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Supporting Information

Heterobimetallic MOF as a Stable Heterogeneous Catalyst with High Activity for Ethylene Oligomerization

Anfeng Peng^a, Gang Li^{*a}, Cong Wang^a, Zheng Huang^a

^a State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian

University of Technology, Dalian 116024, China.

* Corresponding Authors

E-mail address: liganghg@dlut.edu.cn

1. Materials and Instrumentation

1.1 Materials and Reagents

3-Fluoropyridine-4-carboxylic acid (97%) and dysprosium chloride hexahydrate (DyCl₃·6H₂O 99.9%) were purchased from Macklin. Nickel chloride (NiCl₂·6H₂O AR) and Cobalt chloride (CoCl₂·6H₂O AR) were purchased from DaMao Chemical Reagent Factory. Diethylaluminium chloride (Et₂AlCl, 1 mol/L in toluene) were purchased from Aladdin. N, N-dimethylformamide (DMF) and anhydrous ethanol were purchased commercially without further purification. Toluene were dried by refluxing over sodium and benzophenone prior to use. Polymerization-grade ethylene (99.95%) was obtained from Dalian Guangming Special gases Co., Ltd.

1.2 Instruments

The powder X-ray diffraction (XRD) patterns were obtained at a scanning speed of 10° min⁻¹ on a Smart Lab 9 diffractometer with Cu K α radiation operating ($\lambda = 1.5418$ Å, voltage: 45 kV, current: 200 mA) in the range of 5–25° with a step of 0.01°. The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker EQUINOX55 spectrometer, using the KBr pellet technique. Scanning electron microscopy (SEM) imaging and Energy-dispersive X-ray spectroscopy (EDS) elemental analysis were carried out on a Nova NanoSEM 450 apparatus. The N2 adsorption isotherms were measured volumetrically at 77K using Micromeritics ASAP-2425. Nickel and dysprosium analyses were performed on an Agilent Avio500 ICP-OES. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCA Lab250 spectrometer with a monochromatic Al K α X-ray source.

2 Experimental Section

2.1 Synthesis of MOF-1213 (Dy/Ni)

The procedure to synthesize MOF-1213 (Dy/Ni) was inspired by previously reported literature¹ with a few modifications. 3-Fluoropyridine-4-carboxylic acid (0.3175g 2.25mmol), DyCl₃·6H₂O (0.2728g 0.15mmol) and NiCl₂·6H₂O (0.0238g 0.02mmol) were dissolved in 61 mL DMF. Further the mixture was sonicated for 10 minutes until no particulate matter was present. The resulting suspension was then placed in a 100 mL Teflon liner inserted in a stainless steel autoclave and kept at 120 °C for three days to yield green cubic crystals. After cooling to room temperature, crystals were washed with fresh DMF (3×30 mL) and then thermally dried at 60 °C under vacuum.

2.2 Ethylene Oligomerization

The catalytic ethylene oligomerization experiment was performed in a stainless steel autoclave reactor (200 mL), which was flushed with ethylene three times during heating at 130 °C for 1 hour. In a typical run, the catalyst and Et_2AICI were dispersed into 50 ml of toluene in a glove box, and the resulting suspension was injected into the autoclave. Then, the reactor was heated to the desired temperature, stirred and backfilled with ethylene to specified pressure. The reaction stopped after 30 minutes, the gas mixture was collected with gas-bags and ice-cold deionized water was added into the liquid-phase before the organic layer was filtered through a syringe filter. 20 μ L of the internal standard (n- heptane) was added to 1ml of filtered organic solution mentioned above. In different reaction tests, the amounts of catalyst and Et_2AICI , pressure of ethylene, reaction temperature, and reaction time were adjusted as needed.

The samples of the liquid phase products were analyzed by GC (Agilent 6890) equipped with flame ionization detector (FID) and a HP-5 column (30 m × 0.32 mm × 0.25 μ m) at 35 °C for 5 min, heated at 10 °C/min until the temperature achieved 280 °C. The gaseous products were quantified using external standard method by GC (Techcomp/6890F) equipped with a TM-Al₂O₃/S column (50 m × 0.53 mm × 25 um) at 80 °C, direct ramp up to 180 °C.

2.3 The calculation of catalyst activity

As the catalytic activity had closely relationship with ethylene oligomerization products, the active site numbers of catalyst and reaction time, the catalytic activity of catalyst was marked according equation (1-1):

$$TOF = \frac{ethylene \ oligomerization \ products \ (g)}{M_{C_2H_4} \times Ni_{mol} \times Time_h}$$
 1-1

wherein the mass of C_2H_4 consumed is equal to the yield of oligomer products (g).

2.4 Leaching Experiment

In order to test the stability of the catalyst MOF-1213 (Dy/Ni), the catalyst (15mg) was suspended in dry toluene (50 mL) and treated with Et₂AlCl (2 mL, 1mol/L in toluene) in a nitrogen glovebox. The mixture was stirred gently in a Shrek bottle for 1 hour. The suspension was centrifuged three times and subsequently passed through a 0.22 μ m PTFE syringe filter. All of the above processes are carried out in a nitrogen glove box. The reactor was pressurized with ethylene to 10 bar and the reaction lasts for half an hour at 30 °C. Then the gas mixture was collected with gas-bags and ice-cold deionized water was added into the liquid-phase before the organic layer was filtered through a syringe filter.

