

Preparation and Application of the HCA Catalyst Materials

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Abstract: To adsorb the excess hydrocarbons emitted during a period of engine cold-start and to solve the fault that Hydrocarbon (HC) adsorption behavior on Pd-based catalyst appears during a cold-start period of actual driving cycle in the vehicles of Dragon and Cherry, Hydrocarbon Absorber (HCA) material were led in catalytic performance of prepared HCA catalyst and HC adsorption process were tested, and then their applications were studied in the whole vehicle. In this work, Pd/Ce-HZSM-5 was used as the main recipes of HCA materials as well as a combination of zeolite and precious metals. Since Pd-based catalyst shows relatively good light-off performance, the combination of HC adsorption and early light-off activity has led to an improvement of overall HC emission reduction to Pd/Ce-HZSM-5. Usage of zeolite combined with Pd-based catalyst maximizes HC adsorption between 20~30 s during the cold-start period for fresh catalyst. For Dragon and Cherry models, their emission results show Pd/Ce-HZSM-5 catalyst is superior to Al₂O₃ molecular sieve catalyst for HC trap. HCA material has great research potential to meet high standards of HC emissions quality at low temperature.

Key words: exhaust purification; HCA catalysts; HC; molecular sieve; natural gas vehicle

Methane, an economical and clean alternative to fuels, is widely used in power plants and new energy vehicles. However, the emission of the unburned methane will cause the serious greenhouse effect, which is approximately 25 times higher than carbon dioxide^[1]. Dry reforming technology of methane (DRM, $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$, $H^\theta = +261 \text{ kJ mol}^{-1}$) has been investigated intensively and draws industrial attention since it offers advantages of converting CH₄ and CO₂ into liquid fuels and other chemicals (favorable H₂/CO ratio) compared to the classical steam reforming technology^[2-7]. One of the primary limitations of the dry reforming technology is the catalyst deactivation due to carbon deposition during the high temperature process^[8]. The catalytic combustion technology is a promising strategy to solve this problem by directly oxidizing methane into carbon dioxide and water. Noble metal based catalysts, such as platinum and palladium oxide, are effective in the catalytic combustion of methane^[9-14].

Several catalytic systems for CO₂ reforming with methane, including ion-exchanged zeolites, noble metals and metal oxide catalysts have been investigated^[15-18]. Hitherto, the

CeO₂-based materials are well known because of their high oxygen storage capacity (OSC)^[19-23]. Ceria-based, especially ceria-zirconia solid solutions have been reported to exhibit significant improvements in “carbon” formation reduction and catalysts stability compared to other non-reducible metal oxide supports (e.g. $\gamma\text{-Al}_2\text{O}_3$, SiO₂)^[24-33].

Because the exhaust gas temperature is lower than the catalytic converter light-off temperature during the cold start of engine, it makes harder for the conventional three way catalysts light-off. Cold start condition needs a much more concentrated mixture, and HC emissions during cold start process is very high. In automotive gasoline engine equipped with ternary catalytic converters, 60%~80% of the unburned hydrocarbons (HC) was produced during the cold start. To reduce HC emissions is the key to meet strict emission regulations during the cold start process. For Euro V high standard emission regulations, the proportion of the total emissions of pollutants emissions will be higher during the cold start. Processing methods of HC emissions can be divided into two categories during the cold start process. One is to accelerate

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the catalytic converter activation, and the essence is to improve catalytic converter exhaust gas temperature at the entrance. The other kind is to reduce the catalytic converter light-off temperature. The second kind is to set up HC adsorbed in front of the catalytic converter and HC is absorbed when the exhaust system is at low temperature. Catalytic converters can make the HC dealt with at the transformation, because it can reach the light-off temperature just at relatively high temperature.

The HC trap catalyst materials are loaded in preceding stage of closed couple catalyst in single stage double loading catalysts. Molecular sieve is used as the component of the catalyst to enhance physical adsorption capacity during cold start of engine. Because of its ability to capture the HC at low temperature, it can increase conversion rate of HC at low temperature. When the temperature reaches a specific temperature (350 °C), stripping HC after capture was oxidized into H₂O and CO₂ by catalytic oxidation, while CH₄ is hard to be oxidized at low temperature in conventional catalyst. Hitherto, in the present work the HCA materials were applied in the special catalyst on Compressed Natural Gas (CNG) engine for the first time in China, which exhibits good technical innovation.

