Electronic supplementary information (ESI)

The origin of Mo promotion during H_2 pretreament on Fe catalyst for Fischer-Tropsch Synthesis

Liping Li,[a] Caixia Hu,[b] Wen Liu,[a] Peng Fei,[a] Xiaojing Cui,[*c] Yongwang Li[b,c] and Jian Xu [b]

[a]College of Chemistry and Environmental Engineering, Shanxi Datong University, Datong, Shanxi 037009, People's Republic of China

[b]Synfuels China Technology Co. Ltd. Leyuan South Street II, No. 1, Yanqi Economic Development Zone C#, Huairou District, Beijing, 101407, People's Republic of China

[c]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, People's Republic of China

[*] Corresponding Author.

E-mail address: cuixj@sxicc.ac.cn

Figure and Table captions:

Fig. S1 XRD profiles of all the calcined catalysts.

Fig. S2 HRTEM micrographs of all the catalysts

Fig. S3 Raman spectra of $Fe(NO_3)_3 \cdot 9H_2O$, $(NH_4)_6MoO_{24} \cdot 4H_2O$, and 100Fe10Mo catalyst precursors during the preparation

Fig. S4 STEM image (A) and EDS mapping profiles for Fe (B) and Mo (C) in calcined 100Fe10Mo

Fig. S5 HRTEM images of the MoO_3 particles in the calcined FeMo catalysts

Fig. S6 The catalytic activity of all the catalysts with time-on-stream

Fig. S7 HRTEM images of FeMo catalysts pretreated in H_2 at 350 ^oC

Fig. S8 XRD profiles of all the catalysts pretreated at 350^oC for 12 h

Fig. S9 Mössbauer spectra at 20 K of the pretreated and used 100Fe

Fig. S10 Mössbauer spectra at 20 K of the pretreated and used 100Fe5Mo

Fig. S11 Mössbauer spectra at 20 K of the pretreated and used 100Fe8Mo

Fig. S12 Mössbauer spectra at 20 K of the pretreated and used 100Fe10Mo

Table S1 The physicochemical properties of all the calcined catalysts

Table S2 Raman shifts (cm^{-1}) and their assignments

Table S3 The fitted results of the distributions of surface Fe and Mo species for the FeMo catalysts

Table S4 The Mössbauer parameters of all the pretreated and used catalysts

Table S5 The estimated amounts of active Fe sites on the iron carbides for all the catalysts

Fig. S1 XRD profiles of all the calcined catalysts.

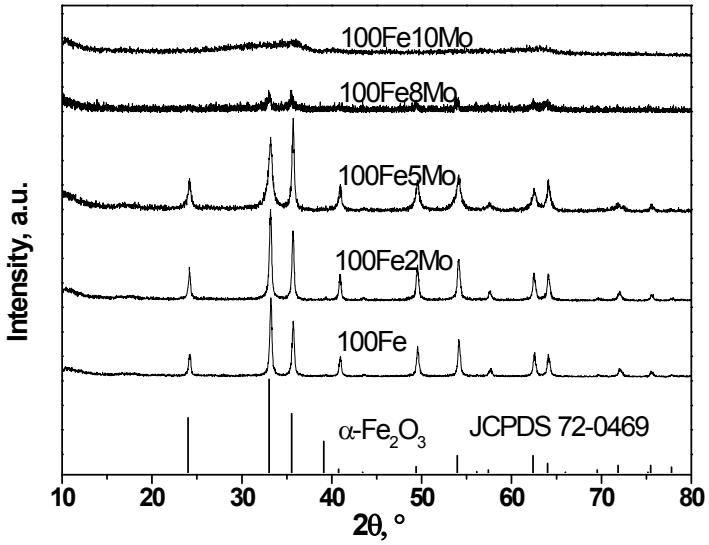


Fig. S2 HRTEM micrographs of all the catalyst precursors: (a) 100Fe; (b) 100Fe5Mo; (c) 100Fe8Mo; (d) 100Fe10Mo

