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Article

Kerosene cracking over supported monolithic Pt catalysts: Effects of SrO and BaO promoters

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ABSTRACT

The cracking of RP-3 fuel over supported monolithic Pt catalysts was studied at atmospheric pressure. The influence of BaO and SrO additives on the cracking reaction was examined. The effect of reaction time on the amount of carbon deposited during cracking was investigated. The catalysts were characterized using an automatic adsorption instrument (for Brunauer-Emmett-Teller analysis), temperature-programmed reduction, X-ray photoelectron spectroscopy, X-ray diffraction, and scanning electron microscopy. The results show that the total amount of gaseous products produced in catalytic cracking over a monolithic Pt/CA(CeO₂-Al₂O₃)-La-Al₂O₃ (CA is a support) catalyst increased by 39.7% compared with that produced by thermal cracking. The addition of BaO or SrO improved the total amount of gaseous products by 25.6% and 37%, respectively. If BaO and SrO were simultaneously added to the monolithic Pt/CA-La-Al₂O₃ catalyst, the catalytic effect improved significantly, and the total amount of gaseous products increased by 96.5%. The addition of BaO or SrO effectively inhibits carbon deposition, and the synergistic effect of BaO and SrO additives improves the cracking reaction.

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1. Introduction

When high-speed aircraft are in flight, air friction produces a large amount of heat, which causes the temperature of the fuselage and power equipment to rise sharply, causing safety problems. When the aircraft speed reaches Mach 6, the fuselage temperature can reach 1300 °C [1,2]. A passive cooling mode such as natural cooling cannot cool the vehicle adequately. The use of endothermic fuel [3–5] as a cooling agent for active cooling is highly desirable. In recent years, endothermic hydrocarbon fuels have become an important new type of fuel. By

exploiting its heat capacity, phase changes, and chemical cracking properties, an endothermic hydrocarbon fuel can absorb the heat from the high-temperature parts of a flight vehicle, and release the heat after arriving in the combustion chamber. This process not only resolves the problem of cooling the flight vehicle, it also produces a small-molecule hydrocarbon fuel with a better combustion performance, thereby improving the efficiency of energy use.

To promote fuel cracking at low temperatures and to improve the heat absorption performance, catalysts that improve the cracking rate and the gas yield of the cracking reaction are

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needed. In the 1990s, the rapid development of catalytic technology established the foundations for endothermic hydrocarbon fuel catalytic cracking research. Researchers in the United States spearheaded studies of endothermic hydrocarbon fuel catalytic cracking [6,7]. The main cracking catalysts are precious-metal, zeolite, and composite oxide catalysts. Among these, precious-metal catalysts were the first to be used in catalytic dehydrogenation. Catalytic dehydrogenation over precious-metal catalysts is simple and the product is stable, but precious-metal catalysts have obvious shortcomings, such as ease of poisoning, short lifetimes, high prices, and ease of carbon deposition [8]. Zeolite catalysts have high catalytic activities, produce little coke, are cheap, and provide higher heat sinks, but the porous zeolite catalysts collapse under high temperature, which makes their high-temperature performances relatively poor. Zhang et al. [9] investigated the cracking reaction of the endothermic fuel NNJ-150 over USHY, HZSM-5, SAPO-34, and USHY+HZSM-5(75:25) catalysts. The results show that the USHY catalyst has the highest selectivity for low-carbon olefins, but it deactivates quickly. The deactivation rate of the HZSM-5 catalyst is relatively slow, but its selectivity for low-carbon olefins is low. Compared with these two catalysts, SAPO-34 exhibits a lower cracking conversion rate and lower selectivity for carbon olefins. Xie et al. [10] investigated cracking of the high-density hydrocarbon fuel JP-10 over a ZSM-5 catalyst. In the temperature range 500–650 °C, the conversion rate by catalytic cracking is 60%–70% higher than that obtained using thermal cracking. This means that the ZSM-5 catalyst significantly improves the cracking conversion. A composite oxide catalyst combines the advantages of individual oxide carriers, giving better high-temperature stability, a stronger surface acid, and better textural properties [11]. A composite oxide catalyst such as $\text{CrO}_3/\text{Al}_2\text{O}_3$ can improve the cracking conversion rate significantly, increase the cracking depth, and achieve the goals of increasing the heat absorption capacity and improving the combustion performance; such catalysts have attracted widespread attention and research interest.

The catalytic dehydrogenation of hydrocarbons has a high heat absorption capacity, excellent specificity, and a high conversion rate. The products are relatively stable and contain a large amount of hydrogen, which is beneficial to combustion. Obviously, increasing the proportion of the catalytic dehydrogenation reaction improves aircraft performance. Depending on the vehicle, a monolithic dehydrogenation catalyst adopting an appropriate coating technology can be used for hypersonic vehicles.

