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Preparation of Reduced Pt-Based Catalysts with High Dispersion and Their Catalytic Performances for NO Oxidation

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Abstract: Pt-based catalysts are widely used in diesel oxidation catalyst (DOC) units, primarily to oxidize the harmful HC, CO, and NO emissions. Notably, NO₂ produced from NO oxidation is beneficial for low-temperature activity in NH₃-SCR and promotes soot oxidation in diesel particulate filters (DPF). Thus, the conversion of NO is an important parameter for determining the performance of DOCs. Considering the increasingly stringent emission regulations and the economic effectiveness, preparation of low-cost and highly active Pt-based catalysts is indispensable. Generally, the Pt⁰ content is crucial as it is an active component of DOCs. Small Pt size is beneficial for improving the catalytic activity. In this study, we applied a modified alcohol reduction-impregnation (MARI) method to synthesize highly active 1% (w, mass fraction) Pt/SiO₂–Al₂O₃ (denoted as MA-Pt/SA) catalyst. Meanwhile, using the conventional impregnation method, we prepared the Pt/SiO₂–Al₂O₃ catalyst with the same Pt loading (denoted as C-Pt/SA) as a reference sample. X-ray photoelectron spectroscopy (XPS) and hydrogen temperature program reduction (H₂-TPR) analyses proved that the MARI method could produce Pt catalysts with higher Pt⁰ content. Pt⁰ content in MA-Pt/SA was ~60.3% while that in C-Pt/SA was only ~23.1%. X-ray diffraction (XRD), CO-diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS), and transmission electron microscopy (TEM) characterization confirmed that the Pt particle size is much smaller over MA-Pt/SA as compared to that over C-Pt/SA. Performance evaluation of MA-Pt/SA and C-Pt/SA was conducted in a simulated diesel atmosphere. The results showed that the maximum NO conversion into NO₂ over MA-Pt/SA is 74% and 68% in the absence and presence of H₂O, respectively, which were much higher than those over C-Pt/SA (42% and 51% NO conversion with and without H₂O, respectively). Furthermore, the temperature for 30% NO conversion over MA-Pt/SA (218 °C) markedly decreased as compared to that over C-Pt/SA (248 °C), indicating the excellent low temperature activity. After the aging treatment with reaction gas at high temperatures, aged MA-Pt/SA maintained 69% NO conversion while aged C-Pt/SA showed only 41% NO conversion. In addition, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of NO + O₂ co-adsorption suggested that higher Pt dispersion and higher Pt⁰ content over MA-Pt/SA could facilitate the formation of bridging nitrates as intermediate species in NO oxidation at lower temperatures and could also facilitate their rapid decomposition (or desorption) at higher temperatures, thus imparting a high catalytic activity. Furthermore, a decrease in the Pt loading to 0.5% (w) resulted in a maximum NO conversion of 64% *via* the MARI method, suggesting a higher catalytic activity compared to that of C-Pt/SA with 1% (w) Pt loading. This work provides a method to prepare highly active Pt-based catalysts with low noble loading.

Performance evaluation of MA-Pt/SA and C-Pt/SA was conducted in a simulated diesel atmosphere. The results showed that the maximum NO conversion into NO₂ over MA-Pt/SA is 74% and 68% in the absence and presence of H₂O, respectively, which were much higher than those over C-Pt/SA (42% and 51% NO conversion with and without H₂O, respectively). Furthermore, the temperature for 30% NO conversion over MA-Pt/SA (218 °C) markedly decreased as compared to that over C-Pt/SA (248 °C), indicating the excellent low temperature activity. After the aging treatment with reaction gas at high temperatures, aged MA-Pt/SA maintained 69% NO conversion while aged C-Pt/SA showed only 41% NO conversion. In addition, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of NO + O₂ co-adsorption suggested that higher Pt dispersion and higher Pt⁰ content over MA-Pt/SA could facilitate the formation of bridging nitrates as intermediate species in NO oxidation at lower temperatures and could also facilitate their rapid decomposition (or desorption) at higher temperatures, thus imparting a high catalytic activity. Furthermore, a decrease in the Pt loading to 0.5% (w) resulted in a maximum NO conversion of 64% *via* the MARI method, suggesting a higher catalytic activity compared to that of C-Pt/SA with 1% (w) Pt loading. This work provides a method to prepare highly active Pt-based catalysts with low noble loading.

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Key Words: DOC; Modified alcohol reduction-impregnation method; NO oxidation; High-performing Pt catalyst; Low Pt loading

高分散还原态Pt基催化剂的制备及其NO氧化的催化性能

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摘要: Pt⁰被认为是NO氧化的活性物种, 而催化剂的制备方法对活性物种的含量起着决定性作用。本文采用非惰性气氛保护的改性醇还原-浸渍法(MARI)合成了高分散高Pt⁰含量的1% (w, 质量分数) Pt/SiO₂-Al₂O₃催化剂(MA-Pt/SA)。X射线粉末衍射(XRD)、CO-漫反射傅里叶变换红外吸收光谱(CO-DRIFTS)和透射电镜(TEM)表征证实550 °C焙烧3 h后催化剂的Pt颗粒仅有3.8 nm。同时, X射线光电子能谱(XPS)和H₂-程序升温还原(H₂-TPR)结果表明催化剂具有高Pt⁰含量(60.3%)。模拟柴油车尾气气氛进行活性测试, 并与传统浸渍法制备的1% (w) Pt/SiO₂-Al₂O₃催化剂(C-Pt/SA)对比, 结果显示MA-Pt/SA具有优异的催化氧化性能, 其NO最大转化率高达74%, 比C-Pt/SA的NO转化率高了23%。经670 °C高温老化15 h后, 老化的MA-Pt/SA的NO转化率仍然高达69%。此外NO + O₂共吸附原位漫反射傅里叶变换红外吸收光谱(*in situ* DRIFTS of NO + O₂ co-adsorption)表明高的Pt分散度和高Pt⁰含量能够促进中间物种桥式硝酸盐的生成及分解, 进而导致了优异的NO氧化活性。最后, 利用同样方法将Pt的负载量降低至0.5% (w)制备催化剂, NO转化率仍达64%。这种制备方法能够获得低贵金属高性能的Pt基催化剂。

