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Electronic Supplementary Information

Sustainable diamine synthesis *via* continuous-flow reductive amination over a stable Re_1O_x–Ni interface

Jiaxiang Qin,[†a] Tongtong Feng,[†a,b] Jiachen Wang,[†c] Wen Cui,[d] Amol Amrute,[e] Xiaoling Mou,[a] Li Yan,[b] Shibo Xi,[d,e] Ronghe Lin,[a*] Javier Pérez-Ramírez,[f,g*] and Yunjie Ding[a,b,h*]

[a]Key Laboratoty of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Key Laboratory of Advanced Catalysis and Adsorption Materials, Hangzhou Institute of Advanced studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou 311231, China. E-mail: catalysis.lin@zjnu.edu.cn.

[b]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China. E-mail: dyj@dicp.ac.cn.

[c]State Key Laboratory of Fine Chemicals, Frontier Science Center for Smart Materials, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China.

[d]Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore.

[e]Institute of Sustainability for Chemicals, Energy and Environment (ISCE^2), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road, Jurong Island, Singapore 627833, Republic of Singapore.

[f]Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland. jpr@chem.ethz.ch.

[g]NCCR Catalysis, 8093 Zurich, Switzerland.

[h]The State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.

[†] These authors contributed equally.

EXPERIMENTAL SECTION

Catalyst synthesis

All the catalysts were prepared by the wetness impregnation method with the nominal Ni content of 15 wt.% and 0-2 wt.% Re. Taking Ni/Al_2O_3 as an example, an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (98.0%, Sinopharm) was prepared to impregnate the commercial γ-Al_2O_3 carrier (20-40 mesh) at room temperature. The solids were fully dried at 373 K in an oven overnight and then calcined in a muffle at 723 K for 5 h (ramping 10 K min^{-1}). For the synthesis of bimetallic catalysts, NH_4ReO_4 (99.99 wt.%, Sinopharm) was co-dissolved with the Ni precursor to impregnate the Al_2O_3 carrier, and followed the same recipe. An additional Re/Al_2O_3 with 1 wt.% Re was prepared following the same method. For the other promoted Ni-Re/Al_2O_3 catalysts, the precursors ($(CH_3COO)_2Cu \cdot H_2O$, 99.0 wt.%, Sinopharm, $Co(NO_3)_2 \cdot 6H_2O$, 99.0 wt.%, Sigma-Aldrich, $Fe(NO_3)_3 \cdot 9H_2O$, 98%, Merck) were co-added with $Ni(NO_3)_2 \cdot 6H_2O$ and NH_4ReO_4 during the impregnation, and the rest procedures are the same as Ni/Al_2O_3.

Catalyst characterization

The porosity of the catalysts was measured by N_2 sorption at 77 K on a Quanta Chrome NT3LX-2 instrument after degassing the samples at 473 K for 3 h.

The Ni and Re contents in the liquid products after stability test were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin-Elmer Optima 7300 DV.

Powder X-ray diffraction (PXRD) was conducted on an X'Pert 3, PANalytical X-ray diffractometer using Cu K_α radiation in a scanning angle of 10-90° 2θ at a speed of 0.2° min^{-1}. The tube voltage and the current were set as 40 kV and 40 mA, respectively. *In situ* PXRD patterns of the catalysts were acquired by introducing 10 vol.%H_2/Ar (20 cm^3 min^{-1}) at temperature ramping (5 K min^{-1}).

The H-D exchange tests were performed on an AutoChem 2910 equipment. The catalysts (ca. 100 mg) were loaded into a U-shaped quartz reactor, preheated at 393 K in flowing Ar for 0.5 h to remove the moisture, and then the sample was ramped to 723 K and reduced by H_2 for an additional 1 h. The gas was switched to He to let the sample cool down to 323 K. After the baseline was stabilized,10 vol.%H_2/10 vol.%D_2/Ar (20 cm^3 min^{-1}) was introduced with temperature ramping (5 K min^{-1}), and the effluents were simultaneously recorded by a mass spectrometer (MS).

Temperature-programmed reduction of H_2 (H_2-TPR) was performed on the same equipment as H-D exchange. The catalysts of ca. 100 mg were loaded onto the U-shaped reactor and temperature was ramped up to 1273 K (10 K min^{-1}) with the H_2 signals followed by MS (m/e = 2).

Temperature-programmed desorption of ammonia (NH_3-TPD) was performed on the same equipment as H-D exchange. The catalysts of ca. 100 mg were loaded into a U-shaped quartz reactor, preheated at 393 K in flowing Ar for 0.5 h to remove the moisture, and then the sample was ramped to 723 K and reduced by H_2 for an additional 1 h. Afterwards, the samples were cooled to 323 K. Ammonia was then repeatedly injected to saturate the samples for 0.5 h, and then flushed with He until the baseline was stabilized. The temperature was then ramped to 773 K (10 K min^{-1}), and the ammonia signals were simultaneously recorded by MS (m/e = 17).

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi spectrometer using a 1.5 keV Al K_α X-ray source as a radiation source. For the reduced catalysts, *in situ* reduction of the fresh catalysts with 10 vol.%H_2/Ar (20 cm^3 min^{-1}) at 723 K for 1 h was performed before the spectrum acquisition. The binding energy was calibrated using the C 1*s* peak at 284.8 eV as the reference. The Ni 3*d* spectra were fitted by mixed Gaussian-Lorentzian component profiles after Shirley background subtraction.

In situ diffuse reflection infrared Fourier transform spectroscopy (*in situ* DRIFTS) measurements were conducted on a Bruker VERTEX 80 V Fourier transform infrared spectrometer in the range of 4000–800 cm− 1 with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen and a high temperature reaction chamber (ZnSe windows).

