Supplementary material

Effect of Re promoter on the structure and catalytic performance of Ni-Re/Al_2O_3 catalysts for reductive amination of monoethanolamine

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Reaction method for MEA reductive amination reaction:

A tubular reactor having an inside diameter of 9 mm and an overall length of about 35cm was used for the reductive amination of MEA with ammonia. Typically, 2.4 g of catalyst was packed into the central portion of the tube using silica sand to fill the void spaces. In each case, the catalyst was in-situ activated by passing approximately 100 ml/min of hydrogen through the tube for 4 hours at 390 or 500 ^{o}C and atmospheric pressure. After reduction, the reactor system was then brought to 170 ^{o}C and 8 MPa while still under hydrogen. The system pressure was controlled by counterbalance valve.

When at the designated conditions, a solution of anhydrous ammonia and MEA (mole ratio between MEA:NH_3 was 1:10) was pumped into the reactor at a MEA liquid hourly space velocity (LHSV) of about 0.5 h^{-1}. Hydrogen was introduced to the MEA:NH_3 feed stream at a space velocity of about 60 h^{-1}. After passing through a preheater, the mixture was passed into the reactor and over the catalyst bed via downward flow. The product was condensed in the receiver at ambient temperature and pressure to allow the ammonia and hydrogen to flash off. The liquid phase products were collected at 5-11 h reaction intervals. Then, the samples were quantified by gas chromatograph (Agilent 7890) fitted with a flame ionization detector and a DB-35 capillary column, and N,N-Dimethylformamide as an internal standard.

S1: *XRD patterns.*

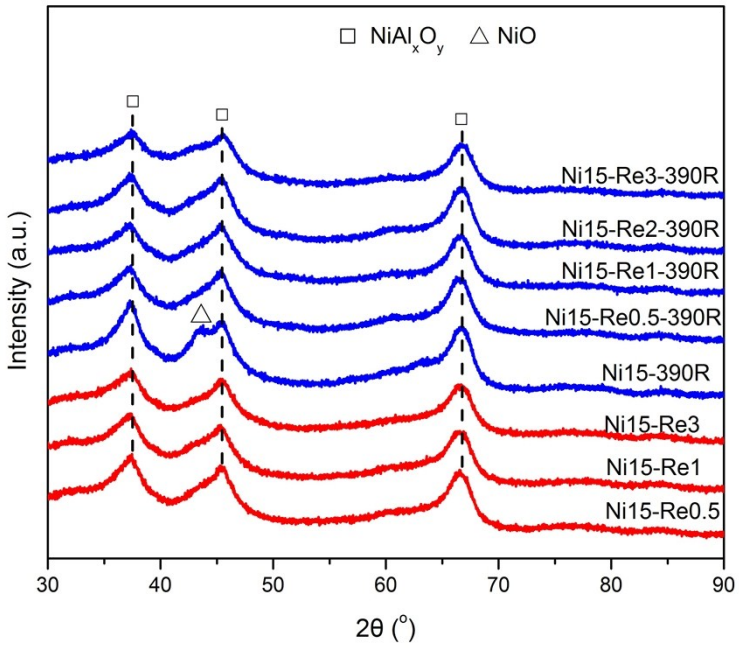

Figure S1 XRD patterns of calcined Ni15-Re0.5, Ni15-Re1, Ni15-Re3 catalysts, and 390 ^{o}C reduced Ni15-390R, Ni15-Re0.5-390R, Ni15-Re1-390R, Ni15-Re2-390R, Ni15-Re3-390R catalysts.

S2: *H_2-TPR data.*

Table S1 H_2-TPR measurement results of the Re2, Ni15, Ni15-Re0.5, Ni15-Re1, Ni15-Re2, and Ni15-Re3 samples.

Samples	Re2	Ni15	Ni15-Re0.5	Ni15-Re1	Ni15-Re2	Ni15-Re3
H_2 consumption[a] ($\mu mol/g_{cat.}$)	262.0	1963.5	2035.2	2109.3	2138.6	2272.4
Theoretical H_2 consumption[b] ($\mu mol/g_{cat.}$)	309.6	2129.5	2151.8	2209.9	2256.3	2372.6
Reduction degree (%)	85	92	95	95	95	96

[a]Calculted by pulse calibration in H_2-TPR; [b]Obtained from ICP-OES results.

