

Catalytic upgrading of palmitic acid to jet fuel range alkanes over Co/H-MCM-49 bi-functional catalysts

Yanchun Shi,^a Rui Li,^b Qingru Shen,^b Mingde Yang,^a Yulong Wu^{*a}

- a) Institute of Nuclear and New Energy Technology, Laboratory of Advanced Reactor Engineering and Safety of Ministry of Education, Tsinghua University, Beijing 100084 (P. R. China)
- b) MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Forestry University, Beijing, 100083 (P. R. China)

* Corresponding authors:

Prof. Yulong Wu

Address: Institute of Nuclear and New Energy Technology, Tsinghua University,
Beijing 100084, PR China

Tel: + 86 010-89796163; Fax: + 86 10-69771464

E-mail: wylong@tsinghua.edu.cn (Y. L. Wu)

Experiments

Catalysts preparation: HMCM-49 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$, Sinopec Research Institute of Petroleum Processing, Beijing, China) was named as HM-49. As-synthesized MCM-49 zeolite were post-synthesized by tetraethylammonium hydroxide (TEAOH) to tailor texture property and acidity,¹ named as HMP-49. Co/HM-49 and Co/HMP-49 were prepared via the solid state impregnation method (& the melt infiltration method) with 5 wt% loading CoO .^{2,3} Additionally, TG curve of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was shown in Fig. S2, and it can be seen that the complete decomposition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ occurred before 300 °C. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (m.p. 55-56 °C, Guangfu Fine Chemical Research Institute, Tianjin, China) was mixed uniformly with HM-49/HMP-49 in a closed vital at 65 °C for 24 h, and molten metal salts could be penetrated into HM-49/HMP-49 pores, supercages and 12 MR cups through capillary forces. After dried at 105 °C overnight, calcined at 550 °C for 5 h in air atmosphere and finally reduced at 500 °C for 4 h (ramp: 10 °C · min⁻¹) in hydrogen flow (flow rate: 80 mL · min⁻¹), Co/HM-49 and Co/HMP-49 bi-functional catalysts were obtained. Thus the complete decomposition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ occurred during calcination. During the solid state impregnation process, no extra water could avoid the adsorption between H_2O and $\text{Co}(\text{NO}_3)_2$ over HM-49/HMP-49 supports, which would be beneficial for Co species dispersion.

Catalysts characterization: XRD patterns of samples were performed with the scanning range of 2θ was 5 - 80° on a D/MAX-III X-ray diffractometer (Rigaku Corporation, Japan), which was filtered Cu K α radiation at a tube current of 35 mA and a voltage of 35 kV. The relative crystallinity (R. C.) of HM-49, Co/HM-49 and Co/HMP-49 were based upon the sum of the peak intensities at 2θ of 14.4°, 22.0°,

22.7°, 23.8° and 26.0° (Fig. S1), and the crystallinity of HM-49 was defined as 100%. Porosity of catalysts was collected via the nitrogen adsorption-desorption isotherms on the Micromeritics ASAP 2010 instrument. According to the BET equation using the relative pressure range of 0.05 - 0.16 in the nitrogen adsorption isotherm as range of linearity (using a molecular cross-sectional area for N₂ of 0.162 nm²), the total surface area was calculated. Based upon the t-plot method, the micropore volume was obtained. TEM characterized the crystal morphology. NH₃-TPD was carried out on an Autochem II 2920 unit equipped with a thermal conductivity detector to characterize the acidity of bi-functional catalysts. H₂-TPR was performed at a rate of 5 °C/min from room temperature up to 600 °C in a flow of 5% H₂/N₂ on a TP-5076 multiple adsorption instrument.

Catalytic HDO tests: In our previous works,⁴⁻⁸ the best conditions to ensure complete deoxygenation of palmitic acid were considered at 260 °C in presence of 4 MPa H₂ for 4 h, which were chosen in this paper. The typical reaction was introduced as follows: palmitic acid (0.5 g), decalin/decane (50 mL), and bi-functional catalysts (0.1 g) were mixed into the autoclave (100 mL) by batch mode. H₂ at ambient temperature was purged into the autoclave for several times to drive away air, and then regulated to 4 MPa H₂. Heating to reaction temperature (260 °C), and then reacting for 4 h at 300 rpm stirring. After reaction, the autoclave cooled to ambient temperature, and the pressure decreased. The final liquid products were analyzed on the Agilent GC-MS (7890-597-5) with a FSFS J & W 122-5532 (30 m × 250 μm × 0.25 μm) column and a flame ionization detector. Conversion of palmitic acid and selectivity of products were calculated:

Conversion of palmitic acid = (moles of converted palmitic acid/ mole of the starting palmitic acid) × 100%.