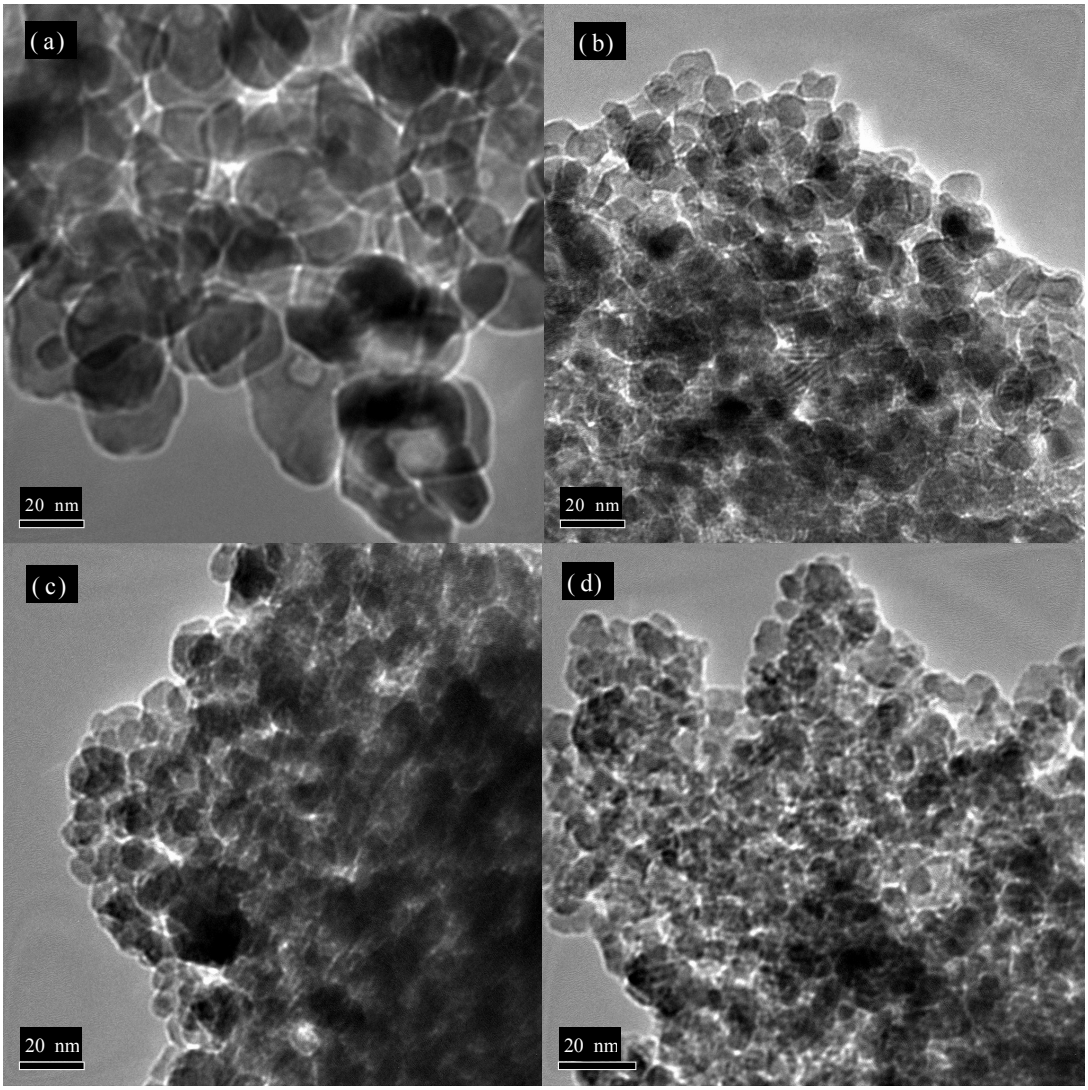
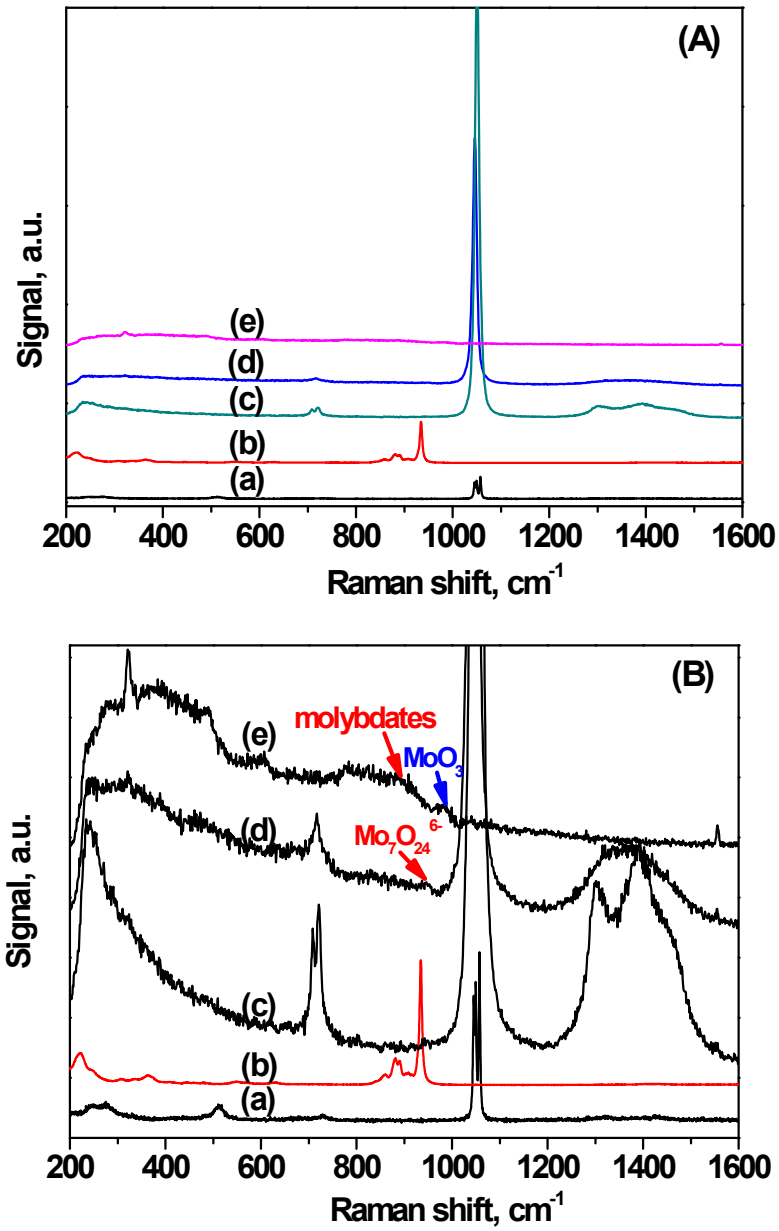


Fig. S3 Raman spectra of (a) $Fe(NO_3)_3 \cdot 9H_2O$, (b) $(NH_4)_6MoO_{24} \cdot 4H_2O$, and 100Fe10Mo catalyst precursors after: (c) filtering; (d) drying at 120 °C; (e) calcining at 375 °C (**Fig. S3A:** the full spectra**; Fig. S3B:** part of the spectra).



