Atomic Pt-Catalyzed Heterogeneous Anti-Markovnikov C–N Formation: Pt$_1^0$ Activating N–H for Pt$_1^\delta^+$-Activated C–C Attack

Xiaodan Ma, Zhe An, Hongyan Song, Xin Shu, Xu Xiang, and Jing He

1. INTRODUCTION

Supported Pt catalysts have been attracting significant attention for decades due to their wide application in the petrochemical industry (including catalytic re-forming and hydrogenation) and the fine chemical field (including C–O conversion and carbonylation). A number of reactions, including the formation or breakage of C–C, C–N, and C–O, have been found as being structure-sensitive so well-dispersed Pt in ensembles, clusters, or even single atoms have been required. Supported atomic Pt has been of interest in the past 10 years due to its impressive activity in CO oxidation, selective hydrogenation of nitro-compounds, CO$_2$ hydrogenation, and methane conversion. However, the application of Pt nanoparticles in the catalytic synthesis of commodity chemicals and staple compounds needs more attention.

The C–N formation is an important strategy to produce N-containing organic compounds, usually accomplished along with homogeneous catalysts. Hydroamination, one mild and atom-economic route for direct production of C–N bonds by the addition of an amine to an unsaturated carbon–carbon bond, is of particular significance and has been focused on for decades. Hydroamination has been known for a long time. With the promotion of phosphorus ligands (PPh$_3$, phosphonium halides, or alkyl phosphites) or the aid of AgOTf, Pt(II) or Pt(IV) complexes have been demonstrated effective for intra- or intermolecular hydroamination. The above Pt-catalyzed C–N addition is based on N–H bond activation followed by olefin...
insertion or the nucleophilic attack of an amine to a coordinated olefin.37–31

For the C–N formation via hydroamination, the regioselectivity control is vital and anti-Markovnikov addition is a great challenge.22,23 Few catalytic systems have been reported to be effective for anti-Markovnikov hydroamination.32–37 The first intermolecular anti-Markovnikov hydroamination has been achieved between a nonactivated aromatic olefin and morpholine with cationic rhodium complexes as catalyst.32 Then Au(I),33 Ru(II),34,35 or Ir(III)36,37 complexes have been reported to catalyze anti-Markovnikov addition. It is interesting that under the promotion of electron-deficient ligands (N-heterocyclic carbene or chelating bisphosphine),32,33 the regioselectivity for the hydroamination on Rh(I) and Au(I) complexes changes to anti-Markovnikov32,33 from Markovnikov.38–41 The C–N addition on Rh(I) is based on N–H bond activation followed by olefin insertion, but the regiochemically controlling element is still not clear.32,36,39 For Au(I), the C–N addition is achieved by nucleophilic attack of an amine to a coordinated olefin,33,40 and the regiocontrol to anti-Markovnikov is ascribed to the sp hybridization of the substrate (alkylidene cyclopropanes).33 More interesting is that Ru(II)34,43 or Ir(II)39,44 has been reported to catalyze Markovnikov C–N addition, while Ru(II)34,35 and Ir(III)36,37 complexes are found to be active for anti-Markovnikov C–N addition, although chelating ligands and Bronsted acid (TOH) are required for Ru(II)36,39 and indispensable thiol as a proton donor and visible light conditions are required for Ir(III).36,37 For Ru(II)42,43 and Ir(II),44 the Markovnikov C–N addition is achieved by amine activation, followed by alkene insertion into the Ru–N or Ir–N bond. Ru(II)34,35 complexes have been suggested to catalyze the anti-Markovnikov hydroamination by attack of amine to the π-arene intermediates. The Ir(III) photocatalyst36,37 has been proposed to oxidize amine/amide to its corresponding aminium radical cation, and then this electrophilic N-centered radical attacks an olefin to furnish a new C=N bond.