Selectivity of products = (moles of each product/ moles of total products) × 100%.

References

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Figure captions:

Fig. S1 Standard XRD patterns of compared samples (a: standard XRD patterns of Co species; b: standard XRD pattern of as-synthesized MCM-22P) and XRD patterns of HM-49, Co/HM-49 and Co/HMP-49 catalysts (c)

Fig. S2 TG curve of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ sample

Fig. S3 N_2 adsorption-desorption curves of HM-49 and post-synthesized HMP-49 zeolites

Fig. S4 SEM images of HM-49 and HMP-49 parent zeolites

Fig. S5 H_2 -TPR curves of Co/HZ-22 and Co/HZ-5 precursors (ref. 19 and ref. 27)

Fig. S6 XPS curve of Co/HM-49 and Co/HMP-49 bi-functional catalysts

Fig. S7 NH_3 -TPD curves of Co/HZ-22 and Co/HZ-5 catalysts (ref. 19 and ref. 27)

Fig. S8 GC-MS spectra of palmitic acid conversion over Co/HM-49 and Co/HMP-49 bi-functional catalysts at 260 °C in presence of 4 MPa H_2 for 4 h

Table S1 Freezing points of some normal and isomethyl paraffins of various carbon numbers

Table S2 Textural properties of zeolitic supports and Co/zeolite bi-functional catalysts

Table S3 Acid properties of H-type zeolites by pyridine-FTIR analysis

Table S4 Comparison of catalytic performance over Co/zeolite bi-functional catalysts at 260 °C in presence of 4 MPa H_2 for 4 h

