Selective continuous synthesis of bis(2-dimethylaminoethyl)ether over Cr and Co modified Cu/Al_2O_3 catalyst

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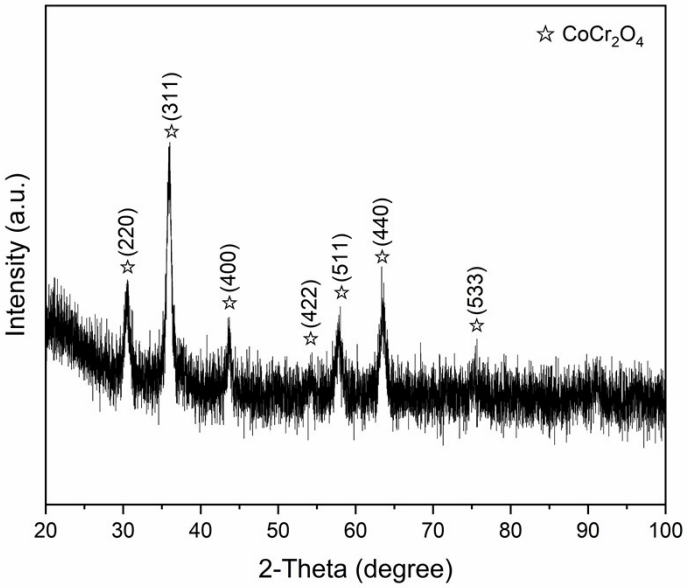

Figure S1 XRD pattern of prepared $CoCr_2O_4$.

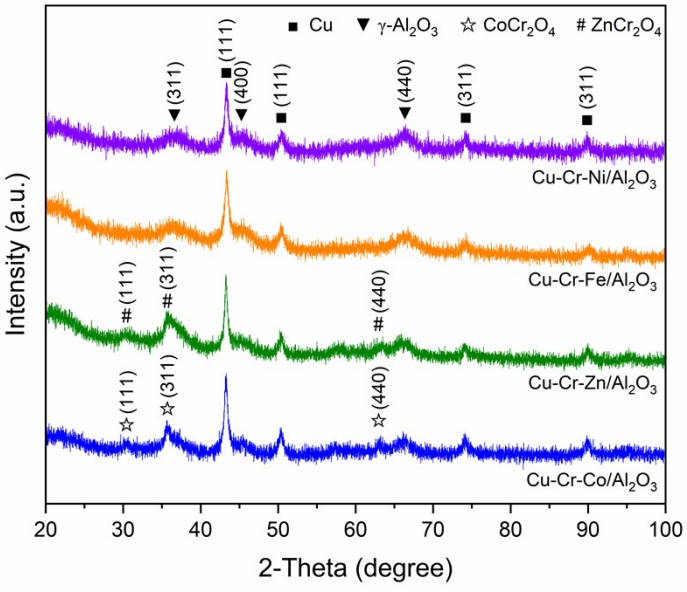

Figure S2 XRD patterns of reduced co-doped Cu-based catalysts.