Despite all the impressive progress in homogeneous catalysis, more intensive efforts are demanded to develop (1) heterogeneous catalysis for anti-Markovnikov hydroamination of olefins and (2) a highly active heterogeneous catalyst for anti-Markovnikov hydroamination. Although Pt(II) or Pt(IV) has been reported as the most active site for hydroamination, no anti-Markovnikov C–N addition has been achieved with Pt(II) or Pt(IV) sites. The regioselective 1,2-insertion of acrylonitrile into the Pt–N bond of cis-[PtH(NHPh)(PET3)2]1 affords anti-Markovnikov product,45,46 but it is a stoichiometric reaction. Here this work reports a highly active and selective heterogeneous hydroamination with supported Pt as catalyst. Atomic Pt has been revealed to effectively catalyze anti-Markovnikov C–N formation, affording a selectivity of up to 92% to anti-Markovnikov product in the hydroamination of styrene with pyrrolidine. It is an original demonstration of (1) heterogeneous catalysis for C–N formation via anti-Markovnikov hydroamination of olefins; (2) Pt-catalyzed anti-Markovnikov hydroamination; and (3) a cooperation between varied metal sites (PtI,47 and Pt0) in monatomic Pt catalysis. The supported Pt reported here (Pt/Zn(Al)O) has been prepared simply by calcination under a H2 atm of Pt-loaded Zn and Al-containing layered double hydroxides (ZnAl-LDHs). LDHs have proved to be excellent precursors for supported Pt.47–49 This strategy is also effective for the anti-Markovnikov addition of aromatic olefins with aromatic/ aliphatic amines, aromatic/aliphatic olefins with aromatic amines, and linear aliphatic olefins with secondary aliphatic amines.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of Pt/Zn(Al)O. Zn(Al)O-supported Pt (Pt/Zn(Al)O) was produced in this work by reduction of Pt-loaded ZnAl-LDHs. ZnAl-LDHs used
for impregnation of Pt in this work were prepared by a pH-constant co-precipitation method.\textsuperscript{30,51} The (003), (006), (009), (015), (018), (110), and (113) reflections characteristic of hydrotalcite structure\textsuperscript{50} are clearly observed in the X-ray diffraction (XRD) patterns (Figure S1). Pt\textsuperscript{2+} was introduced in varied loading by incipient wetness impregnation\textsuperscript{52} of ZnAl-LDHs with positively charged Pt precursor ([(NH\textsubscript{4})\textsubscript{4}Pt]\textsuperscript{2+}). The hydrotalcite structure is well retained according to the XRD patterns (Figure S1). Calcination of Pt-impregnated ZnAl-LDHs under a reduction atmosphere produced Pt/Zn(Al)O and 0.05 wt % Pt/Zn(Al)O-18% Pt\textsubscript{1}, and (k) 0.11 wt % Pt/Zn(Al)O-0Pt\textsubscript{1}. The band to bridge-bound CO on the Pt cluster support (at 1975 cm\textsuperscript{-1})\textsuperscript{55,56} emerges at 0.11 wt % Pt loading and becomes marked (red shift to 1945 cm\textsuperscript{-1} with the emergence of 3D Pt ensembles) at 0.30 wt % Pt loading. At 0.30 wt % Pt loading, the adsorption on Pt–Pt sites\textsuperscript{14,55,56} emerges, consistent with the HAADF-STEM observations of 3D Pt ensembles (Figure 1 and Figure S3).

In the electron paramagnetic resonance (EPR) spectra (Figure 2B), except for the EPR signal resulting from oxygen vacancies\textsuperscript{57} in the Zn(Al)O support (g = 2.003), no other signal is observed for 0.01 wt % Pt/Zn(Al)O, indicating the atomic-scale Pt\textsuperscript{6+} in 0.01 wt % Pt/Zn(Al)O was actually Pt\textsuperscript{2+}. The EPR signal assigned to Pt (g = 1.971) emerges at 0.05 wt % Pt loading and gets more visible for 0.30 wt % Pt/Zn(Al)O, suggesting that the atomic-scale Pt was Pt\textsuperscript{6+} or Pt\textsuperscript{4+} in these cases. The EPR observations well account for the red shift of CO adsorption from 2085 to 2055 cm\textsuperscript{-1} in the FT-IR spectra with Pt loading increasing from 0.01 to 0.05 wt % (Figure 2A). For 0.11 wt % Pt/Zn(Al)O, the signal at g = 1.971 disappears because of the formation of a Pt–Pt bond at 100%. According to literature observations,\textsuperscript{58} the atomic-scale Pt could coordinate with lattice oxygen sites or be located at lattice Zn(Al) sites, as observed here in the HAADF-STEM images (Figure S5). The Pt\textsuperscript{6+} results from the electron transfer from Pt to O atoms, while the Pt\textsuperscript{0} binding to the Zn(Al) sites remains neutral. The ratio of Pt\textsuperscript{6+} to Pt\textsuperscript{4+} in surface Pt is determined as 0.33, 0.89, 2.03, 2.45, and 3.55 for 0.05, 0.11, 0.30, 1.01, and 2.12 wt % Pt/Zn(Al)O, according to the quantitative estimation following the reference method.\textsuperscript{59}