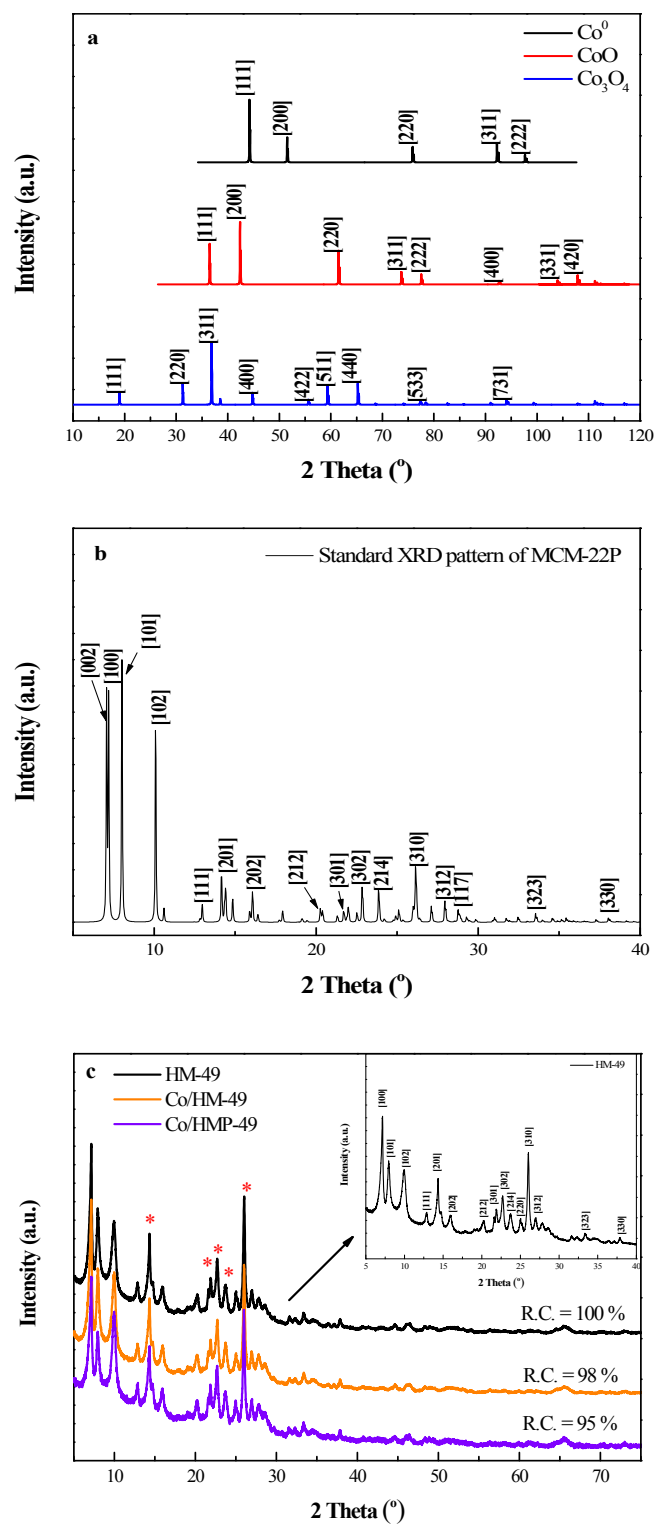


Fig. S1 Standard XRD patterns of compared samples (a: standard XRD patterns of Co species; b: standard XRD pattern of as-synthesized MCM-22P) and XRD patterns of HM-49, Co/HM-49 and Co/HMP-49 catalysts (c)

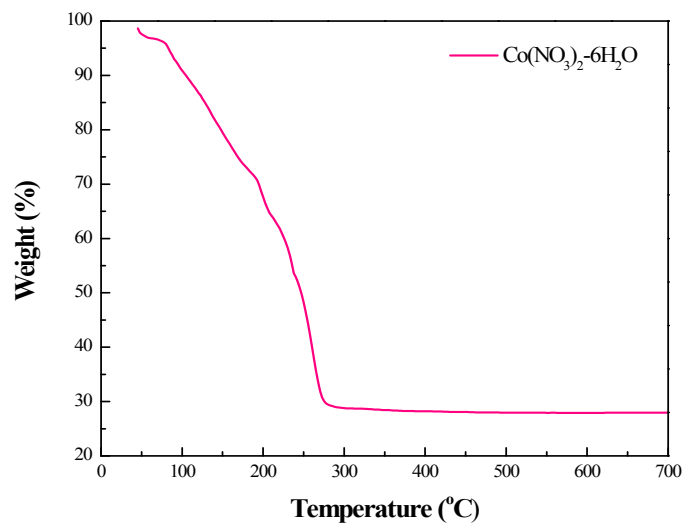


Fig. S2 TG curve of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ sample

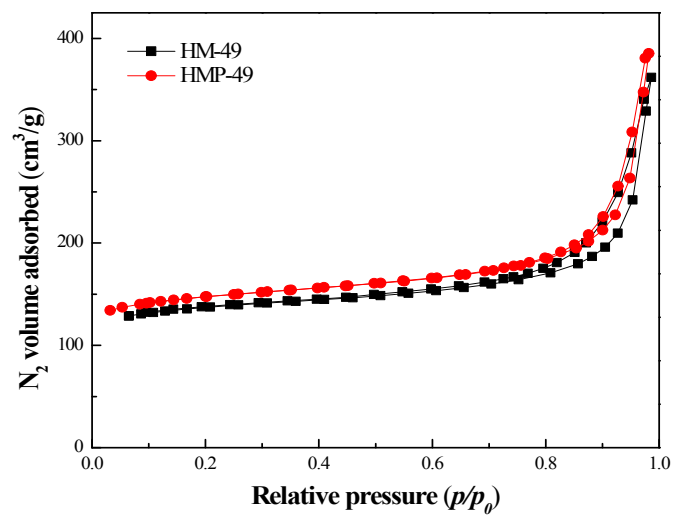


Fig. S3 N₂ adsorption-desorption curves of HM-49 and post-synthesized HMP-49 zeolites (like of the cases in ref. 21)

