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Insight into Platinum Poisoning Effect on Cu-SSZ-13 in Selective Catalytic Reduction of NO_x with NH₃

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Abstract: Platinum's (Pt) poisoning effect on Cu-SSZ-13 and its regeneration were investigated. The Pt enhanced the parallel reactions, such as NH₃ oxidation and NO oxidation reactions, which decreased the deNO_x activities. In the temperature range below 330 °C, the deactivation of Cu-SSZ-13 by Pt poisoning was primarily caused by the overconsumption of NH₃, due to the enhanced NH₃-selective oxidation reaction, while the formation of NO_x in NH₃ oxidation and NO oxidation into NO₂ further aggravated the degradation when the temperature was above 460 °C. The non-selective NH₃ oxidation and non-selective NO_x catalytic reduction reactions resulted in increased N₂O formation over Pt-doped samples. The transformation of Pt⁰ into PtO_x after hydrothermal aging recovered the deNO_x activities of the Pt-poisoned samples.

Keywords: Pt poisoning; Cu-SSZ-13; NH₃-SCR; regeneration

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1. Introduction

Cu-exchanged SSZ-13 has recently been commercialized as a catalyst for the selective catalytic reduction of NO_x with a NH₃ (NH₃-SCR) section in a diesel engine exhaust after-treatment system [1]. For automotive applications, there is a critical requirement for the application life of the SCR catalyst in order to meet the NO_x emission standard [2].

Sulfur poisoning (including SO₂ and SO₃), hydrothermal aging, and chemical contamination (such as Ca, P, Pt, Pd, etc.) would deactivate the Cu-SSZ-13 [3–7]. Specific to the sulfur poisoning, the deactivation caused by SO₂ poisoning is mostly reversible, as NH₄HSO₄ and CuHSO₄ intermediates formed on Cu-SSZ-13 can be decomposed after thermal treatment at high temperatures [8]. However, the deactivation caused by SO₃ poisoning due to the formation of copper sulfate and structural damage is irreversible [3,7].

Specific to hydrothermal treatment, the deactivation of Cu-SSZ-13 is typically attributed to the destruction and transformation of cupric sites from SCR-active to -inactive forms, which is irreversible [5,9]. Nevertheless, the effect of chemical poisoning on Cu-SSZ-13 is more complex than that of sulfur poisoning and hydrothermal treatment. In addition to the poisoning effect of the destruction and transformation of isolated Cu²⁺ ions into inactive forms [6,10–12], the additional chemical contaminants may act as active sites that catalyze side reactions in the NH₃-SCR reaction system.

In general, the standard SCR reaction is the target pathway for the NO_x elimination in the NH₃-SCR system, as shown in Reaction 1 (R.1):

However, some parallel reactions also occur along with the standard reaction, as shown in R.2–R.7.

Without the contaminants, the rate of the standard NH_3 -SCR reaction is much higher than that of the side reactions when using the Cu-SSZ-13 as catalyst, because the isolated Cu^{2+} ions primarily catalyze the standard reaction [13,14]. Therefore, the Cu-SSZ-13 exhibited excellent deNO_x activity. However, the presence of additional chemical contamination sites might help to catalyze the reactions in R.2–R.7, which increases the parallel reactions rate [6]. As such, the competition between the parallel reactions (R.2–R.7) and the standard reaction (R.1) would reduce the SCR activity of Cu-SSZ-13 (R.1) [6].

Pt is a typical chemical contamination species for Cu-SSZ-13 [6]. In an after-treatment system, the SCR catalyst is located downstream of the diesel oxidation catalyst (DOC) and diesel particulate filter (DPF) sections [15]. The Pt coating in DOC and DPF would be volatilized and deposited on the SCR catalyst due to the high exhaust temperature, which significantly decreases the deNO_x activities of the SCR catalysts [16–18]. The previous work in the industry investigated the Pt poisoning effect on Cu-SSZ-13 with Pt loading in the weight range of 0–0.016 wt. % [19]. This work found that 0.008 wt. % was the threshold with little influence on the activity of Cu-SSZ-13, above which the activity decreased significantly. Lezcano-Gonzalez et al. [6] investigated the effect of series pollutants (Pt, Zn, Ca and P) on Cu/SSZ-13 catalysts during the NH_3 -SCR process, and Pt poisoning (with Pt loading of 1–2 wt. %) resulted in the NO_x conversion reduction, which was predicted to be due to the Pt species' oxidation ability that promoted the NH_3 oxidation reaction (R.3–R.6). A similar poisoning effect of Pt was also observed on Cu-SAPO-34 [18]. It should be noted that the amount of Pt has a significant impact on the SCR performance of Cu-SSZ-13 [19]. Therefore, the effect of a Pt loading of 0.01–0.1 wt. % on Cu-SSZ-13 should be investigated. In addition, the hydrothermal treatment effect on the Pt poisoning influence on Pt/Cu-SSZ-13 has also not been reported.

