Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for

A recyclable heterogeneous-homogeneous-heterogeneous NiO/AlOOH catalysis system for hydrocarboxylation of acetylene to acrylic acid

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1. Catalytic performance of catalysts, filtrate and nickel salt

Table S1 The effect of supports on catalytic performance

No.	Cat.	Mass/mg	P/MPa	T/^{o}C	t/min	Yield/ %	STY/h^{-1}
1	10NiO/Al_2O_3	50	4.2	245	60	49.0	387
2	10NiO/SiO_2	100	3.9	242	40	48.0	301
3	10NiO/AlOOH	50	3.9	245	41	49.9	554
4	10NiO/MCM-41	50	3.9	245	60	47.6	381
5	10NiO/Mg-Al LDHs	100	3.8	240	90	28.2	73

Reaction conditions: 150 mL acetone, 15 mL H_2O, 1.2 mM/L $CuBr_2$, CO/C_2H_2 molar ratio of 1.75.

Table S2 The space time yield (STY) of fresh NiO/AlOOH and catalysts from literatures

No.	Cat.	STY/($g_{AA}/g_{cat.}/h$)	Ref.
1	NiO/AlOOH	412	-
2	CuY Zeolite	242.8	*Chem. Eng. J.*, 2017, 313, 663-670
3	Ni-MCM-41	70.6	*RSC Adv.*, 2016, 6, 97285-97292
4	NiY Zeolite	62	*Appl. Catal. A*, 2014, 485, 163-171

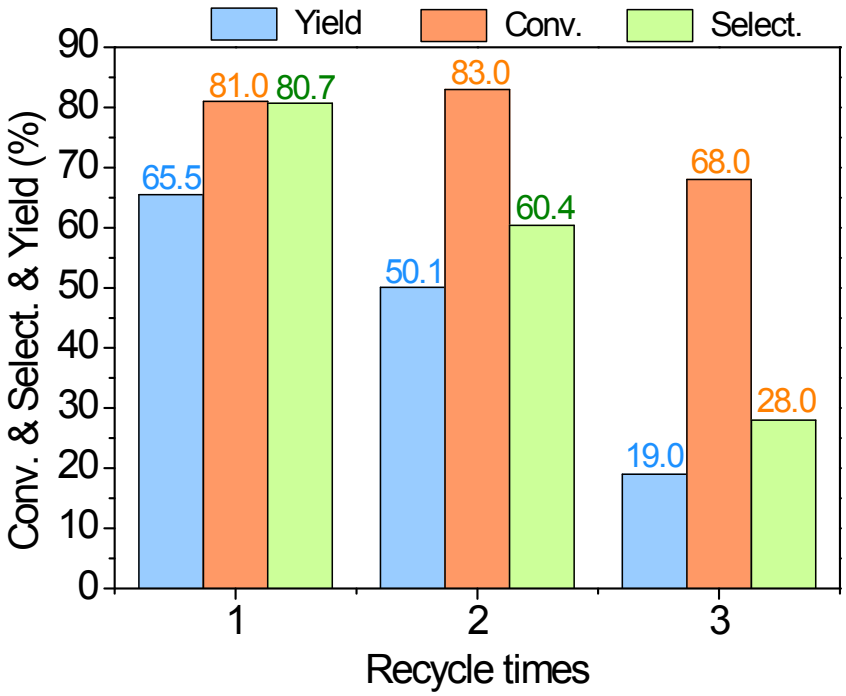

Fig. S1 Catalytic performance of the recovered NiO/AlOOH catalyst. Conditions: 150 mL acetone, 15 mL H_2O, 1.2 mM/L $CuBr_2$, 200 mg NiO/AlOOH catalyst, CO/C_2H_2 molar ratio of 1.75 and initial pressure of 4.5 MPa, reaction temperature of 250 ^oC and reaction time of 90 min.

