

Electronic Supplementary Information

Experimental Section

Catalysts preparation

The Fe-based catalysts were prepared by melting method. Appropriate amounts of Fe_3O_4 and K_2CO_3 powders were melted and held at 1600 K in a vacuum induction furnace for 30 min to ensure the homogeneity of the melt. The molten material was quenched in the water. The brittle alloys were then ground and sieved, and the 60-80 mesh fraction used. The powder was reduced by pure hydrogen at 723 K for 6h. After the reduction, the powder was cooled down to around 323 K, a flow of passivation gas (98% N_2 /2% O_2) was fed into and held for 2 h.

The precipitated Co and Co-Mn catalysts were prepared in the usual batch-wise manner by adding ammonia solution to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution and a solution containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ which had been heated up to near 100°C. The obtained precipitates were washed by deionized water, dried at 100°C for 12 h and calcined in air at 350°C for 4 h. Part of the powder was reduced by pure hydrogen (at 623 K for 6h) and passivated by passivation gas (98% N_2 /2% O_2) to measure their competent and saturation magnetization, and the other part of powder by supported on SiO_2 (BET surface area of 96 m^2/g , pore volume of 0.51 ml/g , pore diameter of 50 nm) to evaluate their catalytic behavior.

Catalysts characterization

The powder component was analyzed by X-ray diffraction (XRD), and the powder XRD profile was collected on a DX-2700 with monochromatic Cu $\text{K}\alpha$

radiation operating at 40 kV and 30 mA, with 2θ from 10° to 90° and a scanning speed of $6^\circ/\text{min}$. The bulk composition was determined by using inductive coupled plasma atomic emission spectroscopy (ICP-AES). The surface composition were examined by using X-ray photoelectron spectroscopy (XPS) with MgK_α radiation as the excitation source. The saturation magnetization was measured by a Superconducting Quantum Interference Device (SQUID). The field strength is between -2 and 2 T on about 13 mg of the sample. All the samples' powder has been reduced by pure hydrogen and passivated by argon. In H_2 temperature programmed reduction (H_2 -TPR), 0.1g catalyst was loaded into the quartz tube reactor, then heated from room temperature to 1000°C the ramp rate of $10^\circ\text{C}/\text{min}$ in $5\%\text{H}_2/95\%\text{N}_2$ flow gas and the consumption of H_2 was monitored via the change in the thermal conductivity of the effluent stream.

Catalytic test

The performance of FTS was evaluated on a fixed-bed equipped with a stainless steel tubular reactor. Prior to the FTS reaction, the as-prepared catalysts were activated in a flow of pure hydrogen at 723 K for Fe-based and 623 K for Co-based catalysts for 6 h ($\text{GHSV}=3000\text{ h}^{-1}$, $P=0.2\text{ MPa}$). During the activation the temperature ramp is $2\text{ K}/\text{min}$. After the activation, the catalysts were cooled down to 300 K, a flow of syngas ($\text{H}_2/\text{CO}=2$) was fed into the catalysts and the temperature was increased at $2\text{ K}/\text{min}$ heating rate to 513K for Fe- and 493K for Co-based catalysts. During the testing, the pressure of syngas was maintained at 2 MPa and the $\text{GHSV}=2000\text{ h}^{-1}$.

The reaction products pass a 403 K hot trap and a 278 K cold trap at working

pressure, and the gaseous products were analyzed on-line by gas chromatography (GC 920). A carbon molecular sieve column connected with a thermal conductivity detector was used to separate and quantify H₂, N₂, CH₄, CO and CO₂, whereas C₁-C₈ hydrocarbons were separated in a capillary porapak-Q column and detected in a flame ionization detector.

