Supplementary Information

Suppressing the active site-blocking impact of ligands of $Ni_6(SR)_{12}$ clusters with the assistant of NH_3 on catalytic hydrogenation of nitriles

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Experimental Procedures

$Ni_6(SR)_{12}$ clusters treated as mentioned three different conditions:

(1) $Ni_6(SR)_{12}$ clusters (15 mg) were mixed in 20 mL methanol. The mixture was transferred in a stainless steel autoclave equipped with an automatic temperature control system and a magnetically driven impeller. The temperature was then raised to 45 °C and the vessel was pressurized by 6 atm H_2 under a stirring of 1000 rpm. After 10 h, the methanol was removed by rotary evaporation, the sample was washed with hexane and then the product was extracted by dichloromethane.

(2) $Ni_6(SR)_{12}$ clusters (15 mg) were mixed in 20 mL methanol with NH_3 atmosphere. The solution was heated to 45 °C under vigorous stirring and maintained at this temperature for 10 h under a stirring of 1000 rpm. After 10 h, the methanol was removed by rotary evaporation, the sample was washed with hexane and then the product was extracted by dichloromethane.

(3) 20 mL methanol was put into a tri-neck flask, NH_3 was introduced with the catheter and the solution was vigorously stirred for 0.5 h in an ice bath. $Ni_6(SR)_{12}$ clusters (15 mg) and the NH_3-infused 20 mL methanol solution were transferred in a stainless steel autoclave equipped with an automatic temperature control system and a magnetically driven impeller. The temperature was then raised to 45 °C and the vessel was pressurized by 6 atm H_2 under a stirring of 1000 rpm. After 10 h, the methanol was removed by rotary evaporation, the sample was washed with hexane and then the product was extracted by dichloromethane.

Supporting Figures and Tables:

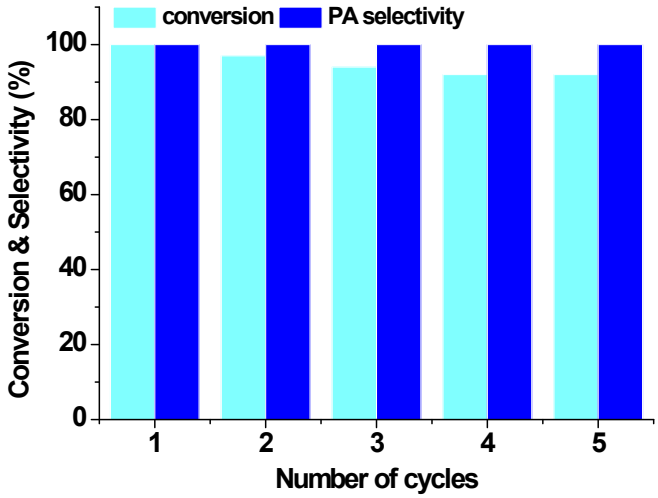

Figure S1. Recyclability of the $Ni_6(SR)_{12}$ cluster catalysts in terms of (a) conversion of 4-cyanotetrahydropyran and (b) selectivity for primary amine.

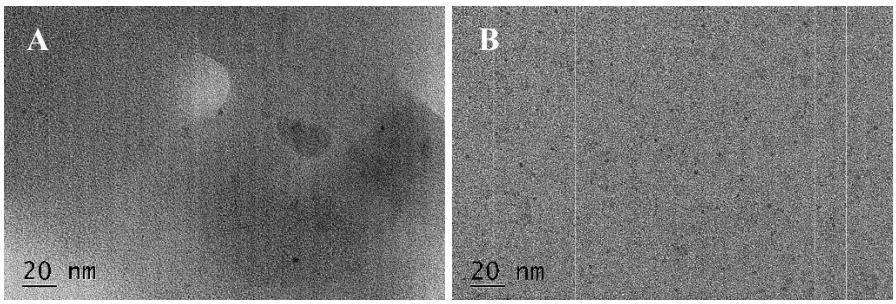

Figure S2. TEM images of (A) fresh and (B) used $Ni_6(SR)_{12}$.

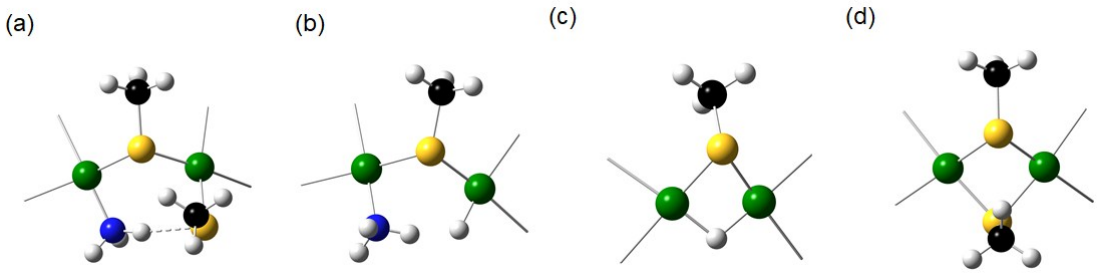

Figure S3. The optimized geometries for initial reaction products for (a) $Ni_6(SR)_{12} + NH_3$, (b) $Ni_6(SR)_{12} + NH_3 + H_2$, and (c) $Ni_6(SR)_{12} + H_2$, and (d) fresh $Ni_6(SR)_{12}$.