In this work, a series of Pt/Cu-SSZ-13 samples with different Pt doping contents (0.01–0.1 wt. %) was prepared to elucidate the poisoning impact of Pt on the NH_3 -SCR performance of the catalysts. The Pt's influence on the NH_3 -SCR reaction network was investigated based on transient reaction experiments. The Pt poisoning effects on the structure and cupric sites of Cu-SSZ-13 were evaluated by XRD and H_2 -TPR measurements. The effect of hydrothermal treatment on the recovery of a Pt-contaminated sample was analyzed.

2. Results and Discussion

2.1. Influence of Pt Poisoning on the Catalytic Performance of Cu-SSZ-13

Figure 1 shows the SCR performance of the Cu-SSZ-13 and Pt poisoning samples with and without hydrothermal treatment. The Cu-SSZ-13 presented above 75% NO_x conversion at 150–550 °C, and the N_2O concentration was below 20 ppm, indicating that the NO and NH_3 were primarily converted via the standard NH_3 -SCR reaction (R.1) pathway over Cu-SSZ-13. For Cu-SSZ-13 doping with Pt (Pt/Cu), the NO_x conversion decreased with increasing Pt loading, particularly in the temperature range above 300 °C. Notably, larger concentrations of N_2O were formed in Pt/Cu samples than in Cu-SSZ-13 (Figure 2). This indicates that the parallel reactions (e.g., R.2–R.7) should be accelerated by Pt sites [18,20]. In addition, the N_2O formation shows a volcanic curve, with the peaks at around 330 °C in the Pt-doped samples. This demonstrates that the parallel reactions (such as R.2 and R.4) contributing to the N_2O formation mainly affect the NO_x conversion below 330 °C. In other words, some other parallel reactions resulted in a decrease in deNO_x activity above 330 °C. This part will be further analyzed in Section 3.2, accompanied by

the transient reaction results. In addition, in our work, the NO_x conversion decreased with the increasing Pt loading from 0.01 to 0.1 wt. % (Figure 1). However, in the work by Lezcano-Gonzalez et al. [6], the Pt-poisoned Cu-SSZ-13 showed a similar loss of NO_x conversion in the Cu-SSZ-13 with Pt loadings of 1 and 2 wt. %. This indicates that the Pt poisoning effect might not change significantly when the Pt loading reaches a high content (around 1 wt.%).

Figure 1. NO_x conversion during standard NH_3 –SCR with the fresh and aged samples. The reaction conditions: 500 ppm NH_3 , 500 ppm NO , 5% O_2 , 5% H_2O , N_2 balance, flow rate at 500 mL/min, 100 mg of catalyst.

Figure 2. N_2O concentration during standard NH_3 –SCR of fresh and aged catalyst samples. The reaction conditions: 500 ppm NH_3 , 500 ppm NO , 5% O_2 , 5% H_2O , N_2 balance, flow rate at 500 mL/min, 100 mg of catalyst.

The NO_x conversion of Cu-SSZ-13 decreased after hydrothermal treatment. However, the hydrothermally aged PtxCu samples showed only slightly inferior NO_x conversions as compared to the Cu-H sample, which was much higher than its fresh counterparts, as shown in Figures 1 and 2. In addition, the N_2O formation over the PtxCu samples decreased after hydrothermal treatment. This demonstrates that the hydrothermal treatment partially recovered the activity of Pt-poisoned Cu-SSZ-13.