Calculation process

According to Crystal Field Surface Orbital (CFSO) [1-3], the interaction energy E_{M-CO} between CO and metal surface can be written as:

$$E_{M-CO} = D_{CO} - E_{C-O} - E_{M-C} - E_{M-O} \quad (1)$$

Where D_{CO} is the CO dissociation energy ($D_{CO}=256$ Kcal/mol), E_{C-O} is the total energy in the C-O bond of the adsorbing molecular on the surface and the value may be given by Bond Energy Bond Order (BEBO) rule [4],

$$E_{C-O} = -13.33n_{C-O}^3 + 56n_{C-O}^2 + 37.33n_{C-O} \quad (2)$$

Where n_{C-O} is bond order of CO.

Besides, E_{M-C} and E_{M-O} is the total energy in the bond formed between the metal surface and adsorbing C and O atom, and the value be also given by BEBO [4],

$$E_{M-C} = E_{M-C S} n_{M-C} \quad (3)$$

$$E_{M-O} = E_{M-O S} n_{M-O} \quad (4)$$

Where $E_{M-C S}$ and $E_{M-O S}$ are the single bond energy of M-C and M-O respectively, and the values can be obtained from reference [5]. For Fe: $E_{M-O S} = 62.8$ Kcal/mol and $E_{M-C S} = 56.2$ Kcal/mol; For Co: $E_{M-O S} = 59.3$ Kcal/mol and $E_{M-C S} = 52.9$ Kcal/mol.

According to “Bond Order Conservation Rule” [5]

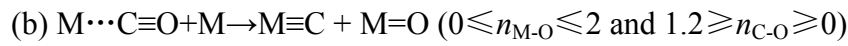
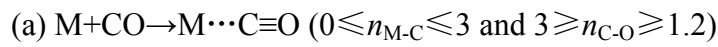
$$n_{M-C} + n_{M-O} = \lambda(n_{C-O}^0 - n_{C-O}) \quad (5)$$

where n_{C-O}^0 is the bond order of gaseous molecular CO at ground state ($n_{C-O}^0 = 3$, because CO is $C \equiv O$ triple bond) and λ is 5/3 for CO, n_{M-C} and n_{M-O} are the forming bond order during chemisorption, n_{C-O} is the residue bond order.

Substituting Eqs. (3), (4), and (5) into Eqs. (1), we can obtain:

$$E_{M-CO} = D_{CO} - E_{C-O} - \lambda E_{M-C S} (n_{C-O}^0 - n_{C-O}) + (E_{M-C S} - E_{M-O S}) n_{M-O} \quad (6)$$

Lots of experimental and theoretical results indicate that adsorbed CO is initially attached through the C atom to metal surface, followed by the dissociation of C≡O bond on some metals due to the direct interaction of the O atom with the metal surface [6]. Considering these facts, CO chemisorption can be divided into two steps, (a) and (b):



The value of 1.2 is a “critical value” of at which point the effective interaction of the O atom with the metal surface begins to operate and it is determined from Eqs. (5).

the interaction energies corresponding to these steps are then given by

for step (a), the E_{M-O} is 0, so the E_{M-CO} can be expressed as:

$$E_{M-CO} = 256 - E_{C-O} - 1.667 E_{M-C S} (3 - n_{C-O}) \quad (7)$$

for step (b)

$$E_{M-CO} = 256 - E_{C-O} - 3 E_{M-C S} - 1.667 (1.2 - n_{C-O}) E_{M-O S} \quad (8)$$

where the $E_{M-C S}$ and $E_{M-O S}$ are given: For Fe: $E_{M-O S} = 62.8$ Kcal/mol and $E_{M-C S} = 56.2$ Kcal/mol; For Co: $E_{M-O S} = 59.3$ Kcal/mol and $E_{M-C S} = 52.9$ Kcal/mol. Therefore, the correlation between Bond Order n_{CO} and interaction energy E_{M-CO} can be obtained (figure 5).

