# Hydrogenation of CO<sub>2</sub> to hydrocarbons over ZnCrO<sub>x</sub>-zeolite composite catalyst

Junfeng Zhang<sup>a</sup>, Meng Zhang<sup>a,b</sup>, Shuyao Chen<sup>a,b</sup>, Xiaoxing Wang<sup>a</sup>, Zeling Zhou<sup>a,b</sup>, Yingquan Wu<sup>a</sup>,

Tao Zhang<sup>a</sup>, Guohui Yang,<sup>a</sup> Yizhuo Han<sup>a</sup>, Yisheng Tan<sup>a,c,\*</sup>,

<sup>a</sup>Shanxi Institute of Coal Chemisitry, Chinese Academy Science, Taiyuan, China 030001;

<sup>b</sup>University of Chinese Academy of Sciences, Beijing, 100049, China

<sup>c</sup>National Engineering Research Center for Coal-Based Synthesis, Institute of Coal

Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

\*Corresponding author: tan@sxicc.ac.cn

### Experimental

#### Catalyst preparation.

The ZnCrO<sub>x</sub> sample (Zn:Cr=1:1) was prepared using a conventional precipitation method. Simply, 20.0 g of CrNO<sub>3</sub>·9H<sub>2</sub>O and 14.98 g of ZnNO<sub>3</sub>·6H<sub>2</sub>O were dissolved into 250 mL of deionized water, then 0.2 mol /L Na<sub>2</sub>CO<sub>3</sub> aqueous solution was added into the above salt solution under the rigorous stirring until the PH reached to 9.0 around, following by the continuous stirring for 3 h. The resulting suspension was aged overnight. After filtering and washing with larger amount of water, the obtained cake was dried and calcined at 400 °C. Finally, the ZnCrO<sub>x</sub> sample with Zn/Cr ratio of 1.0 was obtained and defined as ZnCr. Other samples with different Zn/Cr ratios such as 0.5, 1.5, and 2.0 were also prepared using the above similar method.

Purchased zeolites such as HY and HZSM-5(HZ5) with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 50, 140 and 200 were firstly calcined at 550 °C before the use. Zn-exchanged zeolites were prepared at 60 °C through 300 mL of ZnNO<sub>3</sub> solution (0.1 mol/L) added by 10 g zeolite with the exchange time of 8 h unless specially stated. The exchanged zeolites were defined as ZnY, ZnZ5-50, ZnZ5-140 and ZnZ5-200 respectively, where 50, 140 and 200 represent the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The composite catalyst was obtained through mixing the desired ZnCr and zeolite with grinding for 10 min.

#### Catalyst characterization.

The elemental composition of the catalyst bulk was obtained using a ZSX100e X-ray fluorescence(XRF) spectrophotometer. X-ray diffraction (XRD) patterns of the samples were carried out on an X-ray diffractometer (Rigaku, Ultima IV X-ray diffractometer) using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm).

NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD) profiles were obtained on a selfconstructed instrument equipped with a gas chromatograph. Typically, the samples (100 mg) was pretreated at 250 °C under Ar flow for 0.5 h and then cooled down to 100 °C for adsorbing NH<sub>3</sub>. The TPD profiles were recorded at a temperature rising rate of 5 °C/min from 100 to 600 °C.

N<sub>2</sub> adsorption-desorption isotherms were measured using Micromerities company Tristar 3000 physical adsorption apparatus at 77 K. The samples were outgassed in vacuum at 350 °C for 4 h before the measurements. The specific surface area and pore size distribution were calculated by using the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) desorption branch, respectively.

The FTIR spectra of pyridine adsorption were recorded in the range of 1000-4000 cm-1 on a Bruker TENSOR 27 spectrometer. The samples were pressed into self-supporting wafers containing 20 mg of material, and then the wafers were mounted inside a Pyrex vacuum cell and degassed at 400 °C for 0.5 h. Samples were allowed to cool down to below 55 °C, and pyridine vapor was admitted into the cell and adsorption lasted for 3 min. After 300 °C treatment for 15 min under vacuum, The IR spectra was recorded.

In situ diffuse reflectance infrared Fourier transform spectroscopy over ZnCr sample and composite catalyst are explored at 320 °C under atmospheric pressure, Prior to analysis, the sample employed was in-situ pretreated at 350 °C in a pure H<sub>2</sub> flow (30 mL/min) for 60 min.

The morphology of the catalysts was investigated with a FET XL30S-FEG scanning electron microscopy (SEM) with an accelerating voltage of 10.0 kV. The data of the energy dispersive X-ray spectroscopy (EDS) were also obtained. Morphology of the sample(TEM) was measured by a JEOL JEM-2100 transmission.

#### **Catalyst evaluation.**

The CO<sub>2</sub> hydrogenation was performed in a fixed bed reactor. In a typical experiment, 3 g catalyst was packed in the reactor. The prereduction was conducted using a stream of diluted hydrogen (10vol% H<sub>2</sub> in N<sub>2</sub>) at 340 °C for 12 h. After prereduction, the reactant gas (H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub>=72/24/4) was introduced into the reactor under 5.0 MPa. The pipeline from the catalyst bed to the gas chromatography was heated at 140 °C so as to prevent the possible condensation of the products. The effluent gases were analyzed by on-line gas chromatographs equipped with TCD and FID detectors. N<sub>2</sub> was used as the internal standard.