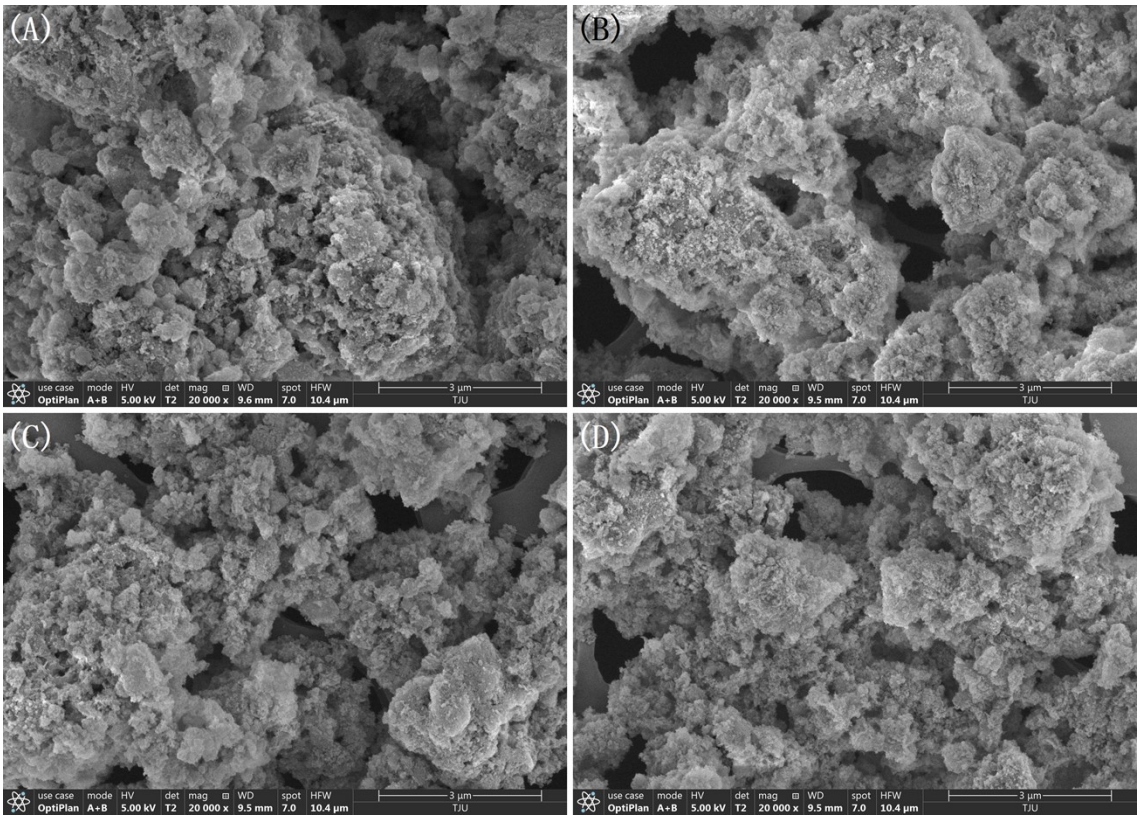

Figure S3 SEM images of reduced (A) Cu/Al_2O_3, (B) $Cu\text{-}Cr\text{-}Co/Al_2O_3$ (C) $Cu\text{-}Cr\text{-}Co/Al_2O_3$ and (D) used $Cu\text{-}Cr\text{-}Co/Al_2O_3$.

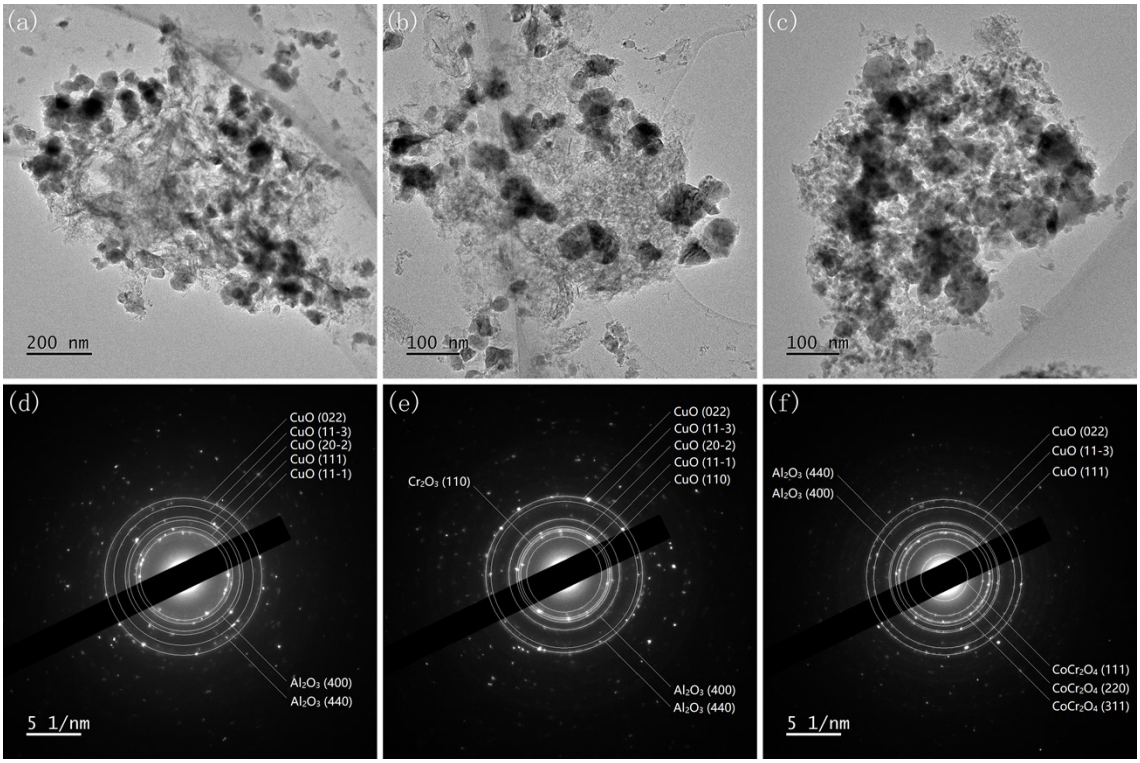

Figure S4 TEM images of unreduced (a) Cu/Al_2O_3, (b) $Cu\text{-}Cr/Al_2O_3$, and (c) $Cu\text{-}Cr\text{-}Co/Al_2O_3$; selected area electron diffraction (SAED) patterns of unreduced (d) Cu/Al_2O_3, (e) $Cu\text{-}Cr/Al_2O_3$, and (f) $Cu\text{-}Cr\text{-}Co/Al_2O_3$.