XRD Pattern

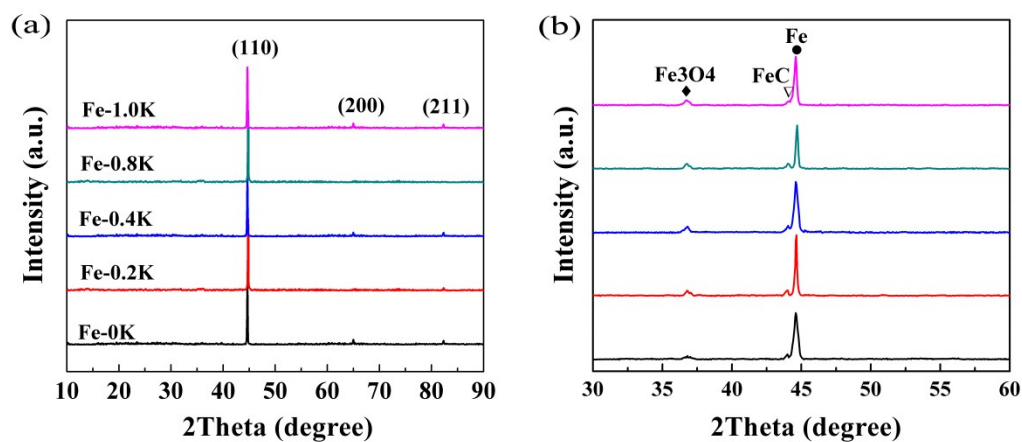


Figure S1, X-ray diffraction pattern of all the fused iron catalysts: (a) after reduction and passivation; (b) after reaction. The mean crystallite size of before reaction is 39 ± 3 nm, which was calculated from the XRD using the Scherrer equation. After reaction, a small amount of Fe was converted into Fe₃O₄ and iron carbides after FT reaction.

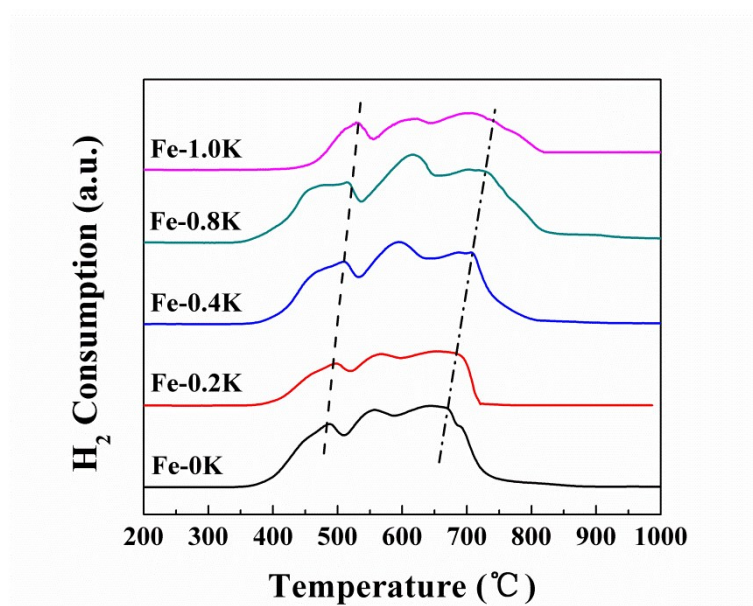


Figure S2, H₂-TPR of fused-iron based catalysts.