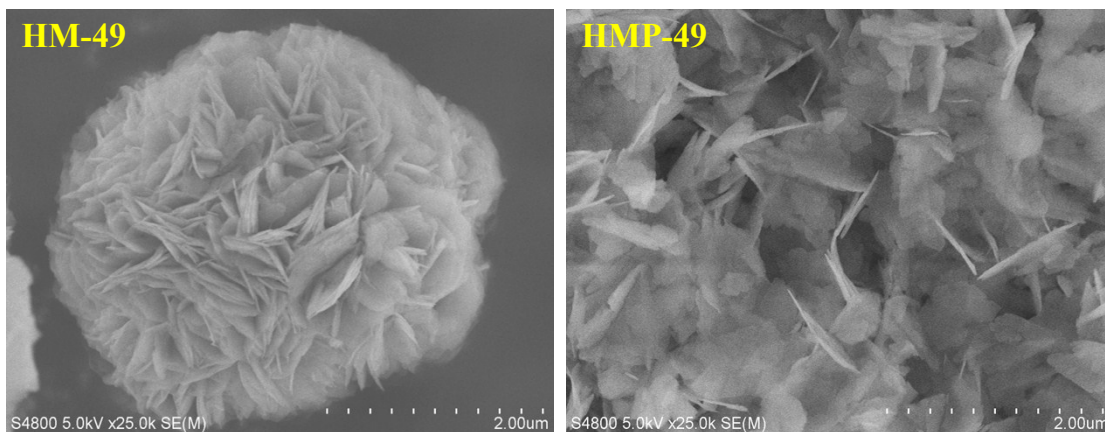


Fig. S4 SEM images of HM-49 and HMP-49 parent zeolites (like of the cases in ref. 21)

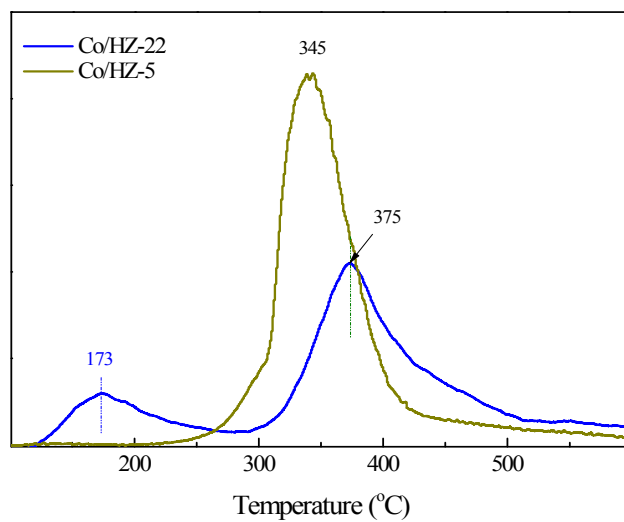


Fig. S5 H₂-TPR curves of Co/HZ-22 and Co/HZ-5 precursors (ref. 19 and 27)

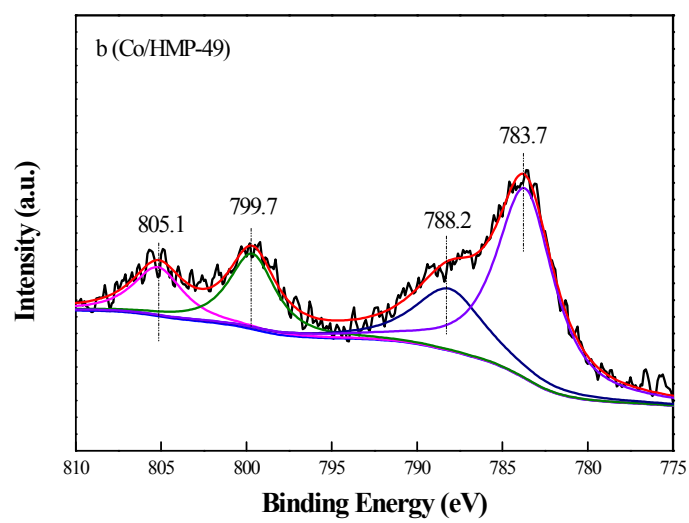
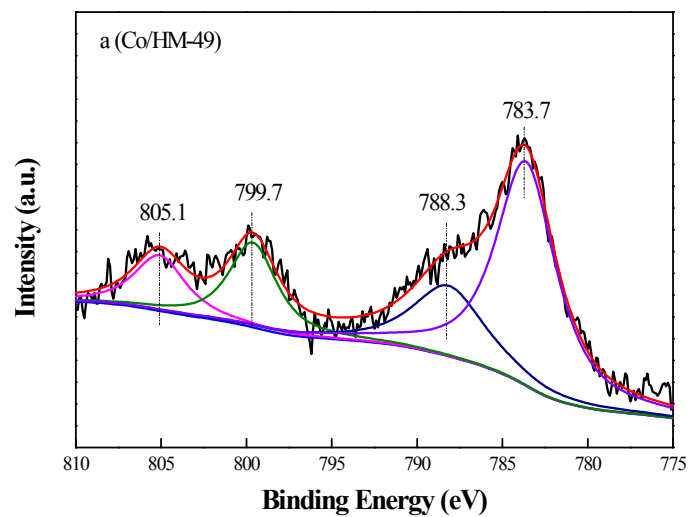