2.2. Catalytic Hydroamination on Pt/Zn(Al)O. 2.2.1. Active Pt Sites for C–N Formation. Pt/Zn(Al)O has then been used as a catalyst for hydroamination. In the addition of styrene and pyrrolidine (Table 1), 0.01 wt % Pt/Zn(Al)O (Table 1, entry 1) affords a TON of 253 in 8 h. No conversion of styrene and pyrrolidine has occurred on Zn(Al)O. The TON increases to 265 on 0.05 wt % Pt/Zn(Al)O (Table 1, entry 2) and then decreases to 225, 156, 103, and 49 for 0.11, 0.30, 1.01, and 2.12 wt % Pt/Zn(Al)O (Table 1, entries 3–6). The TON displays a rapid decrease with decreasing Pt\textsubscript{1} ratio or increasing Pt–Pt site fraction (Figure S6), indicating that Pt\textsubscript{1} sites are the active sites for C–N addition. The 5.05 wt % Pt/Zn(Al)O was found to be totally inactive for the reaction (Table 1, entry 7), confirming that Pt–Pt sites are not active for the reaction.

To define the active sites for C–N formation, 0.11 wt % Pt/Zn(Al)O has been further treated to tailor the ratio of Pt\textsubscript{1} in total Pt to be 100% (0.11 wt % Pt/Zn(Al)O-re-100% Pt\textsubscript{1}, Figure 1) or 14% (0.11 wt % Pt/Zn(Al)O-re-14% Pt\textsubscript{1}, Figure S7). Or in another way, 0.11 wt % Pt/Zn(Al)O has been prepared directly to tailor Pt sites as Pt\textsubscript{1} at 100% (0.11 wt % Pt/Zn(Al)O-100% Pt\textsubscript{1}), 18% (0.11 wt % Pt/Zn(Al)O-18% Pt\textsubscript{1}), or 0 (0.11 wt % Pt/Zn(Al)O-0Pt\textsubscript{1}) (Figures 1 and S8). According to the in situ FT-IR spectra of CO adsorption (Figure 2A), for either 0.11 wt % Pt/Zn(Al)O-re-100% Pt\textsubscript{1} or 0.11 wt % Pt/Zn(Al)O-100% Pt\textsubscript{1}, the band at 2020
cm$^{-1}$) predominates over Pt$_{1}^{0}$ (the band at 2070 cm$^{-1}$) in quantity, and the ratio of Pt$_{1}^{0}$ to Pt$_{1}^{\delta}$ was determined as 2.12 or 1.78. More atomic-scale Pt$_{1}$ are observed to be located at lattice Zn(Al) sites from the HAADF-STEM images (Figure 3).

