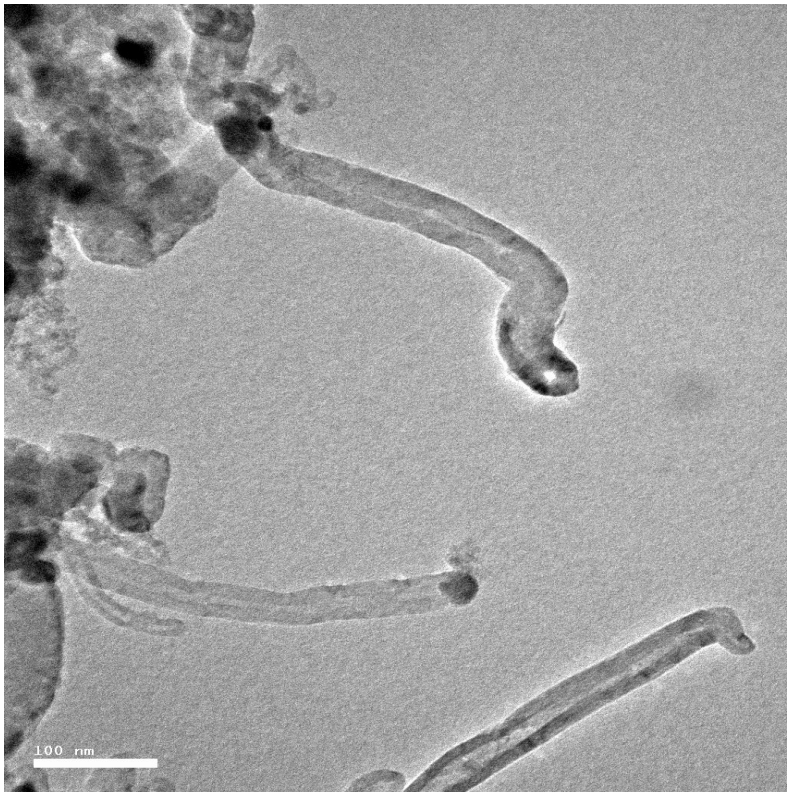


Figure S18. Tip and base grown CNT's over 1Fe-2Co/SiO2 catalysts at T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}.

II. Tables

Table S1. Metal compositions and crystallite size (XRD) values of fresh and spent of mono/bimetallic Ni/Fe/Co catalysts.

Ni-Fe catalysts	Ni:Fe mole ratios	Ni (wt%)	Fe (wt%)	Crystallite size (XRD) (nm)	
				Fresh	Spent
Fe/SiO_2	---	0	60	29	13
$1Ni-2Fe/SiO_2$	1:2	20.67	39.33	19	22
$1Ni-1Fe/SiO_2$	1:1	30.75	29.25	17	20
$2Ni-1Fe/SiO_2$	2:1	38.67	21.33	9	9
$4Ni-1Fe/SiO_2$	4:1	48	12	10	12
$9Ni-1Fe/SiO_2$	9:1	54	6	20	20
Ni/SiO_2	---	60	0	25	25
Ni-Co catalysts	**Ni:Co mole ratios**	**Ni (wt%)**	**Co (wt%)**	**Fresh**	**Spent**
Co/SiO_2	---	0	60	21	24
$1Ni-9Co/SiO_2$	1:9	5.98	54.02	22	26
$1Ni-1Co/SiO_2$	1:1	29.94	30.06	23	24
$2Ni-1Co/SiO_2$	2:1	39.97	20.03	25	25
$4Ni-1Co/SiO_2$	4:1	47.96	12.04	24	26
$9Ni-1Co/SiO_2$	9:1	53.97	6.02	25	25
Fe-Co catalysts	**Fe:Co mole ratios**	**Fe (wt%)**	**Co (wt%)**	**Fresh**	**Spent**
$9Fe-1Co/SiO_2$	9:1	53.70	6.30	28	31
$4Fe-1Co/SiO_2$	4:1	47.48	12.52	26	28
$2Fe-1Co/SiO_2$	2:1	39.27	20.90	23	25
$1Fe-1Co/SiO_2$	1:1	29.19	30.81	17	18
$1Fe-2Co/SiO_2$	1:2	19.29	40.71	17	18
$1Fe-9Co/SiO_2$	1:9	5.70	54.30	17	19

- Higher activity of bimetallic catalysts can be possibly due to decrease in crystallite size, which corresponds to higher active sites.

- Slight variation in catalyst activity was observed after regeneration possibly due to sintering of metal nanoparticles during the course of the reaction.

Table S2. Raman analysis data (I_D/I_G values) of CNT's over mono and bimetallic Ni/Fe/Co catalysts.

Ni-Fe Catalysts	**I_D/I_G**
Fe/SiO_2	1.260
$1Ni\text{-}2Fe/SiO_2$	0.817
$1Ni\text{-}1Fe/SiO_2$	0.944
$2Ni\text{-}1Fe/SiO_2$	0.949
$4Ni\text{-}1Fe/SiO_2$	0.829
$9Ni\text{-}1Fe/SiO_2$	0.874
Ni/SiO_2	0.883
Ni-Co Catalysts	**I_D/I_G**
Co/SiO_2	0
$1Ni\text{-}9Co/SiO_2$	0
$1Ni\text{-}1Co/SiO_2$	0.868
$2Ni\text{-}1Co/SiO_2$	1.084
$4Ni\text{-}1Co/SiO_2$	0.887
$9Ni\text{-}1Co/SiO_2$	0.765
$1Fe\text{-}9Co/SiO_2$	1.042
Fe-Co Catalysts	**I_D/I_G**
$9Fe\text{-}1Co/SiO_2$	0.997
$4Fe\text{-}1Co/SiO_2$	0.896
$2Fe\text{-}1Co/SiO_2$	0.983
$1Fe\text{-}1Co/SiO_2$	1.019
$1Fe\text{-}2Co/SiO_2$	1.021

Table S3. Effect of space velocities on CH4 conversion over Fe/SiO2 catalysts

GHSV (h^{-1})	**CH4 Conversion (%)**
42000	47
21000	36

Reaction conditions: 30% CH4, Catalyst = 0.1g, T = 700 °C, TOS = 60 minutes,