Transmission electron microscopic (TEM) images were obtained using a JEOL JEM-2100 electron microscope with 200 kV accelerating voltage. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the corresponding high-resolution elemental mapping of energy dispersive X-ray (EDX-mapping) images were acquired on a JEM-ARM200F STEM/TEM instrument equipped with a probe Cs-corrector and Super X EDS, with an instrument resolution of 0.08 nm and an accelerating voltage of 200 kV.

Extended X-ray absorption fine structure (EXAFS). *Ex situ* and *in situ* X-ray absorption spectroscopy (XAS) measurements were carried out at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS). The spectra were processed using the standard procedures implemented in the ATHENA module of the Demeter software package. For energy calibration, the corresponding metal foil or powder reference was recorded simultaneously with the samples.

Catalytic tests

The reductive amination of diethylene glycol (DEG) and morpholine (MOR) was studied in a continuous-flow fixed-bed 316L stainless steel reactor (self-made, length of 400 mm, internal diameter of 10 mm). The catalysts of *ca*. 4 cm^3 (20-40 meshes) were packed between glass wools in the middle of a reactor that was placed vertically in a furnace equipped with a temperature controller (Yudian, China). The catalysts were first pre-treated at 473 K for 1 h in N_2 (20 cm^3 min^{-1}) and then reduced by pure H_2 at 723 K for 1 h for the activation. Afterwards, the reactor was cooled to the preset temperatures, and then the reaction was started by introducing the DEG/MOR mixture using a syringe pump (NS, NP-KX-201, Japan). The gas hourly space velocity of H_2 at 200 h^{-1} was set throughout the experiments unless otherwise stated. The liquid samples were collected in a condenser of 150 cm^3 capacity connected to a cooling pump (set at 283 K), and periodically taken at 6 h intervals. The reaction products were analysed offline by using an Agilent 7890B chromatograph equipped with a FFAP column (30 m × 0.53 mm × 10 μm) and a flame ionization detector. For product identification, the reaction effluents were also analyzed offline using an Agilent 7890B chromatograph coupled with a mass spectrometer (Agilent 5977B MSD) and compared with commercial standards.

Table S1. Comparison of the performance of different catalysts for DMDEE synthesis in flow chemistry.

Catalysts	T / K	P_{H2} / MPa	$WHSV$ / h^{-1}	X_{DEG} / %	S_{DMDEE} / %	Y_{DMDEE} / %	STY_{DMDEE} / g kg_{cat}^{-1} h^{-1}	Lifetime / h	refs.
NiCuCr[a]	503	6.8	~1.26	-	~40	-	-	n.a.[c]	3
Cu/Al_2O_3[b]	488-498	1.5	~0.27	84	48	40	~106	n.a.	4 (BASF)
Co/SiO_2	503	13.7	~0.75	92	72	66	495	n.a.	5 (Huntsman)
$NiReCuFe/Al_2O_3$	473	2.0	0.4	100	77	77	~300	>1000	this work

[a] Ni:Cu:Cr = 75:23:2, molar ratios;

[b] 55 wt.%CuO;

[c] Not specified.

Table S2. Characterisation data of the key catalysts and the carrier.

Catalysts	S_{BET} [a] / cm^2 g^{-1}	V_{total} [b] / cm^3 g^{-1}	d_p [c] / nm	Acidity [d] / µmol g_{cat}^{-1}	H_2 adsorption [e] / mmol g_{cat}^{-1}
Al_2O_3	222	0.53	-	-	-
1Re/Al_2O_3	206	0.48	-	21.5	-
Ni/Al_2O_3	166	0.38	3.43±0.83	18.5	25.7
Ni-0.5Re/Al_2O_3	140	0.39	2.53±0.60	23.5	36.9
Ni-1Re/Al_2O_3	143	0.39	2.40±0.54	25.6	46.9
Ni-2Re/Al_2O_3	139	0.39	2.62±0.44	21.1	55.8

[a] BET method.

[b] Pore volume at $p/p_0 = 0.98$.

[d] Mean particle size based on TEM analysis.

[d] Dtermined by NH_3-TPD.

[e] Estimated by H_2 pulse chemisorption.

Table S3. Summary on the performance of different catalysts in the reductive amination between DEG and MOR.

Catalysts	T / K	P_{H2} / MPa	MOR:DEG / mol mol^{-1}	WHSV[a] / h^{-1}	X_{DEG} / %	τ[b] / min	X_{MOR} / %	Product distribution / %			
								DMDEE	HEEM	N-MOR	others
Ni/Al_2O_3	473	2	1.8	0.4	44.4	15	37.6	23.3	66.4	0.7	9.5
Ni0.5Re/Al_2O_3	473	2	1.8	0.4	87.4	15	86.1	72.9	14.9	0.9	11.2
Ni1Re/Al_2O_3	473	2	1.8	0.4	89.8	15	86.2	75.7	11.2	1.1	11.9
Ni2Re/Al_2O_3	473	2	1.8	0.4	95.5	15	88.5	66.6	17.0	5.8	10.6
1Re/Al_2O_3	473	2	1.8	0.4	15.0	15	19.0	11.4	34.2	0	54.4
Ni1Re/Al_2O_3	473	2	1.4	0.4	95.8	15	94.3	56.6	27.8	4.7	10.8
Ni1Re/Al_2O_3	473	2	1.6	0.4	95.0	15	90.1	65.5	12.4	8.7	13.1
Ni1Re/Al_2O_3	473	2	2.0	0.4	89.5	15	73.6	73.7	9.7	5.1	11.4
Ni1Re/Al_2O_3	473	2	2.6	0.4	80.8	15	57.2	65.0	10.6	9.7	14.6
Ni1Re/Al_2O_3	493	2	1.8	0.4	96.8	15	92.9	65.5	3.7	14.2	16.5
Ni1Re/Al_2O_3	513	2	1.8	0.4	96.3	15	90.8	39.9	3.8	42.1	23.2
Ni1Re/Al_2O_3	473	3	1.8	0.4	95.9	15	90.2	64.5	20.0	5.8	9.6
Ni1Re/Al_2O_3	473	4	1.8	0.4	94.1	15	87.5	64.1	23.9	3.8	8.2
Ni1Re/Al_2O_3	473	6	1.8	0.4	94.1	15	77.2	57.7	29.1	5.8	7.3
Ni1Re/Al_2O_3	473	2	1.8	0.2	94.1	30	88.6	71.7	8.0	7.6	12.6
Ni1Re/Al_2O_3	473	2	1.8	0.7	90.2	8.6	78.7	46.5	36.7	6.1	10.7
10CuNi1Re /Al_2O_3	473	2	1.8	0.4	94.6	15	95.6	73.0	12.4	3.8	10.8
10CoNi1Re /Al_2O_3	473	2	1.8	0.4	100	15	97.4	62.3	11.0	4.3	22.4
10Cu2FeNi1Re /Al_2O_3	473	2	1.8	0.4	100	15	98.3	74.3	14.6	2.5	8.6