S3: *Pyridine adsorption FT IR.*

Fourier transform infrared spectroscopy (FT IR) studies were recorded on a Thermo Scientific Nicolet iS50 spectrometer, equipped with a DTGS detector and operated at a resolution of 4 cm^{-1}. For pyridine adsorption IR, about 20 mg catalyst in a powder form was reduced in the cell with H_2 at 390 °C for 1 h. After cooling to 50 °C in N_2, the cell was evacuated to 10^{-2} Pa and the IR spectrum of the sample was recorded as background. Pyridine was introduced into the cell at 50 °C for 10 min. Physically adsorbed pyridine could be desorbed by heating the sample at 200 °C in vacuum for 30 min. After cooling to 50 °C in vacuum, the IR pyridine spectrum was recorded again.

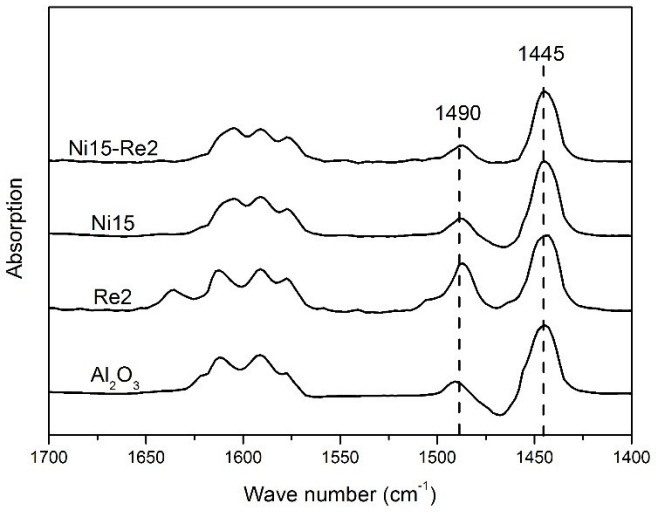

Figure S2 Pyridine adsorption IR spectra of Al_2O_3 support, Re2, Ni15, and Ni15-Re2 samples.

S4: *CO_2-TPD.*

Temperature programmed desorption (TPD) experiments of CO_2 were conducted

using an Altamira Instruments AMI-300 equipped with a thermal conductivity detection (TCD) device. Approximately 100 mg of catalyst was placed in a quartz U-tube and reduced at 390 ^{o}C for 1 h in a 10% H_2/Ar flow (30 mL/min). Next, the sample was degassed under stream of argon (30 mL/min) at 600 ^{o}C for 30 min then cooled to 50 ^{o}C. Further, catalyst was exposed to a flow (30 mL/min) of 100% CO_2 for 2 h. After being purged in He for 1 h, the catalyst was heated linearly at 10 ^{o}C/min to 600 ^{o}C in a flow (30 mL/min) of He.

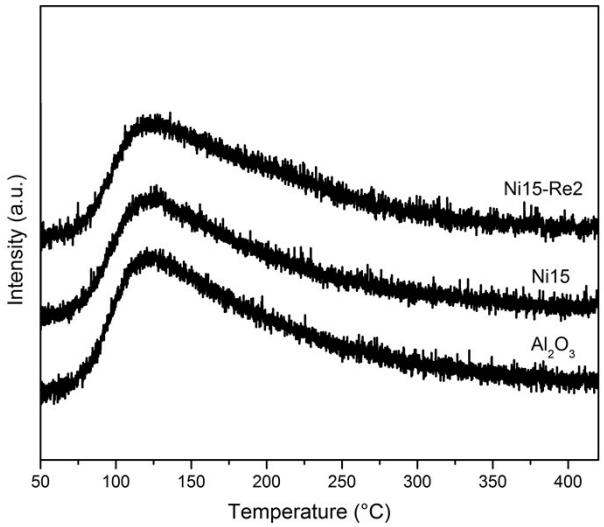

Figure S3 CO_2-TPD profiles of Al_2O_3 support, Ni15, and Ni15-Re2 samples.

Table S2 NH_3-TPD and CO_2-TPD measurement results of the Al_2O_3 support, Re2, Ni15, and Ni15-Re2 samples.

Catalysts / Values	Al_2O_3	Re2	Ni15	Ni15-Re2
CO_2 (μmol/g)	185.0	-	166.3	180.0

S5:*CO adsorption FT IR.*

Fourier transform infrared spectroscopy (FT IR) studies were recorded on a Thermo Scientific Nicolet iS50 spectrometer, equipped with a DTGS detector and operated at a resolution of 4 cm^{-1}.For CO adsorption IR, about 20 mg catalyst in a powder form was reduced in cell with H_2 for 1 h. The cell was evacuated to 10^{-2} Pa and cooled to room temperature. Background spectra were collected before CO adsorption. After exposed to CO for 20 min at room temperature, the cell was evacuated again. Both the spectrum and cell vacuum degrees are recorded.