Fig. S6 XPS curve of Co/HM-49 (a) and Co/HMP-49 (b) bi-functional catalysts

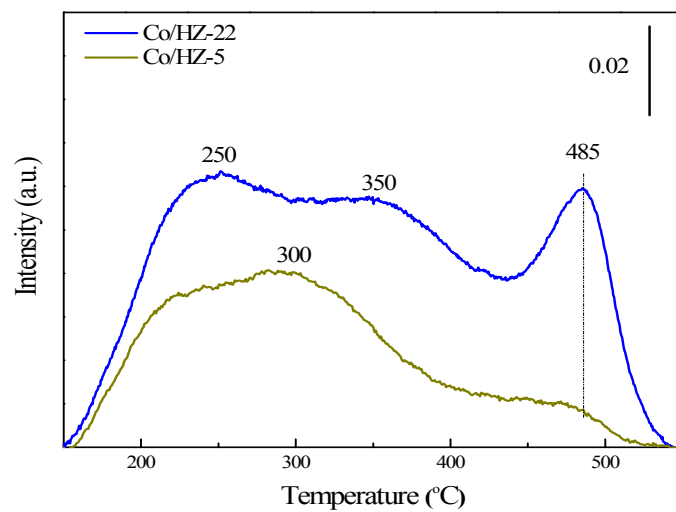


Fig. S7 NH₃-TPD curves of Co/HZ-22 and Co/HZ-5 catalysts (ref. 19 and 27)

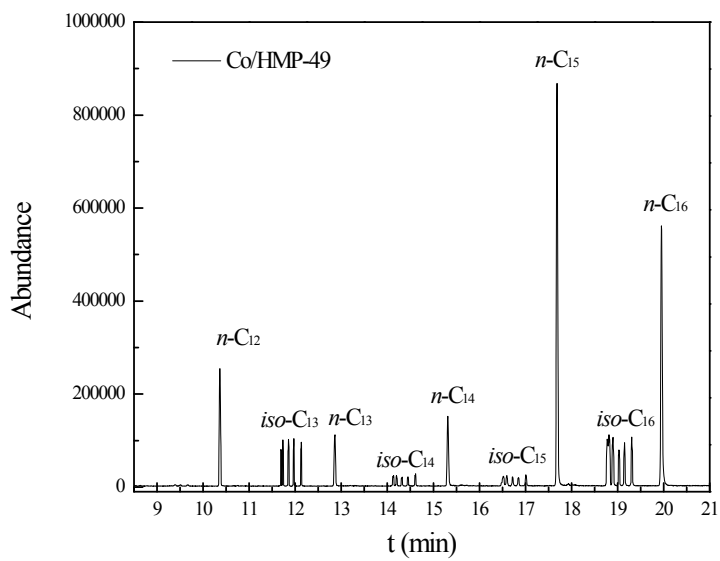
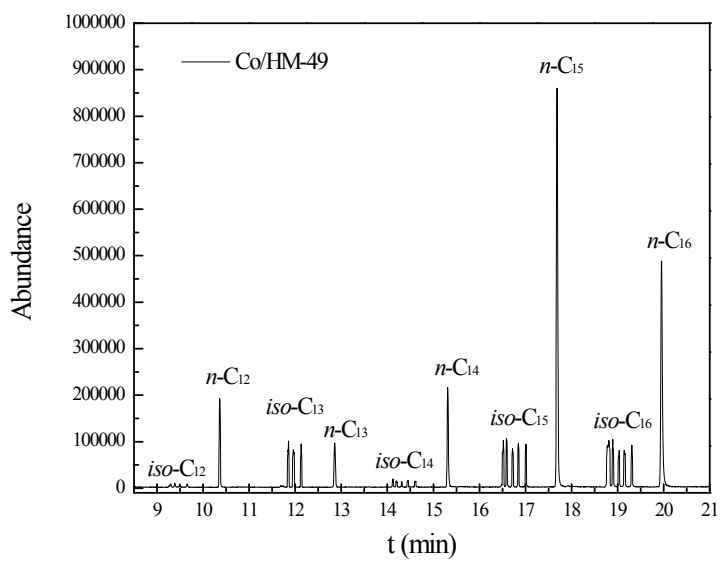