2.2. Transient Reactions

To investigate the effect of Pt on the standard NH_3 -SCR reaction and parallel reactions with Cu-SSZ-13 below and above 330 °C, the transient reactions were conducted, and the results are given in Table 1. The procedure of the transient reactions is shown in Figure 3. The NH_3 oxidation results in Figure S1 reveal that the Pt poisoning enhanced the NH_3 oxidation capacity of PtxCu samples. However, small amounts of NO and NO_2 were formed on the Cu-SSZ-13 and Pt-poisoned samples during the NH_3 oxidation period at 330 °C, as shown in Table 1. This indicates that the Pt sites mainly enhanced the NH_3 selectivity of the oxidation reaction to N_2 (R.3), which led to insufficient NH_3 taking part in the standard SCR reaction, and decreased the NO_x conversion of PtxCu samples (Figure 1) below 330 °C as a result.

Figure 3. The procedure of the transient reactions.

Both the non-selective NH_3 oxidation reaction (NSNO, R.4) and the non-selective NO_x catalytic reduction reaction (NSCR, R.2) contributed to the N_2O formation [21]. The larger content of N_2O in the PtxCu sample than Cu-SSZ-13 (Figure 2) must be attributed to the enhancement of the NSNO and NSCR reaction rates. However, the N_2O formation cannot be attributed to the enhancement of the non-selective NH_3 oxidation reaction (NSNO, R.4), because only a low concentration of N_2O was formed in the NH_3 oxidation period at 330 °C, as shown in Table 1. After the introduction of NO, the N_2O concentration was significantly increased (Table 1). This indicates that the N_2O formation was primarily attributed to the non-selective NO_x catalytic reduction reaction (NSCR, R.2), which was catalyzed by Pt sites.

Table 1. Transient reaction results for the catalyst samples at 330 °C and 460 °C.

Sample T (°C)		Reaction										
		NH ₃ Oxidation				SCR Reaction				NO Oxidation		
		NO	NH ₃	N ₂ O	NO ₂	NO	NH ₃	N ₂ O	NO ₂	NO	N ₂ O	NO ₂
		(ppm)				(ppm)				(ppm)		
Cu-SSZ-13	330	0	59	4	0	0	0	4	0	485	1	5
	460	0	0	1	0	0	0	5	0	479	1	13
Pt ₁ Cu	330	0	0	7	0	85	0	18	11	465	1	12
	460	48	0	4	3	306	0	8	44	437	1	56
Pt ₂ Cu	330	0	0	12	0	152	0	39	14	435	2	23
	460	98	0	4	23	356	0	8	92	397	1	81
Pt ₃ Cu	330	17	0	24	10	232	0	59	29	424	1	35
	460	160	0	5	35	488	0	12	118	404	1	90

More NO was formed during the NH₃ oxidation at 460 °C (R.6) than at 330 °C. This indicates that, in addition to the decrease in reductant involved in the standard SCR reaction due to the enhancement of the NH₃ oxidation reaction by Pt, the oxidation of NH₃ to NO (R.6) also contributed to the decrease in NO_x conversion at high temperatures (460 °C).

Besides this, at 460 °C, a large amount of NO₂ was also produced during the NH₃ oxidation of Pt doping samples, while none was observed in Cu-SSZ-13 (Table 1), indicating that a part of the NH₃ was oxidized to NO₂ by Pt at 460 °C. Meanwhile, NO oxidation into NO₂ (R.7) was also enhanced in the PtxCu samples, as confirmed by the higher concentration of NO₂ formed over PtxCu than Cu-SSZ-13 during the NO oxidation period (Table 1). Furthermore, the total concentration of NO₂ formed in the NH₃ oxidation and NO oxidation reactions was similar to that formed in the NH₃-SCR period. This demonstrates that Pt loading accelerated the reactions in R.6 and R.7, resulting in the increased NO₂ formation in the NH₃-SCR process. Those observations above imply that, beside the overconsumption of NH₃ following R.1, the additional NO and NO₂ production via NH₃ and NO oxidation (R.5-R.7) also led to the decline in NO_x conversion in the PtxCu samples at high temperatures (around 460 °C) [22,23].

2.3. Pt Poisoning Effect on the Texture and Structure

The ICP results of the samples are given in Table 2. The fresh and aged samples showed similar Cu loading contents, and the Pt amount increased with the increment in the Pt loading. The hydrothermal treatment did not change the Pt content.