Table 1. Pt-Catalyzed C–N Addition of Styrene and Pyrrolidine$^{a}$

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<th>entry</th>
<th>catalyst</th>
<th>Pt$_{1}$ ratio in surface Pt$^{b}$</th>
<th>Pt$<em>{1}^{0}$/Pt$</em>{1}^{\delta}$</th>
<th>a-M/%</th>
<th>M</th>
<th>TON$^{c}$</th>
<th>TON$<em>{Pt</em>{1}}$</th>
<th>catalyst</th>
<th>Pt$_{1}$ ratio in surface Pt$^{b}$</th>
<th>Pt$<em>{1}^{0}$/Pt$</em>{1}^{\delta}$</th>
<th>a-M/%</th>
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<th>TON$^{c}$</th>
<th>TON$<em>{Pt</em>{1}}$</th>
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<td>0.01 wt % Pt/Zn(Al)O</td>
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<td>0 (Pt$<em>{1}^{0}$/Pt$</em>{1}^{\delta}$)</td>
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<td>90 (90)</td>
<td>253</td>
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<td>0.05 wt % Pt/Zn(Al)O</td>
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<td>0.33</td>
<td>55 (53)</td>
<td>43 (45)</td>
<td>265</td>
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<tr>
<td>3</td>
<td>0.11 wt % Pt/Zn(Al)O</td>
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<td>0.89</td>
<td>85 (86)</td>
<td>13 (12)</td>
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<td>0.30 wt % Pt/Zn(Al)O</td>
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<td>2.03</td>
<td>90 (92)</td>
<td>8 (7)</td>
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<td>1.01 wt % Pt/Zn(Al)O</td>
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<td>2.45</td>
<td>92 (93)</td>
<td>7 (5)</td>
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<td>2.12</td>
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<td>1.78</td>
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<td>0.11 wt % Pt/Zn(Al)O-re-18% Pt$_{1}$</td>
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<td>0.19</td>
<td>36</td>
<td>61</td>
<td>46</td>
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<td>0.11 wt % Pt/Zn(Al)O-re-0% Pt$_{1}$</td>
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<td>0</td>
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$^{a}$Reaction conditions: styrene (0.6 mmol), pyrrolidine (0.3 mmol), catalysts (exposed Pt = 0.067 mol %), and solvent (isopropanol 1.5 mL) in a Schlenk tube, $T$ = 60 °C, $t$ = 8 h. $^{b}$Pt$_{1}$ and total Pt$_{1}$ were estimated from HAADF-STEM images; Pt$_{1}$ + Pt$_{1}^{\delta}$ = surface Pt. $^{c}$Pt$_{1}^{0}$ was estimated from in situ FT-IR of CO adsorption; Pt$_{1}^{0}$ + Pt$_{1}^{\delta}$ = Pt$_{1}$. $^{d}$TON was calculated based on the number of surface Pt sites. The number of surface Pt sites was estimated from the Pt dispersion ($D_{pt}$ in Table S1). $^{e}$TON$_{Pt_{1}}$ was based on Pt$_{1}$ sites. $^{f}$The numbers in parentheses are reproduced data.
accounting for the higher ratio of Pt\(^{1+}\) to Pt\(^{0}\). The EPR signals assigned to Pt\(^{1+}\) are more visible for 0.11 wt % Pt/Zn(Al)O-re-100% Pt\(^{1+}\) (Figure 2B), consistent with higher Pt\(^{1+}\) sites than 0.11 wt % Pt/Zn(Al)O-re-100% Pt\(^{1+}\) (Table 1, entries 8 and 9), both from the post-treatment of 0.11 wt % Pt/Zn(Al)O, it is found that an increased Pt\(^{1+}\) ratio affords a lower TON (Table 1, entry 9 vs 3), while a decreased Pt\(^{1+}\) ratio affords a lower TON (Table 1, entry 9 vs 3), further demonstrating that Pt\(^{1+}\) are the active sites. Similar catalytic results are observed with 0.11 wt % Pt/Zn(Al)O-re-100% Pt\(^{1+}\) and 0.11 wt % Pt/Zn(Al)O-re-14% Pt\(^{1+}\) (Table 1, entries 10 and 11). An increased Pt\(^{1+}\) ratio affords a higher TON (Table 1, entry 10 vs 3), while a decreased Pt\(^{1+}\) ratio affords a lower TON (Table 1, entry 11 vs 3); 100% Pt–Pt affords no TON (Table 1, entry 12), further confirming that Pt\(^{1+}\) are the active sites for styrene adsorption. The signals of an unpaired electron at 1619 cm\(^{-1}\) on Pt\(^{1+}\), blue-shifting to 1622 cm\(^{-1}\) on Pt\(^{1+}\) and to 1630 cm\(^{-1}\) on Pt\(^{0}\), suggest that the interactions between Pt\(^{1+}\) and C–N becomes weaker with increasing electron density on Pt\(^{1+}\) sites (Figure 3A, a–f). The δ-bonding of styrene to Pt\(^{1+}\) is accorded at 2855, 2910, and 2952 cm\(^{-1}\) when Pt–Pt appears and becomes predominant with the increase in Pt–Pt ratio (Figure 3A, e–h). Relating the catalytic results in Table 1 to styrene adsorption, it can be deduced that the styrene activation in δ-bonding mode on Pt\(^{1+}\) is responsible for the C–N addition, whether on Pt\(^{1+}\), Pt\(^{1+}\), or Pt\(^{0}\).

