Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

PdAg Alloy Nanoparticles Immobilized on Functionalized MIL-101-NH_2: Effect of Organic Amines for Hydrogenation of Carbon Dioxide into Formic Acid

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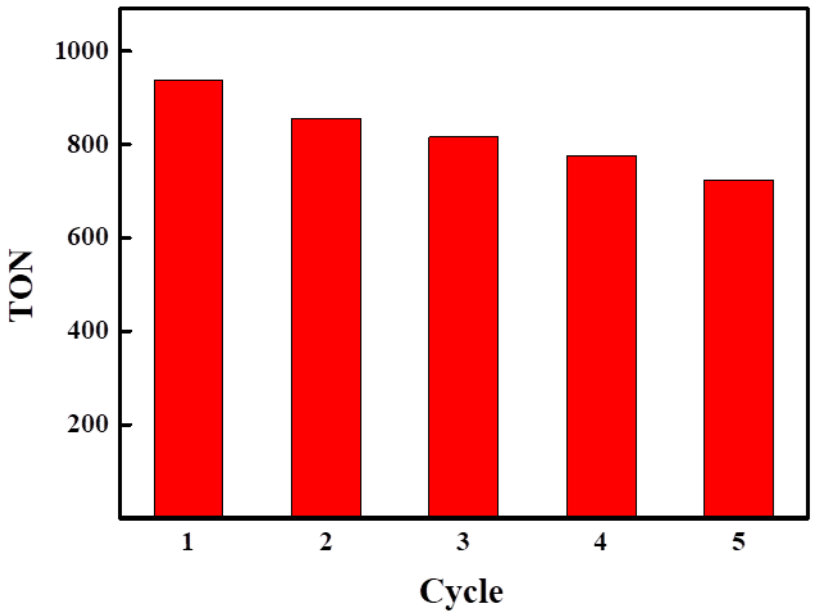

Fig. S1. Recyclability of PdAg/TEDA-MIL-101-NH_2 catalyst during the hydrogenation of CO_2 into formic acid. Reaction condition: 20 mg catalyst, the total pressure of 5.0 MPa (CO_2 : H_2 = 1 : 1, volume ratio) at 70 ^{o}C for 10 h.

We further investigated the reason for the deterioration of catalyst activity by using ICP-AES, XRD, TEM and FT-IR. The Pd contents in fresh catalyst and recycled catalyst after 5 times respectively were 1.77 wt% and 1.59 wt%. The XRD patterns of fresh catalyst and recycled catalyst were shown as Fig. S2 and it noted that PdAg/TEDA-MIL-101-NH_2 was stable during this

reaction. Unfortunately, the particle size of PdAg NPs in recycled catalyst were analyzed by TEM and results as shown in Fig. S3, part of PdAg NPs had agglomeration and the average of MNPs was ~ 7.3 nm. And FT-IR results as shown in Fig. S4, the skeleton characteristic peak of MIL-101-NH_2 and the loaded organic base characteristic peak all still were observed in the recycled catalyst, which indicated catalyst support was unchanged. However, peak at 3370 cm^{-1} signed to $–NH_2$ was emerged after reaction and it was because of the small number of losing and clusters of noble metals. Therefore, basically it can be determined that the cause of catalyst activity loss was the increase of MNPs size.

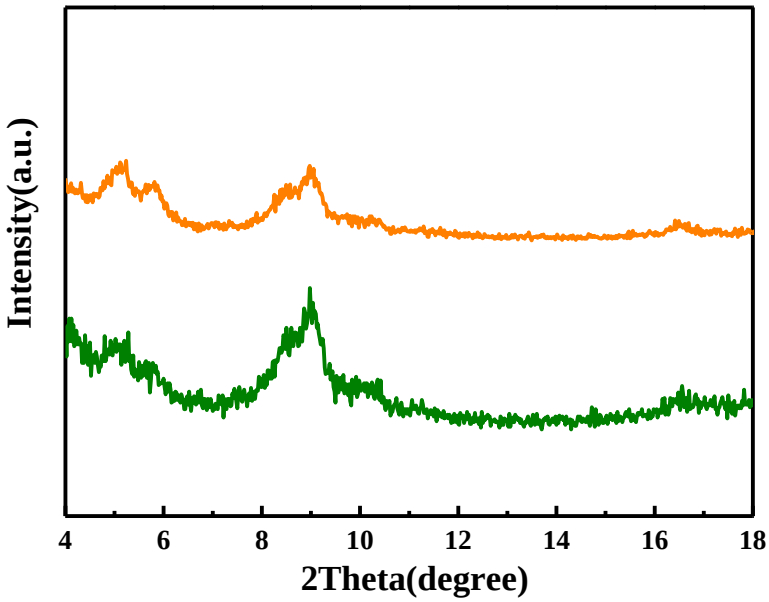

Fig. S2. The PXRD pattern of PdAg/TEDA-MIL-101-NH_2 fresh (green) and recycled (yellow) catalysts.