[a] Liquid weight hourly space velocity;

[b] Contact time.

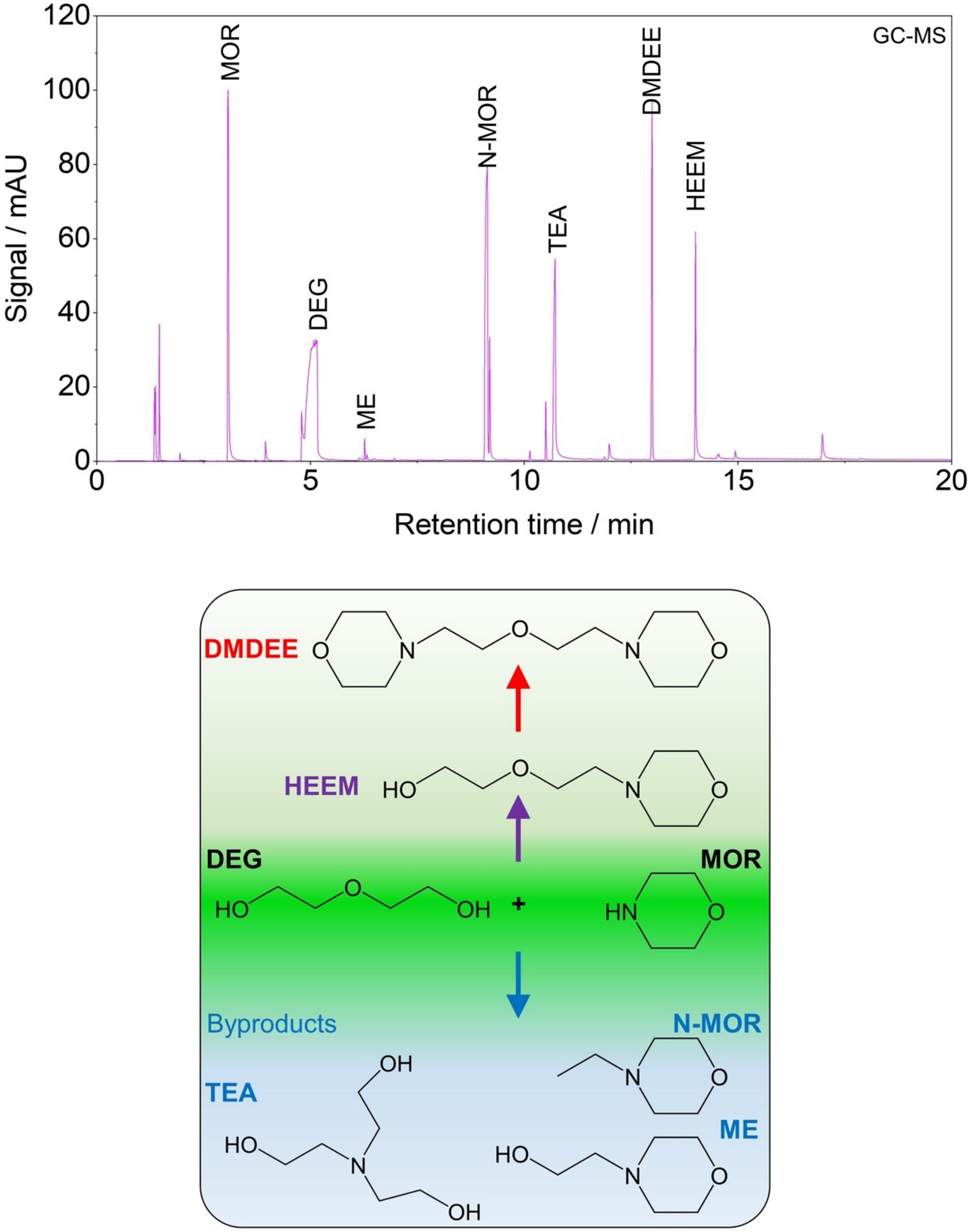

Fig. S1. GC-MS analysis of the liquid products in the reduction amination between diethylene glycol (DEG) and morpholine (MOR), and their structures (bottom). DMDEE: bis(2-morpholinoethyl)ether, HEEM: 4-[2-(2-Hydroxyethoxy)ethyl]Morpholine, N-MOR: N-ethylmorpholine, ME: 4-morpholineethanol, TEA: Triethanolamine.