关键词: 柴油车氧化催化剂; 改性的醇还原-浸渍法; NO氧化; 高性能Pt基催化剂; 低Pt含量
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1 Introduction

The hazardous gas derived from diesel-engined vehicles consists of unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen monoxide (NO) and particulate matter, and their emissions are the main reason of air pollution¹. Given more tightened emission standards, the combined after-treatment systems, consisting of diesel oxidation catalyst (DOC), diesel particulate filters (DPF), selective catalytic reduction (SCR) and ammonia slip catalyst (ASC) are used^{2,3}. DOC is in the front of after-treatment systems, the function of which is to catalyze the oxidation of HC, CO and NO. NO conversion into NO₂ is an important index for evaluating catalytic performances, because NO₂ can facilitate soot oxidation in DPF and fast reduction in SCR⁴. Pt-based catalysts are generally used in exhaust gas after-treatment system due to its excellent catalytic performance. The related studies had proved that small-size Pt particles had an important effect on improving catalytic performance on account of exposing more surface active sites^{5,6}. Many studies have focused on decreasing Pt size to enhance catalytic performance. In our previous work⁷, adding Mg to Pt-based catalysts by the impregnation method obtained higher Pt dispersion due to Pt—O—Mg bond formation, but unfortunately the presence of this covalent bond also caused the formation more PtO which was unfavorable to catalytic reaction for NO oxidation. Metal Pt is widely considered as an active specie for the catalysts of exhaust gas while PtO_x formation is responsible for the decreased activity, and thus it's crucial for Pt catalysts to increase Pt⁰

content of catalysts at same loading^{8,9}. Considering the both factors above, it's necessary to develop new preparation techniques to obtain the Pt catalysts with smaller size of Pt particles and high Pt⁰ content.

In recent years, reducing metal salt by various reductants is the broadest method for preparing supported catalysts with nano-sized metal particles (Pt, Pd, Rh, Au and so on)¹⁰⁻²⁷. García *et al.*²⁸ obtained Pt-based catalysts supported on undoped carbon materials *via* conventional impregnation technology and NaBH₄ reduction method, and the higher activity of hydrodechlorination reactions was observed for the latter. According to the literature reported by Ma and co-workers²⁹, the active metal catalyst of ethanol electrooxidation is metal Pt in acidic media. They used ethylenediamine-tetramethylene phosphonic acid (EDTMP) to coordinate with H₂PtCl₆ to form the complex of EDTMP—Pt^{IV}, and then obtained Pt⁰ nanoparticles due to self-reduction. The size-controlled Pt/C catalyst with 2.5 nm was prepared by this reduction method and showed the highest ethanol electrooxidation activity. However, this reduction technology is less employed in preparing exhaust purification catalysts.

Here, we combined the modified reduction method with impregnation method, namely the modified alcohol reduction-impregnation (MARI) method, to synthesize supported-Pt DOC with high Pt dispersion and Pt⁰ proportion. Firstly, in this method, H₂PtCl₆ was completely reduced in ethylene glycol (EG) and water system, with polyvinylpyrrolidone (PVP) as a coating agent to get homogeneously distributed Pt⁰

nanoparticles. Although EG and PVP has been widely reported to synthesis the Pt nanoparticles, the modified reduction process of MARI method is conciser and easier than other reduction methods^{11,14,30}, without alkaline/acidic reagents and inert atmosphere, and Pt⁰ nanoparticles (less than 3 nm) could be obtained in EG/H₂O solution *via* controlling reduction conditions. And then, loading the products on SiO₂—Al₂O₃ (SA) material by impregnating made Pt nanoparticles homogeneously and individually supported on SA. This spatial distribution of Pt could prevent its particle aggregation at high temperatures. At the same time, the same content of H₂PtCl₆ was loaded on SA only using traditional impregnation to obtain Pt/SA catalyst as a reference sample.

Notably, the prominent advantage of MARI method is that it can obtain small Pt particles and high Pt⁰ content, making the efficient use of precious metal and hence highly boosting the catalytic property of Pt-based catalysts. Moreover, using this method the Pt loading of catalyst was decreased from 1% (w) to 0.5% (w), and its catalytic performance was even superior contrast with 1% (w) Pt sample obtained by conventional impregnation technology, showing that this combined preparative technique is cost-competitive for catalytic application.

At the same time, a series of experiments, including ICP-OES, XPS, XRD, TEM, CO-DRIFTS, H₂-TPR and *in situ* DRIFTS of NO + O₂ co-adsorption, were performed in order to investigate physical and chemical properties of all samples. Our works demonstrated that it is feasible to get cost-efficient and highly active Pt-based catalysts by MARI method.