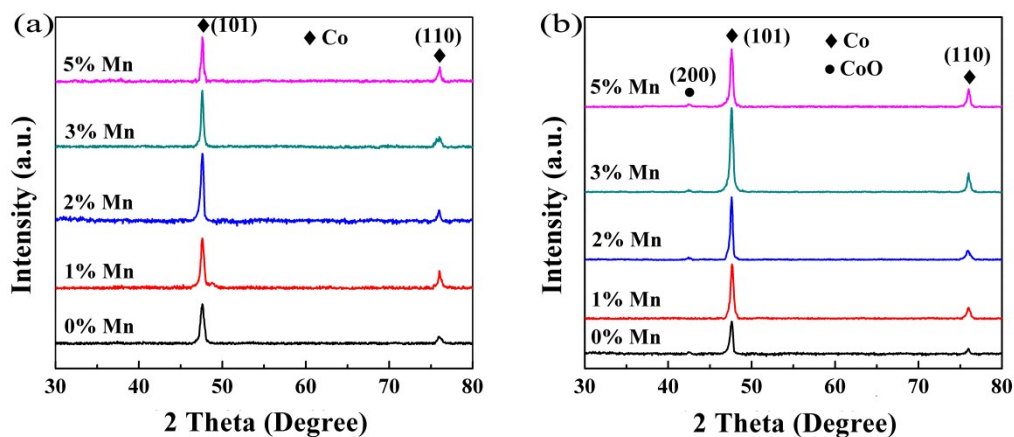


Figure S3, X-ray diffraction pattern of all the fused iron catalysts: (a) after reduction and passivation; (b) after reaction. The mean crystallite size of before reaction is about 25 nm, which was calculated from the XRD using the Scherrer equation. According to the current research results, the saturation magnetization is independent of specimen size, unless the particle size is smaller than 6-8 nm. After the reaction, the grain growth is not obvious but a small amount of Co was oxidized to CoO.

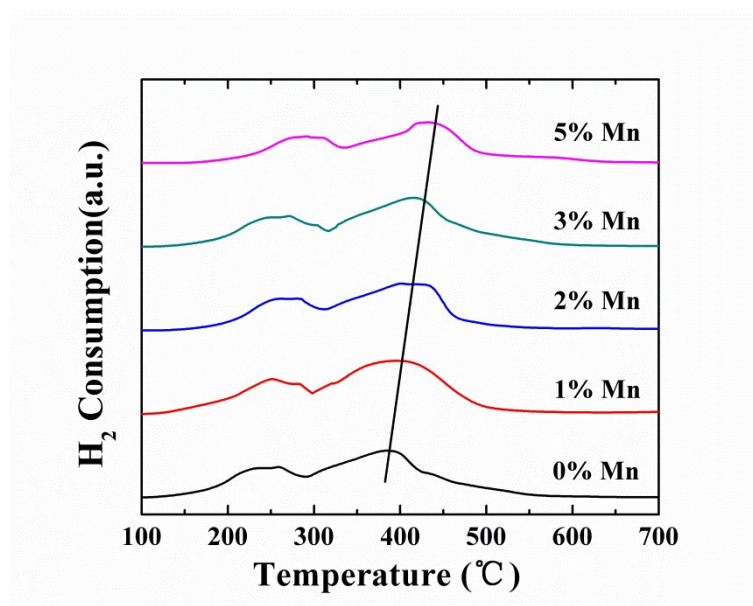


Figure S4, H₂-TPR of Co-based catalysts.