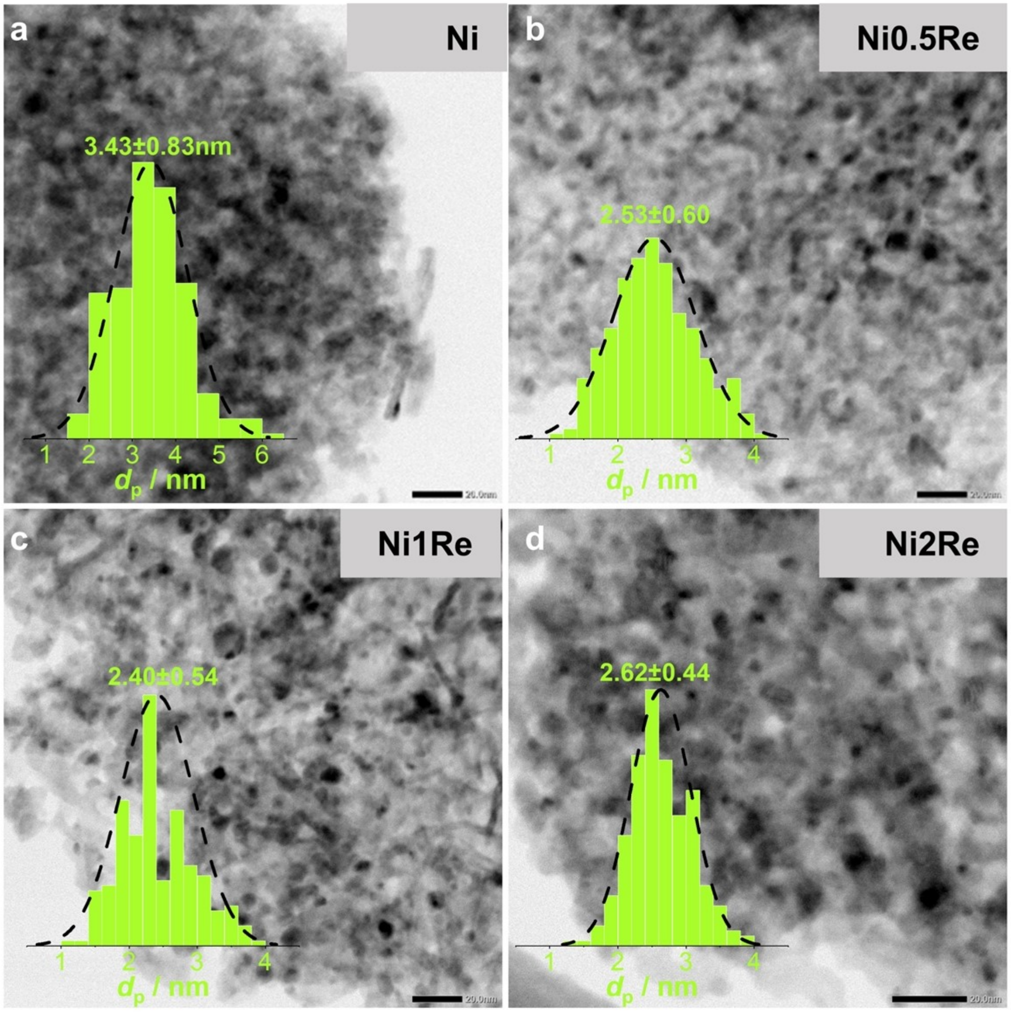

Fig. S2. TEM images of Ni/Al_2O_3 and Ni-*x*Re/Al_2O_3 catalysts. Insets show the particle size distributions and mean particle sizes (scale bars 20 nm). These results demonstrated the generally reduced particle sizes upon Re addition.