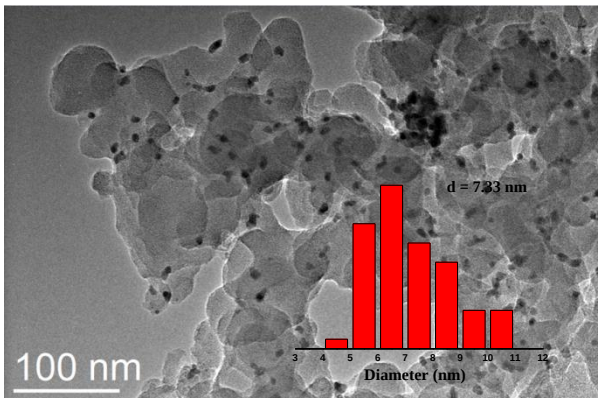

Fig. S3. The TEM of PdAg/TEDA-MIL-101-NH_2 recycled catalyst

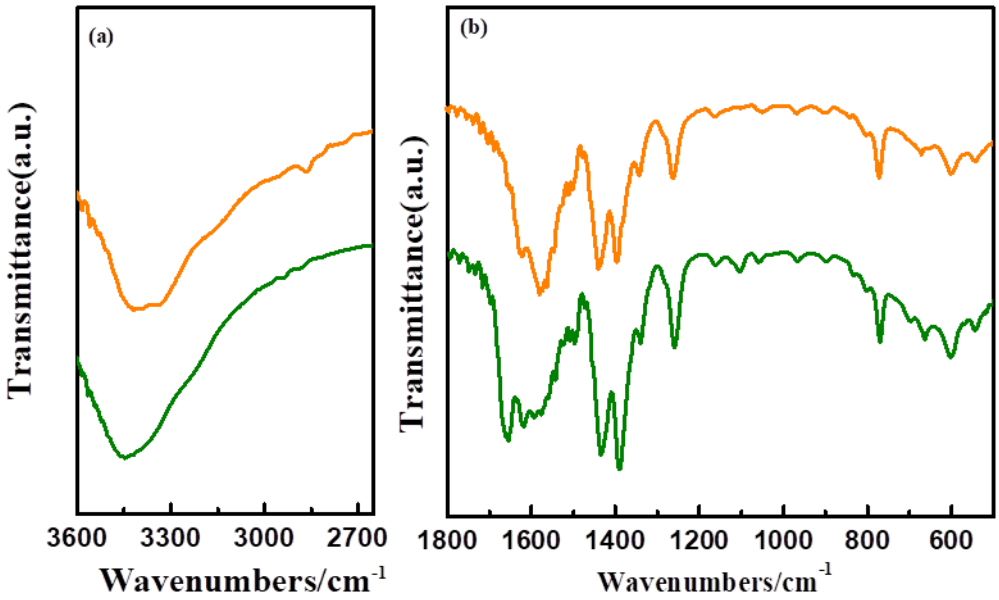

Fig. S4. Partial enlarged view of fresh and recycled catalysts FT-IR spectra. (a) High wavenumbers; (b) Low wavenumbers of fresh PdAg/TEDA-MIL-101-NH_2 (green); recycled PdAg/TEDA-MIL-101-NH_2 (yellow)

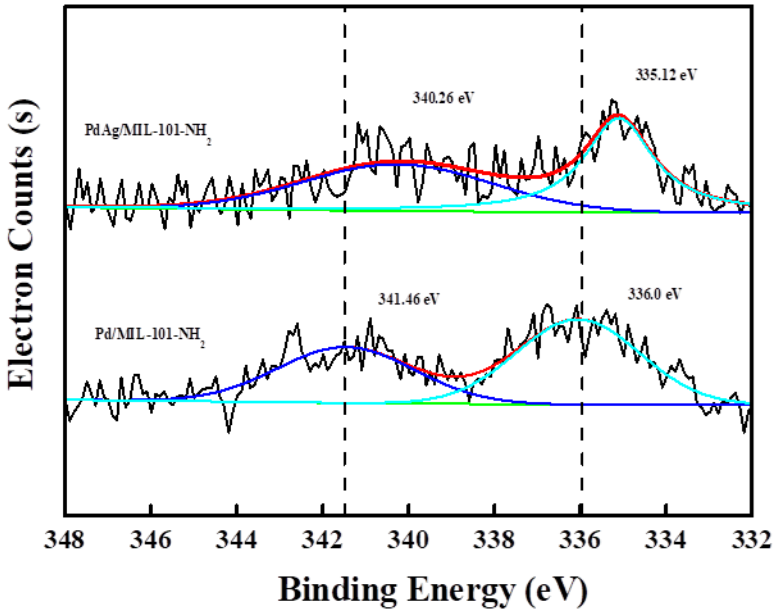

Fig. S5. The Pd 3d XPS of Pd/MIL-101-NH_2 and PdAg/MIL-101-NH_2.