The LRS bands of $Fe(NO_3)_3 \cdot 9H_2O$ at 244、 and 721 cm^{-1}, and NO_3^- at 1050 cm^{-1} were detected after precipitation. After drying at 120 °C, The bands of 709 and 1050 cm^{-1} largely reduced, indicating the decomposition of part $Fe(NO_3)_3$. The LRS bands for $Fe(NO_3)_3 \cdot 9H_2O$ and NO_3^- disappeared after calcination at 375 °C, implying the complete decomposition of $Fe(NO_3)_3$.

Fig. S4 STEM image (A) and EDS mapping profiles for Fe (B) and Mo (C) in calcined 100Fe10Mo

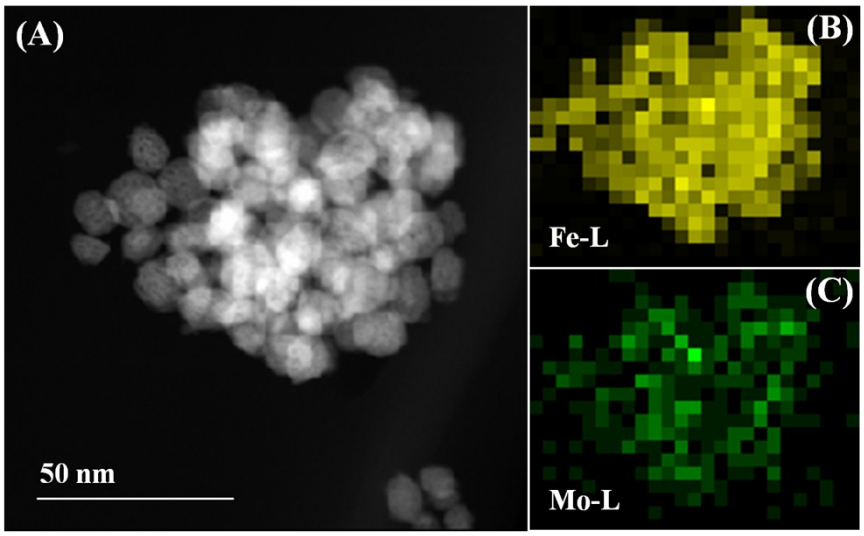


Fig. S5 HRTEM images of the MoO_3 particles in the calcined FeMo catalysts: (a) 100Fe5Mo; (b) 100Fe8Mo; (c) 100Fe10Mo.

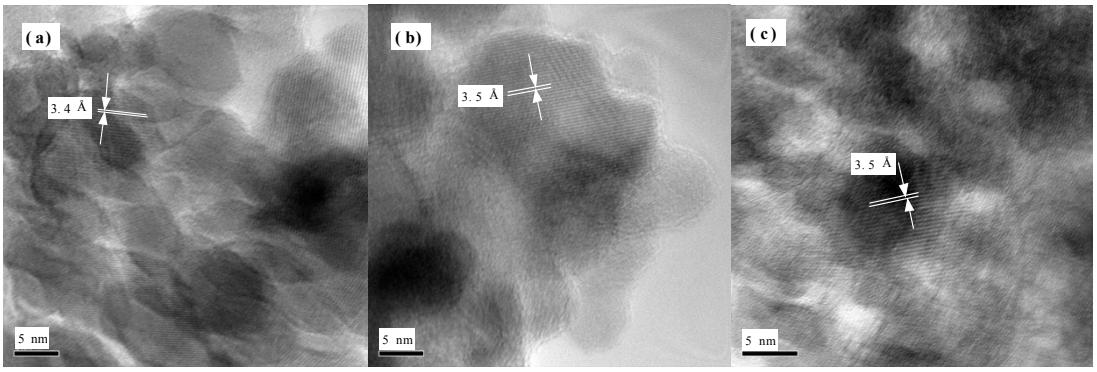


Fig. S6 The catalytic activity of all the catalysts with time-on-stream

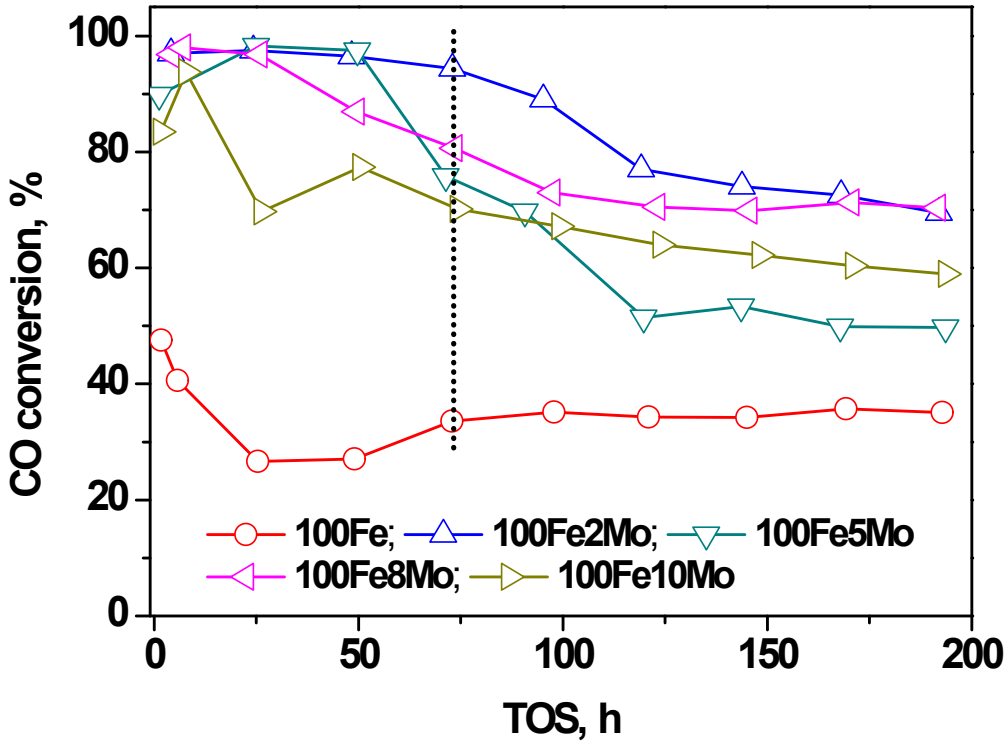


Fig. S7 HRTEM images of FeMo catalysts pretreated in H_2 at 350 °C: (a) 100Fe5Mo; (b) & (d) 100Fe8Mo; (c) & (e)100Fe10Mo