1 Experiment

1.1 Catalyst preparation

A stoichiometric amount of Ce(NO₃)₃·6H₂O was dissolved in 45 ml distilled water, then was impregnated with HZSM-5 (catalyst factory of Nankai University, 400 g) and was stirred for 24 h at room temperature (RT). Finally was dried for 12 h at 120 °C, and then calcinated for 4h at 550 °C.

Pd(NO₃)₂ solution was impregnated with Ce/HZSM-5 and then was weighed (10% of palladium coating amount, the actual content was 9.8±0.07%). After palladium material hydrolysis, metric HCA materials were introduced by ball milling or glue grinding, and then they were prepared into a paste.

The prepared HCA palladium materials were coated to the surface of the catalyst according to the mixed coating or layered coating; the precious metal content and other coating formula kept unchanged; HCA materials were prepared by the method, which would not affect the existing production process because of its small proportion in the coating.

1.2 Catalyst characterizations

Specific surface area of samples was calculated according to the BET method by the N₂ adsorption isotherm at -196 °C, using a Quanta Chrome NOVA 2000e instrument. The powders X-ray diffraction (XRD) experiments were performed on a Japan Science D/max-R diffractometer using Cu K α radiation ($\lambda=0.154\ 06\ \text{nm}$). The X-ray tube was operated at 40 kV and 40 mA. The X-ray diffractogram was recorded at 0.01° intervals in the range of $10^\circ \leq 2\theta \leq 80^\circ$ with 3 s count accumulation per step. The identification of the phase was made with the help of the JCPDS cards (Joint Committee on Powder Diffraction Standards).

For the dispersity of Pd experiments, the sample was treated by the N₂ adsorption isotherm at -196 °C. Firstly, the sample was pretreated in H₂/Ar (80 mL min⁻¹) from RT to 450 °C, and held for 2 h. After the sample was pretreated in pure Ar (80 mL min⁻¹) to get a stable TCD signal baseline, the temperature was raised up to 460 °C and kept for 10 min. After cooling to 80 °C and held for 0.5 h, the sample was titrated by pure CO (300 μL) until peak area was kept constantly, which was recorded. The dispersity of Pd was calculated according to equation.

The catalytic activity tests were carried out in engine bench. Schematic drawing of engine bench is shown in Fig.1.

The engine bench was operated at 2900 r min⁻¹. In the experiment of light-off temperature performance, the entrance temperature was operated from 200 °C to 500 °C evenly, and its accuracy range was $\pm 10\ ^\circ\text{C}$. Working Air/Fuel (A/F) kept 14.6 and SV kept 40000 h⁻¹. In the experiment of A/F performance, the entrance temperature was operated at 450 °C, and its adjustable accuracy was $\pm 20\ ^\circ\text{C}$. Working A/F was operated from 13.6 to 15.6, and SV kept 40 000 h⁻¹.

For the C₃H₆-TPD experiments, the sample was pretreated in pure Ar (80 mL min⁻¹) from RT to 500 °C with a rate of 10 °C min⁻¹, and held for 2 h. After cooling to RT, the sample was treated in C₃H₆/He (80 mL min⁻¹) until it got a stable TCD signal baseline, and held for 0.5 h. Finally, the sample was treated in Ar (80 mL min⁻¹) until a stable TCD signal baseline and, then heated to 800 °C with a rate of 10 °C min⁻¹.

2 Results and Discussion

2.1 Structure properties of the catalysts

Molecular sieve is combined by TO₄ (T=Si, Al, P) tetrahedron structure unit in space in a certain order and it has developed porous structure and large specific surface area. During thermal or hydrothermal aging, the process of hole collapse might occur, which reduces the specific surface area sharply. Table 1 shows Pd/I-Ce-HZSM and Pd/HZSM have larger specific surface area than Pd/Al₂O₃ for fresh catalyst.

