Supporting information

Coupling Conversion of methane with Carbon Monoxide via carbonylation over Zn/HZSM-5 catalyst

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Catalyst preparation

The catalysts were prepared by incipient wetness impregnation. Typically, 1.365g $Zn(NO_3)_2 \cdot 6H_2O$ (Tian jin da mao) was dissolved in 5g deionized water, then 5g HZSM-5(SiO_2/Al_2O_3=40.7, NanKai University) was introduced into the solution. Incipient overnight at atmosphere temperature, then dried 2h at 120℃, and calcined in muffle at 550℃ for 4 h.

NMR Spectroscopy

All the solid-state NMR experiments were performed on a Bruker Avance III 600 spectrometer equipped with a 14.1T wide-bore magnet using a 4mm MAS probe.^{13}C CP/MAS NMR spectra recorded using cross polarization sequence with a spinning rate of 12 kHz.

Catalyst test

The prepared catalyst was tested on a high-pressure fixed bed reactor, with a liner made of quartz inside the stainless steel tube. Typically, 0.4g of catalyst was putting in the reactor, pretreated in He at 350℃ for 2h and increasing to reaction temperature for 30min. After the pretreatment, the reaction gas with a composition of 10% methane, 80% carbon monoxide, and 10% argon as the standard was introduced to the reactor. The reaction products were analyzed by an online gas chromatograph (Agilent 7890B) equipped with a Plot-Q capillary column connected to a flame ionization detector(FID) to detect the hydrocarbons of methane, ethane, ethylene, C_3, benzene and toluene, HP-5 capillary column connected to another FID to detect the aromatics such as BTX, naphthalene, methylnaphthalene and C_{11+} aromatics; besides, a TDX-1 packed column connected to a thermal conductivity detector(TCD) to detect the Ar, CO, CH_4 and CO_2.

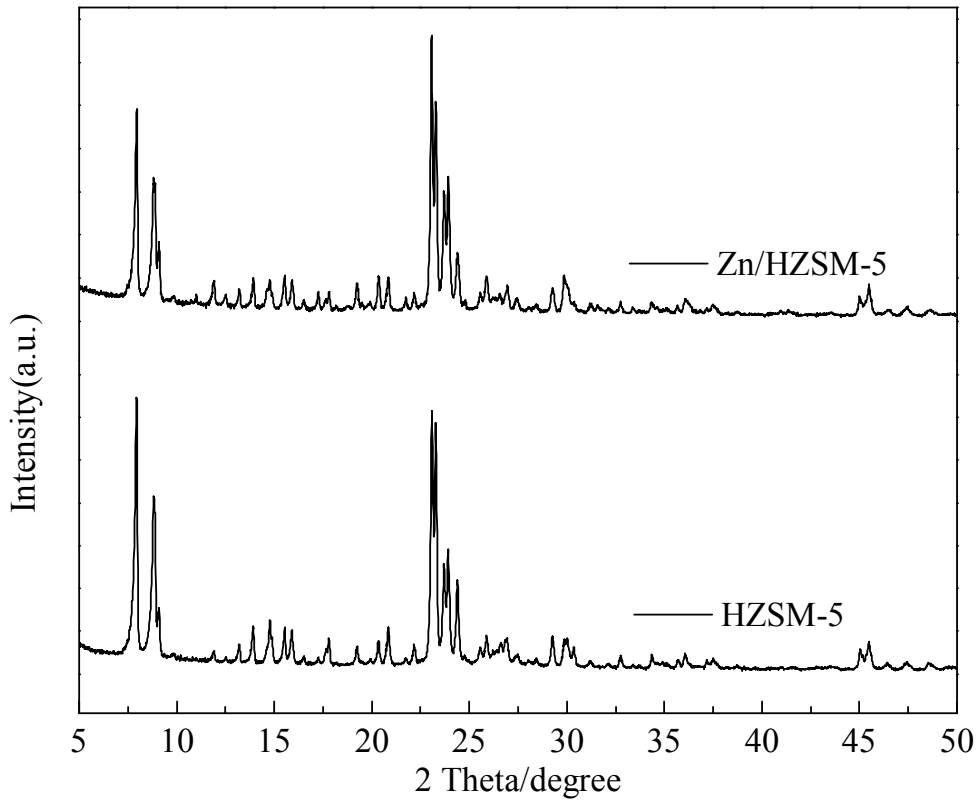

Fig S1. Powder XRD pattern of the HZSM-5 and corresponding Zn/HZSM-5

Introducing of 6%Zn has no effect of the crystal structure of HZSM-5, and ZnO peak was not found in XRD pattern.