In the FT-IR spectra of pyrrolidine adsorption (Figure 3B), the CH\(_2\) stretching vibrations of amine (at 2970 and 2880 cm\(^{-1}\)) are observed for each Pt/Zn(Al)O, suggest that both of Pt\(^{1+}\) and Pt–Pt sites have the ability to adsorb amine. The N–H stretching vibration\(^{65,66}\) is observed at 3220 cm\(^{-1}\) on electron-deficient Pt\(^{1+}\) or Pt\(^{1+}\) (Figure 3B, b and c), but disappears when Pt\(^{0}\) increases (Figure 3B, d–f) and blue shifts to 3230 cm\(^{-1}\) on Pt–Pt sites (Figure 3B, g and h). The results show that in the activation of pyrrolidine, N–H cleavage occurs on Pt\(^{1+}\) while N–H is reserved on the electron-deficient Pt\(^{1+}\) or Pt\(^{1+}\) or Pt–Pt sites. The EPR spectra for Pt/Zn(Al)O with pyrrolidine adsorbed (Figure 3C) confirm the observations in FT-IR spectra. The signal of an unpaired electron at g = 1.971 disappears for Pt\(^{1+}\) and does not change for Pt\(^{1+}\) or Pt\(^{0}\) or Pt–Pt sites after pyrrolidine adsorption, suggesting pyrrolidine is adsorbed with the N radical on Pt\(^{1+}\) sites, adhering an electrophilic N center, while with N electron pairs on Pt\(^{1+}\) or Pt\(^{1+}\) or Pt–Pt sites, adhering a nucleophilic N center. It is consistent with the theoretical prediction\(^{69,70}\) that Pt\(^{0}\) sites can adsorb and activate the amines to be electrophilic. Relating the catalytic results in Table 1 to pyrrolidine adsorption, it can be deduced that the pyrrolidine activation with N–H cleavage on Pt\(^{1+}\), other than Pt\(^{1+}\), Pt\(^{1+}\), or Pt–Pt, is responsible for the anti-Markovnikov C–N addition.

The FT-IR spectra of styrene and pyrrolidine competitive adsorption on either Pt\(^{1+}\) or the Pt\(^{1+}\) with varied Pt\(^{1+}\) or Pt\(^{1+}\) ratio (Figure 3D) show that δ-bonded styrene on Pt\(^{1+}\) (Figure 3D, a) can be completely replaced by pyrrolidine (Figure 3D, b), and the pyrrolidine adsorbed on Pt\(^{1+}\) sites (Figure 3D, c) can be partially replaced by styrene (Figure 3D, d), suggesting both the styrene and pyrrolidine are adsorbed on Pt\(^{1+}\) sites dynamically. The pyrrolidine on Pt\(^{1+}\) is easily replaced by styrene while the replacement becomes harder with increasing...
Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio, suggesting that nucleophilic N–H adsorbed on Pt\textsuperscript{0} or Pt\textsuperscript{0} sites can be easily replaced, but the electrophilic N adsorbed on Pt\textsuperscript{0} cannot be replaced by styrene. Thus, it could be deduced that the nucleophilic N–H and C=C on Pt\textsuperscript{0} or Pt\textsuperscript{0} contribute to the Markovnikov addition, while the C=C activated on Pt\textsuperscript{0} sites and the electrophilic N activated on Pt\textsuperscript{0} sites are proposed to be responsible for the anti-Markovnikov C–N formation.

2.3.2. Cooperating Catalysis between Pt\textsuperscript{0} and Pt\textsuperscript{0}. To figure out the cooperativity between Pt\textsuperscript{0} and Pt\textsuperscript{0} in the anti-Markovnikov C–N formation, the in situ FT-IR spectra of the styrene and pyrrolidine adsorption—desorption on Pt\textsuperscript{0} have been recorded (Figure 4A–C). The styrene is difficult to desorb from the Pt/Zn(Al)O with Pt\textsuperscript{0} dominant (Figure 4A, a) and becomes easier with increasing Pt\textsuperscript{0} (Figure 4A, b), and pyrrolidine is easy to desorb from the Pt/Zn(Al)O with Pt\textsuperscript{0} dominant (Figure 4B, a) and becomes more difficult with increasing Pt\textsuperscript{0} (Figure 4B, b). The results confirm that C=C is preferred to be activated on Pt\textsuperscript{0} and pyrrolidine on Pt\textsuperscript{0} sites. In the coadsorption (Figure 4C), the styrene adsorption predominates over pyrrolidine on the Pt/Zn(Al)O with Pt\textsuperscript{0} dominant (Figure 4C, a), while pyrrolidine adsorption predominates over styrene on the Pt/Zn(Al)O with Pt\textsuperscript{0} dominant (Figure 4C, b). But either styrene or pyrrolidine adsorption hardly changes in the desorption (Figure 4C), indicative of the simultaneous activation of styrene and pyrrolidine. The coadsorption on the Pt/Zn(Al)O with varied Pt dispersion (Figure 4D) displays a decrease in styrene adsorption and meanwhile an increase in pyrrolidine adsorption with the increase of Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio, confirming the simultaneous activation of styrene and pyrrolidine. In the simultaneous activation of styrene with pyrrolidine (Figure S10), C=C is π-bonded to Pt\textsuperscript{0} (1621–1622 cm\textsuperscript{-1}) rather than Pt\textsuperscript{0} sites (1630 cm\textsuperscript{-1}). In the FT-IR spectra of styrene and pyrrolidine coadsorption on Pt–Pt sites (Figure S11), no pyrrolidine adsorption but di-σ-bonded styrene is observed, suggesting the di-σ-bonded adsorption of styrene on Pt–Pt sites is not only inactive itself but also so strong as to prohibit the activation of pyrrolidine.

