Supplementary Information (SI)

Tab. S1. The textural properties of H-ZSM-5, 20%CoB/ZSM-5, and CoB were calculated from N_2 adsorption-desorption isotherms.

Catalyst	BET surface area (m^2 g^{-1})	Pore diameter (nm)	Pore volume (cm^2 g^{-1})
H-ZSM-5	285.96	2.32	0.17
20%CoB/ZSM-5	167.48	2.39	0.10
CoB	29.91	13.09	0.098

Tab. S2. The STY(CO) of different reaction conditions of 20%CoB/ZSM-5.

Reaction conditions	STY (μmol g^{-1} s^{-1})
H_2 atmosphere	$1.62*10^{-3}$
CO_2 atmosphere	Trace
Ar atmosphere	Trace
Quarta sand, without catalyst	Trace

(Unless otherwise stated, the reaction condition is fixed: 500°C reaction temperature, 3000 mL g^{-1} h^{-1}, the stoichiometric ratio of CO_2:H_2 is 1:4, and 3 h reaction period.)

Tab. S3. Comparison of catalytic activity of 20%CoB/ZSM-5 catalyst with highly selective catalysts reported in literature.

Catalyst	T(℃)	P(mPa)	CO_2:H_2	SV (mL h^{-1} g^{-1})	CO STY (μmol g^{-1} s^{-1})	S(CO) (%)	Ref.
20%CoB/ZSM-5	500	0.1	4:1	30000	21.56	97.35	This work
CoZrOx (10)	340	0.1	1:4	10000	2.0	100	1
Cu-CeO_2	300	0.1	1:3	1120	1.6	100	2
Ni/TiO_2	360	0.1	1:3	15000	1.3	100	3
Ni_3-Fe_9/ZrO_2	400	0.1	1:2	9000	6.4	96	4
$CuAl_2O_4$	300	0.1	1:2	15000	2.1	100	5
$NiMgO_x$	300	3	1:4	60000	0.2	100	6
5% Ir/CeO_2	300	1	1:4	11400	2.0	＞99	7
Pt-Co/TiO_2	300	-	1:2	36000	11.4	99	8
Pt/mullite	340	0.1	1:1	27000	12.5	96	9
Ru/Al_2O_3	350	0.1	1:3	72000	21.6	98	10
Au/TiO_2	300	0.1	1:9	20000	7.4	＞99	11

