Supporting Information

Supported Pt-Cu Bimetallic Catalysts: Preparation and the Synergic Effect in Their Catalytic Oxidative Degradation of Aniline

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Contents:

Some extra characterization about the $Pt_{0.5}Cu_{1.5}$ catalysts compared to the catalytic supports.

In the catalytic reaction test section (Section 3.3) it can be seen that the $Pt_{0.5}Cu_{1.5}$/AC-MR catalyst presented desirably good catalytic performance for Fenton oxidation of aniline in water. So, more characterization results focusing on the $Pt_{0.5}Cu_{1.5}$ catalysts were performed, with the results shown in the supporting information including the TG-DSC curves, SEM (SIGMA 500, Zeiss) images and TEM-EDX (Oxford-MAX80) elemental mappings.
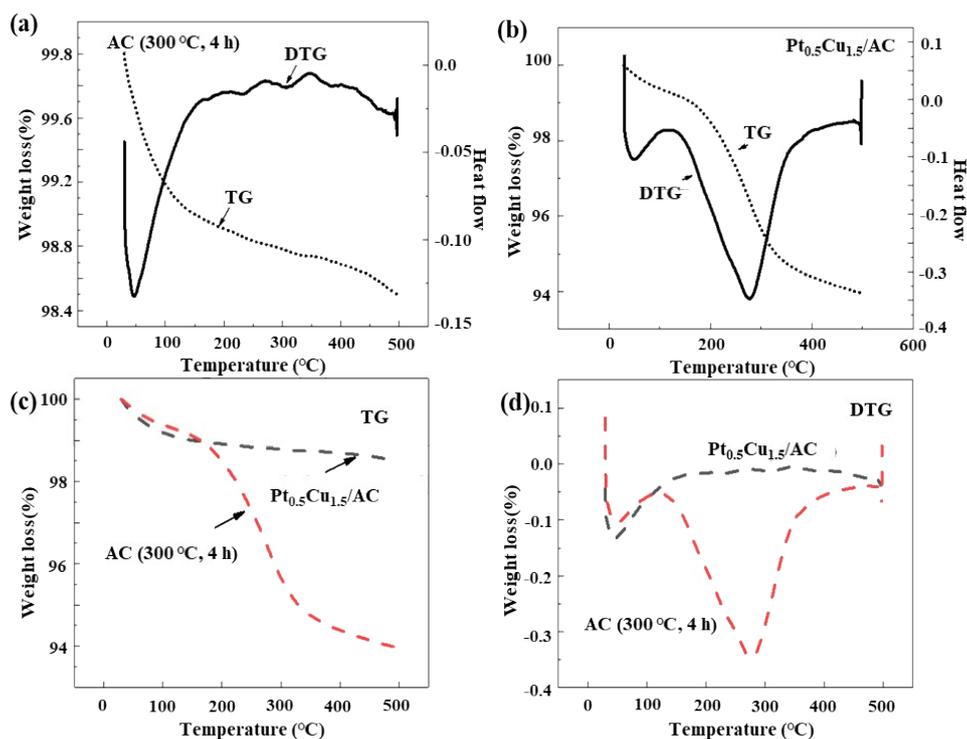
Figure S1. TG-DSC curves of the AC (calcined at 300 °C, 4h) support and the Pt$_{0.5}$Cu$_{1.5}$/AC-MR catalyst in the N$_2$ atmosphere.
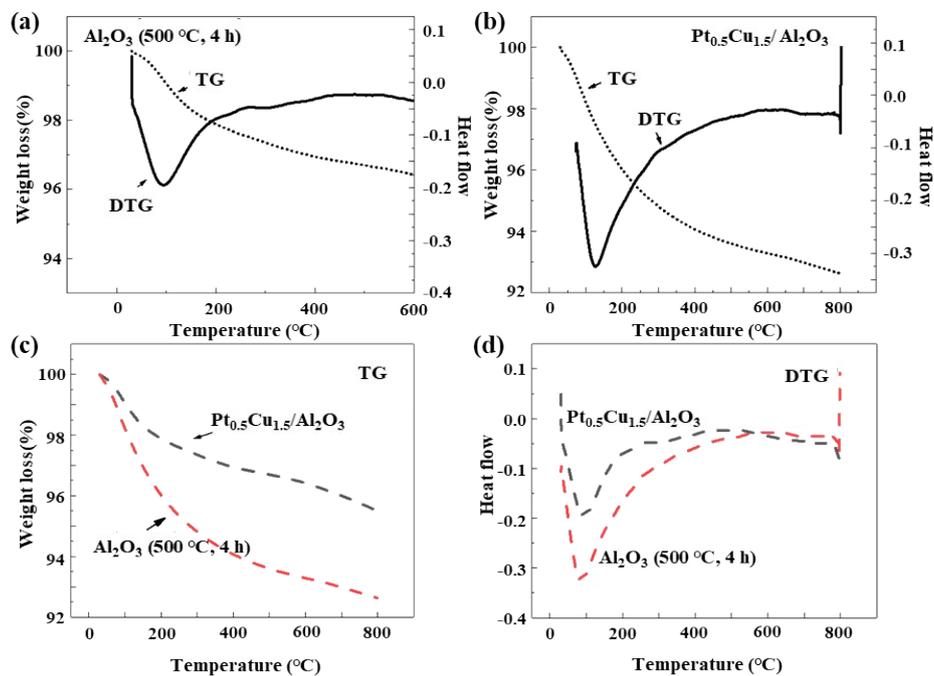
Figure S2. TG-DSC curves of the Al$_2$O$_3$ (calcined at 500 ℃, 4h) support and the Pt$_{0.5}$Cu$_{1.5}$/Al$_2$O$_3$ catalyst in the N$_2$ atmosphere.