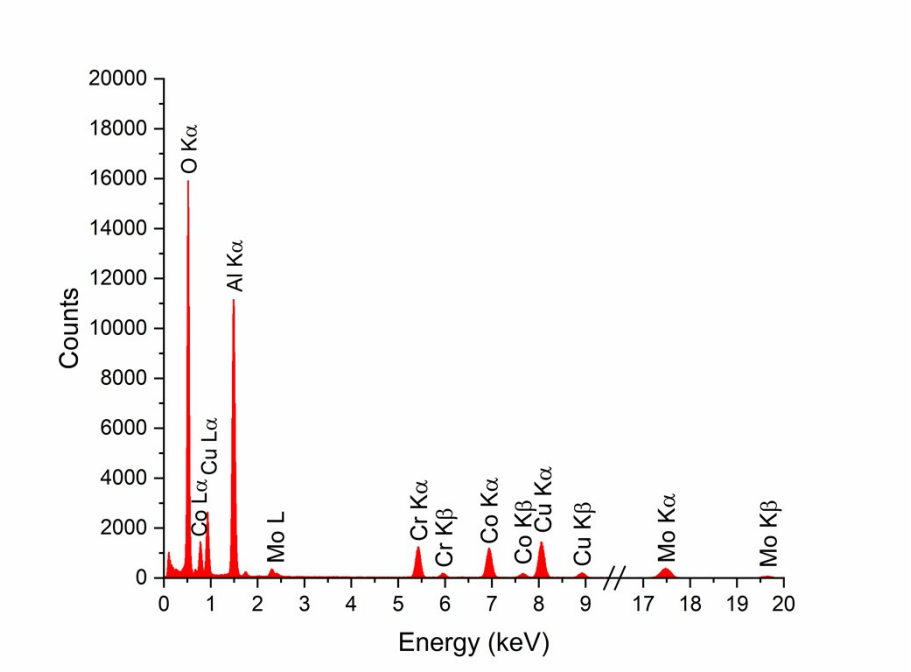

Figure S5 EDS spectrum of reduced $Cu\text{-}Cr\text{-}Co/Al_2O_3$.

Table S1. Cu dispersion and acidic sites concentration of Cu-based catalysts.

Catalyst	Cu Content [a] (%)	D_{Cu} [b] (%)	S_{Cu} [b] (m^2/g)	Acidic sites concentration [c] (mmol/g)				TOF (h^{-1})
				Weak	M-strong	S-strong	Total	
Cu/Al_2O_3	19.75	10.5	13.5	0.31	0.74	0.19	1.24	1.9
$Cu\text{-}Cr/Al_2O_3$	18.86	12.5	15.3	0.34	0.68	-	1.02	2.2
$Cu\text{-}Cr\text{-}Co/Al_2O_3$	17.87	17.8	20.6	0.36	0.77	-	1.13	3.3
$Cu\text{-}Cr\text{-}Fe/Al_2O_3$	19.01	14.1	17.4	0.29	0.58	-	0.87	2.5
$Cu\text{-}Cr\text{-}Ni/Al_2O_3$	18.75	14.9	18.1	0.27	0.56	-	0.83	2.4
$Cu\text{-}Cr\text{-}Zn/Al_2O_3$	17.91	17.1	19.9	0.30	0.66	-	0.96	2.9

[a] Determined by ICP-OES.

[b] Determined by N_2O chemisorption.

[c] Determined by NH_3-TPD.

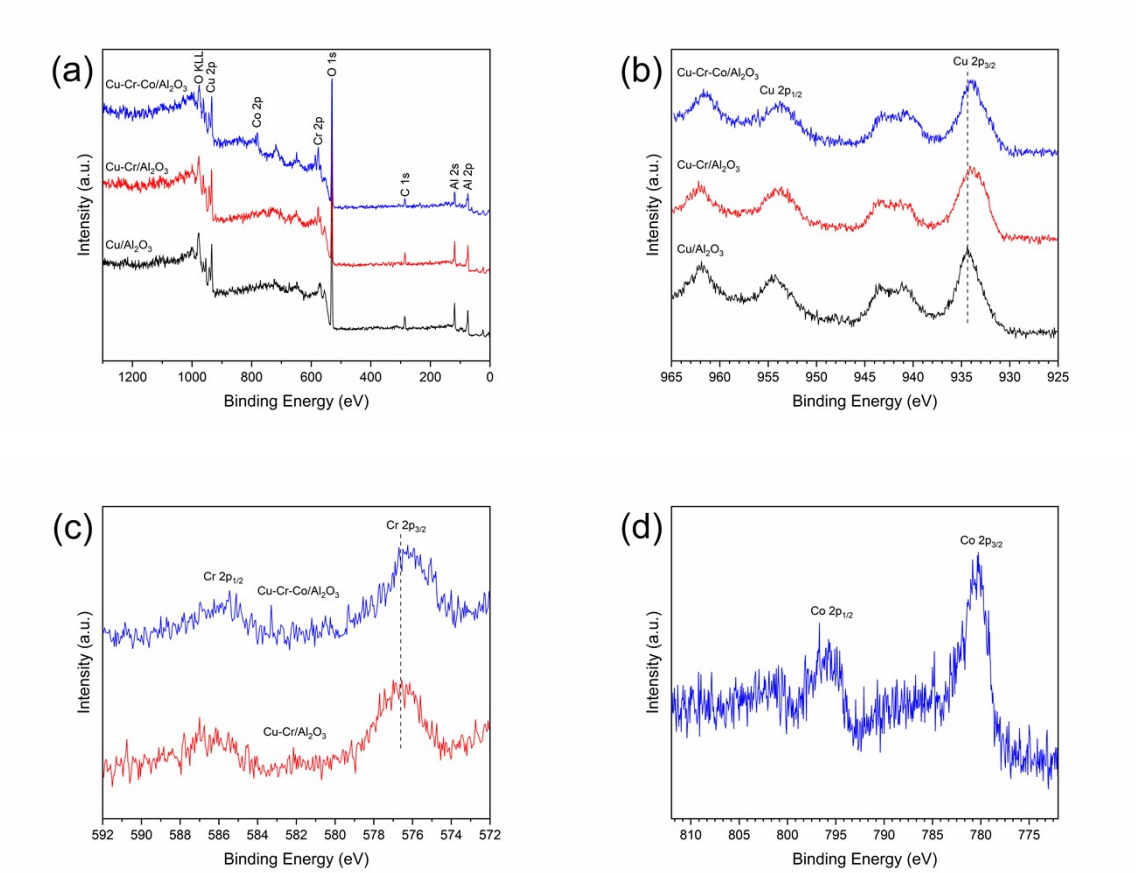

Figure S6 XPS spectra of calcined catalysts. (A) Cu 2p, (B) Cr 2p, (C) Co 2p and (D) survey spectra.

