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Article

The performance of $\text{Pt}/\text{Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ as Kerosene cracking catalysts

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ABSTRACT

$\text{Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ composite oxides for use as supports were prepared by coprecipitation and assessed with regard to their catalytic performance during the kerosene cracking reaction. The catalysts were characterized by N_2 adsorption-desorption, scanning electron microscopy-energy dispersive spectrometry, X-ray diffraction, and temperature-programmed desorption (NH_3 -TPD). The results showed that a support composed of $\text{ZrO}_2\text{:TiO}_2\text{:Al}_2\text{O}_3$ in the ratio of 1:1:3 exhibited the highest surface area and pore volume, and had the strongest surface acidity and highest acidic density. Energy dispersive spectroscopy results showed that catalysts from which carbon deposits were removed by heating under oxygen changed very little, and additional experimental data confirmed that these catalysts are readily regenerated while retaining their functionality. The gaseous reaction products produced over $\text{ZrO}_2\text{:TiO}_2\text{:Al}_2\text{O}_3$ (1:1:3)-supported Pt catalyst generated during catalytic cracking was 2.1 times and 1.4 times higher than that obtained with thermal cracking at 650 °C and 700 °C, respectively. An examination of the catalytic performance of Pt catalyst supported on composite oxides calcined at 1000 °C for 5 h indicated that these materials lost much of their catalytic activity.

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1. Introduction

The so-called "thermal barrier" is currently the greatest challenge associated with hypersonic flight. This phenomenon occurs when high-speed aircraft is in flight and the large amount of heat generated by air friction causes the temperature of the fuselage and power equipment to rise sharply, potentially leading to significant damage to these components [1,2]. In recent years, new endothermic hydrocarbon fuels have become very important. These represent excellent high-performance fuels for propulsion in hypersonic flight while simultaneously working as good coolants for the vehicles [3–5]. The cooling process is based primarily on the endothermic nature

of cracking reactions associated with the hydrocarbon fuel, which may include both thermal and catalytic cracking. Thermal cracking reactions require higher temperatures and are readily subject to coking and so catalytic cracking has become the main research focus in this field. The addition of catalysts reduces the initial reaction temperature, improves the rate and selectivity of the endothermic reactions, and generates a large number of olefins, which increases the heat absorption ability of the fuel. The catalytic cracking of endothermic hydrocarbon fuels is therefore becoming an attractive option [6,7].

In the 1990s, the rapid development of catalytic technology established the foundations for future study of the catalytic cracking of endothermic hydrocarbon fuels, led by researchers

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in the United States. The main cracking catalysts are precious metals, zeolites, and composite oxide catalysts. Among these, precious metal catalysts were the first to be used in catalytic dehydrogenation, because catalytic dehydrogenation over these materials is simple and produces stable reaction products. The precious metal catalysts, however, have obvious shortcomings, such as a susceptibility to poisoning, short lifetimes, high prices, and deactivation by carbon deposition [8]. Although the zeolite catalysts exhibit high catalytic activities, produce little coke, and are cheap and provide better heat sinks, porous zeolites tend to collapse under high temperature, which makes their high-temperature performance 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 showed that the USHY catalyst had the highest selectivity for low carbon olefins, but deactivated quickly. In contrast, the deactivation rate of the HZSM-5 catalyst was relatively slow, but its selectivity for low carbon olefins was poor. Compared with these two catalysts, SAPO-34 exhibited a lower cracking conversion rate and lower selectivity for low carbon olefins.

The support has an important effect on the performance of supported catalysts. TiO_2 and ZrO_2 have been widely used as catalyst supports due to their superior performance [10,11]. Pure TiO_2 and ZrO_2 , however, have relatively low surface area and poor thermal stability and can readily undergo phase changes during use, which will have an effect on the performance of the catalyst. These problems can be mitigated through the use of composite oxides, which usually have larger surface area, better thermal stability and mechanical strength as well greater surface acidity, and often lead to better catalytic performance [12–14]. $\text{ZrO}_2\text{-TiO}_2$ composite oxides not only maintain the unique properties of the original TiO_2 and ZrO_2 but also minimize the respective defects of the pure materials. For this reason, these composite oxides have attracted a great deal of attention in recent years and have been applied widely, such as in the esterification of *n*-butyl alcohol with acetic acid [15], the photo-oxidation of salicylic acid, the photo-reduction of Cr (VI) [16] and the oxidative removal of diesel exhaust particulate matter [17], as well as in NSR catalysts [18] where they serve as supports capable of resisting sulfur poisoning. According to the literatures [19,20], La_2O_3 and Y_2O_3 can be added to $\text{ZrO}_2\text{-TiO}_2$, and it is also possible to form $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ ternary composite oxides by introducing SiO_2 . These modifications produce $\text{ZrO}_2\text{-TiO}_2\text{-MO}_x$ composite oxide supports that show excellent physical and chemical properties and exhibit higher catalytic activity for specific reactions. Al_2O_3 has the advantages of larger surface area, better thermal stability and lack of crystallization at high temperatures, so Al_2O_3 has also been added to $\text{ZrO}_2\text{-TiO}_2$ composite oxide supports to improve their high-temperature stability. While previous studies [21] have shown that Al_2O_3 and $\text{ZrO}_2\text{-TiO}_2$ may be used to produce a two-component support system with superior catalytic properties during water vapor transformation, the application of $\text{ZrO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ supports to kerosene (RP-3) cracking and the petroleum chemical industry has seldom been reported. However, our long-term research concerning the application of