Our research group has been engaged in the preparation and application of monolithic catalysts for a long time. In our previous studies, we investigated the influence of a CaO additive in monolithic loaded Pd-based catalysts on methanol cracking performance. The experimental results showed that the addition of CaO enhanced the interactions between the metal and the support, and increased the Pd electron density, resulting in Pd retaining a partial oxidation state $\text{Pd}^{\delta+}$ ($0 < \delta < 2$), and improved activity of the methanol catalytic cracking reaction. As a result, the temperature for complete cracking of

methanol was reduced by 34 °C [12]. In this paper, we change the dispersion of active Pt centers on the support surface by adding an alkaline-earth metal oxide in a loaded Pt-based catalyst. Alkaline-earth metal oxides have the ability to resist carbon deposition, which not only strengthens the catalytic effect in kerosene fuel dehydrogenation and cracking, but also effectively prevents catalyst deactivation caused by carbon deposition.

2. Experimental

2.1. Support and catalyst preparation

$\text{Ce}_{0.95}\text{Al}_{0.05}\text{O}_x$ was prepared by coprecipitation. $\text{Ce}(\text{NO}_3)_3$ and $\text{Al}(\text{NO}_3)_3$ were dissolved in high-purity water in a certain proportion, and then precipitation was induced with a buffer solution consisting of ammonia and ammonium carbonate. The precipitate was aged, dried, and roasted for 3 h at 600 °C to produce the support material, denoted by CA. An $\text{La-Al}_2\text{O}_3$ support was prepared by peptization, using the methods described in the literature [13,14].

The two as-prepared materials were used as the support and chloroplatinic acid was used as the Pt precursor. The Pt catalyst (Pt content 0.71%) was prepared by an impregnation method, and then roasted for 2 h at 550 °C and dried to give the powdered catalyst. This was then mixed with the two support powders in a 1:1 ratio, and the mixture was divided into four lots, numbered 1, 2, 3, and 4; 4.5% BaO, 4.5% SrO, and 2.3% BaO plus 2.3% SrO, were added to lots 2, 3, and 4, respectively. The mixtures were ball-milled with water, and then coated on a cordierite matrix (2.5 cm³, 62 hole/cm², Corning Corporation), dried at 120 °C, and roasted for 2 h at 550 °C. The monolithic catalysts obtained were denoted by Cat1, Cat2, Cat3, and Cat4.

2.2. Catalytic activity evaluation

RP-3 was chosen as the raw material for testing our laboratory-made experimental device for atmospheric kerosene cracking. The experimental apparatus includes a feed system, temperature-control system, heating system, reaction system, condensing system, and an analysis system, as shown in Fig. 1. A stainless-steel tube of diameter 12 mm was used as the reaction tube, with a preheating section of length 250 mm, and a reaction section of length 300 mm. The temperatures of the preheating section and the reaction section were controlled using a programmed temperature-control device. The temperature of the preheating section was controlled at 250 °C, and the temperature of the reaction section was set at 550, 600, 650, or 700 °C, for testing catalytic activity. Before the reaction, the reaction tube was purged with 99.99% N_2 for 30 min, and the kerosene feed-rate was controlled by the N_2 gas velocity. The reaction time was set at 80, 120, 180, or 240 min.

The gaseous products of kerosene cracking were analyzed by gas chromatography (GC2000 III, Shanghai Institute of Computing Technology). Fifty-meter HP-Al/S capillary separation columns with flame ionization detectors were used to detect small organic hydrocarbon molecules. Two-meter columns

Fig. 1. Schematic diagram of apparatus. 1—N₂; 2—valve; 3—needle valve; 4—mass flow controller; 5—feed tank; 6—temperature controller; 7—off valve; 8—pre-heater; 9—reactor; 10—cold trap; 11—gas chromatograph.

assembled and packed in the laboratory (chromatographic column stationary phase TDX-101), with thermal conductivity detectors, were used to detect hydrogen and other small inorganic molecules. The condensate recovery liquid was analyzed using gas chromatography/mass spectrometry.

2.3. Catalyst and carbon characterization

The textural properties of the catalysts were measured using a QUADRASORB specific surface area analyzer (Quantachrome Instruments, USA). The samples were treated for 1 h at 300 °C under a vacuum. N₂ was used as the adsorbate, and the measurement temperature was −196 °C.

XPS was performed using an XSAM-800 spectrometer (KRATOS Co., UK) with Mg K α excitation under a high voltage (13 kV) and current (20 mA), calibrated internally by the carbon deposit C 1s binding energy at 284.8 eV.