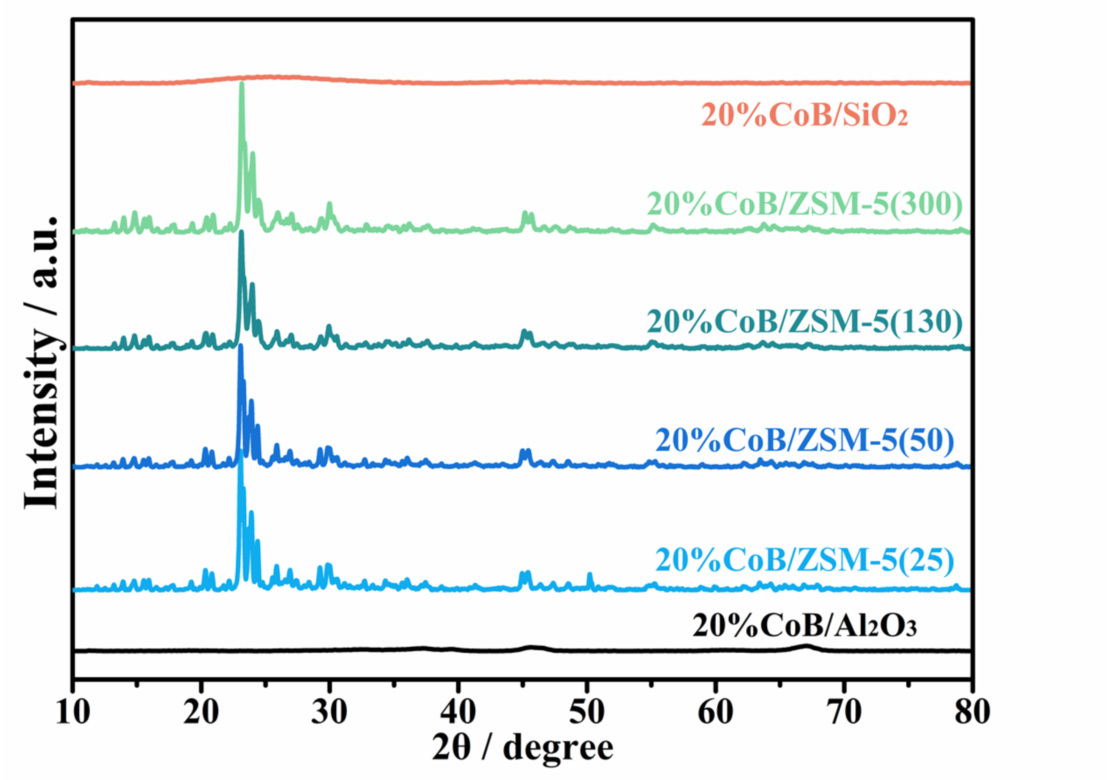

Fig. S1. XRD patterns of different catalyst. The number in brackets in the catalyst name is the SiO_2/Al_2O_3 ratio of H-ZSM-5 zeolites.

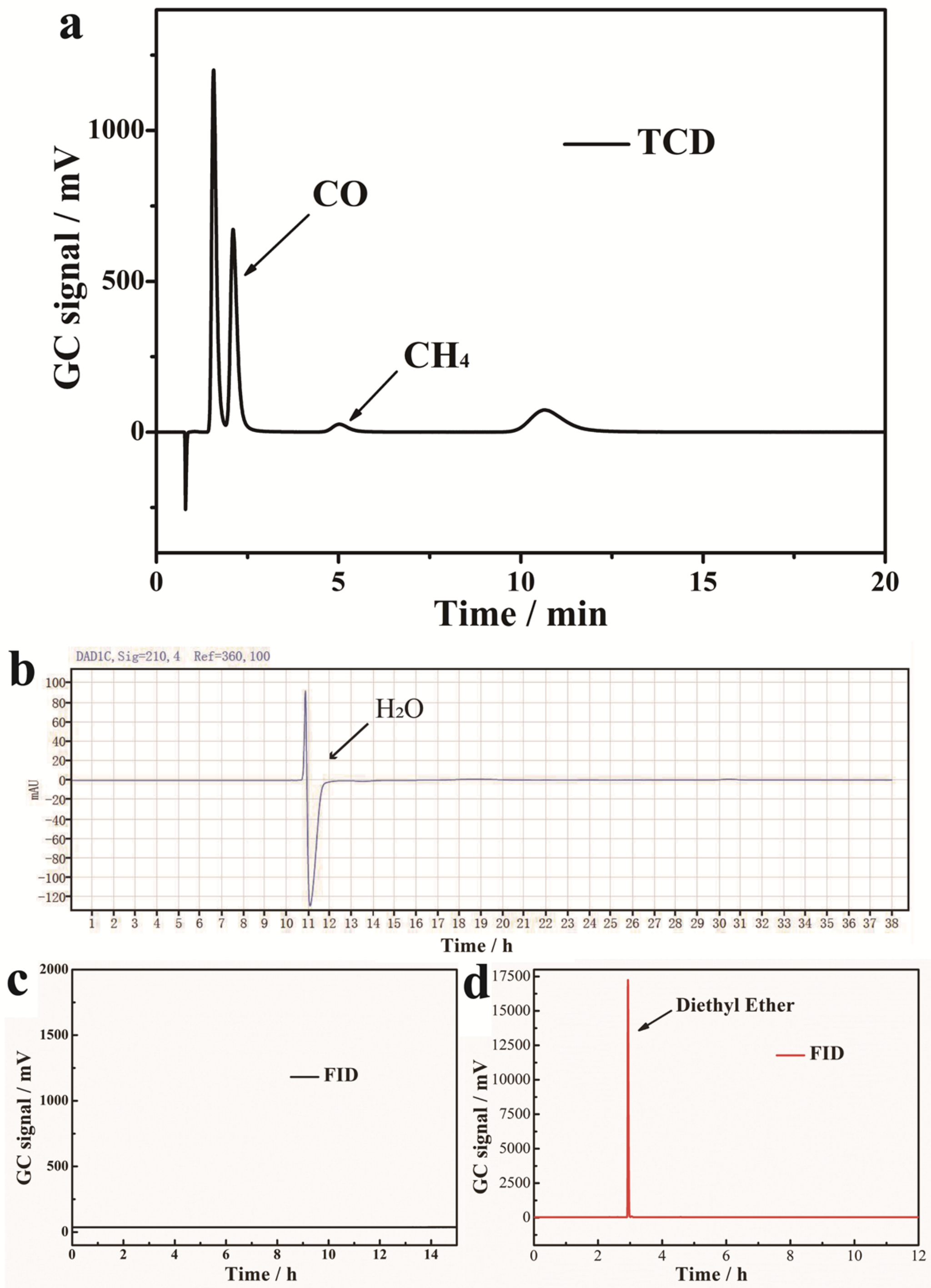

Fig. S2. Product chromatographic signal of 20%CoB/ZSM-5. (a) FID signal of permanent gas products, (b) TCD signal of permanent gas products, (c) RID signal collected in the aqueous phase, (d) FID signal of hydrophilic phase products, and (e) FID signal of organophilic phase products.