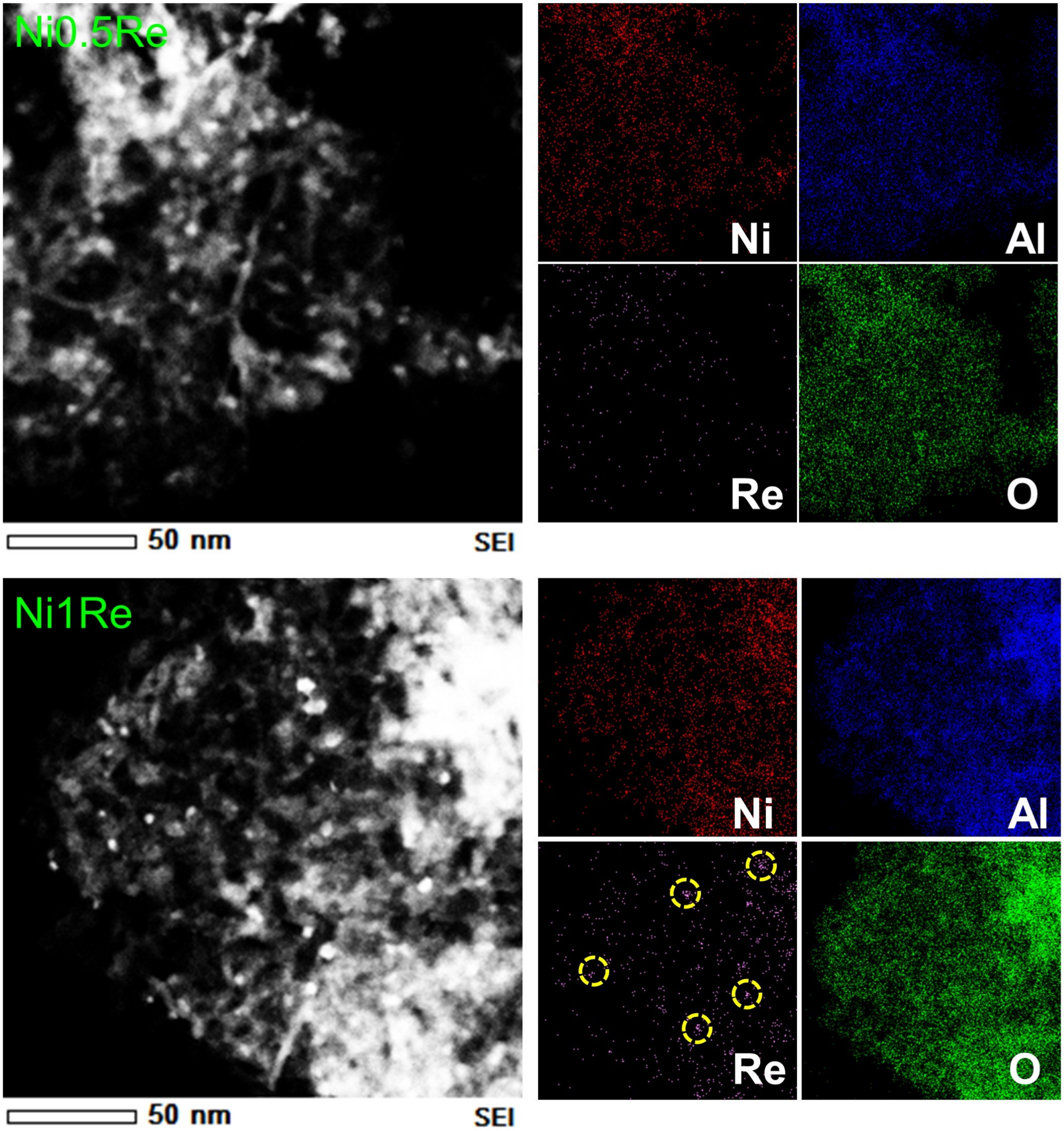

Fig. S3. HAADF-STEM of Ni-*x*Re/Al_2O_3 catalysts, accompanied with the elemental mapping images. Re remained in atomic dispersion on Ni-0.5Re/Al_2O_3, while some clustering of Re species, indicated by the circles, was evidenced in Ni-1Re/Al_2O_3 .

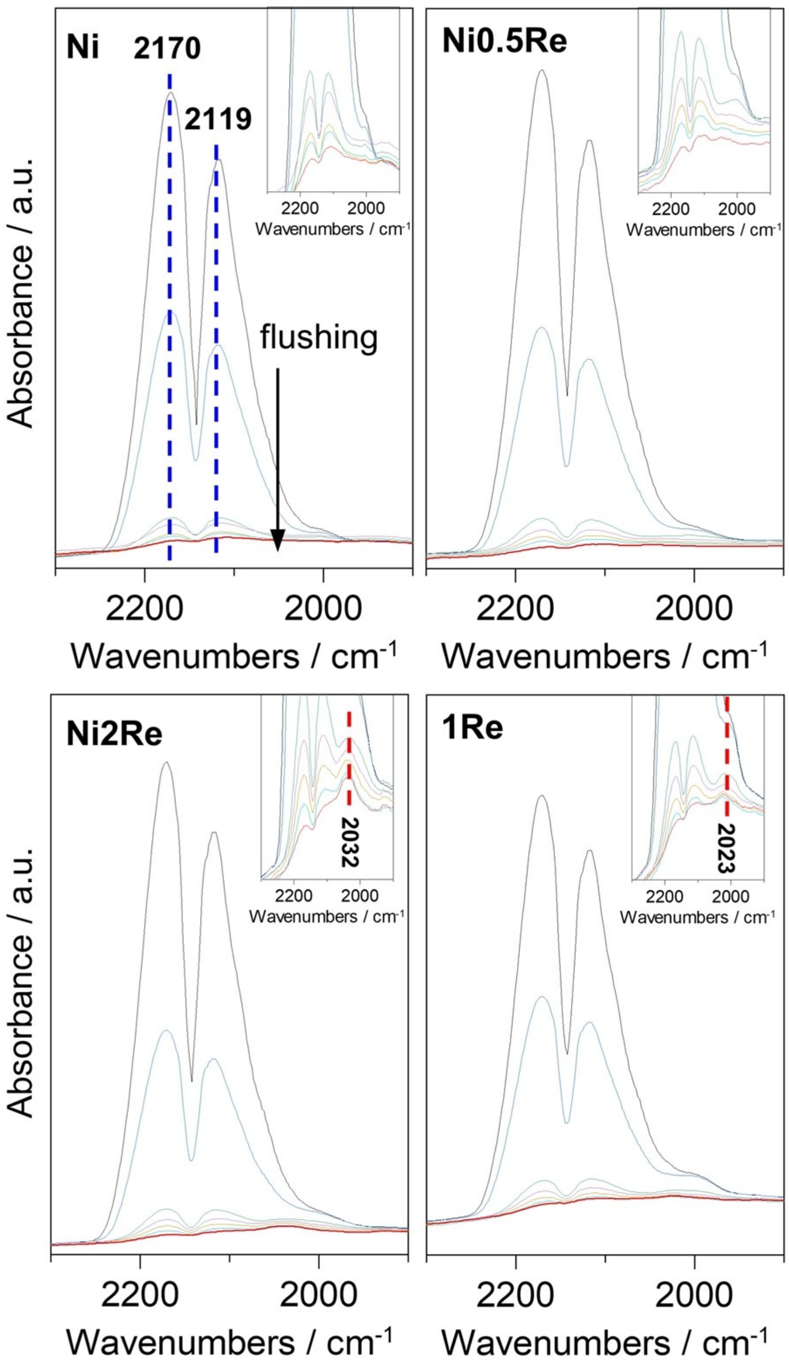

Fig. S4 *In situ* CO-DRIFTS spectra on Ni/Al_2O_3 and Ni-*x*Re/Al_2O_3 catalysts. Insets show the features at 2250-1950 cm^{-1}.