Table 2. The element content and textural properties of the catalysts.

Sample	Cu Content ^a (wt. %)	Pt Content ^a wt. %	Surface Area ^b (m ² /g)	Pore Volume ^b (cm ³ /g)
Cu-SSZ-13	4.11	ND ^e	498	0.21
Pt ₁ Cu	4.13	0.009	412	0.2
Pt ₂ Cu	4.08	0.051	390	0.19
Pt ₃ Cu	4.14	0.1	382	0.19
Cu-H	4.06	ND	406	0.17
Pt ₁ Cu-H	4.10	0.01	355	0.17
Pt ₂ Cu-H	4.10	0.048	342	0.16
Pt ₃ Cu-H	4.09	0.1	335	0.15

^a Determined with ICP. ^b Determined with N₂ physisorption.

The surface area and pore volume decreased with the increasing Pt loading (Table 2). No significant framework dealumination took place as a result of Pt impregnation, as only a slight decline of the peak at 58 ppm, attributed to the tetrahedral Al species, was observed in the Pt-doped samples compared to Cu-SSZ-13 (Figure S4) [14,24]. In addition, no significant formation of octahedrally coordinated Al species (showing a resonance peak at 0 ppm) could be detected [14,24]. These observations above indicate that the dealumination should not be the primary reason for the decline in BET surface area. Actually, SSZ-13 possesses small windows of about 3.8 Å, so mass transfer limitations might be induced due to the deposition of impurities, even at low quantities. Moreover, taking into account the diameter of Pt⁰ and PtO_x (around 1 nm, shown in the TEM results in Figure S6), it is reasonable to assume that some of the Pt might be located in the zeolite micropores, causing a decrease in the micropore volume and the BET surface area. However, those values were largely maintained after hydrothermal treatment, suggesting that the structure of the hydrothermally aged sample remains intact, consistent with the XRD results in Figure S2.

2.4. Pt Poisoning Effect on the Catalytic Active Sites

2.4.1. H₂-TPR

The isolated Cu²⁺ ions are identified as the active sites that catalyze the standard NH₃-SCR reaction [25–27]. H₂-TPR was carried out on the catalysts to detect the state of cupric species, and the results are shown in Figure 4a. For the fresh samples, two peaks in 220–380 °C and in 600–750 °C were observed, representing the reduction of isolated Cu²⁺ to Cu⁺ (R.8) and the reduction of Cu⁺ to Cu⁰ (R.9), respectively [28,29].

Figure 4. (a) H₂-TPR spectra of fresh and aged Cu-SSZ-13 and PtxCu samples; (b) the relative Cu²⁺ ion content in the catalyst samples, using Cu-SSZ-13 as a reference.

After deconvolution, the peak in the 220–380 °C range can be divided into two peaks with tops at 250 °C and 325 °C, assigned to the reduction of isolated Cu²⁺ located in eight- and six-member rings, respectively [30]. After the hydrothermal treatment, the reduction peak below 500 °C was widened, and an additional peak at 190 °C appeared. This can be attributed to the transformation of a part of the isolated Cu²⁺ ions to CuO during the hydrothermal treatment [31].

The isolated Cu^{2+} ions content of each sample was normalized using the area of the reduction peaks of isolated Cu^{2+} ions in Cu-SSZ-13 as a reference, shown in Figure 4b. The Cu-SSZ-13 and Pt_xCu samples contained similar isolated Cu^{2+} ions contents. This suggests that the Pt poisoning has no influence on the cupric sites, which is consistent with previous work [6]. Therefore, the parallel reactions should exclusively be catalyzed by the Pt species, which reduced the SCR activities. Furthermore, the SCR active sites, i.e., isolated Cu^{2+} ions, decreased, and the Pt content remained constant (Figure 4b), while the SCR activity was increased for the Pt_xCu samples after hydrothermal treatment. This indicates that the hydrothermal conditions might change the state of Pt, which plays a critical role in determining the SCR's performance.