Therefore, a possible mechanism for the anti-Markovnikov C–N formation is proposed (Figure 4E). The styrene is initially π-bonded to Pt\textsuperscript{0} sites and the pyrrolidine adsorbed on Pt\textsuperscript{0} sites with N–H cleavage. Then, it is the attack of activated C=C on Pt\textsuperscript{0} sites to the electrophilic N on Pt\textsuperscript{0} sites that is responsible for the anti-Markovnikov C–N formation. Higher TONPt\textsubscript{0} has been achieved with a controlled Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of ca. 2 (Table 1, entry 4 or 10), meaning a Cooperating catalysis between Pt\textsuperscript{0} and Pt\textsuperscript{0} for C–N formation. Two Pt\textsuperscript{0} sites are needed for the Pt–N and Pt–H formation, while one Pt\textsuperscript{0} for the C=C activation, although it is a pity that no Pt–H bands are observed in the FT-IR spectra.

2.4. Reusability. The spent catalyst (0.11 wt % Pt/Zn(Al)O) has been recycled (Figure 5) simply by centrifugation and reused without any regeneration. Almost

Figure 4. In situ FT-IR spectra of (A) styrene, (B) pyrrolidine, and (C) their mixture with the time-dependent desorption on Pt/Zn(Al)O with Pt present as Pt\textsuperscript{0} at 100% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of (a) 0.33 and (b) 1.78. (D) In situ FT-IR spectra for the coadsorption of pyrrolidine and styrene on Pt/Zn(Al)O with Pt present as (a) Pt\textsuperscript{0} at 100% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 0.33, (b) Pt\textsuperscript{0} at 76% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 0.89, (c) Pt\textsuperscript{0} at 100% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 1.78, (d) Pt\textsuperscript{0} at 47% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 2.03, (e) Pt\textsuperscript{0} at 100% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 2.12, (f) Pt\textsuperscript{0} at 38% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 2.45, and (g) Pt\textsuperscript{0} at 50% with a Pt\textsuperscript{0}/Pt\textsuperscript{0} ratio of 3.55. (E) Possible reaction pathway for the anti-Markovnikov C–N formation: red: O2; blue-gray: Zn2+; magenta: Al3+; green: Pt\textsuperscript{0}; aqua: Pt\textsuperscript{0}; gray: C; white: H; blue: N.

Figure 5. (A) Recycling of 0.11 wt % Pt/Zn(Al)O–re-100% Pt\textsuperscript{0} has been recycled (Figure 5) simply by centrifugation and reused without any regeneration. Almost...
no decrease in TON (>310) and the selectivity for anti-Markovnikov (90%) are observed in 10 runs (Figure 5A). Correspondingly, the atomic dispersion of Pt is well retained in the catalysis, according to the HAADF-STEM image (Figure 5B). According to the in situ FT-IR spectra of CO adsorption (Figure 5C), for the used 0.11 wt % Pt/Zn(Al)O-re-100% Pt1, Pt1\(^0\) (the band at 2005 cm\(^{-1}\)) predominates over Pt1\(^{δ+}\) (the band at 2070 cm\(^{-1}\)) in quantity, and the ratio of Pt1\(^0\) to Pt1\(^{δ+}\) was determined as 2.35, being maintained at a similar level to the fresh 0.11 wt % Pt/Zn(Al)O-re-100% Pt1 (a Pt1\(^0\)/Pt1\(^{δ+}\) ratio of 2.12).