Fig. S8 GC-MS spectra of palmitic acid conversion over Co/HM-49 and Co/HMP-49 bi-functional catalysts at 260 °C in presence of 4 MPa H₂ for 4 h

Table S1 Freezing points of some normal and isomethyl paraffins of various carbon numbers
(modified from ref. 8)

Carbon Number	Freezing Point, °C		
	<i>n</i> -Paraffin	2-Methylparaffin	5-Methylparaffin
C12	-10	-46	-70
C13	-5	-26	-69
C16	18	-10	-31

Table S2 Textural properties of zeolitic supports and Co/zeolite bi-functional catalysts

Samples	Si/ Al (XRF)	Co/Si (XRF)	Co/Si (XRF)	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{ext} (m ² /g)	V _{micro} (cm ³ /g)	V _{total} (cm ³ /g)
HM-49	12	/	/	476	394	82	0.18	0.56
Co/HM-49	12	0.0436	0.0244	427	355	72	0.16	0.52
HMP-49	10	/	/	507	409	98	0.18	0.63
Co/HMP-49	10	0.0441	0.0239	428	342	86	0.16	0.57
Co/HZ-22 [ref. 8]	36	/	/	131	94	37	0.04	0.31
Co/HZ-5 [ref. 9]	112	/	/	385	355	30	0.17	0.23

Table S3 Acid properties of H-type zeolites by pyridine-FTIR analysis
(modified from ref. 19)

Samples	200 °C		350 °C	
	Lewis acid ($\mu\text{mol}\cdot\text{g}^{-1}$)	Brönsted acid ($\mu\text{mol}\cdot\text{g}^{-1}$)	Lewis acid ($\mu\text{mol}\cdot\text{g}^{-1}$)	Brönsted acid ($\mu\text{mol}\cdot\text{g}^{-1}$)
HM-49	180	412	155	387
HMP-49	307	538	231	486
HZ-22 [ref. 19]	62	214	48	200

Table S4 Comparison of catalytic performance over Co/zeolite bi-functional catalysts at 260 °C in presence of 4 MPa H₂ for 4 h

(a: *n*-decane one run; b: *n*-decane five runs; c: decalin one run)

Catalysts	Con. (%)	Selectivity (%) of each alkanes								<i>iso/n</i> - (mol/mol)	Cracking selectivity (C ₁₂ - C ₁₄)	Ref. (%)
		alkanes	<i>iso/n</i> -C ₁₂	<i>iso/n</i> -C ₁₃	<i>iso/n</i> -C ₁₄	<i>iso/n</i> -C ₁₅	<i>iso/n</i> -C ₁₆	-CHO	-OH			
Co/HM-49 ^a	> 99.9	100	1.0/5.4	8.7/3.3	2.1/5.8	12.0/26.9	17.8/17.0	-	-	0.7	26.3	-
Co/HMP-49 ^a	> 99.9	100	0/8.2	9.0/3.7	3.0/5.4	3.2/29.4	19.1/19.0	-	-	0.5	29.3	-
Co/HMP-49 ^b	> 99.9	100	-/5.0	6.3/2.5	4.8/3.4	9.8/30.2	15.0/24.0	-	-	0.4	24.0	-
Co/HMP-49 ^c	> 99.9	100	-/5.4	11.7/2.8	4.8/3.8	4.9/33.1	10.4/23.1	-	-	0.5	26.9	-
Co/HZ-22	> 99.9	100	-/-	-/-	-/0.9	9.3/15.4	43.6/30.8	-	-	1.1	0.9	8
Co/HZ-5	> 99.9	100	-/-	-/-	-/3.6	4.5/17.5	24.9/49.5	-	-	0.4	3.6	9