Pt/CA ($\text{CeO}_2\text{-Al}_2\text{O}_3$) in the kerosene cracking reaction resulted in some useful findings [22], and this paper reports the preparation of a series of $\text{ZrO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ composite oxides (ZTA) with varying Al contents by coprecipitation. The structure and surface morphology of these composite oxides may be tuned, along with their surface acidity and high temperature stability, by adding different levels of Al_2O_3 into the support. The resulting materials may be used as catalyst supports in conjunction with Pt (the Pt/ZTA series) in the RP-3 cracking reaction and we have assessed their catalytic performance in this regard. The results show that the Pt/ZTA series exhibit exceptional catalytic effects.

2. Experimental

2.1. Preparation of $\text{Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ composite oxides and catalysts

$\text{Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ composite oxides were prepared by coprecipitation method [23,24]. $\text{Zr}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$, $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in high-purity water in the desired ratio (mass ratio of $\text{ZrO}_2\text{:TiO}_2\text{:Al}_2\text{O}_3 = 1\text{:}1\text{:}x$, where $x = 1, 2, 3, 4, 5$) and precipitation was induced by the addition of a pH 10 buffer solution composed of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$. The resulting precipitate was aged, dried for 2 h at 120 °C and calcined for 3 h at either 600 or 1000 °C to produce the support materials, denoted as ZTA600_x and ZTA1000_x respectively, where $x = 1, 2, 3, 4, 5$.

The two series of as-prepared materials (ZTA600_x and ZTA1000_x) were used as the supports and chloroplatinic acid was used as the Pt precursor. The Pt-loaded catalysts (Pt content 0.70%) were prepared by impregnation, following which the impregnated supports were calcined for 2 h at 550 °C and dried to obtain powdered catalysts. The catalysts were subsequently ball-milled with water and then coated on the inner walls of stainless steel pipes (15 cm, ϕ 3 mm $\times$ 0.5 mm, 0.471 cm³), following which the coated pipes were dried at 110 °C and heated for 2 h at 500 °C. The catalysts produced from the ZTA600_x ($x = 1\text{--}5$) material are denoted as Cat1 through Cat5 while those made from the ZTA1000_x ($x = 1\text{--}5$) are termed as Cat6 through Cat10. The loading of all catalysts is 0.035 g/15 cm.

2.2. Catalytic activity evaluation

RP-3 was chosen as the raw material for assessing kerosene cracking in our laboratory-made experimental device. The experimental apparatus included components for fuel feeding, temperature control, heating, reaction, product condensation and data analysis, as shown in Fig. 1. A stainless-steel tube (15 cm, ϕ 3 mm $\times$ 0.5 mm) was used as the reaction tube, divided into a 250 mm preheating section and a 150 mm reaction section. The temperatures of these two sections were controlled using a programmed temperature control device. The preheating section was held at 300 °C while the reaction section was heated to 600, 650, 700 or 750 °C during the reaction trials. The reactant flow was accurately controlled using a mass flow me-

Fig. 1. Schematic diagram of the experimental apparatus. 1. Nitrogen; 2. Valve; 3. Needle valve; 4. Mass flow meter; 5. Feed tank; 6. Temperature controller; 7. Shut off valve; 8. Pre-heater; 9. Heater; 10. Cold trap; 11. Gas chromatograph.

ter, generating a residence time in the reaction section of 0.3 s. The gaseous products resulting from kerosene cracking were analyzed by gas chromatography (GC2000 III, Shanghai Institute of Computing Technology, Shanghai, China). A 50 m HP-Al/S capillary column coupled with a flame ionization detector was used to detect small organic hydrocarbons while a 2 m column assembled and packed in our laboratory (stationary phase TDX-101) in conjunction with a thermal conductivity detector was used to measure hydrogen, based on an external standard method.