2 Experimental section

2.1 Catalyst preparation

For MARI method, as shown by Scheme 1, H₂PtCl₆·6H₂O (99.9%, purity) was firstly reduced through modified reduction process. Polyvinylpyrrolidone (PVP, K30, purity) in ethylene glycol (EG, purity) was mixed with H₂PtCl₆·6H₂O aqueous solution. The mixture was refluxed at 110 °C, dispensing with alkaline/acidic reagents and inert atmosphere, to obtain transparent dark-brown colloidal solution. Then, the PVP-

stabilized Pt metal nanoparticles were collected by centrifugation with acetone (purity) and finally redispersed in deionized water. Secondly, the obtained products were supported on SiO₂—Al₂O₃ (SA, provided by Solvay) materials by impregnation method with a total 1% (w) Pt loading, and this sample was denoted as uncalcined MA-Pt/SA. And then, it was calcined at 550 °C for 3 h in static air. The homogeneous slurry was obtained by mixing distilled water with the sample powder, and was wash-coated onto honeycomb cordierite (2.5 cm³, USA) with coat-loading amount of about 150 g·L⁻¹. The obtained monolithic catalyst and the residual slurry simultaneously was dried at 60 °C, and then calcined again at 550 °C for 3 h, denoted as MA-Pt/SA-f. After treatments mentioned above, the monolithic catalyst and the catalyst powder (obtained by the residual slurry) was used in catalytic evaluation and catalyst characterization, respectively. The actual Pt loading of the MA-Pt/SA sample was 0.9727% (w) tested by ICP-OES, near to the theoretical loading. It indicated that liquid Pt ions were completely reduced to Pt⁰ nanoparticles after centrifugation were totally supported on SA materials.

For conventional impregnation method, the aqueous solution of H₂PtCl₆·6H₂O was directly impregnated on SA by the equal pore volume impregnation method (1% (w) Pt) and calcined at 550 °C for 3 h in static air. The monolithic catalyst and the powder sample was obtained by the same method above, denoted as C-Pt/SA-f. ICP-OES demonstrated that its actual Pt loading was 0.9692% (w).

The sample of MA-Pt/SA-f and C-Pt/SA-f undergone the aging treatment (aging condition: 0.15% CO, 0.06% C₃H₆, 0.02% NO, 4% CO₂, 5% O₂, and N₂ balance, at 670 °C for 15 h and then 250 °C for 15 h), and was denoted as MA-Pt/SA-a and C-Pt/SA-a, respectively. Besides, we also synthesized Pt/SA with 0.5% (w) Pt loading by MARI method, denoted as MA-0.5 Pt/SA. The actual Pt loading of MA-0.5Pt/SA sample was 0.4740% (w) proved by ICP-OES.

2.2 Catalytic evaluation

The catalytic performance evaluation of all samples was completed in a fixed bed quartz flow reactor. The monolithic catalysts were inserted into quartz tube, and then were placed in the constant temperature zone of a cylindrical furnace. A K-thermocouple was positioned on the top of catalysts to monitor the catalyst bed temperature (presented in this paper). Another K-thermocouple was positioned in a middle place between the quartz tube and the furnace connected with a temperature controller. The reactant gases contained CO (0.1%), C₃H₆ (0.033%), NO (0.02%), CO₂ (8%), O₂ (10%), N₂ balance with/without H₂O (7%), GHSV 60000 h⁻¹. The gas flow was controlled by mass flow controllers. Before catalytic performance evaluation, all samples were pre-treated under simulative exhaust gases, including CO (0.1%), C₃H₆ (0.033%), NO (0.02%), CO₂ (8%), O₂ (10%), N₂ balance with/without H₂O (7%), GHSV 30000 h⁻¹ at 550 °C for 3 h to get stable catalysts during the reaction. Nicolet Antaris IGS-6700 gas analyzer

Scheme 1 The diagrammatic drawing of preparation process for two methods.

(Thermo Fisher Scientific, USA) was used to monitor the content of the outlet gas (CO, C₃H₆, NO and NO₂). The CO, C₃H₆ and NO conversion were calculated by the following equations:

$$\text{CO conversion} = (C_{\text{CO}}^{\text{in}} - C_{\text{CO}}^{\text{out}}) / C_{\text{CO}}^{\text{in}} \times 100\% \quad (1)$$

$$\text{HC conversion} = (C_{\text{HC}}^{\text{in}} - C_{\text{HC}}^{\text{out}}) / C_{\text{HC}}^{\text{in}} \times 100\% \quad (2)$$

$$\text{NO conversion} = (C_{\text{NO}_2}^{\text{out}} - C_{\text{NO}_x}^{\text{in}}) \times 100\% \quad (3)$$

2.3 Catalyst characterizations

Electron spectrometer (XSAM-800, KRATOS Co., England) was exploited to obtain XPS data with an Al K α radiation. The binding energies were calibrated by C 1s (284.6 eV). The Rigaku Ultima IV diffractometer were used to obtained the XRD (Rigaku, Japan) patterns employing Cu K α radiation (40 kV, 40 mA, $2\theta = 20^\circ$ – 80° , scanning step = 0.02° , $\lambda = 0.15406$ nm). The particle size of Pt could be roughly evaluated by Pt (111) FWHM (the full width at half maximum) based on Debye-Scherrer equation: $d = 0.89\lambda / (\beta \cos \theta)$, where θ is the angle of the peak, β is FWHM, λ is the wavelength of X-ray. The Pt loading of catalysts was determined by inductively coupled plasma/optical emission spectroscopy (ICP-OES, Perkin-Elmer plasma 8000, USA). Using a tubular quartz micro-reactor with TCD (thermal conductivity detector) collected H₂-TPR (TP-5074, China) profiles. The preprocessing of the samples (0.1 g) were finished by He flow at 450 °C for 30 min. Whereafter, the samples were reduced by 5.0% (ϕ , volume fraction) H₂/N₂ from ambient temperature to 400 °C with a heating rate of 8 °C·min⁻¹.