XRD patterns of the as-prepared materials were obtained using a DX-2500 X-ray diffractometer (China Dandong Fangyuan Instrument Co., Ltd.) with a graphite monochromator and Ni filter, using Cu K α radiation, operated at 40 kV and 25 mA. The samples were scanned in the 2θ range 10°–90° with a step size of 0.03°/s.

The reduction performances of all the catalysts were tested using H₂-TPR. The sample (100 mg) was heated to 400 °C at a heating rate of 8 °C/min in a flow of N₂, kept at that temperature for 45 min, and then cooled to room temperature. The flow gas was switched to H₂ (5%) in N₂ (flow rate 20 ml/min). The reduction was carried out from room temperature to 700 °C, at a heating rate of 8 °C/min (thermal conductivity detector).

The micro-morphologies of the sediments were observed by SEM using a Hitachi-S-4800 (Japan) instrument.

3. Results and discussion

3.1. Influence of BaO and SrO additives on carbon deposition and catalytic activity

Figure 2 shows the changes in the amount of carbon deposited with reaction time over different catalysts at 650 °C. For Cat1, which had no addition of BaO and SrO, carbon deposition increased with increasing reaction time. Carbon deposits aggregate in the channels of catalysts and cover the catalytic active centers [15], causing a decrease in catalytic activity and

even deactivation. With the addition of BaO, carbon deposition was partly suppressed. Increasing the reaction time by 2 h significantly reduced the ability of Cat2 to suppress carbon deposition. With the addition of SrO, also exhibited some ability to inhibit carbon deposition, but after 2 h the inhibition effect decreased. The co-addition of SrO and BaO not only improves the efficiency of the catalytic activity, but also prolongs the time for which it is able to inhibit carbon deposition. For Cat2, carbon deposition was reduced by 66.5% after 2 h, but 3 h later, the effect of carbon inhibition decreased significantly. After reaction for 2 h, Cat3 can effectively inhibit 74.2% of carbon deposition. Cat4 can effectively reduce the quantity of carbon deposited by 91.2% after 2 h, 89.9% after 3 h, and 67.0% after 4 h. The experimental results show that BaO and SrO inhibit carbon deposition to some extent, and the synergistic effect of BaO and SrO gives much better resistance to carbon deposition.

Table 1 gives the quantities of different gases produced by cracking at 650 °C. It shows that the catalysts extend the cracking reaction significantly, lower the activation energies of the reactant molecules, increase the reaction rate, and improve the yields of all small hydrocarbon molecules. For Cat1, the total volume of gas increased by 39.7% at the same temperature as that for thermal cracking. For Cat2, the total amount of gaseous products increased by 25.6% compared with Cat1. For Cat3, the total volume of gaseous products increased by 37% compared with Cat1. For Cat4, containing both BaO and SrO, the total volume of gaseous products was improved 1.75-fold compared with thermal cracking, and increased by 96.5% compared with Cat1.

Fig. 2. Influence of different additives on amount of carbon deposited.

Table 1

Influence of different additives on amounts of gaseous products from catalytic cracking of RP-3 at 650 °C.

Sample	Product (mmol/g)									
	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	<i>n</i> -C ₄ H ₈	<i>i</i> -C ₄ H ₈	C ₄ H ₆	Total
Pyrolysis	0.680	0.249	0.036	0.211	0.005	0.220	0.062	0.048	0.028	1.539
Cat1	1.177	0.330	0.084	0.183	0.023	0.229	0.052	0.055	0.017	2.150
Cat2	1.480	0.351	0.060	0.284	0.012	0.330	0.059	0.071	0.055	2.702
Cat3	1.614	0.388	0.064	0.322	0.016	0.352	0.064	0.064	0.062	2.946
Cat4	2.520	0.525	0.090	0.448	0.013	0.437	0.064	0.069	0.059	4.225

Thus it can be seen, adding BaO and SrO can effectively reduce the amount of carbon deposited, improve the catalytic activity, and increase the lifetime of the catalyst. In addition, the catalytic mechanism of the cracking reaction shows that the catalytic cracking reaction, the hydrogen transfer reaction, and aromatization reactions are competing reactions. It has also been pointed out in the literature that adding an alkaline-earth metal oxide can effectively inhibit aromatization reactions, reduce carbon deposition, and favor the cracking reaction [16].

3.2. Influence of BaO and SrO additives on catalyst textural properties

3.2.1 Textural properties of catalysts

Table 2 is the textural properties of catalysts. Small amounts of BaO and SrO do not affect the catalyst texture, which means that the different effects are not caused by differences among the specific surface areas of the catalysts.