2.3. Catalyst characterization

The textural properties of the catalysts were assessed using a Quadrasorb specific surface area analyzer (Quantachrome Instruments, USA). Samples were initially held under vacuum for 1 h at 300 °C, then cooled to −196 °C using liquid N₂, at which point their N₂ adsorption was measured. The micro-morphological characteristics of the catalyst coatings were observed using a Hitachi-S-4800 scanning electron microscope (SEM). Qualitative and quantitative analyses of elemental distributions in microscopic regions of the catalyst powders were performed using an Oxford-IE-250 energy dispersive spectrometer (EDS). X-ray diffraction (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 with Cu K α radiation, operated at 40 kV and 25 mA. The samples were scanned over a 2θ range of 10°–80° at a step rate of 0.03°/s.

The surface acidity of each catalyst was measured by NH₃-temperature programmed desorption (NH₃-TPD) using a TP-5076 TPD instrument. During these measurements, a sample of 100 mg was heated to 400 °C at a rate of 8 °C/min in a flow of N₂, maintained at 400 °C for 45 min and then cooled to room temperature. The gas was then switched to 2% NH₃ in N₂ (20 mL/min) for absorption for 60 min and then over the temperature was increased from ambient to 850 °C at a heating rate of 8 °C/min, employing a thermal conductivity detector.

3. Results and discussion

3.1. Catalytic activity evaluation

Table 1 presents the data obtained from thermal and catalytic cracking trials at 650 and 700 °C. These results indicate that the total gas quantities over Cat1 through Cat5 materials during catalytic cracking were much greater than these from thermal cracking. The addition of the catalysts thus reduces the cracking reaction temperature while increasing the reaction rate, generating an increased quantity of numerous low molec-

Table 1
Gaseous reaction products resulting from catalytic cracking of RP-3 at 650 and 700 °C.

Sample	Product amount (mmol/g)															
	H ₂		CH ₄		C ₂ H ₆		C ₂ H ₄		C ₃ H ₈		C ₃ H ₆		C ₄		Total	
	650 °C	700 °C	650 °C	700 °C	650 °C	700 °C	650 °C	700 °C	650 °C	700 °C	650 °C	700 °C	650 °C	700 °C	650 °C	700 °C
None	3.10	5.33	0.07	0.54	0.02	0.1	0.06	0.52	0	0.02	0.06	0.47	0	0.26	3.31	7.24
Cat1	6.23	7.94	0.21	1.25	0.05	0.27	0.13	0.91	0.02	0.07	0.23	1.16	0.14	0.65	7.01	12.25
Cat2	8.05	8.22	0.27	1.35	0.07	0.43	0.16	1.01	0.03	0.12	0.28	1.20	0.13	0.82	8.99	13.15
Cat3	9.16	10.73	0.36	2.08	0.09	0.44	0.21	1.35	0.04	0.11	0.33	1.69	0.22	1.03	10.41	17.43
	(9.12)	(10.65)	(0.32)	(2.12)	(0.11)	(0.48)	(0.25)	(1.35)	(0.05)	(0.11)	(0.36)	(1.71)	(0.26)	(0.96)	(10.47)	(17.38)
Cat4	7.24	9.73	0.21	1.14	0.05	0.23	0.12	0.85	0.02	0.06	0.20	1.13	0.09	0.62	7.93	13.76
Cat5	6.53	7.65	0.22	1.30	0.06	0.27	0.13	0.94	0.02	0.08	0.23	1.25	0.15	0.77	7.34	12.26
Cat6	—	4.11	—	0.28	—	0.04	—	0.24	—	0.01	—	0.25	—	0.29	—	5.22
Cat7	—	4.45	—	0.28	—	0.04	—	0.23	—	0.01	—	0.25	—	0.28	—	5.54
Cat8	—	4.64	—	0.50	—	0.08	—	0.41	—	0.02	—	0.44	—	0.51	—	6.60
Cat9	—	3.76	—	0.43	—	0.07	—	0.39	—	0.01	—	0.39	—	0.48	—	5.53
Cat10	—	3.96	—	0.29	—	0.05	—	0.25	—	0.01	—	0.27	—	0.31	—	5.14

Reaction conditions: residence time = 0.3 s, the reaction temperature section = 600, 650, 700, or 750 °C.