2.2 C₃H₆-TPD curves of Pd/I-Ce-HZSM, Pd/HZSM and Pd/Al₂O₃ samples

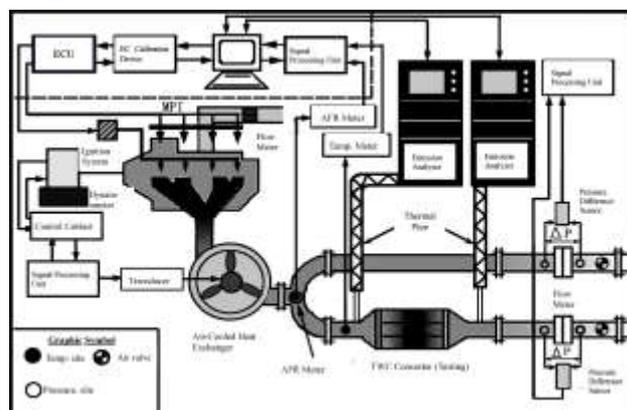


Fig.1 Schematic drawing of engine bench

Table 1 Specific surface area (SSA), pore volume, diameter (D), and dispersity of Pd of the catalysts

Samples	SSA _(BET) /m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	D/nm	Dispersity of Pd/(D%)
Pd/I-Ce-HZSM	272	0.1422	1.4902	60.0
Pd/HZSM	302	0.1521	1.20	23.0
Pd/Al ₂ O ₃	137	0.3377	49.47	40.0

Because the main component of the HC is C₃H₆, in the process of automobile exhaust, C₃H₆ was used as an imitated gas source of the HC in the experiment. Fig.2 shows that Pd/I-Ce-HZSM has low temperature adsorption performance for HC in exhaust emission, and the catalyst helps to reduce cold start emissions of the engine. It can be seen that Pd/I-Ce-HZSM has good catalytic activity. Therefore, the performance of Pd/I-Ce-HZSM will be discussed in the following sections.

2.3 HCA content on impact of the catalytic performance

2.3.1 Bench tests of DPCA N68 models

The effect of HCA content on the catalytic performance were shown in Fig. 3. It can be found that, with HCA content increasing, the HC conversion rate rises up clearly. It is clearly found from Fig.3 that the HC conversion rate reaches 24% when HCA content is 10% and the HC conversion rate reaches 35% when HCA content is 20%. Thus, it is concluded that with HCA content increasing, HC absorption ability is stronger during cold start. In addition, as can be seen in Fig.3, catalyst work window changes narrowly, making it hard to adapt automobile A/F ratio fluctuation at work. Therefore, HCA content should be controlled at 8%~12% in the catalyst.

2.3.2 Emission results of the DPCA N68 models

In order to validate further performance and usage of HCA catalyst in the whole vehicle, three kinds programs were designed. Compared with 10% HCA content, 0% HCA content catalyst and 20% HCA material were placed in the front and back of the catalyst, respectively. The results shown in Table 2 declare HC initial conversion rate changes largely; however, light-off temperature decreases slightly. HC initial conversion rate is best, and reaches 34% when 10% HCA materials is placed in the front of the catalyst. At the same time, the intersection point conversion of HCA catalyst decreases. In particular, the intersection point conversion of HCA catalyst decreases