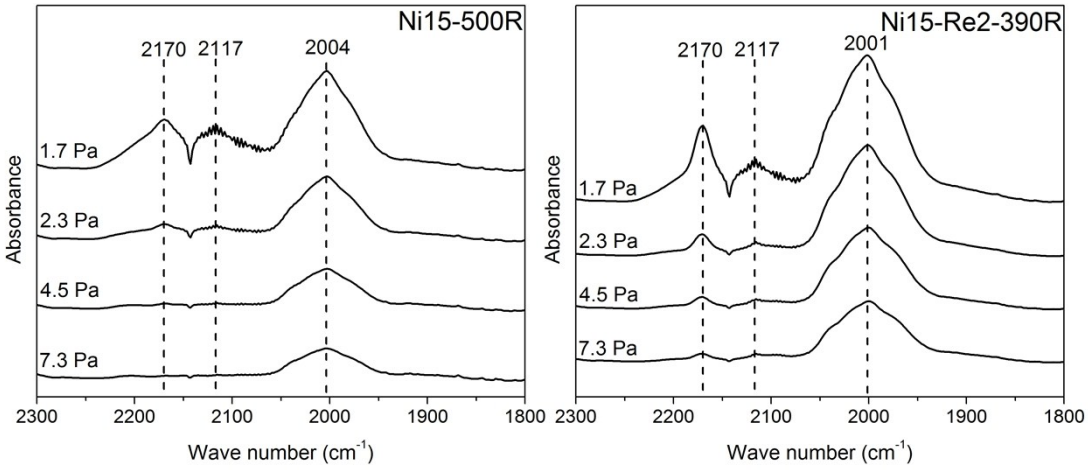

Figure S4 In situ Fourier-transformed infrared spectra of CO adsorption on Ni15-500R and Ni15-Re2-390R catalysts.

S6: *Calculating data of TOF for Ni15-Re0.5, Ni15-Re1, Ni15-Re2, and Ni15-Re3.*

Table S3 Calculating data of TOF for catalysts with varied Re loading.

Catalysts	C_{MEA}[a] (μmol $g_{cat.}^{-1}$ h^{-1})	Ni^0 total[b] (μmol $g_{cat.}^{-1}$)	Ni particle size[c] (nm)	Ni^0 surface[d] (μmol $g_{cat.}^{-1}$)	TOF[e] (h^{-1})
Ni15-Re0.5-390R	2417	283	31	11	213
Ni15-Re1-390R	3227	385	33	14	223
Ni15-Re2-390R	4811	494	32	19	251
Ni15-Re3-390R	7150	764	34	28	256

[a] Conversion of MEA per gram catalyst per hour. The data were obtained at about 30% MEA conversion; [b] Total metal Ni atoms estimated by H_2-TPR at 390 °C for 4 h; [c] Mean diameter of Ni particles in spent catalyst estimated by TEM; [d] Surface metal Ni atoms estimated with formulas suggested by Mortensen et al. (Catalysis Today, 2016. 259(2): 277-284); [e] TOF of catalyst per surface Ni atoms.

S7: *TEM.*

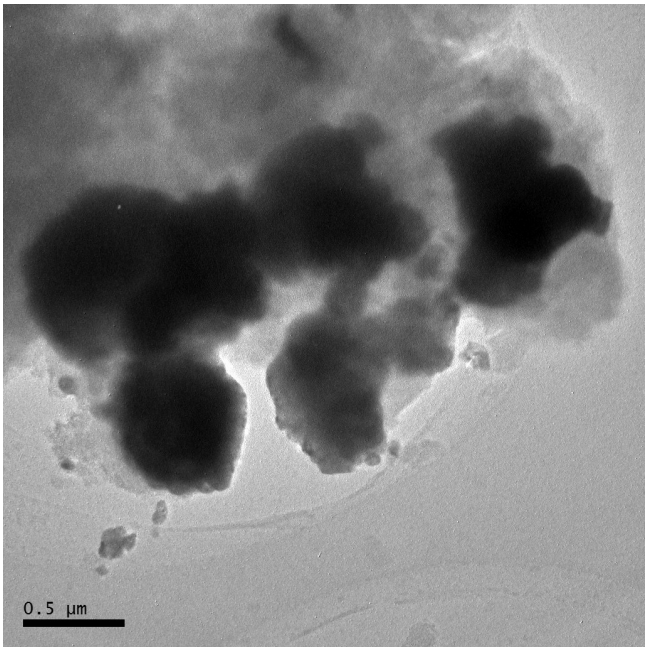

Figure S5 TEM image of spent Ni15-500R sample.