The numbers in parentheses represent the product amount over regenerated Cat3.

ular weight reaction products. Cat3 exhibited the best catalytic activity, generating gases rate at 650 and 700 °C were 10.41 and 17.43 mmol/g respectively, which were 2.1 and 1.4 times higher than the results of thermal cracking (3.31 and 7.24 mmol/g). The Pt/ZTA600_x series catalysts have large surface area, which is advantageous during the catalytic cracking reaction. Cat3 demonstrates that superior catalytic activity is associated with the largest surface area, which is not unexpected because a large surface area is conducive to contact between the reactant molecules and the catalyst, thus increasing the probability of interactions and improving the catalytic efficiency. The Pt/ZTA1000_x series of catalysts does not exhibit efficient catalytic activity at 700 °C, because their total gas production are less than that obtained from thermal cracking. The total gas production obtained from Cat8 is the largest in the group and the closest to the results from thermal cracking. Because the Pt/ZTA1000_x supports were calcined at 1000 °C, their surface area and acid contents were decreased dramatically, such that the catalytic activities of the Cat6 to Cat10 materials are very low. It is possible that the stainless steel pipe itself may also play a catalytic role; however, the Cat6 to Cat10 catalysts were coated on the inner surface of the pipe, which should prevent contact between reactant molecules and the stainless steel.

Carbon deposition on used Cat3 was removed by oxygen-enriched heating, and the performance of this regenerated Cat3 was assessed by again in the reaction vessel. The total product amounts obtained with the reused catalysts were 10.47 and 17.38 mmol/g at 650 and 700 °C, respectively, which are quite close to the results obtained with the fresh material. The Cat3 catalyst is therefore capable of regeneration.

Figure 2 plots the quantities of different gases produced by cracking at several temperatures when using Cat3. These data show that the gas phase products are primarily methane, ethane, ethylene, propane, propylene, butene, butane and butadiene. The cracking reaction evidently proceeds slowly below 650 °C. With increases in temperature, the reactant molecular motion is accelerated, and thus it is expected that the rate of the cracking reaction increases. Methane, ethylene and propylene are produced in greater amounts than ethane, propane, butane and butene during the catalytic reaction. This occurs because

Fig. 2. Gaseous product distributions resulting from catalytic cracking over Cat3.

the reactant molecules initially adsorb on the catalyst surface and then move into pore channels where they react with active sites. During this stage of the reaction process, secondary cracking of C4 products takes place to generate increased quantities of C1 and C2 products [25].

3.2. Textural properties of catalysts

Table 2 summarizes the specific surface area, pore volume, and average pore diameter of the ZTA600_x and ZTA1000_x materials. It can be seen that the surface area of the Pt/ZTA600_x series initially decreases with increase in the Al₂O₃ content after which they begin to increase, with maximized surface area and pore volume (336.8 m²/g and 0.73 ml/g) obtained at an Al₂O₃ content of 60%. The surface area of Cat8 and Cat10 drop to 38.1 and 33.5 m²/g after calcination at 1000 °C. A larger surface area is beneficial with regard to uniform dispersion of active sites and thus plays a positive role by reducing the sizes of the active centers, preventing active sites from agglomerating during sintering. In contrast, small surface area reduces the dispersion of active sites and can lead to agglomeration, affecting the catalytic activity. As noted above, the larger surface area of Cat3 correlates with its superior catalytic activity. N₂ adsorption data show that the ZTA600_x and ZTA1000_x support materials exhibit typical type IV adsorption isotherms as well as a hysteresis loop during H₂ adsorption (as per the IUPAC classification), showing that both slit and bottle-type pore shapes are present. The pore size distribution as calculated by the BJH method shows that only pores with openings of less than 6 nm exist [26,27].

3.3. SEM results

Figure 3(a) shows the internal morphologies of the reaction pipes following thermal oxidation at high temperatures. The pipe walls are evidently coated with 4 to 6 μm particles following the high-temperature oxidation process. As the pipe walls become increasingly coarse, the growth of the catalysts along the wall will become more pronounced. Fig. 3(b) shows the pipe wall morphology following the application of a coating of catalyst, from which it is evident that the catalyst is uniformly deposited on the inner pipe wall, and that the catalyst particles are 2 to 4 μm in size. Fig. 3(c) shows the pipe wall after it has been subjected to carbon deposition during the cracking reaction; the carbon deposits cover the surface of the catalyst and block the pore channels. Fig. 3(d) shows the pipe wall after carbon has been dislodged from the catalyst by high-tempera-

Table 2
Textural properties of different catalysts.