Fig. S5. HAADF-STEM of 1Re/Al_2O_3 catalyst, accompanied with the elemental mapping images. Insets show the clustering of Re species.

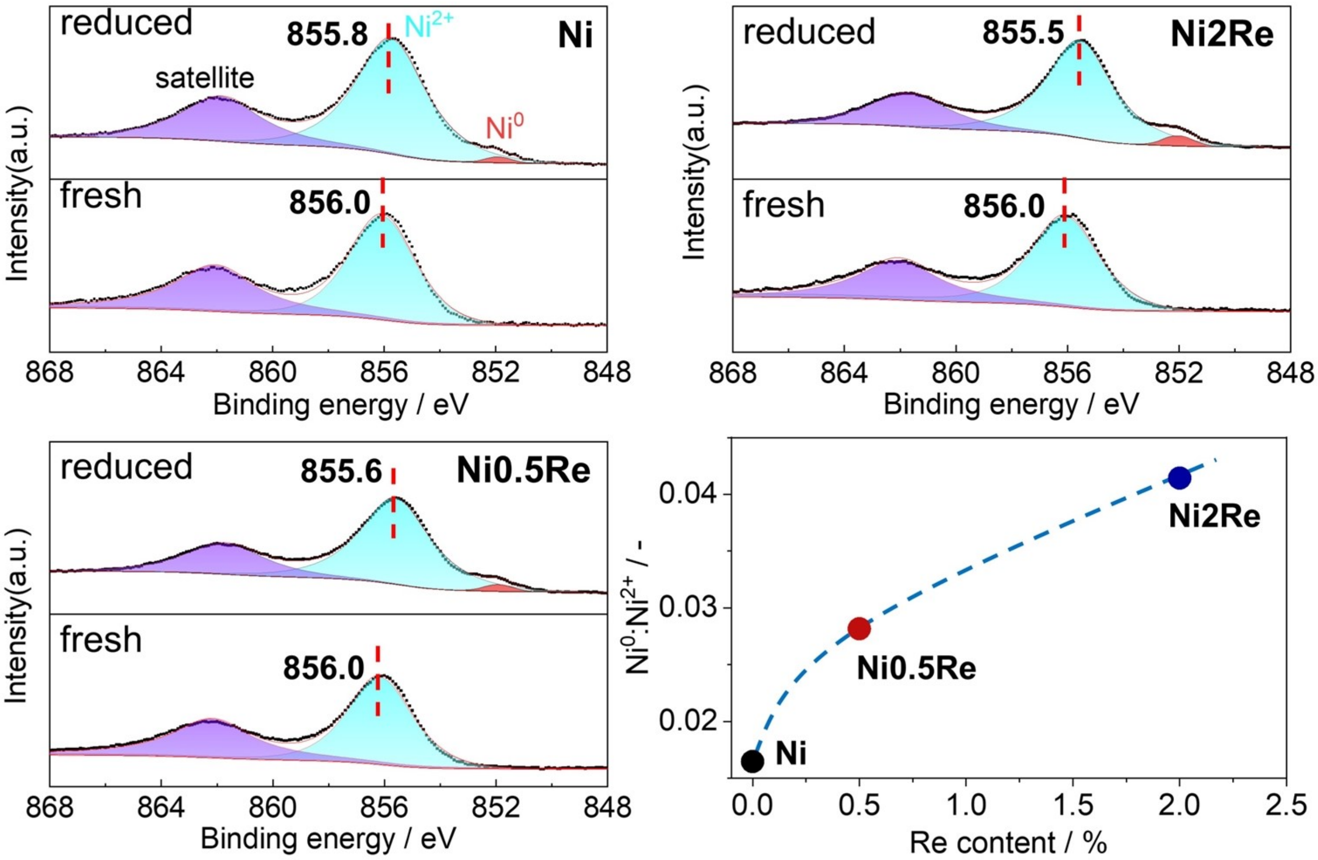

Fig. S6. The Ni 3*d* XPS spectra of the fresh and *in situ* H_2-reduced 1Re/Al_2O_3, and Ni-*x*Re/Al_2O_3 catalysts, as well as the Ni^0:Ni^{2+} ratios as a function of the Re contents, based on the XPS fitting results of the reduced catalysts.