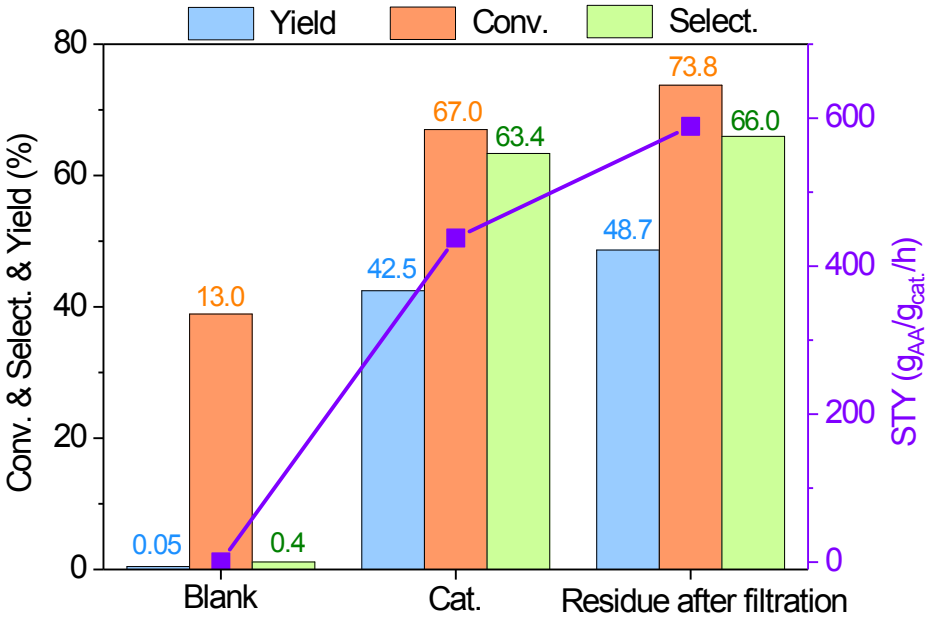

Fig. S2 Catalytic performance of the filtrate. Reaction conditions: CO/C_2H_2 molar ratio of 1.75 and initial pressure of 4.5 MPa, reaction temperature of 250 °C and reaction time of 30 min.

It is worth noting that the reaction conditions for the catalyst is as follows: 50 mg NiO/AlOOH, 1.2 mM/L $CuBr_2$, 150 mL acetone, 15 mL H_2O, CO/C_2H_2 molar ratio of 1.75 and initial pressure of 4.5 MPa, reaction temperature of 250 °C and reaction time of 30 min.

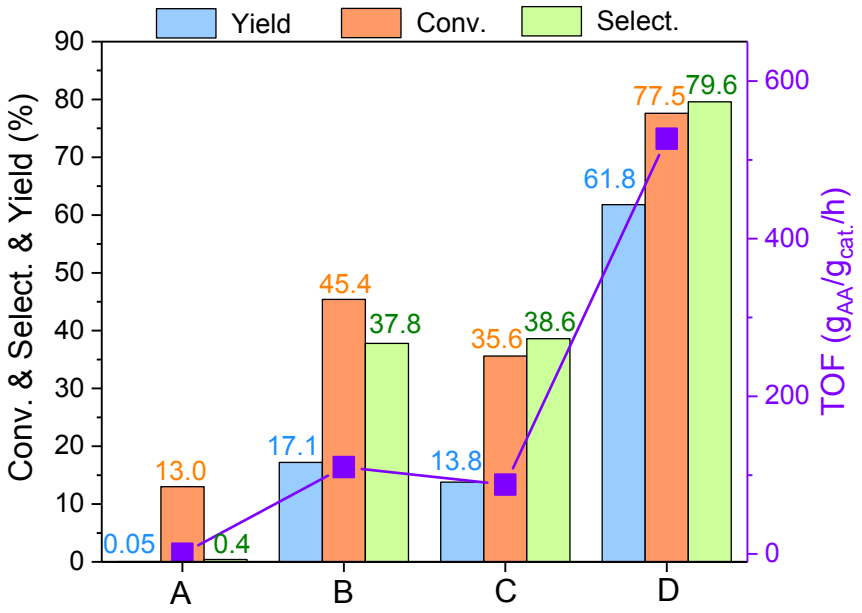

Fig. S3 Catalytic performance of contrast samples (A of blank, B of nickel salt of nickel nitrate, C of nickel salt of nickel nitrate with blank AlOOH, D of fresh catalyst). Conditions: 150 mL acetone, 15 mL H_2O, 1.2 mM/L $CuBr_2$, CO/C_2H_2 molar ratio of 1.75 and initial pressure of 4.5 MPa, reaction temperature of 250 ^oC and reaction time of 30 min.

2. Controlled experiments

2.1 Effect of gas atmosphere

We investigated the effect of gas atmosphere on the nickel leaching. In a typical experiment, known quantities of catalyst powders (0.1 g) and acetone (150 mL) were charged into the stirred pressure reactor. The reactor was firstly flushed with nitrogen for several times and subsequently pressurized with different gases (N_2, N_2-C_2H_2 mixture or CO) to 4.5 MPa of initial total pressure. The reactor was then heated to 250 ^oC and kept for 30 min under constant agitation (800 rpm). Finally, the autoclave was quickly cooled to room temperature and the liquid was collected and analyzed by ICP measurement.

2.2 Effect of additives

We investigated the effect of additives on the nickel leaching. In a typical experiment, known quantities of catalyst powders (0.1 g), acetone (150 mL) and additive (1.2 mM/L, $CuBr_2$, $Cu(NO_3)_2$ or KBr) were charged into the stirred pressure reactor. The reactor was firstly flushed with nitrogen for several times and subsequently pressurized with different gases (N_2-C_2H_2 mixture or CO) to 4.5 MPa of initial total pressure. The reactor was then heated to 250 ^oC and kept for 30 min under constant agitation (800 rpm). Finally, the autoclave was quickly cooled to room temperature and the liquid was collected and analyzed by ICP measurement.