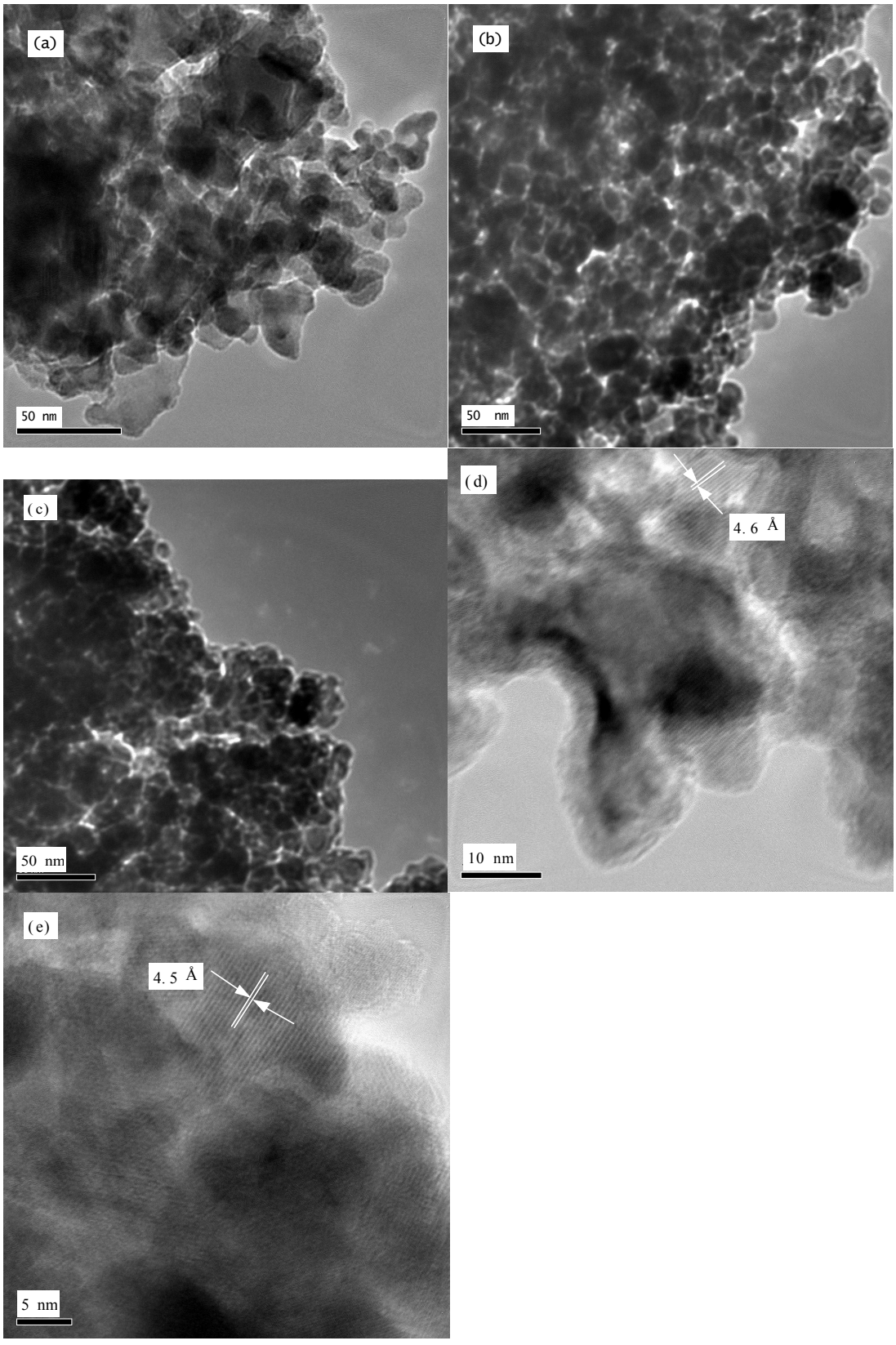


Fig. S8 XRD profiles of all the catalysts pretreated at 350°C for 12 h

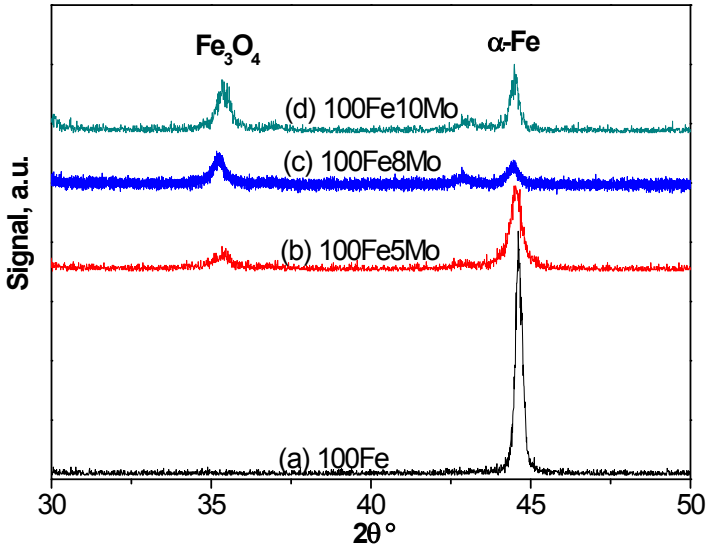


Fig. S9 Mössbauer spectra at 20 K of the pretreated and used 100Fe

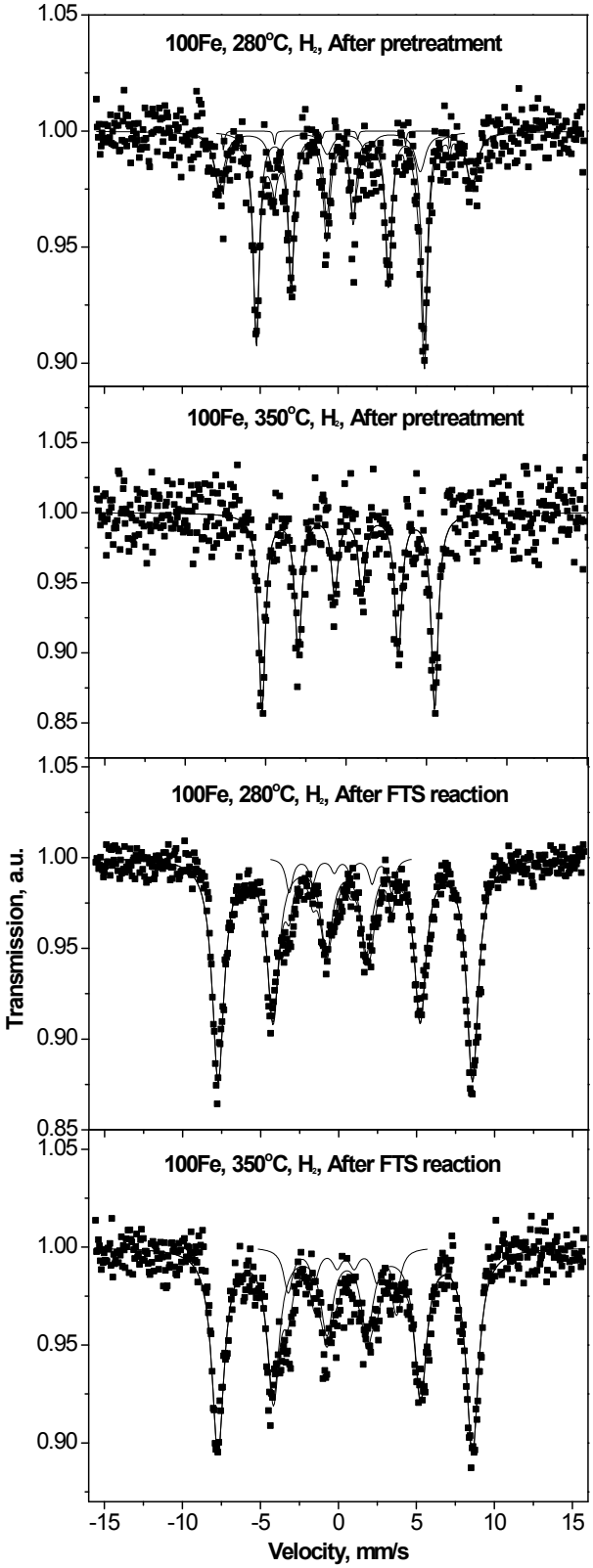


Fig. S10 Mössbauer spectra at 20 K of the pretreated and used 100Fe5Mo

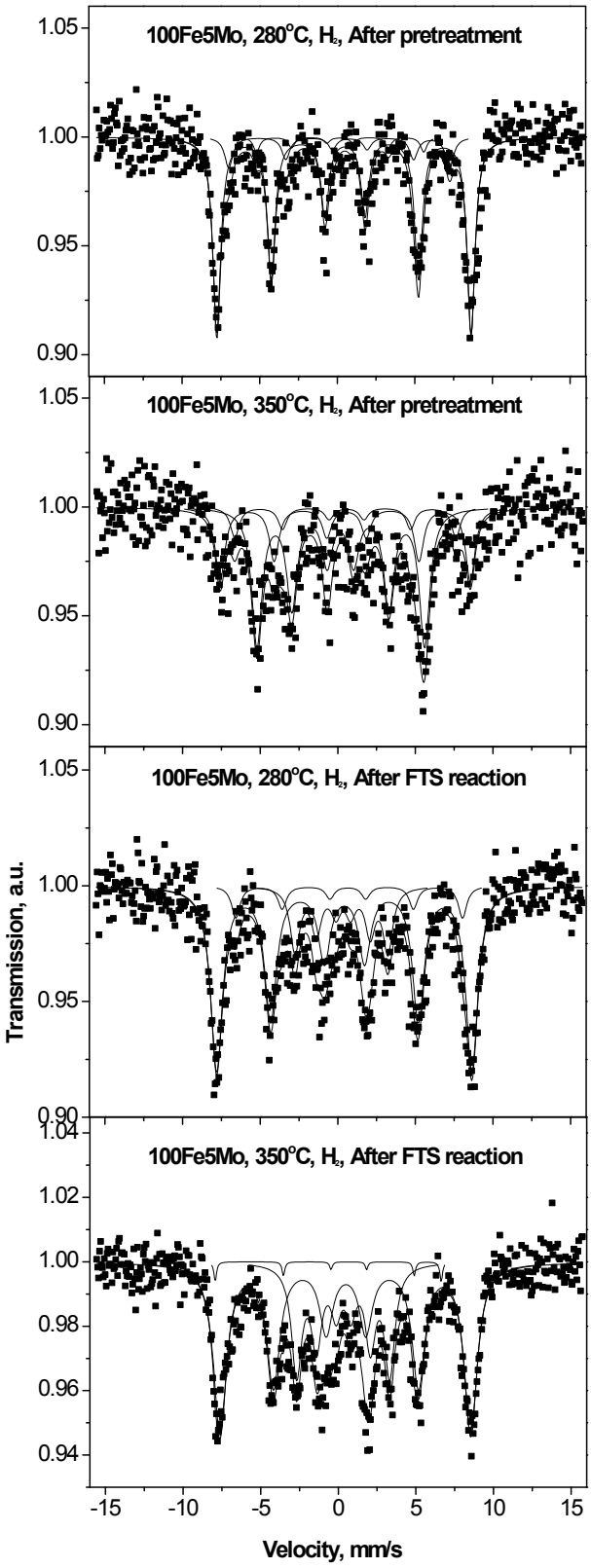


Fig. S11 Mössbauer spectra at 20 K of the pretreated and used 100Fe8Mo

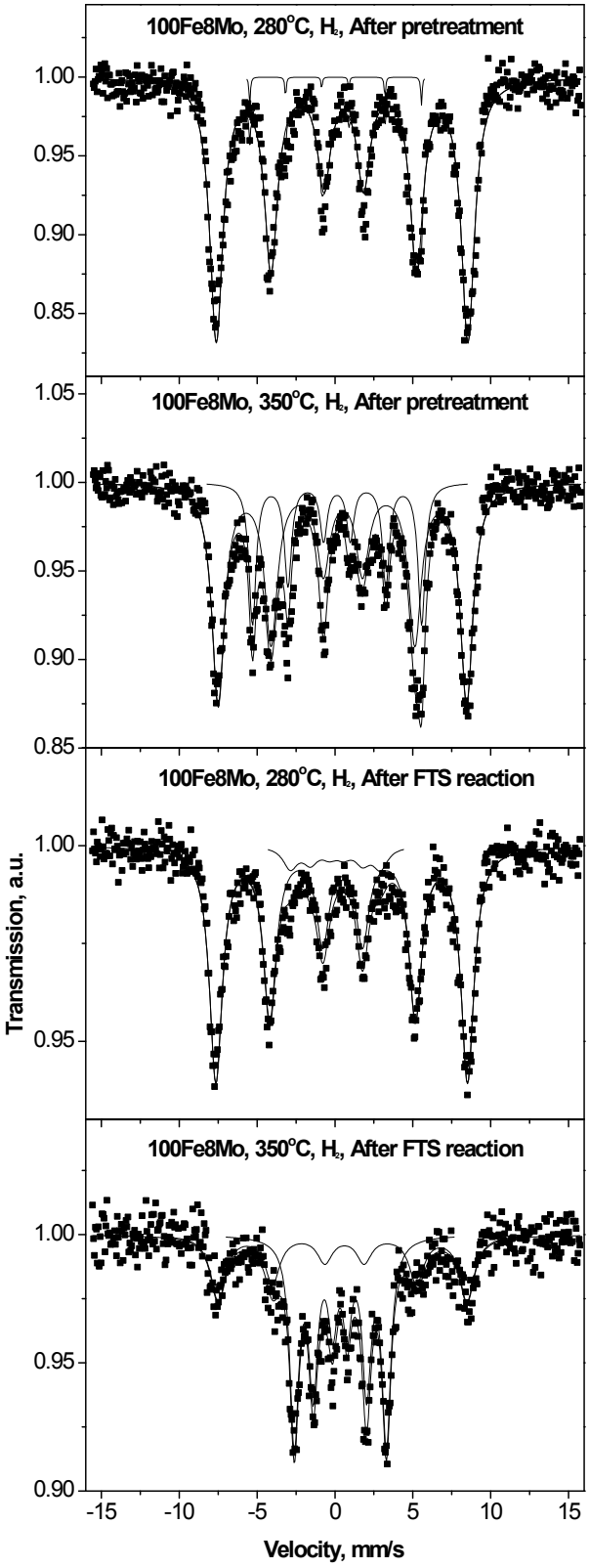


Fig. S12 Mössbauer spectra at 20 K of the pretreated and used 100Fe10Mo

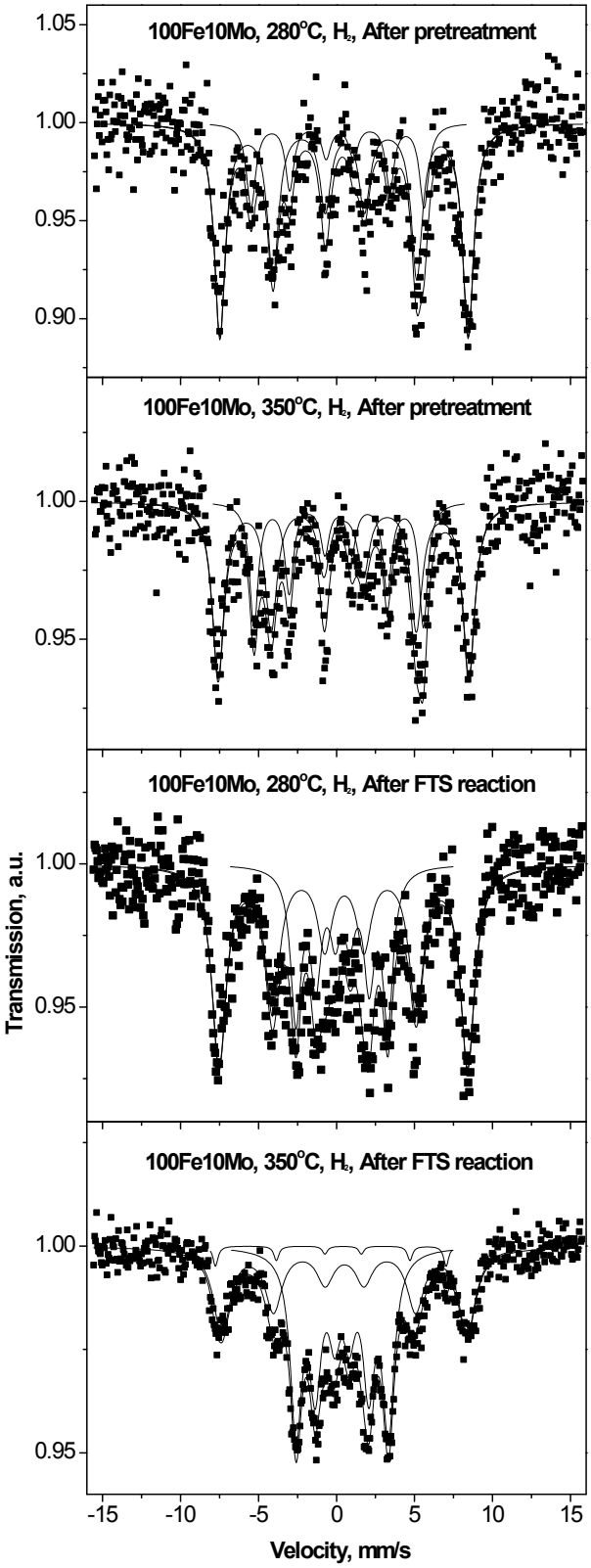


Table S1 The physicochemical properties of all the calcined catalysts

Catalyst	S_{BET} [a] (m^2/g)	V_p [a] (cm^3/g)	d_p [a] (nm)	Particle size (nm)	
				XRD[c]	TEM[d]
100Fe	23	0.08	9.6	32	27
100Fe2Mo	41	0.08	5.5	30	23