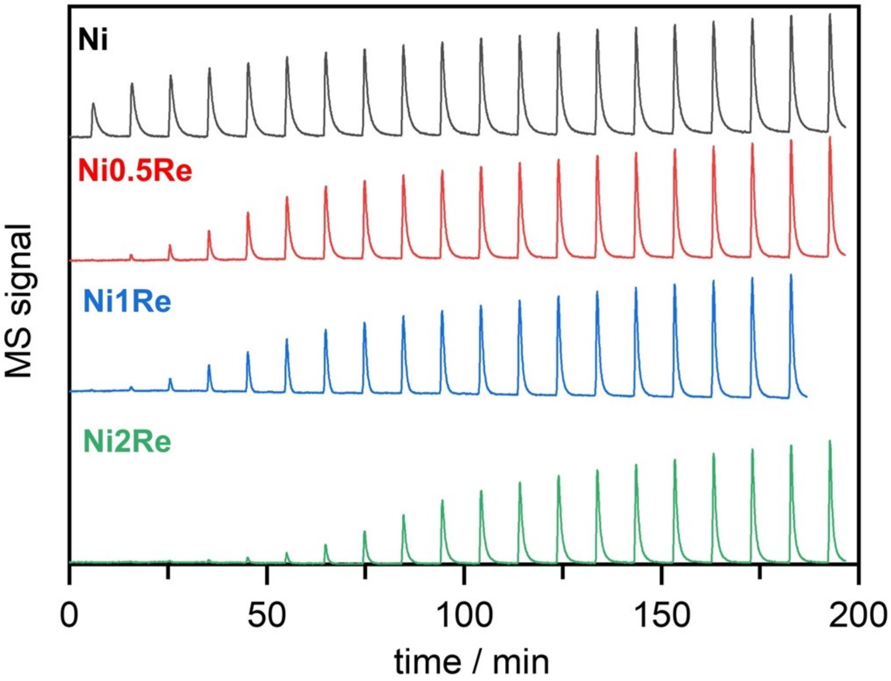

Fig. S7. The H_2 pulse chemisorption properties of Ni-*x*Re/Al_2O_3 catalysts. These results indicate the enhanced H_2 adsorption propensity of the catalysts upon increasing Re addition as summarised in **Table S2**.

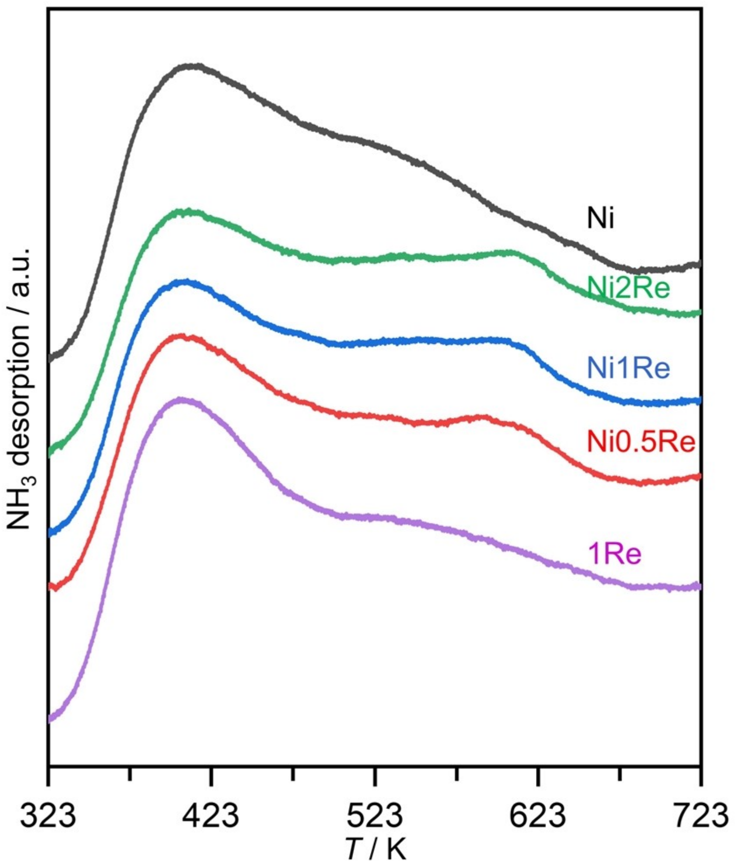

Fig. S8. The NH_3-TPD profiles of $1Re/Al_2O_3$, and Ni-*x*Re/Al_2O_3 catalysts. Quantification of the acid sites (shown in **Table S2**) indicate minimal influence after the metal loading.

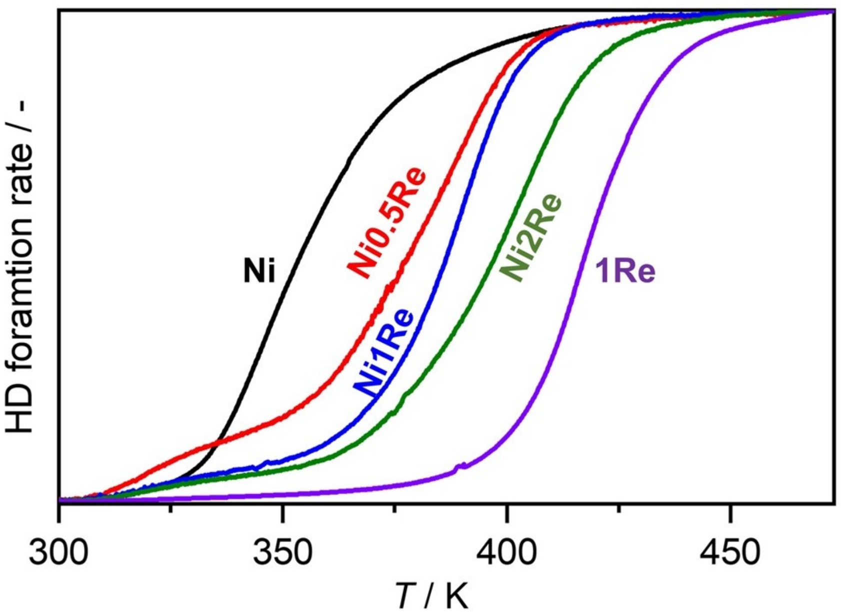

Fig. S9. The H/D exchange propensity of $1Re/Al_2O_3$, and Ni-*x*Re/Al_2O_3 catalysts. These results indicate the reduced H/D exchange properties of the catalysts upon increasing Re addition.