Transmission electron microscopy (TEM) characterization of all catalysts were completed by Tecnai G2 F20 S-TWIN (FEI Company, US), using an acceleration voltage of 200 kV. The distributions of particle size were obtained by the Digital Micrograph software. The equation of the average particle size is as followed:

$$d = \sum_i n_i d_i / \sum_i n_i \quad (4)$$

where n_i is the particle number (about 100 particles) and d_i is particles diameter.

Besides, according to the reference reported by Peng *et al.*³¹, the dispersion of Pt was calculated by the following equations:

$$D_{\text{Pt}} = 600 M_{\text{Pt}} / \rho d a_{\text{Pt}} N_{\text{A}} \quad (5)$$

where M_{Pt} is 195.08 g·mol⁻¹ (the molar weight of Pt); ρ is 21.45 g·cm⁻³ (the density of Pt); a_{Pt} is 8.06×10^{-20} m²·atom⁻¹; N_{A} is 6.02×10^{23} mol⁻¹ (the Avogadro constant); d is the mean size of Pt obtained by TEM.

CO-DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) experiments were carried out using a DRIFTS spectrometer (Thermo Nicolet 6700, Thermo Scientific, USA), equipped with a reaction cell and KBr windows. The preconditioning of catalyst powder was accomplished by N₂ at 450 °C for 30 min. The catalyst was cooled to 25 °C and then contacted with 1% (ϕ) CO/N₂ until saturation. After that, the CO-DRIFTS spectra were obtained after N₂ purging. The spectra were collected by subtracting atmospheric background and the background of samples without adsorption. Each spectrum was accumulated with a resolution of 4 cm⁻¹ in 64 scans.

NO + O₂ co-adsorption experiments were performed using a DRIFTS spectrometer, similar to CO-DRIFTS (Thermo Nicolet 6700, Thermo Scientific, USA). The samples were mixed with KBr with a weight ratio of 1 : 20, and were pretreated in N₂ at 450 °C for 30 min. After cooling, 0.1% NO + 10% (ϕ) O₂ in N₂ (300 mL·min⁻¹) were flowed at 50 °C. *In situ* spectra were recorded at the range of 50 to 300 °C.

3 Results and discussion

3.1 Surface state of Pt

3.1.1 XPS

The Pt valence states are a crucial factor for the catalytic activity. In the light of the reported literature³², the possible reaction pathways of NO oxidation were presented as follows: the gaseous O₂ adsorbed on Pt particles and disassociated into atomic oxygen and yielded Pt–O component, and then it reacted with gaseous NO (Eley-Rideal model, Pt–O + NO → Pt–NO₂) or adsorbed NO (Langmuir-Hinshelwood model, Pt–O + Pt–NO → Pt + Pt–NO₂) to produce NO₂. Moreover, the literature⁹ reported that, compared with metal Pt⁰, the binding ability of PtO₂ toward O₂, O and NO is weak, and the dissociation of O₂ on the oxidized Pt is pretty hard. Other literature also reported that Pt oxide formation resulted in the decrease of activity^{8,33}. That is, metal Pt is regarded as an active center for NO oxidation reaction^{8,9}. So, XPS analyses were performed for revealing the effects of two preparation methods on the chemical state of Pt. Unfortunately, the intensity of Pt 4d peak over two samples is too weak to analyze. Thus, the spectra of Al 2p and Pt 4f are shown by Fig. 1 (the whole spectra of Al 2p and Pt 4f could be seen as Fig. S1 (in Supporting Information)), and all binding energies were calibrated by C 1s (284.6 eV). The Al 2p core level spectra had no difference over C-Pt/SA-f and MA-Pt/SA-f samples, which were located at about 74.4 eV. Though Pt 4f peak was overlapped by Al 2p at 74.4 eV, the peaks at 70.9 eV (Pt⁰), 77.3 eV (Pt²⁺) and 78.2 eV (Pt⁴⁺) could be observed. The curve-fitting of Pt 4f was performed for the quantitative calculation of the Pt chemical states^{34,35}. The binding energies of Pt 4f_{7/2} and Pt 4f_{5/2} were 70.9/74.3 eV, 73.6/77.3 eV, and 74.8/78.2 eV, assigned to Pt⁰,

Fig. 1 XPS spectra of Al 2p and Pt 2p for C-Pt/SA-f and MA-Pt/SA-f samples.

Pt²⁺ and Pt⁴⁺ respectively. Visibly, the peak intensity of MA-Pt/SA-f at 70.9 eV (Pt⁰) was stronger than that of C-Pt/SA-f. In other words, the content of metallic Pt over MA-Pt/SA-f markedly increased compared with C-Pt/SA-f. The information involving Pt species ratio (Pt⁰, Pt²⁺ and Pt⁴⁺) was presented in Table 1. The Pt⁰ proportion of MA-Pt/SA-f was about 60.3%, while that of C-Pt/SA-f was about 23.1%. This result also demonstrated that a portion of Pt⁰ was reoxidized for MA-Pt/SA-f after calcination at 550 °C in air.