100Fe5Mo	100	0.17	4.9	17	12
100Fe8Mo	116	0.19	5.0	14	11
100Fe10Mo	157	0.17	3.3	-	6

[a]: represent the BET surface area, the pore volume and the pore diameter of the calcined catalysts. [b]: the calcined catalysts. [c]: the average iron crystallite size of the calcined catalysts was calculated using Scherer's equation taking the diffraction peak at $2\theta = 33^o$. [d]: the average iron crystallite size of the calcined catalysts was calculated from HRTEM data.

Table S2 Raman shifts (cm^{-1}) and their assignments

Raman shift (cm^{-1})	Assignment	References
1044, 1050, 1057	NO_3^- from ferric nitrate	[1]
988~992	Terminal Mo=O vibrations in MoO_3	[1]
947	Symmetric stretching of terminal Mo=O	[2-3]
717~721	Ferric nitrate	[1]
~600, ~487, ~402	α-Fe_2O_3	[4]
325	LRS laser	
241-246	Ferric nitrate	[1]

Refs:

[1] G.B. Raupp, W.N. Delgass, Mössbauer Investigation of Supported Fe and FeNi Catalysts II. Carbides Formed by Fischer-Tropsch Synthesis. J. Catal., **1979,** 58: 348-360.

[2] J.W. Niemantsverdriet, J. van Grondelle, A.M. van der Kraan, Mössbauer Spectroscopy of Supported Bimetallic Catalysts: 1:5 Fe-M/SiO_2 (M= Ru, Rh, Pd, Ir, Pt). Hyperfine Interact., **1986,** 28: 867-870.

[3] M.Y. Ding, Y. Yang, B.S. Wu, J. Xu, C.H. Zhang, H.W. Xiang, Y.W. Li, Study of Phase Transformation and Catalytic Performance on Precipitated Iron-Based Catalyst for Fischer–Tropsch Synthesis. J. Mol. Catal. A: Chem., **2009,** 303: 65-71.

[4] M.Y. Ding, Y. Yang, J. Xu, Z.C. Tao, H.L. Wang, H. Wang, H.W. Xiang, Y.W. Li, Effect of Reduction Pressure on Precipitated Potassium Promoted Iron-Manganese Catalyst for Fischer-Tropsch Synthesis. Appl. Catal. A: Gen., **2008,** 345: 176-184.