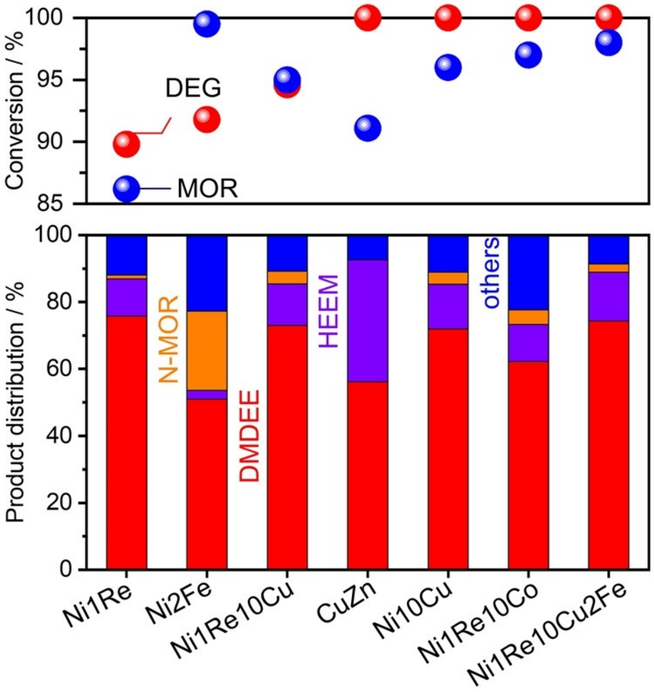

Fig. S10. The impact of different promoters on the catalytic performance of Ni-1Re/Al_2O_3 catalyst in the reductive amination between diethylene glycol and morpholine: top, conversions, bottom, product distribution. The catalysts without the addition of Re and a reference CuZn catalyst[6] were also evaluated for comparison purpose. Reaction conditions: MOR:DEG = 1.8 mol mol^{-1}, WHSV = 0.4 h^{-1}, T = 473 K, and P = 2 MPa.

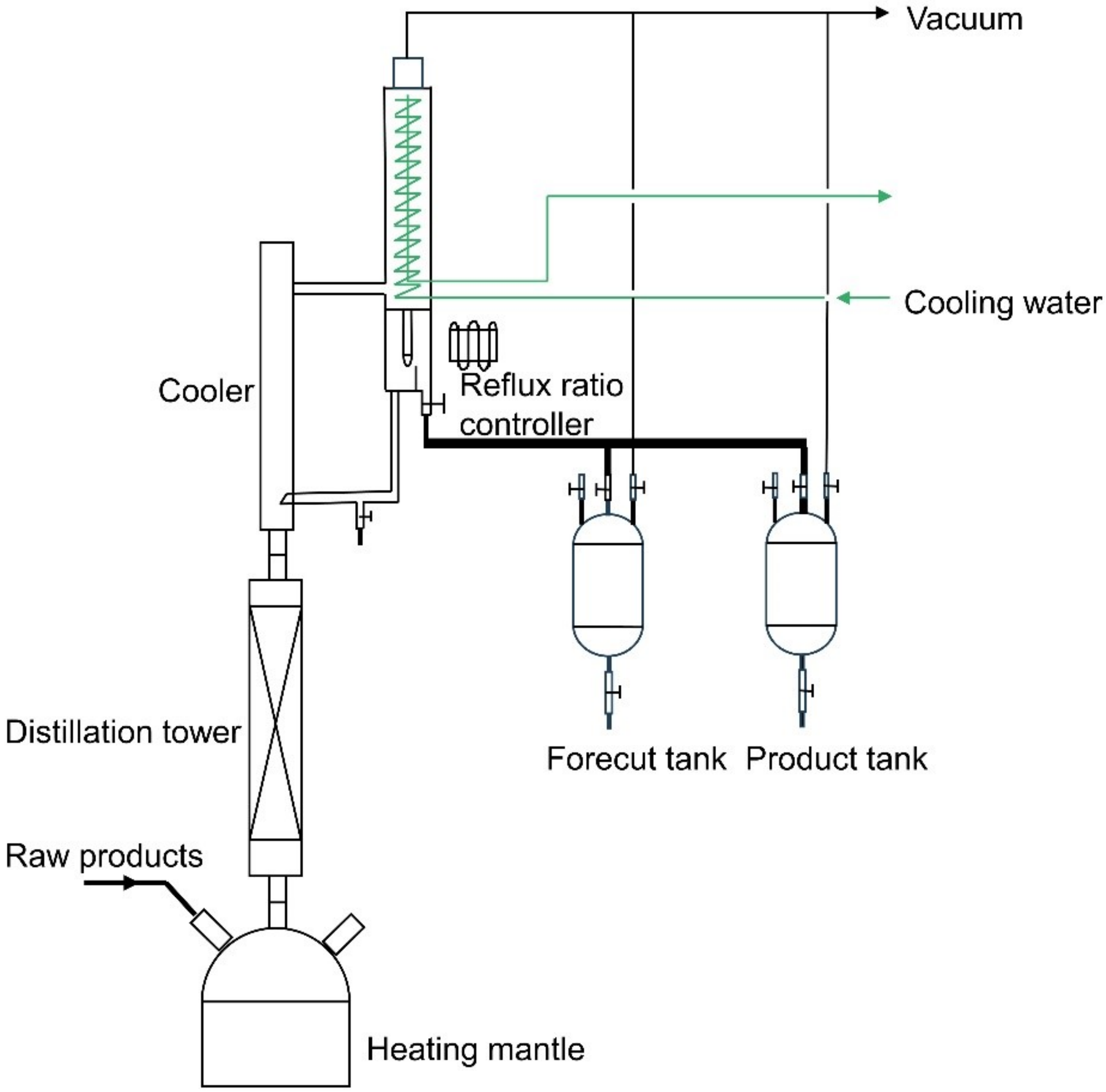

Fig S11. Illustrations for the distillation setup.

Fig. S12. The light-yellow DMDEE product from distillation (left) and supplier (right, Deyin Chemical).

Supplementary references

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