3.2.2 N₂ adsorption-desorption isotherms of catalysts and pore size distributions

Figure 3 shows the N₂ adsorption-desorption isotherms of the catalysts. All the samples exhibit the typical IV-type adsorption isotherm, which is characteristic of mesoporous materials. All the samples have an obvious hysteresis loop because of the capillary condensation phenomenon [17]. The isotherms of these samples are typical H2 type, showing that the pore shapes are slit type and bottle type [18]. It also can be seen that the adsorption amount increased rapidly at $p/p_0 = 0.8–0.9$. This indicates that the samples have large average pore openings, relatively narrow pore size distributions, and pore sizes in the range 2–50 nm. The hysteresis loops show that the pore sizes and shapes are not completely uniform. When the relative pressure (p/p_0) is close to 1, the adsorption-desorption curves reach equilibrium. Figure 4 shows the pore size distribution of each catalyst. It shows that the pore size of each catalyst is concentrated in the region 2–14 nm, and the most probable pore size is about 6 nm. These results show that the additives do not significantly affect the textural properties of the materials.

Table 2

Textural properties of the catalysts.

Sample	Surface area (m ² /g)	Pore volume (ml/g)	Average pore diameter (nm)
Cat1	129.2	0.34	5.28
Cat2	120.1	0.29	4.86
Cat3	120.8	0.32	5.23
Cat4	119.1	0.32	5.42

Fig. 3. N₂ adsorption-desorption isotherms of the catalysts.

3.3. XPS

From Table 3, it can be seen that the Pt 4f_{5/2} binding energies of Cat1, Cat2, Cat3, and Cat4 are 76.78, 77.3, 77.07, and 76.71 eV, respectively. The Pt XPS curves are changed slightly, showing that the impacts of BaO and SrO on the Pt electronic valence is not obvious. The molar contents of Pt dispersed on the surfaces of Cat1, Cat2, Cat3, and Cat4 were 0.20%, 0.31%, 0.44%, and 1.29%, respectively, showing that the addition of BaO and SrO favors Pt dispersion on the catalyst surface, forming a shell-type catalyst with an uneven distribution of the active component. The contents of Pt dispersed on the catalyst surfaces are in the following order: Cat4 > Cat3 > Cat2 > Cat1. Because Pt acts as the active center of the catalyst, better dispersion of the Pt results in better catalytic activity. These re-

Fig. 4. Pore diameter distributions of the catalysts.

Table 3

Electronic binding energy and surface contents of Pt, Ba, and Sr in different catalysts.

Catalyst	E_b/eV		Surface concentration (%)		
	Pt 4f _{5/2}	Pt 4f _{7/2}	Pt	Ba	Sr
Cat1	76.78	73.40	0.20	0.00	0.00
Cat2	77.30	74.00	0.31	1.17	0.00
Cat3	77.07	73.82	0.44	0.00	1.07
Cat4	76.71	73.38	1.29	0.62	0.92

sults are in agreement with the catalytic activities for the cracking reaction and the carbon inhibition results.

3.4. XRD

Figure 5 shows the XRD patterns of the as-prepared catalysts. The diagram shows that at 28.8°, 32.9°, 47.4°, 56.4°, and 76.7°, indicating the presence of the cubic fluorite structure of the CeO₂ crystal. The diffraction peak at 67.1° is caused by the presence of γ -Al₂O₃. The XRD results show that the catalysts modified with BaO and SrO mainly exist in the CeO₂ cubic fluorite structure and the γ -Al₂O₃ phase. In the four diffraction patterns, no diffraction peak associated with Pt appears, indicating that the Pt species are amorphous or that they are highly dispersed on the support [19], which is beneficial to the catalytic activity.

3.5. H₂-TPR

The H₂-TPR results for the catalysts are shown in Fig. 6. The lower the reduction temperature of the Pt, which plays a key role in the catalyst, and the larger the peak area, the better the reduction performance of the catalyst and the better the catalytic activity, which increases the cracking reaction of RP-3. Figure 6 shows that the catalysts have an obvious reduction peak at about 250–300 °C. The peaks in the temperature region is caused by reduction of Pt [21]. The Pt reduction peak temperature moves to low temperature illustrating that adding BaO and SrO could improve the reduction performance of the catalyst, thereby promoting the catalytic cracking reaction. These results are also consistent with those for the cracking reaction. The reduction peak of Pt for Cat4 moved to 257 °C,

Fig. 5. XRD patterns of different catalysts. **Fig. 6.** H₂-TPR results for different catalysts.

illustrating that BaO and SrO have a synergistic effect. Therefore, the performance of the Cat4 improves further.