Table S3 The fitted results of the distributions of surface Fe and Mo species for the FeMo catalysts [a]

Catalyst	Assignment	Peak temperature, ^{o}C	Peak area, a.u. × 10^3	The Mo coverage (θ_{Mo}) [b]
100Fe2Mo	Surface Fe	83.1	132.8	
	Surface Fe	120.3	76.5	
	Surface Fe	220.4	352.7	
	Surface Mo	393.4	31.0	**5.2%**
100Fe5Mo	Surface Fe	85.8	45.5	
	Surface Fe	122.9	94.8	
	Surface Fe	226.2	125.1	
	Surface Mo	398.4	27.4	**9.4%**
100Fe8Mo	Surface Fe	89.8	31.8	
	Surface Fe	145.0	112.4	
	Surface Fe	225.1	263.1	
	Surface Mo	366.7	402.9	**49.7%**
100Fe10Mo	Surface Fe	160.8	44.1	
	Surface Fe	250.8	337.9	
	Surface Mo	394.2	382.9	
	Surface Mo	518.9	49.8	**53.1%**

a: pretreated at 350 ^{o}C in 5%H_2/Ar for 12 h; [b]: the coverage ratio of Mo is calculated as following: 100× the peak area(s) of surface Mo/(the peak area(s) of surface Mo+ the peak areas of surface Fe)