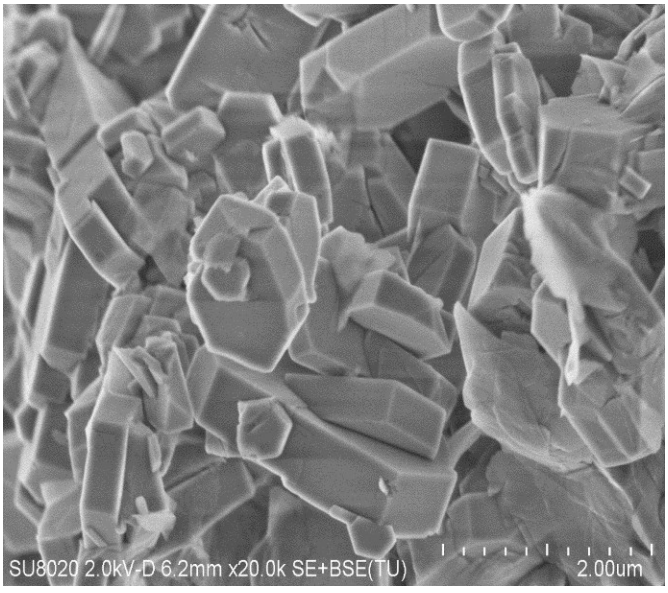

Figure S2. SEM images of HZSM-5.

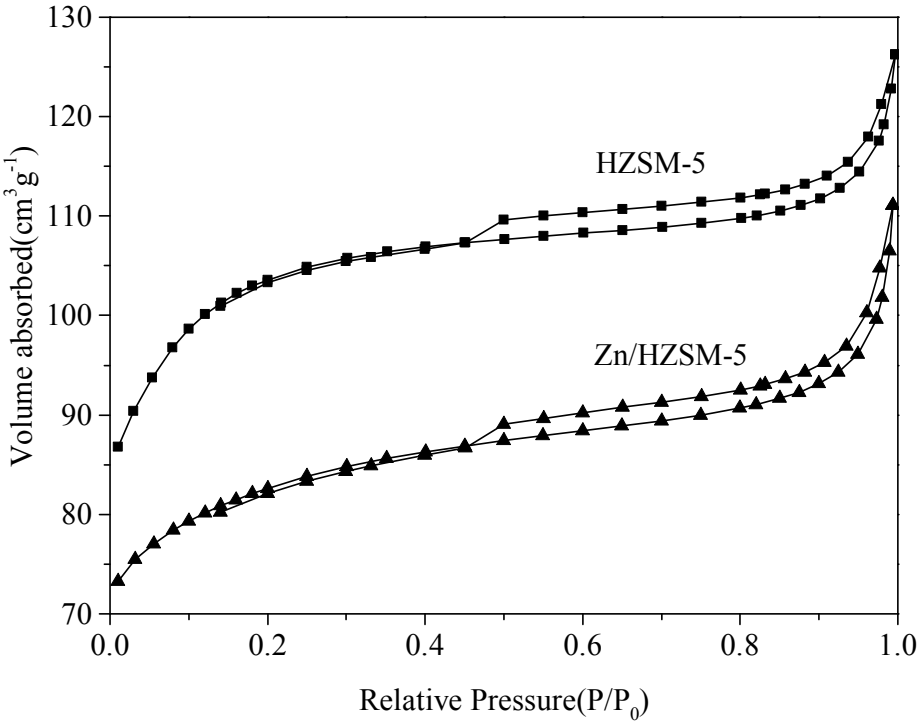

Fig S3. N_2 adsorption-desorption isotherms of the HZSM-5 and corresponding Zn/HZSM-5