Saturation magnetization

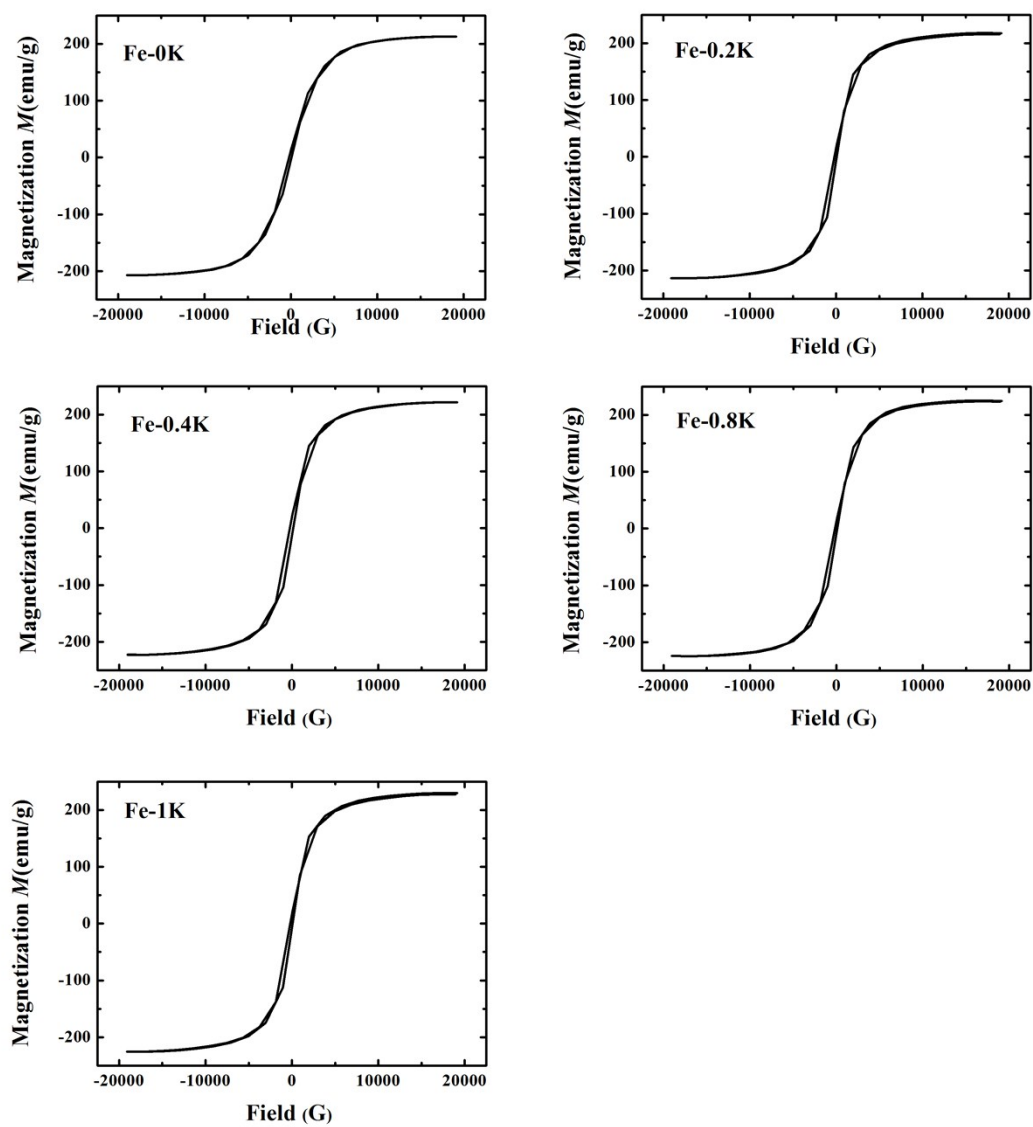


Figure S5. The magnetic hysteresis loops of all the fused iron catalysts after reduction and passivation