3. Stability of NiO/AlOOH catalyst after recovery of leached nickel

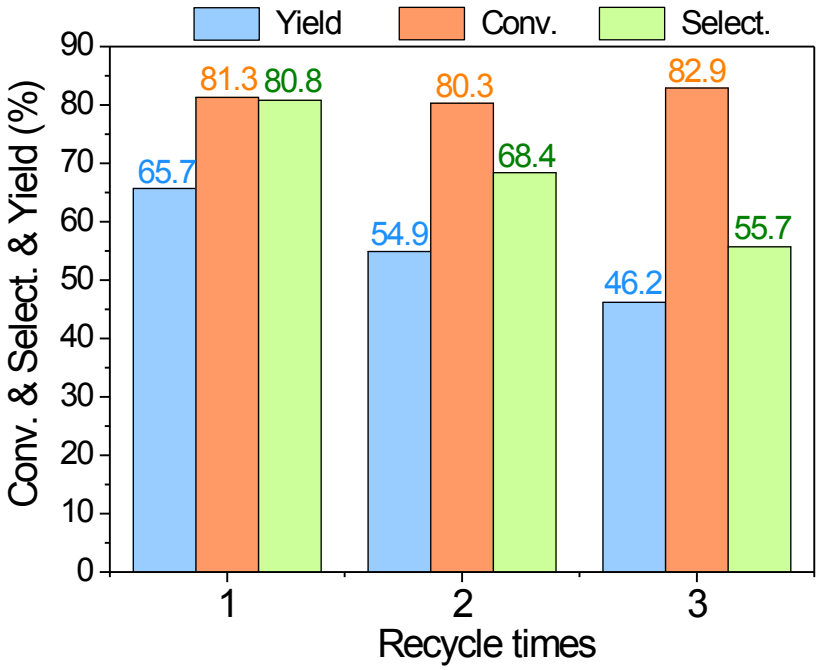

Fig. S4 Stability of NiO/AlOOH catalyst after recovery of leached nickel. Conditions: 150 mL acetone, 15 mL H_2O, 1.2 mM/L $CuBr_2$, 200 mg NiO/AlOOH catalyst, CO/C_2H_2 molar ratio of 1.75 and initial pressure of 4.5 MPa, reaction temperature of 250 °C and reaction time of 90 min.

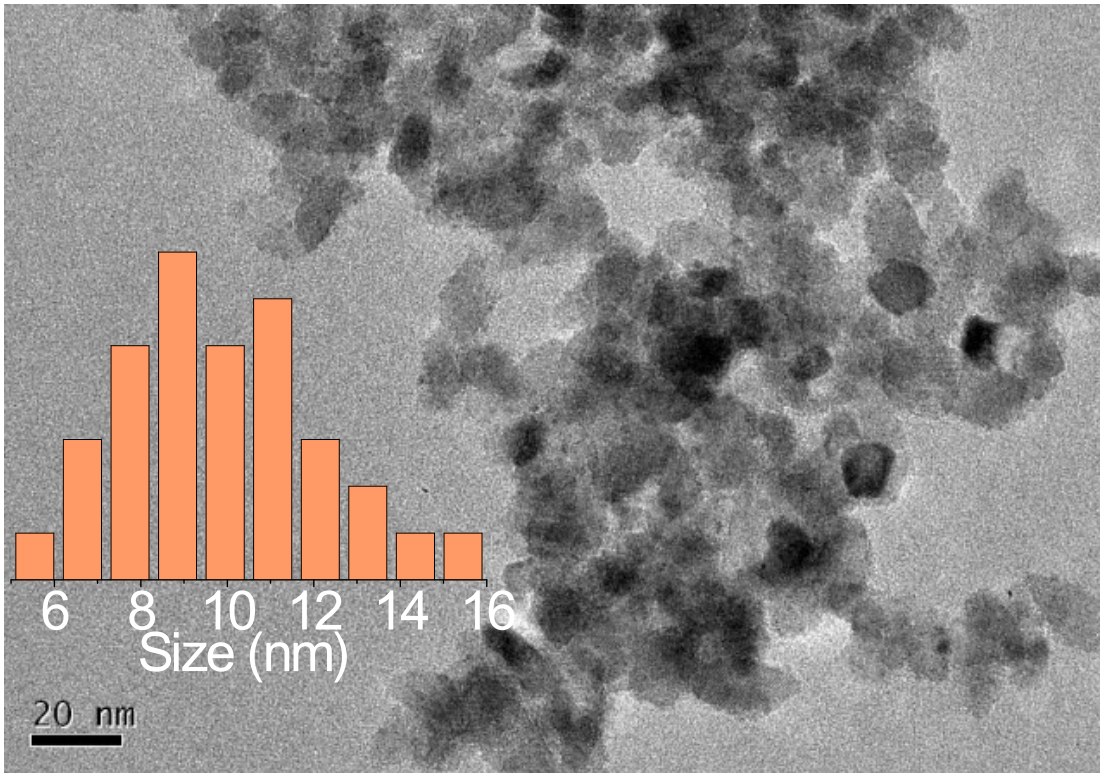

Fig. S5 TEM image and size distribution of Ni particles (inset) of NiO/AlOOH sample after one cycle.