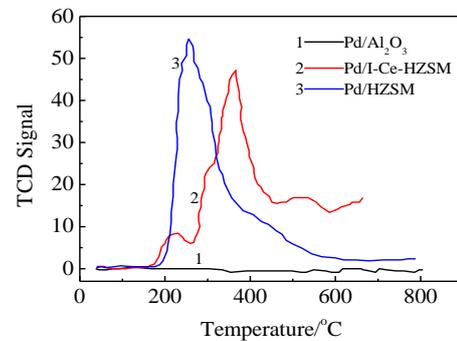


Fig.2 C₃H₆-TPD curves of Pd/I-Ce-HZSM, Pd/HZSM and Pd/Al₂O₃

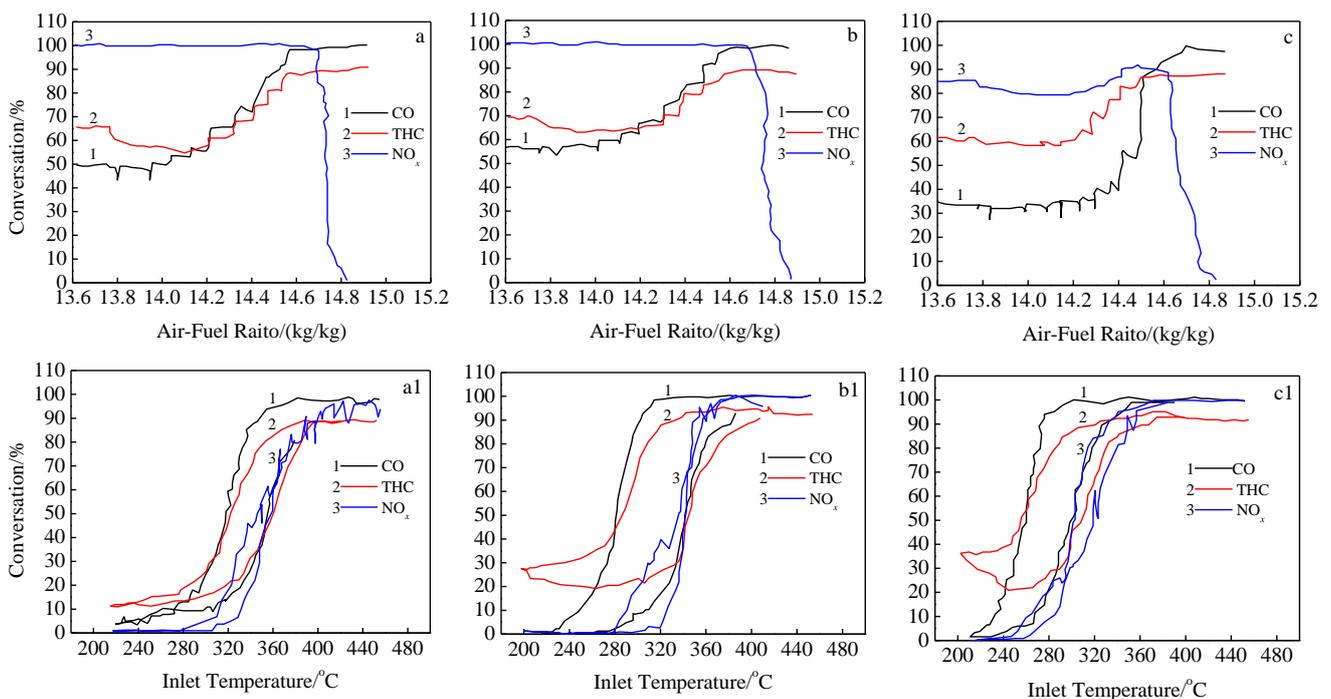


Fig.3 Effect of HCA content on the catalytic performance: (a) 0%, (b) 10%, and (c) 20%

Table 2 Emission results of the DPCA^a N68 models

Item		N68-8	N68-18	N68-19
Structure	CCC ^b	+0% HCA	+10% HCA	+10% HCA
	UFC ^c	+0% HCA	+0% HCA	+10% HCA
Test Result	Light off	230	288	334
	Max-conv.	98.5%	97.4%	97.3%
	Start-conv.	0%	34%	27%
	Crossing-conv.	99.3	98.4%	90%

a: Dong Feng Peugeot Citroen Automobile Company Ltd; b: closed couple catalyst, 123.3×76.2, 400/6.5, 50@0:7:1 (precious metals content @ Pt:Pd:Rh); c: under floor catalyst 123.3×88.9, 400/6.5, 50@0:7:1

from 98.5% to 90% when 10% HCA materials is placed in the back of the catalyst. The results show the catalyst is best when HCA material is placed in the front of the catalyst.

The DPCA N68 emissions results shown in Fig.4 explain why HCA materials has significant improvement in vehicle emissions for HC. Emission results are better when catalyst with HCA material is used in preceding stage than that of the catalyst with HCA materials used in preceding stage and back stage. While the NO_x emission results increase when HCA material is excessive in N68-19 samples.

From the transient emissions curves of the cold start, HC emissions peak decreases with HCA content increasing, but the duration of the peak is longer and longer. It illustrates that with the increase of the content of HCA, HC adsorption performance strengthens, but also increases catalyst light-off temperature.

2.3.3 Emission results of Cherry models

To give further insight into the performance and usage of HCA catalyst in the whole vehicle, emission results of Cherry models were also studied. Basic state and emission results of the Cherry models samples are presented in Table 3 and Table 4, respectively.