After the photothermal reaction, the gas is washed with 50 mL of water. Suppose that the non-permanent gas in the reaction product is dissolved in water.

First, the permanent gas will be injected directly into the online GC as the feed gas is continuously injected. Then, the purge water sample is detected by the FID detector of GC and the RID detector of LC. Alcohols and small fatty acids in the products can be found. Finally, the organophilic phase products in the hypothetical non-permanent gas in the water sample were extracted using ether and detected by the FID detector of GC.

The results show that only CO and CH_4 were found in the products of CO_2 hydrogenation reaction by 20%CoB/ZSM-5.

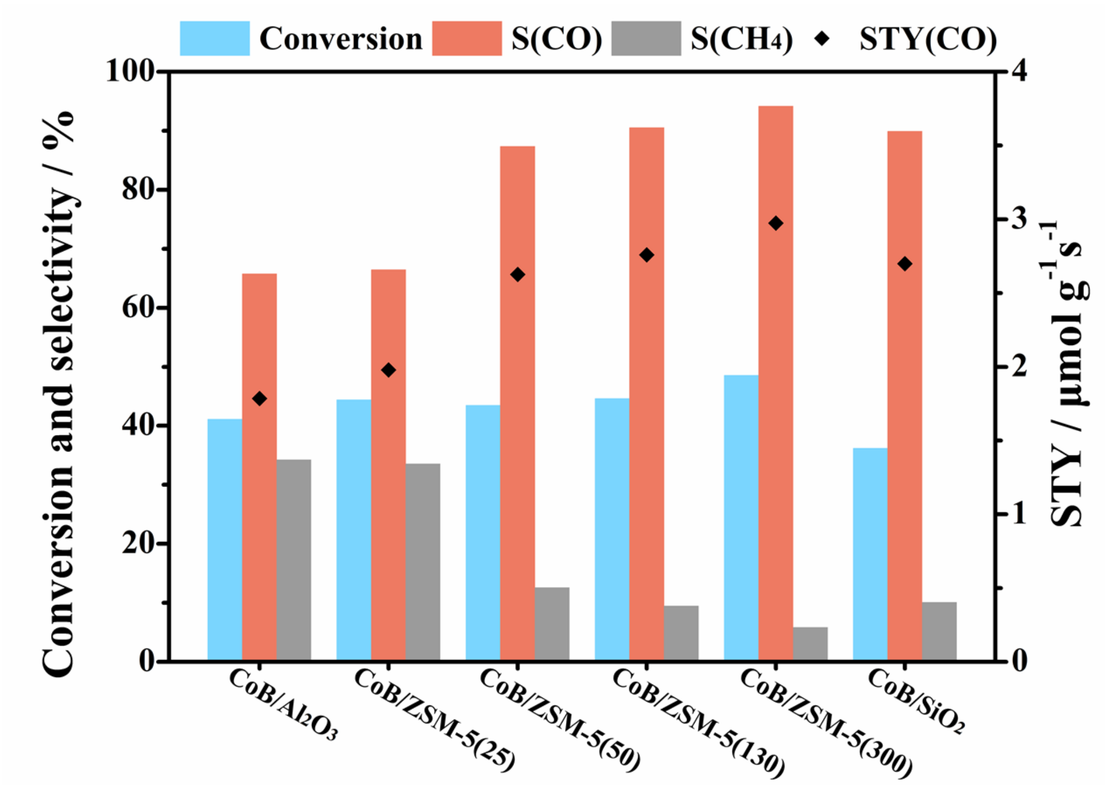

Fig. S3. Different vector catalyst in CO_2 hydrogenation. The number in brackets in the catalyst name is the SiO_2/Al_2O_3 ratio of H-ZSM-5 zeolites. The reaction condition is fixed: 20% CoB loading, 500℃ reaction temperature, 3000 mL g^{-1} h^{-1}, the stoichiometric ratio of CO_2:H_2 is 1:4, and 3 h reaction period.)

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