Table S2 XPS Peaks position of Cu-based catalysts.

Catalysts	B.E. (eV)			$X_{Cu(0)/(Cu(I)+Cu(0))}$
	Cu $2p_{3/2}$	Cr $2p_{3/2}$	Co $2p_{3/2}$	(%)
Calcined Cu/Al_2O_3	934.4	-	-	-
Calcined $Cu-Cr/Al_2O_3$	934.0	576.6	-	-
Calcined $Cu-Cr-Co/Al_2O_3$	934.0	576.2	780.5	-
Reduced Cu/Al_2O_3	932.1	-	-	63.6
Reduced $Cu-Cr/Al_2O_3$	931.8	576.7	-	89.0
Reduced $Cu-Cr-Co/Al_2O_3$	931.8	576.2	780.5	92.3

Table S3 Structural properties and chemical compositions of catalysts.

Catalysts	Metal loading[a] (%)			S_{BET}[b]	V_p[b]	d_p[b]	Acid sites [c] (mmol/g)			Cu particle sizes (nm)	
	Cu	Cr	Co	(m^2/g)	(cm^3/g)	(nm)	LA [d]	BA [e]	Total	XRD [f]	TEM [g]
Cu/Al_2O_3	19.75	-	-	150.0	0.32	8.4	0.0873	0.0138	0.1011	24.3	27.7
$Cu-Cr/Al_2O_3$	18.86	6.11	-	112.6	0.33	10.7	0.0652	0.0114	0.0766	18.4	16.1
$Cu-Cr-Co/Al_2O_3$	17.87	6.54	4.06	124.8	0.35	11.1	0.0817	0.0139	0.0956	17.9	15.3

[a] Determined by ICP-OES.

[b] Determined by N_2 adsorption.

[c] determined by pyridine-FTIR.

[d] Lewis acidic sites.

[e] Brønsted acidic sites.

[f] determined by Scherrer equation.

[g] determined by TEM.

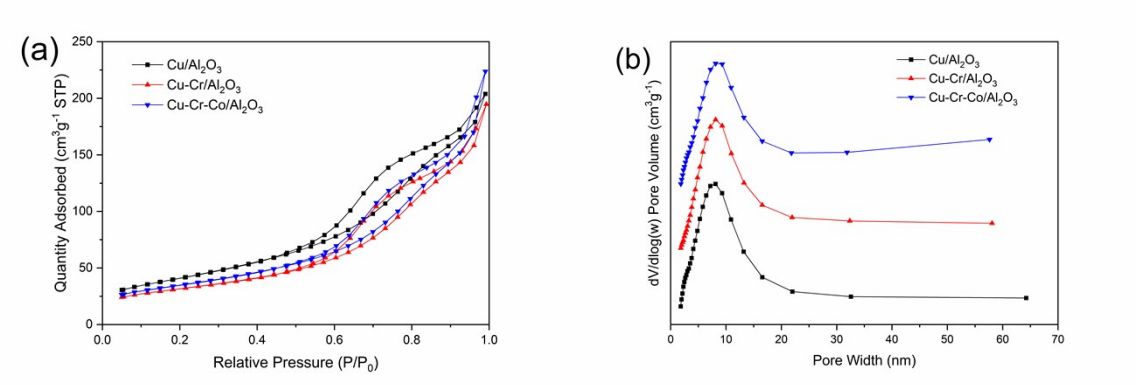

Figure S7 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of catalysts.