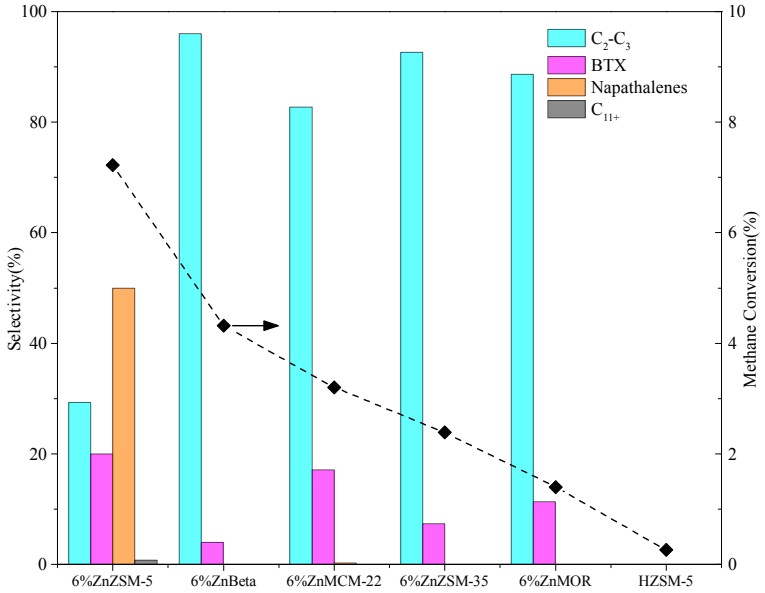

Fig S4. The conversion of methane and the hydrocarbons selectivity on Zn-Zeolite with different topology structure

Reaction conditions: T=773 K, P=2.0 Mpa, $CO/CH_4/Ar$=8:1:1, space velocity=2250 $ml/g_{cat}\cdot h$, time on stream=30 min

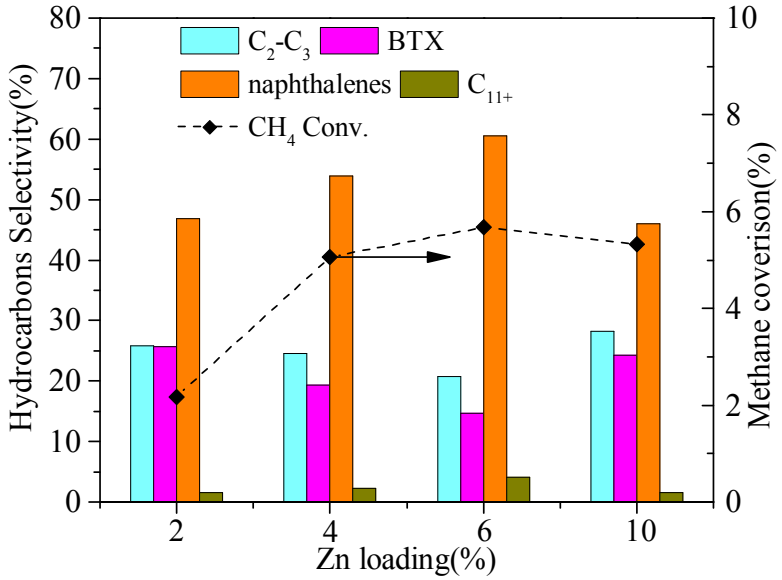

Fig S5. The hydrocarbons selectivity and methane conversion on Zn/HZSM-5 catalyst with different Zn content

Reaction conditions: T=773 K, P=2.0 Mpa, $CO/CH_4/Ar$=8:1:1, space velocity=4500 $ml/g_{cat}·h$, time on stream=30 min