From TG-DSC curves shown in Figures S1 and S2 it can be seen that the temperature of weight loss of AC was between 0-100 °C and that of Al_2O_3 was between 0-150 °C. These weight losses were due to the loss of moisture. A second stage of weight loss of AC took place between 400-500 °C, while it was between 700-800 °C for the case of Al_2O_3. At this stage, the main loss was the coordinated water. The weight loss rate was not too much, which was mainly due to the thermal decomposition of carriers and the internal pore structure partially collapsed at high temperatures. The TG and DTG curves of the Pt-Cu/AC samples were rather different compared to the case of AC (Figure S1). There were two distinct weight losses in Pt-Cu/AC.

The rapid weight loss between 0-50 °C was due to the loss of water in the catalyst, and the reason of significantly faster weight loss between 200-300 °C was the thermal decomposition of the AC carrier. The poor interaction between AC and active components cut down the thermal stability of AC (Panels (c) and (d) in Figure S1). Therefore, it was not feasible to reduce Pt and Cu in hydrogen atmosphere at high-temperature when AC was used as the carrier, and it also explained the necessity of methanal reduction at 80 °C and the rationality of pre-calcination of AC at 300 °C.

The TG and DTG curves of the PtCu/Al_2O_3 (Figure S2) were basically consistent with those of the Al_2O_3 support. There were also two obvious position of weight loss (Panels (c) and (d) in Figure S4), 0-150 °C and 700-800 °C, but the weight loss rate in the entire temperature range was not obvious. The reason was the same as that of the AC case, but the Pt and Cu components helped improve the thermal stability of the Al_2O_3, which strengthen the force of the support and active metal components. Therefore, the feasibility of reducing Pt and Cu with Al_2O_3 in hydrogen atmosphere and pre-calcination of the Al_2O_3 carrier at high temperatures was confirmed. In