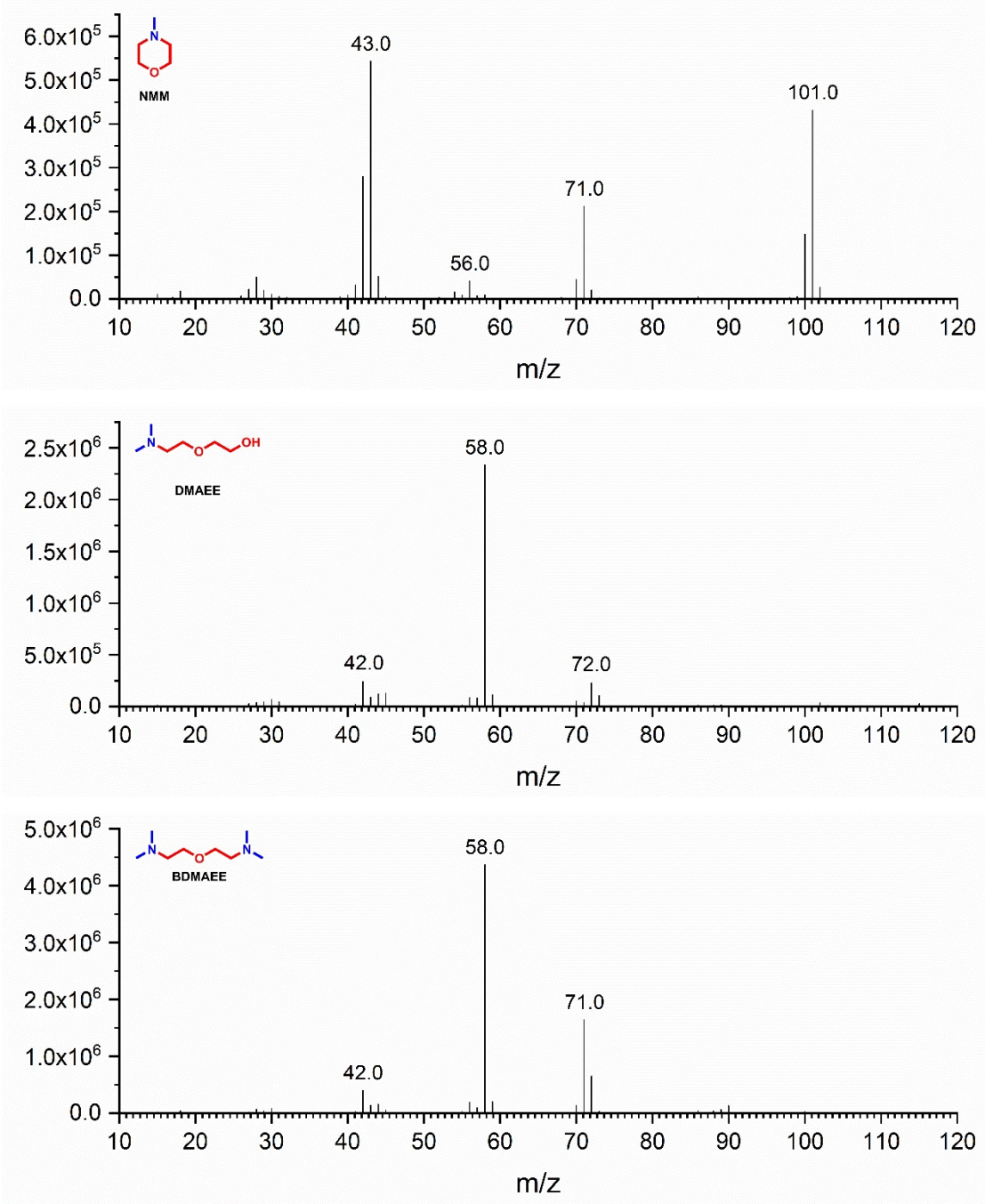

Figure S8 Mass spectra of the products in reaction mixture.

Table S4 Reaction of DEG with dimethylamine over different temperature.

Temperature (°C)	DEG Conversion (%)	Selectivity (%)				BDMAEE/NMM
		DMAEE	BDMAEE	NMM	Other	
150	39.7	84.0	4.6	6.4	5.0	0.7
170	97.9	27.9	21.7	42.0	8.4	0.5
190	99.6	9.1	55.2	26.7	9.0	2.1
210	99.5	4.5	37.8	29.2	28.5	1.3

Reaction conditions: Catalyst, Cu-Cr-Co/Al_2O_3; DMA/DEG (molar ratio) = 4:1; H_2 pressure, 3 MPa; LHSV, 0.3 h^{-1}; Solvent, Methanol.

Table S5 Reaction of DEG with DMA over different H_2 pressure.

H_2 pressure (MPa)	DEG Conversion (%)	Selectivity (%)				BDMAEE/NMM
		DMAEE	BDMAEE	NMM	Other	
2	99.7	13.1	28.9	47.4	10.6	0.6
3	99.6	9.1	55.2	26.7	9.0	2.1
4	99.8	10.4	56.1	27.3	6.2	2.1

Reaction conditions: Catalyst, Cu-Cr-Co/Al_2O_3; DMA/DEG (molar ratio) = 4:1; Temperature, 190 °C; LHSV, 0.3 h^{-1}; Solvent, Methanol.

Table S6 Reaction of DEG with DMA over different substrate molar ratio.

DMA/DEG (molar ratio)	DEG Conversion (%)	Selectivity (%)				BDMAEE/NMM
		DMAEE	BDMAEE	NMM	Other	
2:1	87.8	21.3	16.8	57.2	4.7	0.3
3:1	99.1	16.9	44.6	29.9	8.6	1.5
4:1	99.6	9.1	55.2	26.7	9.0	2.1
5:1	99.5	8.9	55.0	27.8	8.3	2.0

Reaction conditions: Catalyst, Cu-Cr-Co/Al_2O_3; Temperature, 190 °C; H_2 pressure, 3 MPa; LHSV, 0.3 h^{-1}; Solvent, Methanol.

Table S7 Comparison studies on catalytic performance toward DEG amination with DMA over reported catalysts

Entry	Catalyst	DMA/DEG (molar)	Temperature (°C)	Time (h)	BDMAEE yield (%)	Reference
1	Cu-Cr-Co/Al_2O_3 (Cu 20wt.%)	4	190	Continuous	55	This work
2	Cu/Al_2O_3 (Cu 55wt.%)	-	210	Continuous	~40	1
3	$IrH_2Cl[(^iPr_2PC_2H_4)_2NH]$	3	140	20	~15	2
4	NHC-Ir	6	120	40	55	3