3.6. Carbon morphology

Figure 7 shows the morphology of the carbon deposits. The results show that the carbon deposits consist mainly of amorphous carbon (granular carbon) and filamentous coke. Filamentous carbon is formed by the reaction of some metal impurities (such as iron, nickel, and chromium) with the fuel, generating unstable metal carbides. Carbides can decrease the activation energy of fuel pyrolysis. After the carbide has been formed, it can decompose again to produce carbon and a metallic phase. When the carbonization process and decomposition process reach a balance, the produced carbon deposit is further dehydrogenated to form filamentous coke. The metals react with fuel again to form metal carbides [22–24]. Amorphous carbon is formed through the following processes: the cracking

Fig. 7. SEM micrographs of coke morphology on the catalysts surface.

of long-chain alkanes to form small-molecule olefins, formation of cycloparaffins or ring olefins by condensation, dehydrogenation to form alkyl benzenes, dehydrogenation again, condensation to form polycyclic aromatic hydrocarbon, and finally carbon deposit formation [25]. Some of the deposit is formed by another route: the cracking products of dienes and ring olefins form polycyclic olefins through Diels-Alder addition reactions, followed by dehydrogenation to form polycyclic aromatic hydrocarbons, and eventually carbon deposit formation [26].

4. Conclusions

The experimental results for the catalytic cracking of RP-3 kerosene show that the total amount of gaseous products produced in catalytic cracking over monolithic Pt/CA(CeO₂-Al₂O₃)-La-Al₂O₃ is increased by 39.7% compared with thermal cracking. Additions of BaO and SrO to the catalyst further improve the total amount of gaseous products by 25.6% and 37%, respectively. When BaO and SrO are simultaneously added to the monolithic Pt/CA-La-Al₂O₃, the total amount of gaseous products is increased by 96.5%. Studies have found that adding BaO and SrO to the Pt/CA catalyst had little impact on the crystal phase structure and textural properties, but the additives significantly reduced the reduction temperature of Pt, and increased Pt dispersion on the catalytic support surface. There are two major types of carbon deposit from RP-3 kerosene catalytic cracking, namely granular carbon (amorphous carbon) and filamentous carbon.

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Graphical Abstract

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Kerosene cracking over supported monolithic Pt catalysts: Effects of SrO and BaO promoters

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It shows that the simultaneous addition of BaO and SrO to a monolithic Pt/CA-La-Al₂O₃ catalyst significantly improves the catalytic effect and effectively inhibits carbon deposition.

整体式担载型Pt基催化剂上航空煤油的裂解：助剂SrO和BaO的影响

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摘要: 考察了整体式担载型Pt基催化剂上国产3号航空煤油(RP-3)的常压裂解反应, 着重探讨了添加BaO和SrO助剂对裂解效果的影响, 以及裂解时间对积炭量的影响. 采用全自动吸附仪、程序升温还原、X射线光电子能谱以及X射线衍射和扫描电镜等方法对催化剂进行了表征. 结果表明, 在整体式担载型Pt基催化剂上RP-3裂解的总产气量比热裂解提高了39.7%; BaO或SrO助剂的添加又使其总产气量又分别提高了25.6%和37.0%; 同时添加BaO和SrO的催化剂, 其催化裂解总产气量则提高了96.5%. BaO和SrO助剂均可有效地抑制积炭的生成, 而两者间的协同作用, 进一步抑制了RP-3催化裂解过程中积炭的生成.

关键词: 催化裂解; 积炭; 碱土金属氧化物; 吸热燃料; 整体式催化剂

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1. 前言

飞行器高速飞行时, 与空气摩擦将产生大量的热, 导致飞行器机身和动力设备温度急剧升高, 对飞行器安全带来隐患. 当飞行速度达到6马赫时, 机身温度可达1300 °C^[1,2]; 依靠自然冷却等被动冷却方式已不能满足飞行器的降温需求, 必须采用吸热燃料^[3-5]作为冷却剂进行主动冷却. 近年来吸热型碳氢燃料成为研究的热点之一. 它利用燃料自身的热容、相变和化学裂解, 吸收飞行器高温部位的热量, 并在进入燃烧室后释放出来, 既解决了飞行器的冷却问题, 又可得到燃烧性能更优的小分子碳氢燃料, 从而提高能量的利用率.

为促进燃料在较低温度下进行裂解, 提高吸热性能, 需要采用催化剂来提高裂解反应的裂解率和产气率. 20世纪90年代, 催化技术的迅猛发展为吸热型碳氢燃料的催化裂解研究奠定了基础. 美国率先开展了吸热型碳氢燃料催化裂解的研究^[6,7]. 裂解催化剂主要包括贵金属、沸石和复合氧化物等. 其中, 贵金属催化剂早先用于催化脱氢, 该反应简单, 产物稳定, 但该催化剂容易中毒, 寿命短, 价格昂贵, 容易积炭^[8].