The XPS results showed that the MARI method could obtain Pt catalysts containing more Pt⁰ species, which was confirmed by CO-DRIFTS and H₂-TPR, efficaciously enhancing the Pt utilization.

3.1.2 CO-DRIFTS

To further investigate the surface states of catalysts, CO-DRIFTS were performed after N₂ pretreatment. According to the intensity and position of CO absorption bands, surface composition of Pt could be monitored sensitively. Fig. 2 exhibits the DRIFTS spectra of CO adsorbed on the fresh catalysts at 25 °C. It was commonly recognized that the region of 2000–2100 cm⁻¹ over the two samples could be belonging to linearly adsorbed CO–Pt⁰. The stretching frequency at about 2122 cm⁻¹ was attributed to CO adsorbed on PtO_x.³⁶ Two CO absorbed bands (a main band at 2079 cm⁻¹ and a weak peak at 2122 cm⁻¹)

in the infrared spectrum were observed over C-Pt/SA-f and MA-Pt/SA-f, indicating metal Pt and Pt oxide exist simultaneously. Moreover, the intensity of CO adsorption peak at 2122 cm⁻¹ over C-Pt/SA-f was relatively stronger than that over MA-Pt/SA-f, whereas the intensity of peak at 2079 cm⁻¹ for MA-Pt/SA-f was higher. This result illustrated that MA-Pt/SA-f had more Pt metallic states than C-Pt/SA-f, which was one of reasons for outstanding catalytic activity of Pt catalysts. This is in good agreement with XPS results.

3.2 Particles size of Pt

3.2.1 XRD

Besides the Pt valence state, the structure of catalysts has significant influence on catalytic performance. Here, XRD technology was used to investigate the structure of all catalysts. As shown in Fig. 3, the diffraction peaks at 45.8° and 66.8° were assigned to γ-Al₂O₃. Beyond that, the XRD analysis revealed typical Pt (111), Pt (200) and Pt (220) crystallographic planes at 2θ angles 39.8°, 46.2° and 67.5°, respectively. XRD patterns show that the diffraction pattern peak intensity of Pt (111) over all catalysts was different.

For fresh samples, the peak of Pt (111) over MA-Pt/SA-f was broad with low intensity, while the peak of it over C-Pt/SA-f was sharp and strong, suggesting that the Pt particles size over MA-Pt/SA-f was smaller. In the light of Debye-Scherrer equation, the Pt size of C-Pt/SA-f and MA-Pt/SA-f was 27.5 and 8.2 nm, respectively (listed in Table 2). In MARI method, EG was employed as a mild reducing agent. Teranishi *et al.* had proved that the type of alcohol could greatly affect the size of Pt particles, which decreased with the boiling points of alcohol increasing in alcohol/water system, by comparing methanol,

Fig. 2 CO-DRIFTS spectra of fresh samples.

Fig. 3 XRD patterns of all catalysts.

Table 2 The detail results of TEM and NO oxidation over different samples.

Catalyst	Pt size (nm)	Pt dispersion % (%)	T ₅₀ /T ₉₀ (°C)		NO Max conversion (%)	Temperature (°C) ^d	TOF (s ⁻¹)
			CO	HC			
C-Pt/SA-f	27.5 ^a /7.8 ^b	14.5	221/236	229/237	51	248	0.06 ^c
MA-Pt/SA-f	8.2 ^a /3.8 ^b	29.6	197/209	208/212	74	218	0.22 ^c
C-Pt/SA-a	34.1 ^a /9.2 ^b	12.3	233/248	245/253	41	278	0.03 ^f
MA-Pt/SA-a	9.5 ^a /5.1 ^b	22.0	204/217	215/222	69	226	0.21 ^f

^a Pt size was obtained by XRD; ^b Pt size was obtained by TEM; ^c The dispersion of Pt was obtained by TEM results; ^d The temperature of 30% NO conversion;

^e Catalyst bed temperature = 212 °C; ^f Catalyst bed temperature = 216 °C.

Fig. 4 TEM images and size distribution of Pt nanoparticles over uncalcined MA-Pt/SA (a), MA-Pt/SA-f (b) and C-Pt/SA-f (c) catalysts.

ethanol and 1-propanol¹⁰. Therefore, EG with high boiling points was used as a reductant for reducing Pt^{4+} ions to Pt^0 . Besides, in this process, Pt nuclei firstly formed when reaching a critical point, after that the nucleation and particle growth of Pt simultaneously occurred^{37,38}. Adjusting the reaction conditions made the Pt^{4+} ions be instantly reduced in a short time and formed more Pt nuclei. That is, the nucleation rate was higher than the rate of particles growth, which could get smaller Pt nanoparticle.

The XRD patterns of aged samples were also shown. And the diffraction peaks corresponding to $\gamma\text{-Al}_2\text{O}_3$ had no obvious change before and after aging, indicating that it was stable support material because it was pretreated at 1000 °C for 4 h. Inversely, the intensity of Pt (111) phase increased in the aged samples, which revealed a certain degree of the aggregation of platinum particles. Observingly, the peak intensity of Pt (111) over MA-Pt/SA-a was weaker than that over C-Pt/SA-f, suggesting that the Pt particles over the aged MARI-obtained sample were also smaller than that over fresh impregnation-prepared sample.