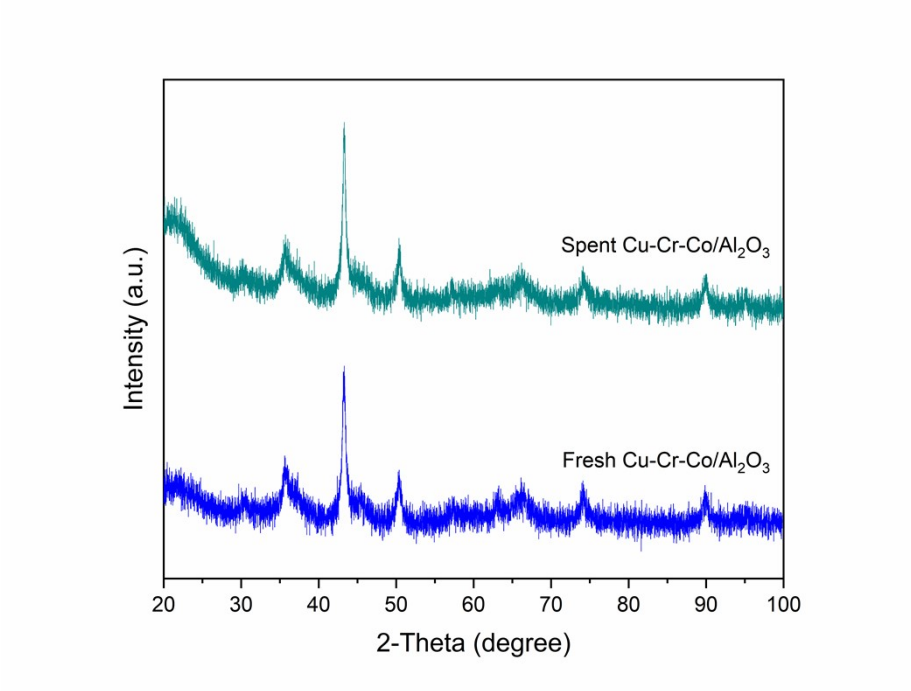

Figure S9 XRD patterns of fresh and spent Cu-Cr-Co/Al_2O_3 catalysts.

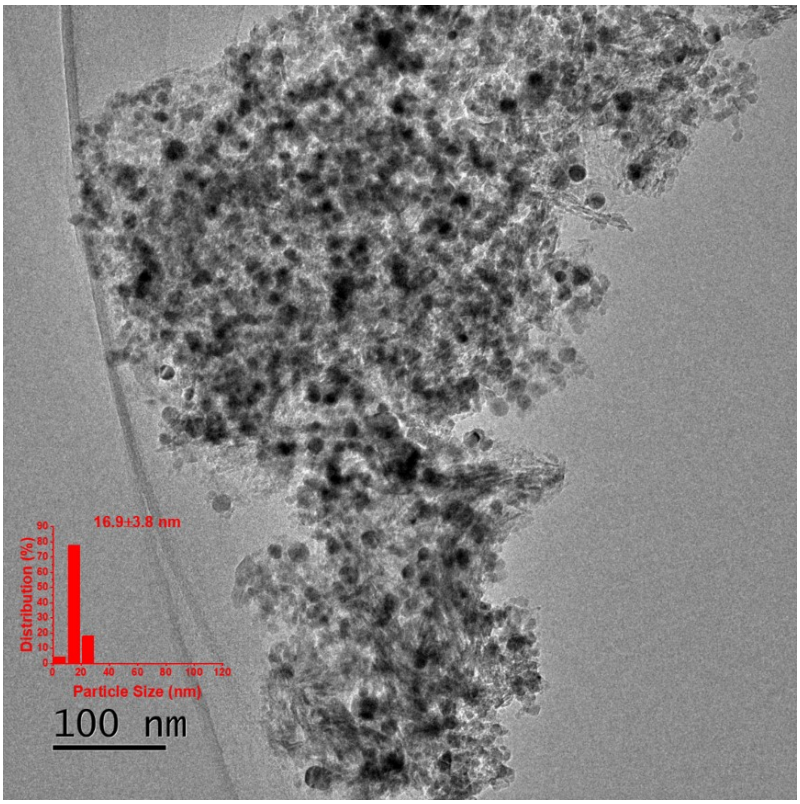

Figure S10 TEM image of spent Cu-Cr-Co/Al_2O_3.

Table S8 Metal loading of the fresh and spent Cu-Cr-Co/Al_2O_3 catalysts determined by ICP-OES

Catalyst	Metal loading (%)		
	Cu	Cr	Co
Fresh Cu-Cr-Co/Al_2O_3	17.87	6.54	4.06
Spent Cu-Cr-Co/Al_2O_3	17.63	6.41	3.97