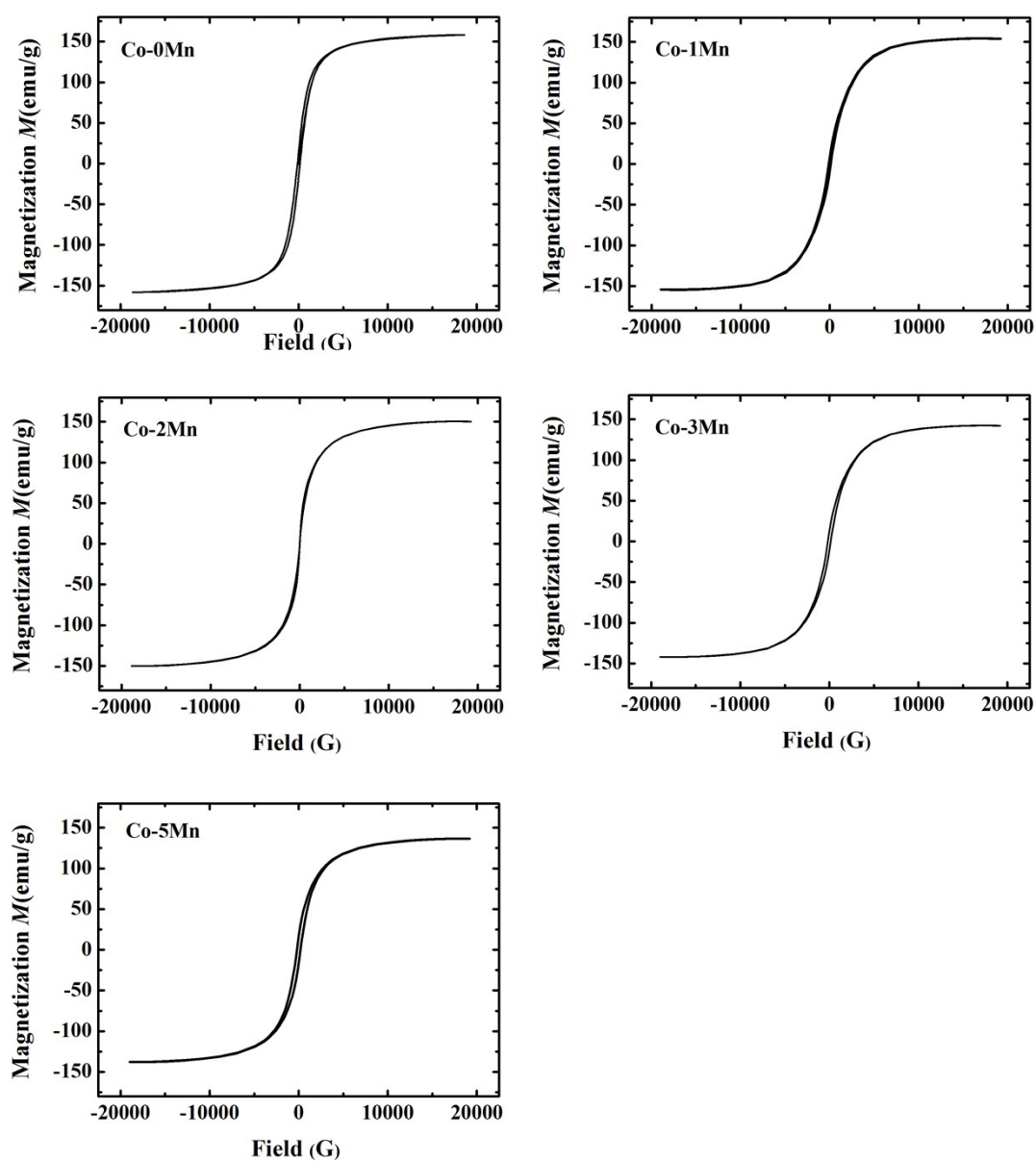


Figure S6. The magnetic hysteresis loops of all the Co-based samples after reduction and passivation.

Table S1: Bulk and surface compositions (Fe/K weight ratio) of all the Fe-based catalysts

Sample	FeK ₀	FeK _{0.2}	FeK _{0.4}	FeK _{0.8}	FeK ₁
bulk	100/0	99.86/0.14	99.58/0.42	99.22/0.78	98.88/1.12
surface	100/0	99.84/0.16	99.61/0.39	99.24/0.76	98.85/1.15

Table S2: Bulk and surface compositions (Co/Mn weight ratio) of all the Co-Mn samples.

Sample	CoMn ₀	CoMn ₁	CoMn ₂	CoMn ₃	CoMn ₅
bulk	100/0	99.03/0.97	98.11/1.89	97.06/2.94	94.71/5.29
surface	100/0	98.92/1.08	98.06/1.94	96.85/3.15	94.88/5.12

Reference

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- [6] W. Erley, H. Wagner, H. Ibach, *Surface Sci.* 80(1979), 612.