2.4.2. X-ray Photoelectron Spectroscopy

To detect the changes of state in Pt, the XPS technique was utilized, and the Pt 4f spectra of the fresh and aged samples are given in Figure 5a,b, respectively. The Cu-SSZ-13 sample displayed no Pt signals, and a broad peak at 70–80 eV was observed in the Pt_xCu samples. The signals for the Pt 4f_{7/2} peaks with a binding energy value at 71.32 eV confirmed the presence of platinum in the zero oxidation state (Pt^0) [32]. The Pt 4f_{7/2} signals at around 72.96 and 74.01 are attributed to PtO and PtO₂ species, respectively, which were formed due to the Pt^0 oxidation during the catalyst's calcination in preparation [33]. In comparison, only reduced Pt was observed in the previous work on Pt-poisoned Cu-SSZ-13 [6]. This might be attributed to the different Pt precursors used in the work by Lezcano-Gonzalez et al. ($[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$) and in our work ($\text{Pt}(\text{NO}_3)_2$), as the different precursors have an influence on the state of the Pt [6,34]. After the hydrothermal treatment, the XPS spectra of the hydrothermally aged samples changed. Only the PtO and PtO₂ species remained in the aged samples. This indicates that all the Pt^0 was oxidized during the aging process, which is consistent with the previous works that reported that the Pt^0 would be easily oxidized at high temperatures [16,18].

Figure 5. Pt 4f XPS results of the catalyst samples. (a) Fresh samples, (b) aged samples, (c) Pt^0 content in Pt_xCu samples.

The Pt⁰ content of each sample was calculated, as shown in Figure 5c (details shown in Figure S3). The Pt⁰ content increased in the order of Pt₃Cu > Pt₂Cu > Pt₁Cu > Cu-SSZ-13, consistent with the extent of the deactivation of the Pt-loaded samples (Figure 1). Combined with the transient reaction results in Table 1, it is suggested that the Pt⁰ catalyzed the R.2–7, decreasing the deNO_x activities of the PtxCu samples (Figure 1). In addition, the aged Cu-SSZ-13 and PtxCu exhibited similar SCR activities after hydrothermal treatment, although a large content of PtO_x still existed in the PtxCu-H samples (Figures 1 and 5b). This demonstrates that the PtO_x is ineffective in catalyzing the parallel reactions. In other words, the transformation of Pt⁰ into PtO_x results in the regeneration of PtxCu samples after hydrothermal treatment.

3. Experimental

3.1. Catalyst Preparation

The Cu-SSZ-13 was synthesized via one-pot hydrothermal synthesis using copper-tetraethylenepentamine (Cu-TEPA, Guangfu, Tianjin) as a structure-directing agent. In total, 180 mL of gel was prepared with a molar ratio of 2.5 Na₂O:1 Al₂O₃:10 SiO₂:150 H₂O:2 Cu-TEPA, which was then transferred into a 250 mL autoclave with a Teflon liner and crystallized at 140 °C for 4 days. The solid product was filtrated, washed with water, and then dried at 120 °C for 6 h. Then, 15 g of as-synthesized sample was ion-exchanged with 300 mL NH₄NO₃ solution (1 mol/L) at 80 °C and kept for 9 h to remove excess Cu. After filtration, washing, and drying at 100 °C, the sample was calcinated in synthetic air at 600 °C for 6 h to obtain Cu-SSZ-13. The Si/Al ratio of Cu-SSZ-13 is 4, as determined by ICP-OES. The details of the preparation can be found in our previous work [14].

The Pt-doped Cu-SSZ-13 catalysts (Pt/Cu-SSZ-13 = 0.01, 0.05, 0.1 wt. %) were prepared by incipient wetness impregnation. Typically, 0.6 mL Pt(NO₃)₂ solution (Guangfu) at different concentrations (0.088, 0.44 and 0.88 mol/L, respectively) was dropped onto 1 g of Cu-SSZ-13. After calcination at 550 °C for 4 h, the catalysts with different Pt loadings were obtained. The samples were denoted as Pt₁Cu, Pt₂Cu and Pt₃Cu for short, respectively.

All catalysts were treated at 750 °C in air with 10% H₂O for 12 h. The flow rate was kept at 500 mL/min. The hydrothermally aged samples with Pt loading were distinguished with the suffix of (-H), and Cu-H was used as the abbreviation for the aged Cu-SSZ-13.