2.5. Substrate Scope and Tolerance. The substrate scope and tolerance were then explored (Table 2). In addition to styrene (Table 1), aliphatic olefin (n-octene here) can also carry out anti-Markovnikov hydroamination with pyrrolidine, affording an anti-Markovnikov selectivity of 83% and TON of 61 (Table 2, entry 1). In addition to pyrrolidine (Table 1), aromatic aniline, aliphatic linear secondary amines (n-ethyl-n-butylamine here), and aliphatic linear primary amines (n-pentylamine here) can carry out hydroamination with styrene, affording an anti-Markovnikov selectivity of 86–91% and a TON of 83–296 (Table 2, entries 2–4). Substituted styrene (cyano, methyl, methoxy substituents) and aliphatic olefin (n-octene here) can all carry out anti-Markovnikov hydroamination with aromatic aniline, which is more challenging than with pyrrolidine, affording an anti-Markovnikov selectivity of 85–93% and TON of 72–325 (Table 2, entries 5–8). An intramolecular C–N addition of N-4-hexen-1-yl-benzenemethanamine to anti-Markovnikov product has also been successfully accomplished in a selectivity of 87% and a TON of 155. It is a pity that the C–N addition of aliphatic olefins with aliphatic linear amines (n-pentylamine with n-octene, n-hexene, 2-methylpentene, 1-methylhexene, or 4-nitrilehexene; n-octene with N-ethyl-n-butylamine, N-ethyl-n-hexylamine, or N-methylcyclohexylamine here), which has not been achieved in previous report,\(^{22,23}\) was also not available with this catalyst. According to the literature,\(^{22,23}\) the benzene ring serves as an electron-withdrawing ligand for the C\(_{\equiv}\)C or NH moiety. Thus, the electrophilic N activated by the Pt1\(^0\) can be more electrophilic with the benzene ring, and nucleophilic β-C activated by Pt1\(^{δ+}\) can be more nucleophilic. Without an electron-withdrawing aromatic moiety, aliphatic linear olefins or aliphatic linear amines are more difficult to be activated.

3. CONCLUSIONS

This work has demonstrated successful C–N addition via hydroamination of olefins with amines on supported atomic-scale Pt. Atomic Pt sites have been identified as the active sites by tailoring Pt dispersion. Relating the chemical state of atomic Pt to the activity and regioselectivity in intermolecular
hydroamination, it has been found that Pt\textsuperscript{2+} is active for Markovnikov C–N formation, while atomic Pt (Pt\textsuperscript{0} and Pt\textsuperscript{6}) contributes to anti-Markovnikov C–N formation. A TON of up to 331 and a selectivity of 92\% to anti-Markovnikov has been afforded over atomic Pt. A cooperating catalysis between Pt\textsuperscript{6} and Pt\textsuperscript{0} in the anti-Markovnikov C–N formation of styrene and pyrrolidine has been revealed by EPR spectra and in situ FT-IR spectra of adsorption–desorption of styrene and/or pyrrolidine. The Pt\textsuperscript{0} sites are revealed to activate N for the attack of Pt\textsuperscript{2+}-activated C=C. This strategy is also effective for the anti-Markovnikov addition of aromatic amines, aromatic/aliphatic amines, aromatic/aliphatic olefins with aromatic amines, and linear aliphatic olefins with secondary aliphatic amines.

4. EXPERIMENTAL SECTION

4.1. Preparation. ZnAl-LDHs. ZnAl-LDHs were prepared in a pH constant-co-precipitation method. Typically, Zn\textsubscript{(NO\textsubscript{3})\textsubscript{2}} \cdot 6H\textsubscript{2}O (0.04 mol) and Al(NO\textsubscript{3})\textsubscript{3} \cdot 9H\textsubscript{2}O (0.02 mol) in 100 mL of deionized water and a solution of NaOH (0.08 mol) and Na\textsubscript{2}CO\textsubscript{3} (0.01 mol) in 100 mL of deionized water were simultaneously added drop by drop to a round-bottomed flask with 300 mL of deionized water under constant pH (10.0), and then the mixture was aged at 60 °C for 12 h under stirring. The solid was filtrated, washed thoroughly with deionized water until the filtrate was neutral, and dried at 60 °C in an air oven overnight.

\[ \text{Pt(NH\textsubscript{3})\textsubscript{2}}\textsubscript{2+} \text{ZnAl-LDHs} \]  

Pt was loaded on ZnAl-LDHs by the incipient wetness impregnation method. Typically, 1.5 g of ZnAl-LDHs was impregnated with 1 mL of aqueous solution containing 270 \( \mu \)mol of platinum tetrathiaimine (PTA, \[ \text{Pt(NH\textsubscript{3})\textsubscript{4}}\textsuperscript{2+} \]) \textsuperscript{12}, giving 3.54 \% Pt loading on ZnAl-LDHs. In the same method, \[ \text{Pt(NH\textsubscript{3})\textsubscript{2}}\textsubscript{2+} \text{ZnAl-LDHs} \] in Pt loadings of 0.008, 0.04, 0.07, 0.09, 0.22, 0.73, and 1.50 \% were prepared with aqueous solution containing 0.6, 3.0, 5.2, 7.2, 15.7, 53.2, and 112.0 \( \mu \)mol of PTA.