general, the addition of Pt and Cu affects the thermal stability of the catalytic supports which was closely related to the properties of Al_2O_3 and AC.
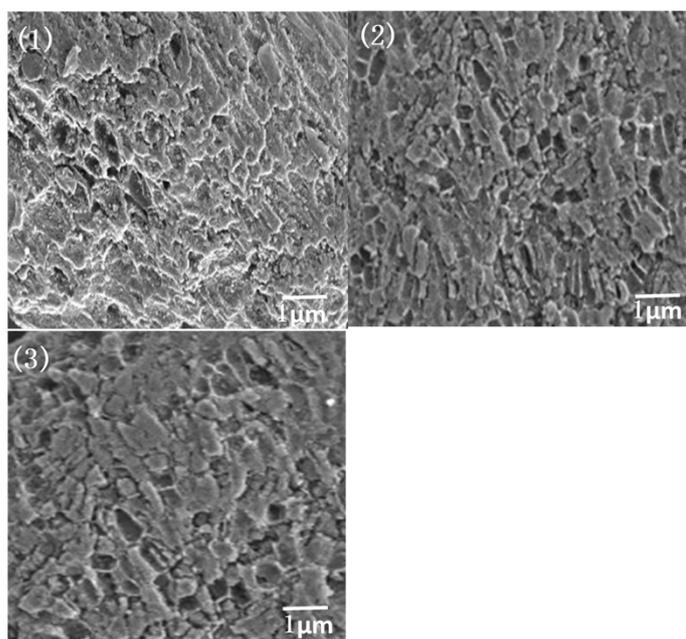
Figure S3. The SEM images (1) uncalcined AC, (2) AC calcined at 300 ℃ in air for 4h and (3) $Pt_{0.5}Cu_{1.5}$/AC-MR

There was little difference between the images of the untreated AC support sample and calcined AC support (Figure S3), reinforcing the rationality of calcining at 300 ℃ for 4 h. Furthermore, the images of the calcined AC and $Pt_{0.5}Cu_{1.5}$/AC-MR also did not change obviously, indicating that the morphology and structure of the supports was not changed during the preparation process. This may be due to the case that the AC support was basically stable when reduced in a liquid phase method at low temperatures. The specific surface area of AC was large, which made the metal components uniformly distributed, and the addition of imidazolidinyl urea during the reduction made the reaction slower and the damage to carrier smaller.
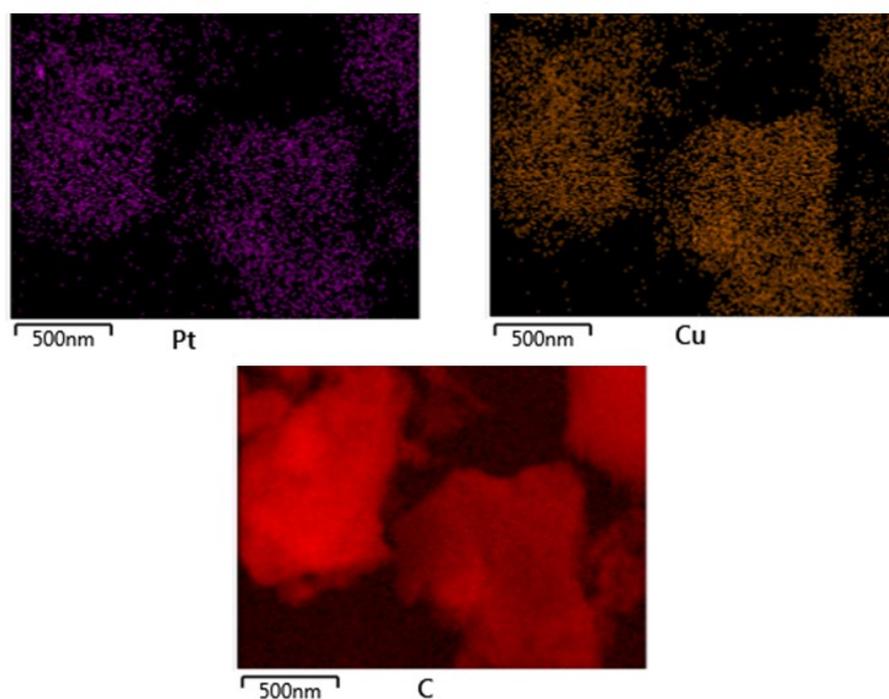
Figure S4. The TEM-EDX elemental mapping of the $Pt_{0.5}Cu_{1.5}$/AC-AR catalyst for Pt, Cu and C element as indicated in the figure.

The TEM-EDX elemental mapping chart (Figure 4S) clearly shows that the distributions of Pt, Cu and C were rather uniform. The distribution of carbon depended on the carrier AC, which further supported that the distribution of Pt and Cu elements on the AC surface was relatively uniform in a 100 nm scale. The distribution of Pt and Cu elements partially overlapped, indicating that there could be interactions between the Pt and Cu components, as reflected by the XRD results (see also in Figure 2 and Table 2).