The observed emission results shown in Table 4 illustrate that after the introduction of molecular sieve, HC emission value declines obviously. Adopting different precious metals for collocation, HC declines by 24%, 28.8% and 37.5%. It suggests that improving coating reduces the effect of HC emissions in whole.

In addition, it is worth noting that with the NO_x emission values increasing, by different precious metals for collocation,

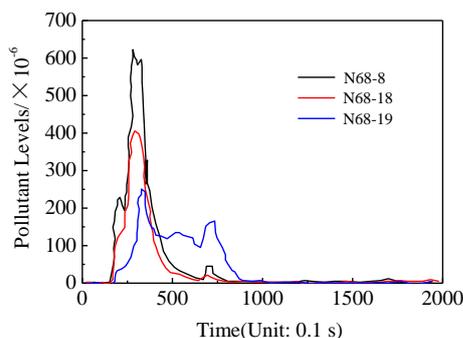


Fig.4 Emission results of DPCA N68 models

Table 3 Basic state of samples

No.	Input zone stage	Output zone stage	State	Remark
S11-C	80@0:75:5	16@0:14:2	Fresh	C
S11-U	80@0:19:1	16@0:14:2	Fresh	U
	+10%HCA ^a	+10%HCA		

a: 10 wt% HCA was added to samples

Table 4 Emission results

No.	CO		HC		NO _x		Remark
	g/km	%	g/km	%	g/km	%	
Cat.1	0.274	27.4	0.104	104	0.023	28.8	C+C
Cat.2	0.173	17.3	0.079	79	0.053	66.3	U+U
Cat.3	0.183	18.3	0.074	74	0.047	58.8	C+U
Cat.4	0.164	16.4	0.065	65	0.039	48.8	U+C

the rise of NO_x emission is 130%, 104% and 70%. Although the rise of NO_x emission is larger, in the end of discharge results still can meet regulatory requirements because NO_x of the models is relatively low (The Euro V standards state is as follows: emissions of CO is 1.0 g/km, emissions of HC is 0.1 g/km, emissions of NMHC is 0.068 g/km, emissions of NO_x is 0.06 g/km).

The test results show CO is descendant in general, and descendant range is between 33% and 40%.

In terms of the matching structure before and after level, the overall effect is that cat.4 is best, and cat.3 is better, while cat.2 is weakest.

3 Conclusions

1) HC capture effect is obvious when the HCA catalyst material is set up during cold start. The optimization model of Pd/HZSM-5 HCA catalyst is superior to commercial catalyst for trap effect of HC. It has great research potential to meet high standards of HC emissions quality at low temperature.

2) When HCA catalyst is used in preceding stage, compared with Al₂O₃ molecular sieve catalyst, HC and CO of HCA catalyst decline by 37.5% and 40.1%, respectively.

3) Loading method and the process of HCA materials in catalyst have a greater influence on the performance. Although the rise of NO_x emission is larger, in the end of discharge the results still can meet regulatory requirements.

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HCA 材料的制备与应用

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摘要: 为满足越来越严格的汽车尾气排放标准且有效降低冷启动时碳氢化合物(HC)排放以及解决神龙、奇瑞车型在冷启动时钯基催化剂的碳氢吸附(HCA)性能消失的缺点, 重点探究了所制备的HCA催化剂在发动机台架上的催化性能、HC吸附性能以及其在整车上的应用。在本研究中, 采用沸石和贵金属连接体的Pd/I-Ce-HZSM-5为HCA材料的主要组分, 对神龙和奇瑞车型而言, 其排放结果表明: 冷启动时, Pd/I-Ce-HZSM-5型HCA催化剂对HC捕集效果明显优于传统方式制备的催化剂, 由于钯基催化剂具有良好的起燃特性, 碳氢吸附的连接体及低起燃性使得Pd/I-Ce-HZSM-5催化剂的碳氢排放进一步减少。冷启动20-30s时, 沸石负载钯基催化剂的碳氢吸附量最大。HCA材料对于满足高标准的低温HC排放质量方面具有很大的研究潜力。

关键词: 尾气净化; HCA催化剂; 分子筛; HC; 天然气车

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