Table S4 The Mössbauer parameters of all the pretreated and used catalysts

Catalyst	Pretreatment	Phases	Mössbauer parameters		
			IS(mm/s)	QS(mm/s)	Hhf(KOe)
100Fe	H_2, 280°C	α-Fe	0.14	0.03	336
		Fe_3O_4	0.54	-0.09	504
			0.02	-0.21	452
	H_2, 350°C	α-Fe	0.14	0.00	334
	H_2, 280°C-r [a]	χ-Fe_5C_2	0.18	-0.12	204
		Fe_3O_4	0.47	-0.08	507
	H_2, 350°C-r [a]	χ-Fe_5C_2	0.36	-0.21	216
		Fe_3O_4	0.49	-0.11	507
100Fe5Mo	H_2, 280°C	α-Fe	0.18	0.01	335
		Fe_3O_4	0.46	-0.06	509
			0.46	-0.68	442
	H_2, 350°C	α-Fe	0.18	0.03	336
		Fe_3O_4	0.52	-0.08	501
			0.53	-0.08	443
	H_2, 280°C-r [a]	ε'-$Fe_{2.2}C$	0.30	-0.12	186
		Fe_3O_4	0.69	0.09	454
			0.43	-0.01	511
	H_2, 350°C-r [a]	ε'-$Fe_{2.2}C$	0.32	-0.02	186
		Fe_3O_4	0.01	-1.33	453
			0.48	-0.04	502
100Fe8Mo	H_2, 280°C	α-Fe	0.03	0.02	343
		Fe_3O_4	0.51	-0.11	502
	H_2, 350°C	α-Fe	0.13	0.01	338
		Fe_3O_4	0.50	-0.03	496
	H_2, 280°C-r [a]	ε'-$Fe_{2.2}C$	0.06	-0.07	180
		Fe_3O_4	0.46	-0.06	502
	H_2, 350°C-r [a]	ε'-$Fe_{2.2}C$	0.33	0.03	184
		Fe_3O_4	0.55	-0.12	497
100Fe10Mo	H_2, 280°C	α-Fe	0.14	-0.14	345
		Fe_3O_4	0.51	-0.05	495
	H_2, 350°C	α-Fe	0.12	0.03	338
		Fe_3O_4	0.46	-0.01	500
	H_2, 280°C-r [a]	ε'-$Fe_{2.2}C$	0.36	-0.04	183
		Fe_3O_4	0.47	-0.06	496
	H_2, 350°C-r [a]	ε'-$Fe_{2.2}C$	0.36	0.02	184
		Fe_3O_4	0.03	-0.79	460
			0.51	-0.01	489

[a]: after the FTS reaction for 120 h.

Table S5 The estimated amounts of active Fe sites on the iron carbides for all the catalysts [a]

Catalysts	Total mass of catalyst g	Total Fe mmol [b]	Volume of per Fe NPs [c] nm^3	Numbers of Fe atoms per Fe NP [d] -	Number of Fe NPs [e] -	Total surface Fe [f] mmol
The size of Fe NPs estimated from XRD						
100Fe	2	25	24429.0	3051421	4.93×10^{15}	0.03830
100Fe2Mo	2	24.1	11494.0	1435717	1.01×10^{16}	0.06101
100Fe5Mo	2	22.8	4188.7	523220	2.62×10^{16}	0.11310
100Fe8Mo	2	21.8	3591.4	448596	2.99×10^{16}	0.12001
100Fe10Mo	2	21.1	1150.3	143689	8.84×10^{16}	0.24780

[a]: Pretreated in H_2 at 350 °C for 12h; [b]: Total moles of Fe in each catalyst = the weight percent of Fe (obtained by ICP, listed in Table S1) × the mass of total catalyst; [c]: Volume of per Fe NPs = $4\pi R^3/3$, where R is the radii of per Fe NP in the pretreated catalysts and can be calculated from the average particle size that estimated by HRTEM/XRD (see Table 1 in the manuscript); [d]: The volume of each Fe atom = $4\pi r^3/3 = 0.008\ nm^3$, where r is the radii of per Fe atom (0.1241 nm), the numbers of Fe atoms per Fe NP in each catalyst = (the volume of per Fe NPs / the volume of per Fe atom); [e]: Total Fe atoms in each catalyst = the mole of the total Fe atoms × N_A (Avogadro constant), the numbers of Fe NPs in each catalyst = (total Fe atoms / the numbers of Fe atoms per Fe NP); [f]: The moles of the total surface Fe in each catalyst = $(1-\theta_{Mo})$(the numbers of Fe NPs × $S_{Fe\ NP}$)/(N_A × $S_{Fe\ atom}$), where θ_{Mo} represents the coverage of surface Mo, the θ_{Mo} for FeMo catalysts are listed in Table S3 in ESI, $S_{Fe\ NP}$ represents the surface area of per Fe NP in each catalyst: $S_{Fe\ NP} = 4\pi R^2$ (R is the radii of per Fe NP), N_A is the Avogadro constant, $S_{Fe\ atom}$ represents the cross-sectional area of per Fe atom: $S_{Fe\ atom} = \pi r^2$ (r is the radii of per Fe atom, r=0.1241 nm). [e]: TOF = mmol converted $_{CO}$/($mmol_{Fe}$•h), where $mmol_{Fe}$ represents the mole of the total surface Fe atoms in each catalyst which are obtained based on HRTEM result.