20 ul of the internal standard (n- heptane) was added to 1ml of filtered organic solutions mentioned above. The sample was analyzed via gas chromatography.

2.5 Recycling Experiment

The cyclic procedure was as follows: after reaction, the reactor was depressurized. The catalyst is collected by centrifugation and the upper solvent was poured off quickly. Afterwards, the catalyst was washed three times with absolute EtOH. Before the next ethylene oligomerization, the catalyst was also fully vacuum-dried under 60 °C.



(b)



Figure. S1. (a) PXRD patterns of MOF-1213(Dy/Ni) and MOF-1213(Dy/Co). (b) FT-IR spectra of MOF-1213(Dy/Ni).

(a) (**b**) 12 10 (c) Al 200 µ

Figure. S2. (a) Scanning electron micrographs (SEM) images and (b) energy dispersive spectroscopy (EDS) mapping of samples MOF-1213(Dy/Ni). (c) SEM image and EDS mapping of used MOF-1213(Dy/Ni).



(b)



Figure. S3. N2 isotherm at 77 K of (a) fresh and (b) used MOF-1213(Dy/Ni). The calculated BET surface area is 449.4 and 11.8 m2/g, respectively. In this case, the material was activated using the following protocol: as-synthesized crystals were washed with DMF (3x) followed by solvent exchange with acetonitrile (3x) and then dried under N2 flow. The sample was then degassed at room temperature under vacuum for ~24 hours until the pressure change rate was no more than 3.5 mTorr/min.

(a)



Figure. S4. The full-range XPS spectra of (a)fresh and (c)used catalyst MOF-1213(Dy/Ni), and the high-resolution Ni2p XPS spectra of (b) fresh and (d) used catalyst MOF-1213(Dy/Ni).



Figure. S5. Chromatogram of ethylene oligomerization catalyzed by MOF-1213(Dy/Ni) under conditions (30 °C, 40 bar).



Figure. S6. PXRD patterns of fresh and used catalyst MOF-1213(Dy/Ni).

Samples	Ni amount (wt%)	Dy amount (wt%)	Al amount (wt%)	Ni/Dy	
Fresh catalyst	4.5	25.5	-	0.2	
Used catalyst	2.9	13.3	15.5	0.2	

Table. S1. ICP-OES elemental analysis results of MOF-1213 (Dy/Ni) before (freshcatalyst) and after reaction (used catalyst).



Figure. S7. Chromatogram after a control ethylene oligomerization experiment with Et_2AlCl . No detectable product is observed.

entry	Pressure	Temperature	Al/Ni	TOF ^a	Selectivity (wt %)			
	bar	°C		(h ⁻¹)	$C_4{}^b$	α -C ₄ ^c	C_6^d	reference
Ni-ZIF-8(0.7%)	50	35	4640	1,116,000	97.0	87.7	3	2
45Ni-ZIF-L	40	30	15784	430,960	96.4	89.5	3.6	3
20Ni-MOF-5	50	35	300	352,000	96.3	84.2	3.7	4
MOF-1213(Dy/Ni)	40	30	200	160,000	98.0	84.0	2.0	This work
Ni ₂ Zn ₂ (BDC) ₂ DABCO	15	10	50	135,000	92.0	36	8	5
Ni(1%)-MFU-41	50	25	500	41,500	97.4	94.5	2.6	6
Ni(7.5%)-CFA-1	50	22	2000	37,100	95.5	91.2	4.5	7
MixMOF-Ni-b	20	40	100	16,400	92.7	6.1	N.R.	8
Ni@(Fe)MIL-101	15	20	70	6,300	95	N.R.	4.5	9
Fe ₁₀ Ni ₉₀ -BTC	30	58	100	5,917	47.6	21.0	33.9	10
Ni-UMOFNS-190	10	25	500	5,536	75.6	N.R.	0.4	11
PCN-160-47%Ni	40	25	300	3,360	95.7	86.1	N.R.	12
1D-Ni-MIL-77	30	10	100	2,858	99.0	93.4	0.96	13
3D-Ni-MIL-77	15	30	180	2,226	99.6	90.0	0.22	
IRMOF-3-Ni-a	20	20	100	2,200	35.0	9.3	N.R.	8
NU-1000-(bpy)NiCl ₂	15	21	N.R.	1,950	94	N.R.	N.R.	14
Ni-MCM-48	35	150	N.R.	47,400	42.0	N.R.	37	15
Ni-MCM-36	40	150	N.R.	16,000	45.0	35.0	N.R.	16
Ni-Y	40	50	N.R.	10,482	67	N.R.	10	17
NiO/Al ₂ O ₃	27.5	150	N.R.	190	85.4	100	9.6	18

Table. S2. Catalytic results and reaction conditions of some selected Ni-based heterogeneous catalysts for ethylene oligomerization.

^aMoles of ethylene converted per mole of nickel per hour. N.R.= not reported. ^bThe Percentage of C_4 olefins in the oligomerization product. ^cThe percentage of 1-butene relative to all C_4 products. ^dThe Percentage of C_6 olefins in the oligomerization product.

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