## **Supplementary Tables and Figures**

	CO. Comu	Sel. (C-mol %)			Hydrocarbon distribution		
ZnCr/Zeolite	(%)	HC( or HC <sub>t</sub> )	СО	Oxy	C≠/HC	ct C <sub>5+</sub> /HCt	Ar/C <sub>5</sub>
2:1	29.35	6.46	83.64	9.9	24.4	57.03	10.1
1:1	27.98	38.9	61.1	0	15.8	61.69	26.7
1:2	30.97	26.9	73.1	0	15.8	48.74	11.0

Table S1 The catalytic performance over the catalyst composited with HZ5-200

Reaction condition: 350 °C, 5.0 MPa, 2000 mL/(g·h), with reactant gas  $H_2/CO_2/N_2=72/24/4$ ; Weight ratio of ZnCr to Zeolite =2:1.

**Table S2** Texture properties of the zeolites with and without Zn-exchanged of the represent Zn

Course la	BET Surface	BET Surface micropore t		micropore
Sample	Area(m <sup>2</sup> /g)	Area(m <sup>2</sup> /g)	$(cm^{3}/g)$	volume (cm <sup>3</sup> /g)
HY	747	701	0.338	0.273
ZnY	743	674	0.370	0.263
HZSM-5(50)	354	263	0.158	0.106
ZnZSM-5(50)	337	263	0.148	0.105
HZSM-5(140)	343	232	0.161	0.094
ZnZSM-5(140)	343	216	0.169	0.0889

Torrestore (9C)	$CO$ Conv $\frac{1}{2}$	Sel. (C-mol%)			
Temperature (*C)		НС	СО	Oxy	
350	38.3	0.84	54.1	45.1	
330	31.7	0.61	28.7	70.6	
320	29.2	0.51	24.3	75.2	

Table S3 The evaluation results of single ZnCr sample at different temperatures with 2000 mL/(g·h) and 5.0 MPa with reactant gas  $H_2/CO_2/N_2=72/24/4$ 

**Table S4** XRF results of the ZSM-5 by ion-exchanging with different conditions

Zeolite	Al	Si	Zn
HZSM-5(140)	1.25	96.2	0
ZnZ5-140	1.09	96.0	0.164
ZnZ5-140 (T)	0.97	96.3	0.248
ZnZ5-140(M)	1.15	96.2	0.240

Zeolite employed	CO <sub>2</sub>	Sel. (C-mol %)			Hydroca	arbon distribution		
	Conv.	HC( or	СО	Oxy	C <sup>≠</sup> /HCt	C <sub>5+</sub> /HC <sub>t</sub>	Ar/C <sub>5+</sub>	
	(70)	HC <sub>t</sub> )						
ZnZ5-140	24.95	36.8	63.2	0.00	3.94	64.5	78.3	
ZnZ5-140 (T)	20.31	48.7	51.3	0.00	10.3	60.7	72.3	
ZnZ5-140(M)	22.55	39.6	60.4	0.00	7.92	64.1	62.5	

**Table S5** Effect of Zn content on catalytic performance in CO<sub>2</sub> hydrogenation into hydrocarbon

Reaction condition: 330 °C, 5.0 MPa, 2000 mL/(g  $\cdot$  h), with reactant gas H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub>=72/24/4; Weight ratio of ZnCr to Zeolite =2:1.

**Note:** ZnZ5-140(T) was prepared by ion-exchanging at 80 °C in 0.1 mol/L  $Zn(NO_3)_2$  aqueous solution, and the ZnZ5-140(M) is corresponding to ion-exchanging in 0.2 mol/L  $Zn(NO_3)_2$  aqueous solution at 60 °C.



Figure S1 Hydrocarbon distribution over the the ZnCrOx-zeolite catalyst with different zeolites



Figure S2 Pyridine FTIR of the representative zeolites



Figure S3 XRD patterns of the representative zeolites



Figure S4 X-ray diffraction patterns of single ZnCr and the composite catalysts



Figure S5 SEM images of ZnCr, (Zn or H)Z5-140 and the composited samples



Figure S6 TEM images of ZnCr, (Zn or H)Z5-140 and the composited samples



**Figure S7** Effect of the ratio of Zn/Cr (a) and the reaction pressure on catalytic performance over ZnCr+HZ5-140 catalyst. Reaction condition: 330 °C, 5.0 MPa, 2000 mL/(g  $\cdot$  h), with reactant gas H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub>=72/24/4; Weight ratio of ZnCr to Zeolite =1:1. **Noting:** in Figure S7(b), Zn/Cr ratio is 2.



**Figure S8** The stability test for CO<sub>2</sub> hydrogenation over ZnCr+ZnZ5-140. Reaction condition: 330 °C, 5.0 MPa, 2000 mL/(g  $\cdot$  h), with reactant gas H<sub>2</sub>/CO<sub>2</sub>/N<sub>2</sub>=72/24/4; Weight ratio of ZnCr to Zeolite =1:1



Figure S9 XRD patterns of the ZSM-5 by ion-exchanging with different conditions