沸石催化剂具有催化活性高, 结焦量少, 价格便宜等优点, 可使吸热型碳氢燃料获得更高的热沉, 但高温时孔易坍塌, 抗高温性能较差. 张波等^[9]考察了USHY, HZSM-5, SAPO-34和USHY+HZSM-5(75:25)等催化剂对吸热燃料NNJ-150裂解的催化作用. 结果表明, USHY对低碳烯烃选择性最高, 但失活较快; HZSM-5的失活速率较慢, 但对低碳烯烃选择性低; SAPO-34的裂化转

化率和低碳烯烃选择性均低于前两者. 谢文杰等^[10]考察了ZSM-5分子筛催化高密度碳氢燃料JP-10的裂解情况. 发现在500~650 °C时, 催化裂解转化率要高出热裂解的60%~70%, 说明ZSM-5分子筛催化剂可以明显提高燃料裂解转化率. 复合氧化物催化剂拥有几种复合载体本身性质的同时, 表现出更好的高温稳定性, 更强的表面酸性, 更好的织构性能^[11]; 如CrO₃/Al₂O₃等可以显著提高吸热型碳氢燃料的裂解转化率, 增加裂解深度, 达到增加吸热量、改善燃烧性能的目的, 因此受到广泛重视和研究.

另一方面, 碳氢化合物催化脱氢反应的吸热量大, 专一性好, 转化率高, 产物相对稳定, 且含有大量氢气, 利于燃烧. 显然, 增加吸热型碳氢燃料中催化脱氢反应的比例, 有利于飞行器性能的提高. 根据飞行器实际情况分析, 脱氢催化剂可通过整体型催化剂和相关的涂层技术用于高超声速飞行器上.

本课题组长期从事整体型催化剂的制备和应用研究. 曾考察了担载型Pd基催化剂中添加助剂Ca所制备的整体型催化剂对甲醇裂解性能的影响. 结果表明, Ca的添加使得金属和载体间相互作用增强, 增加了Pd周围的电子密度, 使Pd保持在部分氧化状态Pd^{δ+} (0 < δ < 2), 进而提高了甲醇催化裂解反应的活性, 使甲醇完全裂解温度降低了34 °C^[12]. 本文通过在担载型Pt基催化剂中添加碱土金属氧化物助剂, 改变活性中心Pt在载体表面的分散情况; 另外, 碱土金属氧化物具有一定的抗积炭作用, 增强对航空煤油燃料脱氢和裂解的催化效果, 以及有效防止因积炭而造成的催化剂失活.

2. 实验部分

2.1. 催化剂的制备

采用共沉淀法制备 $\text{Ce}_{0.95}\text{Al}_{0.05}\text{O}_x$ 。将 $\text{Ce}(\text{NO}_3)_3$ 和 $\text{Al}(\text{NO}_3)_3$ 分别用高纯水溶解后按一定比例配成盐溶液, 与氨水及碳酸铵配制的缓冲溶液并流滴定共沉淀; 沉淀完成后, 经陈化, 干燥, 600°C 焙烧 3 h, 即得所需载体材料, 标记为 CA。同时采用胶溶法制备 $\text{La-Al}_2\text{O}_3$ 载体, 其制备方法详见文献[13,14]。

以上述两种材料为载体, 氯铂酸为前驱体, 采用浸渍法制备 Pt 催化剂(Pt 含量均为 0.71%), 经干燥后于 550°C 焙烧 2 h, 得到粉末状催化剂。再将焙烧后的两种粉料按 1:1 混合, 分成四份, 记为 1#, 2#, 3#, 4#。在 2#, 3# 和 4# 中依次分别再加入 4.5% BaO, 4.5% SrO, 2.3% BaO 和 2.3% SrO, 加水球磨制浆, 然后涂覆到堇青石基体(8 mm × 8 mm × 27 mm, 62 孔/ cm^2 , 康宁公司)上, 然后在 120°C 烘干, 550°C 焙烧 2 h, 即可得整体式催化剂, 分别记作 Cat1, Cat2, Cat3 和 Cat4。

2.2. 催化剂的评价

以航空煤油 RP-3 为原料, 在自制的常压航空煤油裂解实验装置上进行催化剂评价。实验装置包括进料系统, 温度控制系统, 预热系统, 反应系统, 冷凝系统, 分析系统等六个子系统, 如图 1 所示。反应管为内径 12 mm 的不锈钢管, 反应管预热段长 250 mm, 反应段长 300 mm, 预热段和反应段采用程序控温装置控制温度, 预热段的温度控制在 250°C , 反应段的温度分别设定在 550, 600, 650, 700°C 下进行反应测试催化剂活性。反应前用 99.99% 的 N_2 吹扫 30 min, 并通过控制 N_2 流速来控制航空煤油的进料速度, 反应时间分别为 80, 120, 180 和 240 min。