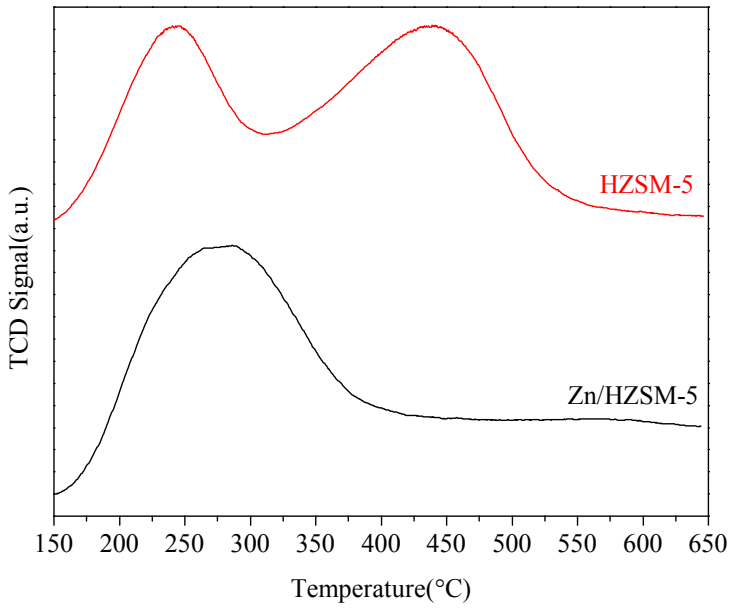

Fig S6. NH_3-TPD of HZSM-5 and corresponding Zn/HZSM-5

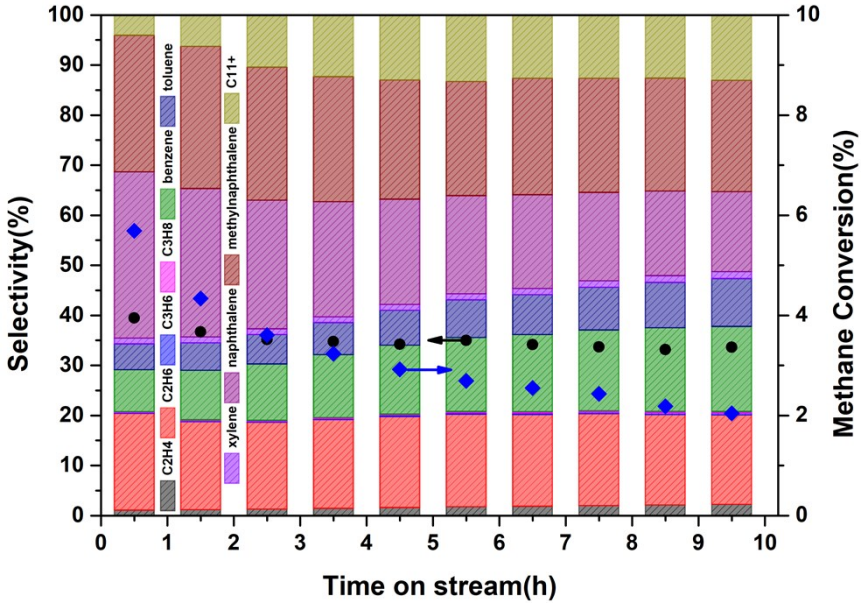

Fig S7. The time on stream of methane conversion (diamond), the selectivity of different hydrocarbons and carbon dioxide (circle).

Reaction conditions: 6%Zn/HZSM-5, Temperature=773 K, Pressure=2.0 MPa, space velocity=4500 mL/g_{cat}·h, CO/CH_4/Ar=8:1:1

Table S1. The products of the co-reaction of CO and methane on Zn/HZSM-5

CO/CH_4 [mol ratio]		0：1[a]	1：1	8：1
Methane conversion(%)		0.28	1.84	5.68
Hydrocarbons Selectivity[%]	ethylene	-	2.75	1.08
	ethane	-	34.86	19.36
	C_3	-	0.60	0.34
	benzene	-	17.32	8.37
	toluene	-	5.33	5.15
	xylene	-	0	1.16
	naphthalene	-	20.78	33.20
	methylnaphthalene	-	8.20	27.29
	C_{11+} aromatics	-	10.14	4.03

Reaction condition: 6%Zn/H-ZSM-5, Temperature=773 K, Pressure=2.0 MPa, space velocity=4500 mL/g_{cat}.h, CO/CH_4/Ar=8:1:1, Time on stream=30 min

[a]: without CO

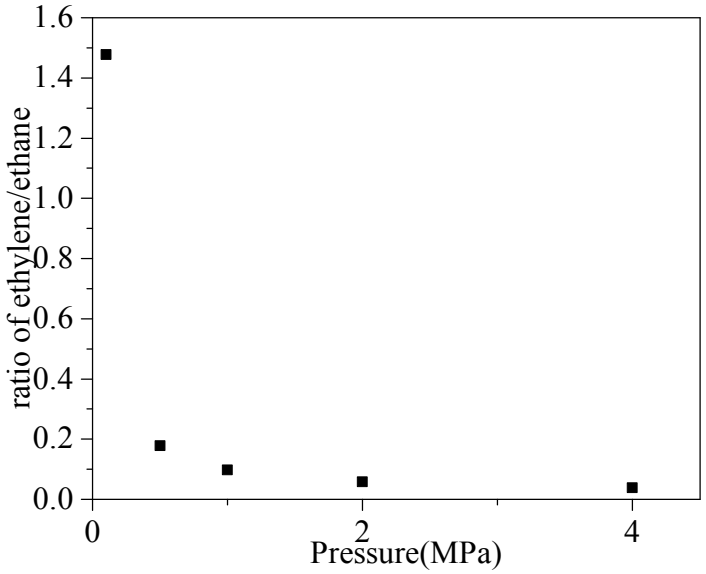

Figure S8. The ratio of ethylene/ethane at different reaction pressure

Reaction conditions: T=773 K, $CO/CH_4/Ar$=8:1:1, space velocity=4500 ml/g_{cat}·h, time on stream=30 min