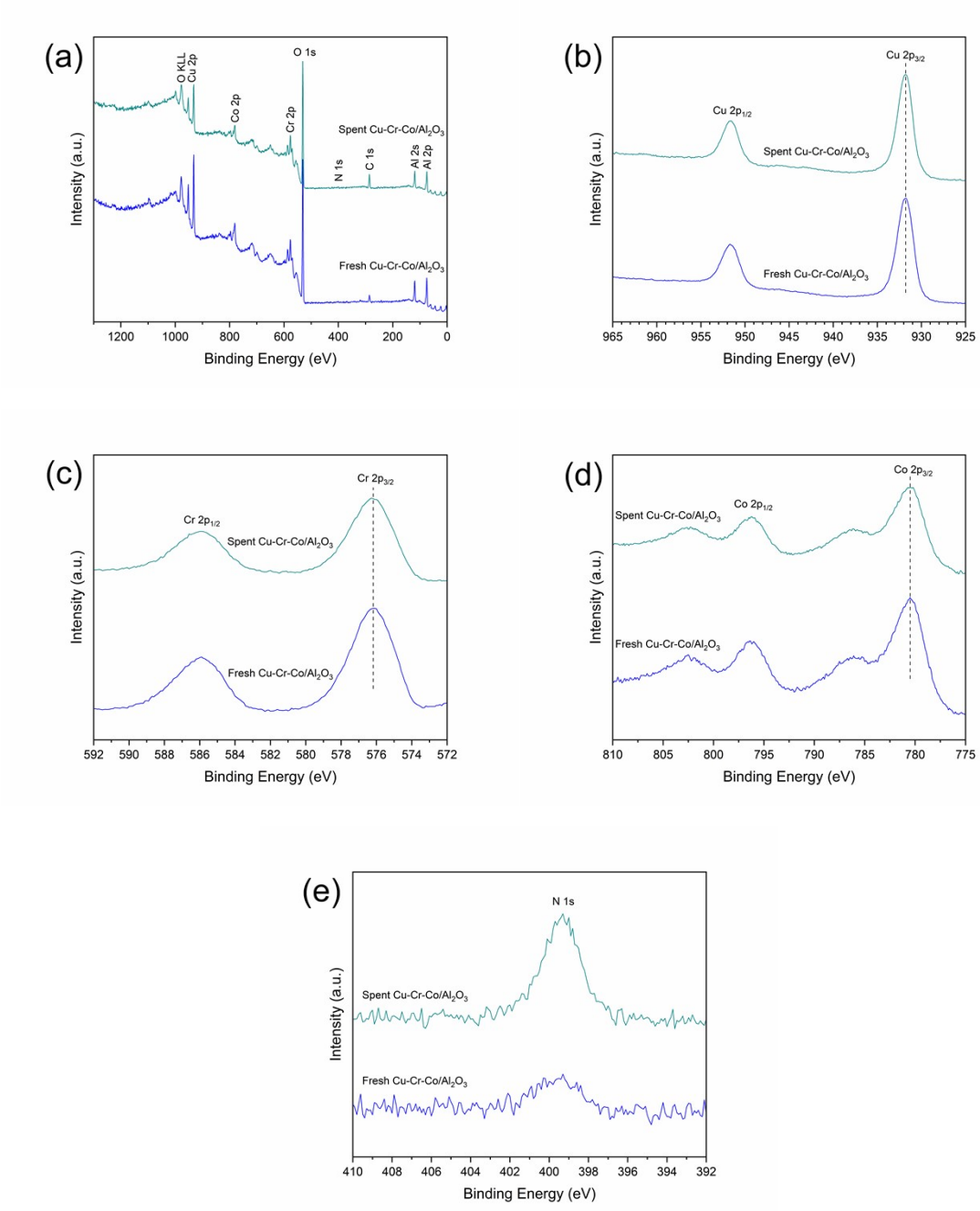

Figure S11 (a) XPS survey, (b) Cu 2p, (c) Cr 2p, (d) Co 2p and (e) N 1s spectra of fresh and spent Cu-Cr-Co/Al_2O_3 catalysts.

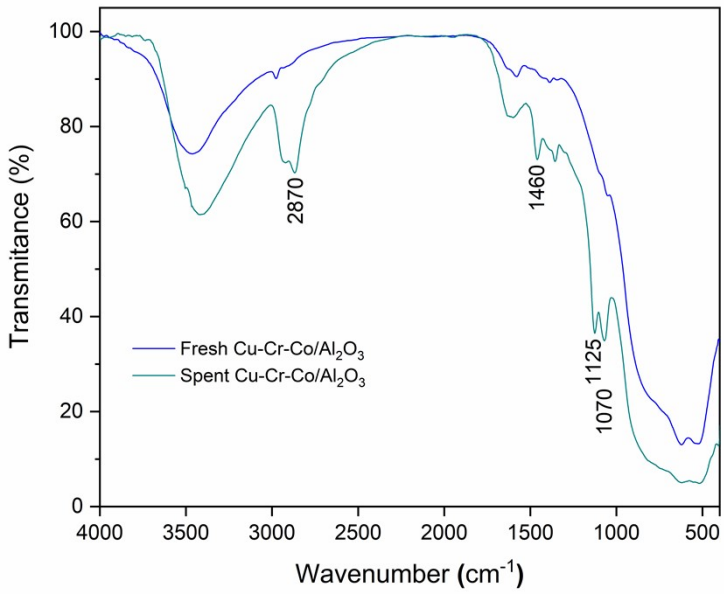

Figure S12 FT-IR spectra of fresh and spent Cu-Cr-Co catalysts. ~2870 cm^{-1} for $\upsilon_{C\text{-}H}$, 1460 cm^{-1} for $\delta_{C\text{-}H}$, ~1125-1070 cm^{-1} for $\upsilon_{C\text{-}N}$.