裂解气相产物采用气相色谱仪(GC2000 III型, 上海技术计算研究)进行分析, HP-Al/S 毛细管分离柱 50 m, FID 检测器检测有机小分子烃类; 用实验室装配的 TDX-101 填充柱(2 m)和 TCD 检测器检测氢气等无机小分子; 冷凝回收液采用 GS/MS 分析。

2.3. 催化剂及积炭表征

催化剂的织构性能用美国康塔公司 QUADRASORB 型比表面仪测定。样品首先在 300°C 抽真空处理 1 h, 用 N_2 作为吸附质, 在 -196°C 下进行测量。

催化剂的 X 射线光电电子能谱(XPS)测定在英国 KRATOS 公司的 XSAM-800 型电子能谱仪上进行, Mg K_α 激发。X 射线高压和电流分别为 13 kV 和 20 mA, 电子结合能数值用 C 1s (284.8 eV) 标定。

材料的物相结构采用 DX-2500 旋转阳极 X 射线衍射仪(中国丹东方圆仪器有限公司)进行分析, Cu K_α 辐射, 石墨单色器, Ni 滤波片, 管电压 40 kV, 管电流为 25 mA, 扫描速率 $0.03^\circ/\text{s}$, 扫描范围 $2\theta = 10^\circ \sim 90^\circ$ 。

采用 H_2 程序升温还原(H_2 -TPR)测试催化剂的还原性能, 样品用量 100 mg。首先样品在流 N_2 (20 ml/min) 吹扫下, 以 $8^\circ\text{C}/\text{min}$ 升温到 400°C , 恒温 45 min 后降温, 然后切换为 5% H_2 -95% N_2 混合气(20 ml/min), 待降至室温后, 以 $8^\circ\text{C}/\text{min}$ 升温至 700°C , TCD 检测耗 H_2 量。

采用日本 Hitachi-S-4800 型扫描电镜(SEM)观察反应后催化剂中沉积物的微形貌特征。

3. 结果与讨论

3.1. 助剂 BaO 和 SrO 对裂解积炭量和催化反应活性的影响

图 2 为 650°C 反应时不同催化剂上积炭量随时间的变化。由图可见, 随着反应的进行, 没有添加 BaO 和 SrO 的 Cat1 上的积炭量逐渐增加, 积炭进入了催化剂孔道中, 覆盖了催化活性位^[15], 致使催化剂的效果降低甚至失活。BaO 的添加使得 Cat2 积炭有所抑制, 反应 2 h 后抗积炭效果明显减少; SrO 的添加, 也使 Cat3 具有一定的积炭抑制作用, 但 2 h 后抗积炭效果也有所降低。SrO 和 BaO 的同时添加, 既有效提高了相应 Cat4 样品的催化活性, 也有效延长了抑制积炭的时间; 反应 2 h 后 Cat2 能有效减少 66.5% 的积炭, 但 3 h 后, 抑制积炭效果明显降低; Cat3 在 2 h 反应后能有效抑制 74.2% 的积炭; Cat4 则能有效抑制积炭量 91.2%, 反应 3 h 后仍可抑制 89.9% 的积炭, 至 4 h 后仍可达 67.0%。可见, BaO 和 SrO 都有一定的抑制积炭效果, 而两者的协同作用使得混合使用时效果更佳。

表 1 为 650°C 时各催化剂上裂解反应生成各气相产物的量。由表可见, 催化剂的加入明显增加了裂解的反应深度, 使得反应物分子的活化能降低, 反应速率增加, 提高了各种小分子烃类产物的生成量。Cat1 的加入使得总产气量可提高 39.7%; 添加 BaO 的 Cat2 催化剂活性又有所提高, 总产气量可提高 75.6%; 而 SrO 的添加则使总产气量提高 91.4%; BaO 和 SrO 的同时添加则导致 Cat4 样品上总产气量较热裂解提高了 1.75 倍, 较 Cat1 提高了 96.5%。

由此可见, 助剂 BaO 和 SrO 的添加能有效减少积炭量, 提高催化剂的活性和有效利用时间。催化裂解反应机理的研究表明, 催化裂解反应与 H_2 转移反应、芳构化反应是竞争反应, 碱土金属氧化物的添加能够有效抑制芳构化反应, 从而减少积炭, 有利于裂解反应的进行^[16]。

3.2. 助剂BaO和SrO对催化剂织构性能的影响

3.2.1. 催化剂的织构性质

表2为各催化剂的织构性能. 可以看出, 添加少量的BaO 和 SrO, 对催化剂的织构性能影响不大, 表明各样品上裂解反应性能的差异主要不是因比表面积所致.