3.2.2 TEM

The transmission electron microscopy (TEM) micrograph and the Pt size distribution histogram, obtained by counting about 100 Pt nanoparticles, were shown in Fig. 4. The corresponding mean size and dispersion of Pt particles were listed in Table 2. Fig. 4c shows that the average size of Pt particles over C-Pt/SA-f was 7.8 nm and the size distribution was broad, revealing that its particle size was bigger and not uniform. The Pt particles of uncalcined MA-Pt/SA catalyst were homogeneously and individually dispersed on the surface of supports, and the mean size was about 2.6 nm, as shown by Fig. 4a. This phenomenon

demonstrated that the reduction condition of MARI method could control the synthesis of small-sized and uniform Pt nanoparticles (< 3 nm) *via* adjusting the nucleation rate and the growth rate. And the impregnation process made Pt nanoparticles supported on SA singly as shown by Scheme 2. Here, PVP, with functional groups including C—N, C=O and CH_2 , could coordinated with Pt^{4+} ions by the O and/or N atom of the repeating unit¹⁰. And then, Pt^{4+} ions were reduced to Pt^0 in alcohol/water system and thus yielded PVP-protected Pt^0 nanoparticles. Here, the O atoms of the carbonyl group or N atoms of PVP still coordinated with surface Pt atoms^{39,40}. Simultaneously, its carbon chains were hydrophobic and had the repulsive forces thus resulting in the steric hindrance effect, thus preventing Pt nanoparticles aggregation.

For MA-Pt/SA, it could be discovered that the Pt particle size changed before and after calcination. Fig. 4b presents that the metal particle size raised in certain degree after calcining process, and the mean size of Pt over MA-Pt/SA-f was 3.8 nm. This is because the PVP capping layer would decompose above 300 °C, and then the aggregation of Pt particles occurred on account of high-temperature calcination. Notably particularly,

Scheme 2 The diagrammatic drawing of MARI preparation process.

most of Pt particle size over MA-Pt/SA-f catalyst was primarily in the range of 2–3 nm, which still was smaller compared with C-Pt/SA-f catalyst (7.8 nm). As shown by Table 2, the Pt dispersion of MA-Pt/SA-f and C-Pt/SA-f catalyst was 29.6% and 14.5%, respectively.

At the same time, the size distribution of Pt on the aged samples was also analyzed. Fig. S2a,b (in Supporting Information) exhibit that the size of the obtained metal particles in MA-Pt/SA-a and C-Pt/SA-a catalyst was 5.1 and 9.2 nm, respectively. Here, the Pt particles over MA-Pt/SA were far apart, which led to less sintering during aging process basing on sintering mechanisms of Ostwald ripening as well as particle migration and coalescence⁴¹.

Besides, there was a difference in Pt sizes obtained by XRD and TEM, because that the testing principles of two characterization techniques are different. Anyhow, whether XRD or TEM results showed that MARI strategy could get the supported Pt catalysts with smaller particles compared with the impregnation process.

3.3 Redox properties

H₂-TPR tests were performed on all catalysts to investigate the redox property, and the TPR profiles were shown in Fig. 5. It is found that the species of various platinum oxides were reduced below 500 °C without the reduction of SA material. For fresh sample, the differences in the temperature and area of reduction peak over two samples were observed. The reduction peak temperature of MA-Pt/SA-f (123 °C) turned out to be lower than that of C-Pt/SA-f (136 °C). Previous studies reported that the smaller particle size of platinum oxides would be related the reduction at lower temperature⁴². Therefore, the lower reduction temperature of PtO_x over MA-Pt/SA-f was due to the smaller Pt size verified by TEM and XRD. Besides, as shown in Table S1 (in Supporting Information), the total area of PtO_x reduction peak for C-Pt/SA-f (2684) was approximately 1.6 times than that for MA-Pt/SA-f (1691). Especially at higher temperature, there were obvious differences in reduction peak area between MA-Pt/SA-f and C-Pt/SA-f. Negligible peak area was shown at 250–400 °C for MA-Pt/SA-f, while the large peak area was shown at same temperature range for C-Pt/SA-f. This result indicated that more PtO_x species existed in C-Pt/SA-f, consistent with the

results of XPS which demonstrated that the PtO_x ratios of C-Pt/SA-f and MA-Pt/SA-f were 76.9% and 39.7% respectively. Additionally, similar phenomenon was also observed in two aged samples. However, the temperature and area of peak over aged catalysts increased compared with fresh catalysts, which might be due to bigger and more PtO_x particles formed under aging conditions. Combining with the other characterization results (XPS/CO-DRIFTS and TEM/XRD), the H₂-TPR results suggested that the catalysts synthesized by the MARI method had less PtO_x species and exhibited low-temperature redox property resulting from the smaller Pt size, which could promote the catalytic performance.

3.4 CO, HC and NO catalytic performance

The catalytic performances of MA- and C-Pt/SA catalysts for CO, C₃H₆ and NO oxidation were evaluated in the simulated diesel atmosphere. The conversion curves of CO and C₃H₆ oxidation were shown in Fig. 6a, b, respectively. It could be seen that, whether fresh samples or aged samples, MA-Pt/SA catalyst displayed better activity compared to C-Pt/SA at the same Pt loading. On the one hand, in order to easily compare the activities data of CO and C₃H₆ oxidation, *T*₅₀ and *T*₉₀ (the temperatures for 50% and 90% conversion) of CO and C₃H₆ were shown in Table 2. For the fresh samples, it could be seen that the *T*₅₀ of CO and C₃H₆ for MA-Pt/SA-f sample decreased by 20 °C compared to that for C-Pt/SA-f sample. Besides, the *T*₉₀ of CO and C₃H₆ in MA-Pt/SA-f was about 210 °C, while the *T*₉₀ of that in C-Pt/SA-f was about 240 °C. According to the results of activity tests, it demonstrated that MA-Pt/SA-f had excellent low-temperature oxidation properties, in accord with H₂-TPR. For the aged samples, the decrease of reaction activity for CO and C₃H₆ oxidation was observed. But, MA-Pt/SA-a still had a better lower-temperature reactivity than C-Pt/SA-a, completely removing CO and C₃H₆ at a temperature about 220 °C.

