Supporting Information

Protective Dissolution: Generating Secondary Pores in Zeolite by Mechanochemical Reaction

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Fig. S1 PXRD patterns of Silicalite-1 treated with different contents of NH_4F alone in the solvent-free mechanochemical treatment: (a) $NH_4/SiO_2=0.54$, (b) $NH_4/SiO_2=1.08$, (c) $NH_4/SiO_2=1.62$, (d) $NH_4/SiO_2=2.70$.



Fig. S2 PXRD patterns of Silicalite-1 treated with different content TPABr alone in solvent-free mechanochemical treatment: (a)TPABr/SiO₂=0.075, (b) TPABr/SiO₂=0.15, (c)TPABr/SiO₂=0.225, (d) TPABr/SiO₂=0.375.



Fig. S3 TEM images of Silicalite-1 treated with different content of NH_4F -TPABr in the solvent-free mechanochemical treatment: (a) $NH_4/SiO_2=0.3$, TPABr/SiO_2=0.075; (b) $NH_4/SiO_2=0.6$, TPABr/SiO_2=0.075; (c) $NH_4/SiO_2=1.0$, TPABr/SiO_2=0.075; (d) $NH_4/SiO_2=0.54$, TPABr/SiO_2=0.10; (e) $NH_4/SiO_2=0.54$, TPABr/SiO_2=0.15; (f) $NH_4/SiO_2=0.54$, TPABr/SiO_2=0.225.



Fig. S4 TEM images and SAED patterns of (a, b) pristine silicalite-1 zeolite, (c, d) ground products and (e, f) ground-heated sample.



Fig. S5 TEM images of Silicalite-1 treated by solvent-free method at 80 °C,100 °C, 120 °C, 150 °C, 180 °C, 220 °C for 15 h.



Fig. S6 TEM images of Silicalite-1 treated by solvent-free method at 180 $^\circ \! C$ for 7 d.



Fig. S7 TEM images of commercial Silicalite-1(a), ZSM-5 with Si/AI =50 (b), ZSM-5 with Si/AI=14 (c), ZSM-5 with Si/AI=13 (d) treated by solvent-free method.



Fig. S8 TEM images of Silicalite-1 treated with different contents of TPABr alone in the solvent-free mechanochemical treatment: (a) TPABr/SiO₂=0.075, (b) TPABr/SiO₂=0.15, (c) TPABr/SiO₂=0.225, (d) TPABr/SiO₂=0.375.



Fig. S9 TEM images of (a, b) Co@Silicalite-1 and (c, d) Pd@Silicalite-1 after mixing and heating process but without calcination and reduction.



Fig. S10 TEM images of Co@Silicalite-1 at different tilting angles.