3.2. Catalytic Performance Test

The NH₃-SCR activities of the catalysts were tested in a fixed-bed quartz reactor (10 mm in diameter). Typically, 100 mg of the catalyst (40–60 mesh) was used, which was pre-activated in 5% O₂/N₂ flow at 550 °C for 1 h. The reactant gases contain 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, and N₂ as balance. The gas flow was kept at 500 mL/min, and the corresponding GHSV was 150,000 h⁻¹. The concentrations of the products (NO, N₂O and NO₂) were recorded on an FTIR gases analyzer (Thermo Nicolet iS10, Madison, WI, USA) with a 2 m gas cell when the reaction reached a steady state (less than 1 ppm change in ten minutes). The NO_x (NO_x = NO + NO₂) conversion was calculated according to R.10:

$$NO_x = \left(1 - \frac{[NO_x]_{out}}{[NO_x]_{in}}\right) \times 100\% \quad (10)$$

3.3. Transient Reaction

Transient reactions were carried out at 330 and 460 °C. First, a similar reaction condition as in the standard SCR measurement mentioned above was adopted for the NH₃ oxidation reaction, in which NO was not introduced into the gas mixture. After the reaction reached a steady state, 500 ppm NO was switched into the reaction system. The concentrations of the gases (NO, NO₂, N₂O and NH₃) were measured with the FTIR gas analyzer (Thermo Nicolet iS10).

The surface area and pore volume were determined by N₂ physisorption measurement at −196 °C using a Quantachrome Autosorb-1, with pre-degassing at 250 °C for 6 h. The

chemical composition of the sample was determined by ICP-OES (VISTA-MPX, Varian, Palo Alto, CA, USA). The H₂ temperature-programmed reduction (H₂-TPR) was conducted on an AutoChem II 2920 (Micromeritics, Norcross, GA, USA) instrument. The samples were treated at 550 °C in 10%O₂/N₂ for 1 h before testing. X-ray photoelectron spectroscopy (XPS) was performed with a PHI-1600 ESCA system spectrometer (Perkin-Elmer Co., USA) using Mg K α as the X-ray source (1253.6 eV) under a residual pressure of 5×10^{-6} Pa. The error of the binding energy was calibrated using C1s at 284.6 eV as the standard.

4. Conclusions

The Cu-SSZ-13 suffered severe deactivation after Pt impregnation, resulting in a decrease in NO_x conversion. The Pt⁰ species accelerated the NH₃ selective oxidation reaction to N₂ in the temperature range below 330 °C, reducing the deNO_x activity of Pt/Cu samples due to the insufficient amount of reductant taking part in the standard NH₃-SCR reaction. In addition to the over-consumption of NH₃ due to NH₃ oxidation, the formation of NO and NO₂ via NH₃ and NO oxidation (R.3–R.7) further increased the loss of deNO_x activity in Pt-poisoned samples at high temperatures (around 460 °C). The NSCR (R.2) reaction contributed to the increased N₂O formation in Pt-poisoned samples at around 330 °C. After hydrothermal treatment, the activity was mostly recovered due to the transformation of Pt⁰, which catalyzed the parallel reactions, into PtO_x species.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11070796/s1>, Figure S1: NH₃ conversion as a function of temperature during NH₃ oxidation experiment for the Cu-SSZ-13 and Pt/Cu samples. Reactant feed contains 500 ppm NH₃, 5% O₂, 5% H₂O, balanced with N₂; flow rate at 500 mL/min, GHSV: 150,000 h^{−1}, Figure S2: NO₂ formation as a function of temperature during NH₃-SCR reaction. The reactant feed contains 500 ppm NH₃, 5% O₂, 5% H₂O, balanced with N₂; flow rate at 500 mL/min, GHSV: 150,000 h^{−1}, Figure S3: XRD patterns of the (a) fresh and (b) aged catalysts, Figure S4: Solid state ²⁷Al MAS NMR spectra of the Cu-SSZ-13 and Pt-poisoned samples, Figure S5: Ratio of different Pt species in the Pt loading samples quantified by the XPS spectra in Figure 5, Figure S6: TEM images of (a) Pt₃Cu and (b) Pt₃Cu-H samples.

Author Contributions: H.Z.: literature search, figures, study design, data collection, writing; L.H.: literature search, figures, study design; Y.W.: figures, study design; J.Z.: data analysis. All authors have read and agreed to the published version of the manuscript.

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