On the other hand, the results of NO oxidation over all samples were illustrated in Fig. 6c and Table 2. In this work, NO oxidation into NO₂ was controlled by thermodynamics, but this reaction was affected by other reactants under simulated diesel conditions. The presence of C₃H₆ and CO could suppress NO oxidation due to competitive adsorption of active sites, and simultaneously lead to N₂O formation by reducing NO.

Fig. 5 H₂-TPR profiles of fresh (a) and aged (b) samples.

Fig. 6 CO (a), HC (b) and NO conversion (c) of all catalysts without H₂O.

Therefore, the NO conversion into NO₂ didn't reach the thermodynamic equilibrium even at high temperature, as shown by Fig. S3 (in Supporting Information). It turned out that MA-Pt/SA-f was greatly more active than C-Pt/SA-f for the oxidation of NO. The maximum NO conversion of MA-Pt/SA-f could reach up to 74% at about 265 °C, while that of C-Pt/SA-f was about 51% at about 310 °C. Furthermore, the temperature of 30% NO conversion over MA-Pt/SA-f (218 °C) markedly decreased compared with C-Pt/SA-f (248 °C). Based on the Pt dispersion, the turnover frequency (TOF) of NO oxidation, which was defined as the number of NO molecules converted per active site per second, was calculated to explore the intrinsic activity of NO oxidation (the detail information could be seen in supporting information). In Table 2, the TOF value of MA-Pt/SA-f with smaller Pt particles (0.22 s⁻¹) was almost 4 times higher than that of C-Pt/SA-f with higher Pt particles (0.06 s⁻¹) at 212 °C. Besides, the influence of H₂O on catalytic activity of NO oxidation was also investigated. As shown by Fig. S4 (in Supporting Information), the maximum NO conversion of MA-Pt/SA-f was 68% in the simulated diesel atmosphere with 7% H₂O, which increased by 26% compared with C-Pt/SA-f (42%). Additionally, Pt-based catalysts for NO oxidation reported in literature were compared with our results, as shown in Table S2 (in Supporting Information). After aging treatment in reaction gas at high temperature, the maximum NO conversion of MA-Pt/SA-a yet could reach up to 69%, while that of C-Pt/SA-a was only 41%. All experimental results above indicated that MA-

Pt/SA catalyst had the outstanding low-temperature activity and high NO conversion due to its high Pt dispersion and Pt⁰ content.

3.5 Effect of particle size and valence state of Pt on NO oxidation activity

The NO + O₂ co-adsorption experiments were performed by *in situ* DRIFTS at 50 °C, for detecting the formation NO_x species over MA-Pt/SA-f and C-Pt/SA-f. In Fig. 7, the bands at the range of 1700–1200 cm⁻¹ for fresh samples could be ascribed to different nitrates and nitrites species. The band at 1634 and 1540 cm⁻¹ were associated with bridging nitrates and monodentate nitrates, respectively^{43,44}. The band at 1520 cm⁻¹ was assigned to the coordinate nitrites⁴³. A weak band at 1433 cm⁻¹ could be ascribed to the monodentate nitrites^{44–46}. Besides, the two bands at 1395 and 1369 cm⁻¹ were belonged to the asymmetric ionic nitrates, with a shoulder at 1324 cm⁻¹ corresponding to the bridging nitrites^{45,47}. For MA-Pt/SA-f, as shown in Fig. 7A, after 1 min of NO + O₂ co-adsorption, a strong band at 1634 cm⁻¹ (the bridged nitrates) was observed, together with two relatively weak bands at 1540 and 1520 cm⁻¹ (the monodentate nitrates and coordinate nitrites). Additionally, the extremely weak and broad peaks were also observed, related to the coordinate nitrites, asymmetric ionic nitrates and bridged nitrites. As the increased adsorption time, the variation of the band intensity belonging to the bridged nitrates was different from other nitrates or nitrites. The band intensity of bridged nitrates reached to maximum after 5 min and then began to decrease, while the band intensity of other nitrogen oxides gradually increased with increasing

Fig. 7 *In situ* DRIFTS spectra of NO + O₂ co-adsorption of MA-Pt/SA-f (A) and C-Pt/SA-f (B) in different adsorption time at 50 °C.

contact time. The DRIFTS spectra of NO + O₂ co-adsorption over C-Pt/SA-f were shown in Fig. 7B, the bands of which were similar with that of MA-Pt/SA-f although the intensity of these bands was diverse. After 1 min of adsorption, the bands of the bridging nitrates, monodentate nitrates and coordinate nitrites were presented, and no bands at 1450–1250 cm⁻¹ could be observed. Visibly, the band intensity corresponding to the bridging nitrates over C-Pt/SA-f was greatly lower than MA-Pt/SA-f, while the band intensity involving monodentate nitrates and coordinate nitrites over two samples was analogous. After 10 min, the monodentate and bridging nitrites (at 1433 and 1324 cm⁻¹) were presented, along with the ionic nitrates (at 1395/1369 cm⁻¹). Unlike MA-Pt/SA-f, the intensity of all bands increased with exposure time and reached up to maximum at 30 min. Besides, it's noteworthy that the band intensity of bridging nitrates over C-Pt/SA-f still was lower than MA-Pt/SA-f after 20 min, but the intensity of asymmetric ionic nitrates over C-Pt/SA-f was higher than MA-Pt/SA-f.