\[ \text{Pt/Zn(Al)} \]  

Pt-loaded Zn-AlDO was produced by calcination of \[ \text{Pt(NH\textsubscript{3})\textsubscript{2}}\textsuperscript{2+} \text{ZnAl-LDHs} \] under a reduction atmosphere. Typically, \[ \text{Pt(NH\textsubscript{3})\textsubscript{2}}\textsuperscript{2+} \text{ZnAl-LDHs} \] in varying Pt loadings was calcined at 550 °C in hydrogen flow for 2 h with the temperature programmed from room temperature to 550 °C at a rate of 5 °C min\textsuperscript{-1}. The samples are denoted as 0.01 wt % Pt/Zn(Al)O, 0.05 wt % Pt/Zn(Al)O, 0.11 wt % Pt/Zn(Al)O, 0.30 wt % Pt/Zn(Al)O, 2.12 wt % Pt/Zn(Al)O, and 5.05 wt % Pt/Zn(Al)O, according to the inductively coupled plasma emission spectrometer (ICP-ES) determination.

\[ \text{Pt/Zn(Al)} \]  

The quantitative analysis for Pt was performed on a Micrometric Chemisorb 2750 chemisorption instrument with a thermal conductivity detector by the HOT method and the procedure reported in the literature (see details in SI 2.2.1). In situ FT-IR of CO adsorption in transmission mode was recorded on a Nicolet 380 model (Thermo Electron Corporation) equipped with a high-temperature cell fitted with BaF\textsubscript{2} windows and an MCT-A detector, with a resolution of 2 cm\textsuperscript{-1} using 64 scans (see details in SI 2.2.2). In situ FT-IR of styrene and pyrrolidine adsorption in transmission mode was recorded on a Nicolet 380 model (Thermo Electron Corporation) equipped with a high-temperature cell fitted with BaF\textsubscript{2} windows and an MCT-A detector, with a resolution of 2 cm\textsuperscript{-1} using 64 scans (see details in SI 2.2.3).

4.2. Characterizations. The powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu K\alpha radiation (\( \lambda = 0.154 \) 18 nm) at 40 kV and 30 mA, with a scanning rate of 5 °C min\textsuperscript{-1}. The quantitative analysis for Pt was performed on a Shimadzu ICPS-7500 ICP-ES. Before measurements, 5 mg of the sample was dissolved by nitric acid and transferred to a volumetric flask, diluted to 10 mL with deionized water. HAADF-STEM images were taken on a JEM-ARM 200F electron microscope capable of high-resolution. The samples for STEM measurements were pretreated in air at 550 °C for 2 h, cooled to room temperature, and then reduced at 280 °C in H\textsubscript{2} for 1 h. The temperature was programmed from room temperature to 550 or 280 °C at a rate of 5 °C min\textsuperscript{-1}.

The 0.11 wt % Pt/Zn(Al)O-re-100% Pt, Pt/Zn(Al)O (0.11 wt %) was first treated in air at 550 °C for 2 h, cooled to room temperature, and then reduced at 280 °C in H\textsubscript{2} for 1 h. The temperature was programmed from room temperature to 550 or 280 °C at a rate of 5 °C min\textsuperscript{-1}.

The 0.11 wt % Pt/Zn(Al)O-re-14-14% Pt, 0.11 wt % Pt/Zn(Al)O-re-18-18% Pt, 0.11 wt % Pt/Zn(Al)O-re-18-21% Pt, and 0.11 wt % Pt/Zn(Al)O-re-40% Pt were also prepared (see details in SI 2.1).

Experimental details and characterizations (PDF)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c02997.

AUTHOR INFORMATION

Corresponding Author

Jing He – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China;  
oicr.org/0000-0002-9240-6675; Phone: +86-10-64425280; Email: jinghe@263.net.cn, hejing@mail.buct.edu.cn; Fax: +86-10-64425385

Authors

Xiaodan Ma – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

Zhe An – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

Hongyan Song – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

AUTHOR INFORMATION

Corresponding Author

Jing He – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China;  
oicr.org/0000-0002-9240-6675; Phone: +86-10-64425280; Email: jinghe@263.net.cn, hejing@mail.buct.edu.cn; Fax: +86-10-64425385

Authors

Xiaodan Ma – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

Zhe An – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

Hongyan Song – State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

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Experimental details and characterizations (PDF)
Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China
Xin Shu — State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China
Xu Xiang — State Key Laboratory of Chemical Resource Engineering & Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c02997

Notes
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