3.2.2. 催化剂的N₂吸附-脱附等温线和孔径分布

图3为各催化剂的N₂吸附-脱附等温线. 由图可见, 各样品均表现为典型的具有介孔材料特征的IV型吸附等温线, 并且由于毛细管凝聚现象, 所有样品均有明显的H2型滞后环^[17]. 表明样品的孔形状为狭缝型和瓶型^[18]. 还可以看出, 吸附支曲线在 $p/p_0 = 0.8 \sim 0.9$ 处吸附量迅速增大, 表明样品具有较大的平均孔径和相对集中的孔径分布, 且以2~50 nm的介孔为主. 同时表明样品的孔大小形状不完全均一. 由滞后环可判断在 p/p_0 接近1时, 吸附-脱附曲线才达到平衡. 图4为各催化剂的孔径分布. 由图可见, 各催化剂的孔径均集中在2~14 nm, 最可几孔径为6 nm左右, 表明助剂的添加并没有明显影响到材料的织构性能.

3.3. XPS结果

表3列出Cat1, Cat2, Cat3, Cat4中Pt 4f_{5/2}的结合能, 分别为76.78, 77.30, 77.07和76.71 eV, 表明BaO和SrO的加入对Pt的电子价态影响不大. 分散在Cat1, Cat2, Cat3和Cat4催化剂表面的Pt摩尔含量依次分别为0.20%, 0.31%, 0.44%和1.29%, 表明BaO和SrO的加入有利于Pt在催化剂表面的分散, 形成了活性组分不均匀分布的“蛋壳型”催化剂, 分散后的表面Pt含量的大小变化为Cat4 > Cat3 > Cat2 > Cat1. 由于Pt为催化剂的活性中心, 活性组分Pt的分散程度越好, 活性中心越多, 催化活性越高, 这可解释裂解反应结果.

3.4. XRD结果

图5为各催化剂的XRD谱. 由图可见, 各催化剂均在 $2\theta = 28.8^\circ, 32.9^\circ, 47.4^\circ, 56.4^\circ, 76.7^\circ$ 等处出现谱峰, 可归属为立方萤石结构CeO₂晶体; 在 $2\theta = 67.1^\circ$ 处为 γ -Al₂O₃的衍射谱峰. 可见BaO和SrO改性的催化剂主要以CeO₂立方萤石结构和 γ -Al₂O₃晶相存在. 另外, 各样品均未出现Pt的衍射峰, 说明Pt是以无定形态存在或者高

度分散于载体中^[19], 有利于催化剂活性的提高.

3.5. H₂-TPR结果

图6是各催化剂的H₂-TPR谱. 催化剂中起主要作用Pt的还原温度越低, 峰面积越大, 催化剂的还原性能越高, 其催化剂的活性越好^[20], 同时也越有利于RP-3裂解反应的进行. 由图可知, 各催化剂中在250~320 °C有一个明显的还原峰, 对应于Pt的还原^[21]. 但BaO或SrO的添加均使样品中Pt还原峰向低温位移, 说明催化剂的还原性能得到改善, 从而可促进催化裂解反应的进行, 与裂解反应结果一致. BaO和SrO的同时添加则使还原峰进一步位移至257 °C, 说明两者存在一定的协同作用, 因而Cat4样品的催化性能进一步提高.

3.6. 积炭的形貌

图7为反应后催化剂积炭的形貌. 由图可见, 炭沉积物主要有无定形碳(颗粒状碳)和丝状焦碳组成. 丝状碳则是由一些金属杂质(如铁、镍或铬等)与燃料反应生成不稳定的金属碳化物组成, 这些碳化物可降低燃料的裂解活化能, 但碳化物生成后又分解为碳和金属相, 当碳化过程和分解过程达到平衡时, 分解出的碳沉积下来, 随后进一步脱氢形成丝状的焦碳, 金属部分再次与燃料反应形成金属碳化物^[22-24]. 而无定形碳是由长链烷烃裂解后形成小分子的烯烃, 然后缩合形成环烷烃或环烯烃, 脱氢后形成烷基苯, 烷基苯经反复脱氢、缩合形成多环芳烃, 最终形成碳沉积^[25]; 还有一部分是裂解形成的二烯烃与环烯烃先经Diels-Alder加成形成多环环烯烃, 脱氢后形成多环芳烃并最终形成沉积^[26].

4. 结论

考察了整体式担载型Pt/CA-La-Al₂O₃催化剂上RP-3航空煤油催化裂解反应性能. 结果表明, 650 °C时催化裂解总产气量要比热裂解提高39.7%; 添加BaO或SrO后可分别提高25.6%和37%; 同时添加BaO和SrO时则可进一步提高96.5%. 研究发现, BaO和SrO的添加对Pt/CA催化剂晶相和织构性能的影响不大, 但明显促进了Pt的还原, 及其在催化载体表面的分散. RP-3航空煤油催化裂解反应积炭主要是纤维丝状碳和颗粒状碳(无定形碳).