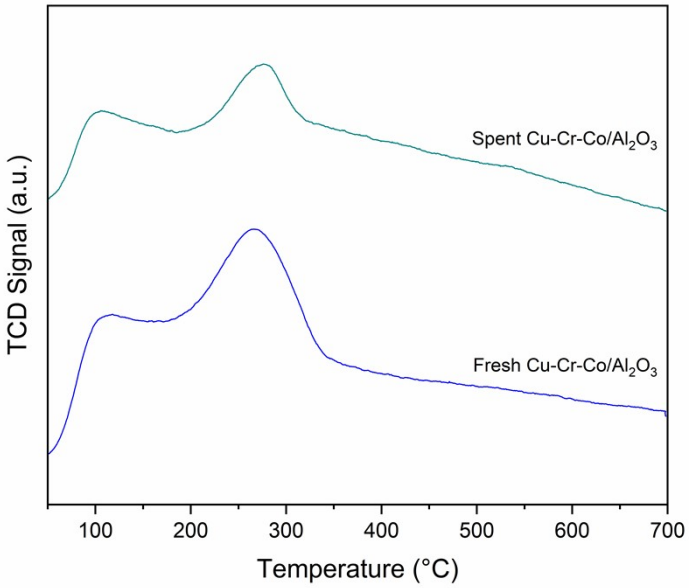

Figure S13 NH_3-TPD profiles of fresh and spent Cu-Cr-Co/Al_2O_3 catalysts.

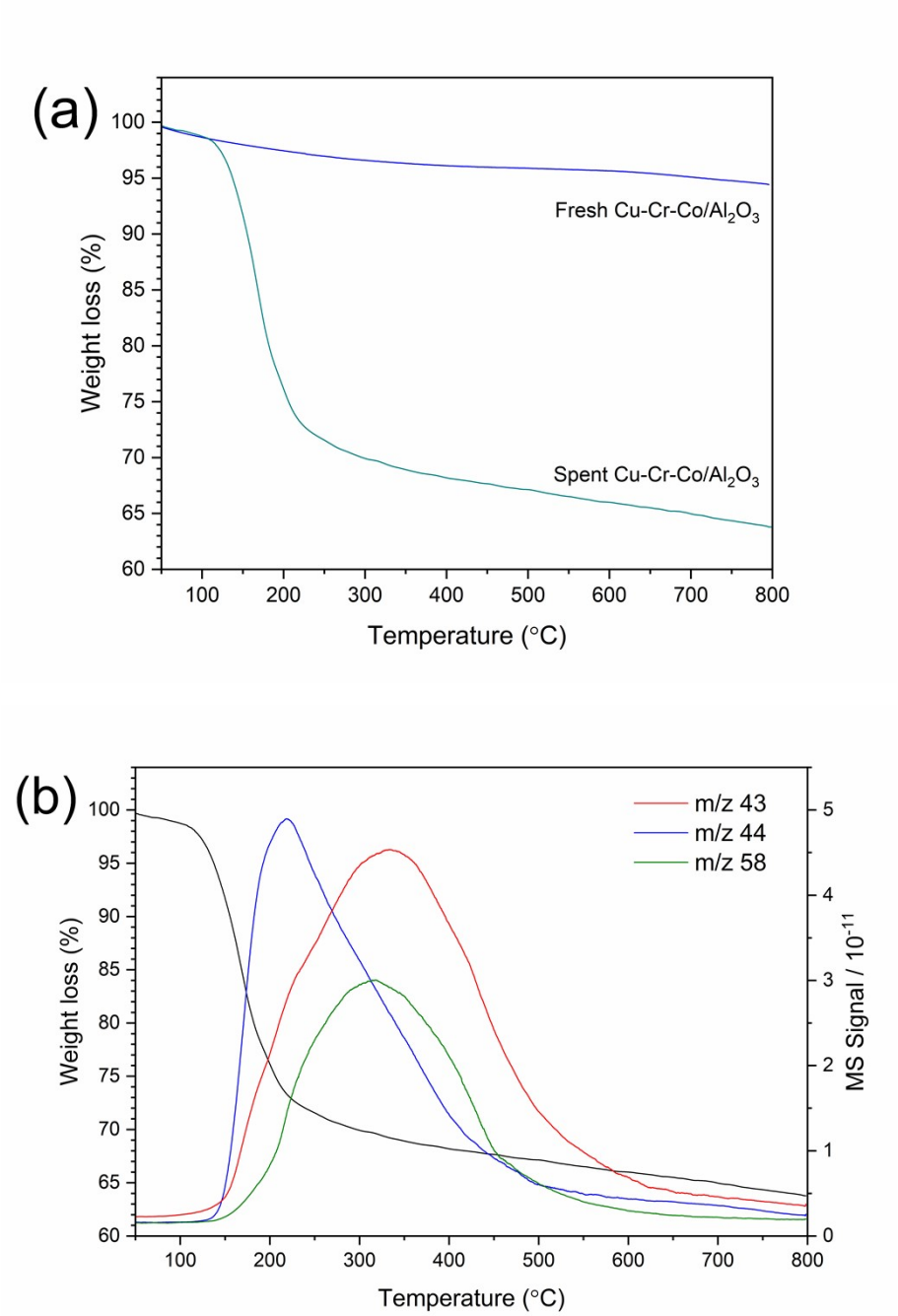

Figure S14 (a) TG spectra of fresh and spent Cu-Cr-Co/Al_2O_3 catalysts and (b) selected MS ion intensity curves and TG spectrum spent Cu-Cr-Co/Al_2O_3 catalysts.

1. WO2010031719, 2015.
2. N. Andrushko, V. Andrushko, P. Roose, K. Moonen and A. Börner, *ChemCatChem*, 2010, **2**, 640-643.
3. J. Jeong and K.-i. Fujita, *ChemCatChem*, 2021, DOI: 10.1002/cctc.202101499.