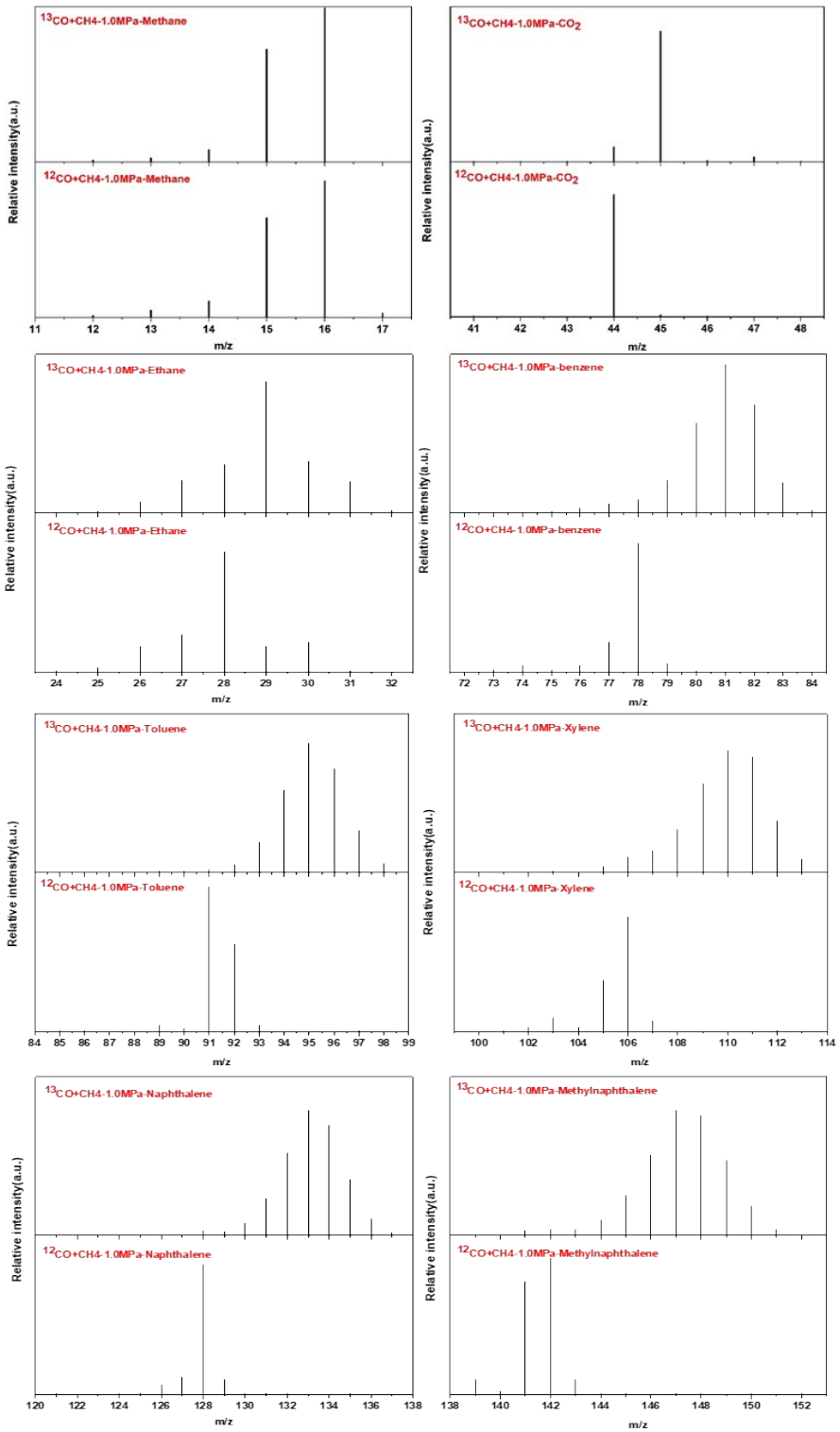

Fig S9. MS spectra of ethane, benzene，toluene，xylene ，naphthalene and methylnaphthalene from different feeds(^{12}CO (bottom) and ^{13}CO (top)) during the CH_4-CO reaction.

Reaction conditions: catalyst weight, 0.15 g; T=773 K; P=1.0 MPa $CO/CH_4/Ar$=8:1:1 space velocity=3000 mL/g_{cat}·h reaction time=60 min