Our previous work⁴³, by comparing PtPd/SA with different particle size (9.9 and 16.5 nm), proved that the formation of the bridging nitrates could be liable to take place on smaller particles while ionic nitrates were easier to form on larger particles. Considering the experimental results mentioned above including XRD, TEM and CO-DRIFTS, it could be proposed that the smaller Pt particles over MA-Pt/SA-f led to the increased amount of bridging nitrates, which was good for NO oxidation. Moreover, according to the literature⁴⁸, introducing Pt into TiO₂ could facilitate the formation of surface nitrate species. Ji and

co-workers, by contrasting pre-oxidized and pre-reduced Pt/Al₂O₃, proposed that the amount of nitrates and NO₂ could be improved on Pt⁰ sites compared to PtO_x⁴⁴. In the light of the XPS and CO-DRIFTS, which confirmed that MA-Pt/SA-f had high Pt⁰ content and exposed more Pt sites, it could conclude that more surface nitrates, as intermediate products, could adsorb on MA-Pt/SA-f due to the smaller Pt particles and high Pt⁰ proportion at lower temperatures, compared to C-Pt/SA-f.

After the same adsorption time (30 min) over C- and MA-Pt/SA-f at 50 °C, *in situ* DRIFTS spectra were recorded at elevated temperatures from 50 °C to 300 °C, as shown in Fig. 8 A,B. For MA-Pt/SA-f, during raising temperature, the intensity of bands at the range of 1700–1600 cm⁻¹ involving the bridging nitrates progressively declined. This phenomenon might be owing to that nitrates decomposed and produced NO₂⁴⁹. The bands intensity of 1450–1250 cm⁻¹ presented a slight decrease from 50 °C to 300 °C, indicating that the asymmetric ionic nitrates and bridging nitrites transformed in part into other N_xO_y species. For C-Pt/SA-f, the intensity of those bands (bridging nitrates, ionic nitrates and bridging nitrites) also decreased with increasing temperature. Moreover, it was a remarkable fact that the amount of bridging nitrates adsorbed on MA-Pt/SA-f was distinctly more than C-Pt/SA-f before 200 °C. However, when the temperature rose up to 200 °C, their amount over two samples almost had no difference. In brief, these results revealed that MA-Pt/SA-f with small Pt size and high Pt⁰ proportion facilitated the formation of bridging nitrates as intermediate species for NO oxidation at lower temperatures, as well as rapid

Fig. 8 *In situ* DRIFTS spectra of NO + O₂ co-adsorption of MA-Pt/SA-f (A) and C-Pt/SA-f (B) at different temperature.

Fig. 9 CO (a), HC (b) and NO (c) conversion of MA-0.5Pt/SA-f and C-Pt/SA-f without H₂O.

decomposition (or desorption) of those at higher temperatures, bringing about an outstanding NO oxidation activity.

3.6 Reaction activity of MA-0.5Pt/SA-f

Meanwhile, MA-0.5Pt/SA-f was prepared and was compared with C-Pt/SA-f. The results of activity evaluation of two fresh samples could be seen in Fig. 9 and Table S3 (in Supporting Information). It was found that, although the loading of noble metal was reduced by a half, the T_{50} and T_{90} of CO or C₃H₆ conversion over MA-0.5Pt/SA-f reduced by 10–15 °C, contrasted with C-Pt/SA-f. For another one, the maximum conversion of NO over MA-0.5Pt/SA-f was 64%, which was obviously higher than that of C-Pt/SA-f. The phenomena mentioned above denoted that the MARI approach was able to greatly decrease the loading of Pt-based catalysts, simultaneously showing better catalytic performance.

4 Conclusions

In this work, the modified alcohol reduction-impregnation method was utilized to obtain high-performance Pt-based catalysts. XPS, CO-DRIFTS and H₂-TPR analysis indicated that the MARI method could get Pt catalysts with more active centers. Meanwhile, the results of XRD and TEM revealed that this synthetic technology could availably synthesize the Pt/SA catalyst with small Pt size and promote the efficacious utilization of Pt as well as enhance catalytic performance, compared to the traditional impregnation method. The maximum NO conversion of MA-Pt/SA-f reached up to 74%, which increased by 23% compared to C-Pt/SA-f without H₂O. After aging, MA-Pt/SA-f still had a pretty good catalytic performance (69% NO conversion). In presence of 7% H₂O, the maximum NO conversion of MA-Pt/SA-f was 68%. In addition, we prepared MA-0.5Pt/SA-f sample, and its NO conversion was 64% which still higher than that of C-Pt/SA-f (51%). Besides, *in situ* DRIFTS of NO + O₂ co-adsorption revealed that the smaller Pt particles and higher Pt⁰ content over MA-Pt/SA-f facilitated the formation of bridging nitrates as intermediate species for NO oxidation at lower temperature, as well as rapid decomposition (or desorption) of those at higher temperature, bringing about an outstanding NO oxidation activity. Here, this work showed that MARI method could apparently improve the catalytic activity of Pt-based catalyst even for lower loading of Pt. This method is significantly important for preparing highly active Pt catalysts with lower Pt loadings.

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Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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