Sample	Surface area (m ² /g)		Pore volume (ml/g)		Average pore diameter (nm)	
	600 °C	1000 °C	600 °C	1000 °C	600 °C	1000 °C
ZTA1	272.1	15.2	0.58	0.03	4.27	4.44
ZTA2	319.2	14.1	0.64	0.04	4.01	5.51
ZTA3	336.8	38.1	0.73	0.13	4.08	5.95
ZTA4	315.6	14.7	0.69	0.04	4.64	5.51
ZTA5	307.6	33.5	0.67	0.11	4.34	5.81

Fig. 3. SEM micrographs of the inner walls of the catalyst-loaded tubes. (a) Inner wall of the reaction pipes; (b) Catalyst coating; (c) Carbon deposition of the catalyst surface; (d) Regenerative catalyst coating.

Table 3

EDS data for Cat3 and deposited coke.

Sample	O K		C K		Al K		Ti K		Zr L		Pt M		Total (%)
	wt%	atom%	wt%	atom%	wt%	atom%	wt%	atom%	wt%	atom%	wt%	atom%	
Fig. 3(b)	44.3	67.8	—	—	24.0	21.8	12.0	6.1	12.6	3.4	7.1	0.9	100
Fig. 3(c)	25.0	27.3	41.4	63.9	0.8	0.5	13.8	5.3	11.1	2.3	8.1	0.8	100
Fig. 3(d)	49.1	72.7	—	—	21.4	18.3	10.2	5.0	11.5	3.0	7.8	1.0	100

ture oxidation. It can be seen that the catalyst is once more exposed and that the catalyst structure has not been degraded. EDS analyses (Table 3) were conducted to elucidate the changes in the catalyst before and after carbon deposition and removal. The results show that fresh and regenerated Cat3 materials both have the same atom percentages. Taken together with the SEM images, which indicate that the structure of the catalyst does not change, these results explain why the regenerated catalyst functions as well as it does after regeneration. Scanning the reaction pipe inner wall after carbon deposition shows that the carbon content of the catalyst following reaction is 63.9%. As noted, this level of carbon deposition on the surface of the catalyst blocks the catalyst pores and hinders contact between the catalyst and reactant, thus slowing the cracking reaction. For this reason, carbon deposition is one of the primary causes of cracking catalyst deactivation [28].

3.4. XRD results

Figure 4 presents the XRD patterns of the as-prepared catalysts, showing that Pt/ZTA600_x catalysts exist as basic amorphous structures. Neither the anatase TiO₂ crystal phase nor ZrTiO₄ were observed. This may be due to the addition of Al³⁺, which may transfer a portion of the Ti⁴⁺ and Zr⁴⁺ into the interior of the material during the precipitation process, preventing the formation of ZrTiO₄ crystals and the anatase crystal phase [29]. Crystallization of the composite oxide will decrease both the surface area and surface acidity with concurrent lessening

of the catalytic activity. The addition of Al₂O₃ shifts the crystallization temperature of the TiO₂ and ZrTiO₄ crystal phases, however, preventing this degradation of the surface area and surface acidity and thus improving the activity of the catalysts. Fig. 4(b) indicates that the crystal structures of Cat6 to Cat10

Fig. 4. XRD patterns of Pt/ZTA600_x (a) and Pt/ZTA1000_x (b).

have been altered such that their XRD patterns present diffraction peaks attributed to a ZrTiO_4 (PDF = 07-0290) phase at 30.5° [30], an $\alpha\text{-Al}_2\text{O}_3$ (PDF = 05-0712) phase at 25.7° , 35.3° , 37.9° , 43.5° , 57.7° , 66.5° , and 68.4° [31] and an anatase TiO_2 (PDF = 65-0190) phase at 27.5° , 36.3° , 54.3° , and 63.8° [32]. The diffraction peaks associated with the $\alpha\text{-Al}_2\text{O}_3$ crystal phase increase in intensity with increasing Al_2O_3 content, while the peaks attributed to ZrTiO_4 weaken.

3.5. NH_3 -TPD

Figure 5 shows the NH_3 -TPD profiles of Pt/ZTA600_x catalysts. Adsorbed NH_3 was continuously stripped from the catalyst surfaces, showing that the acidic surface sites of these catalysts have a homogeneous, continuous distribution and that there is many types of surface acidity [33]. It can also be seen that each catalyst has a strong desorption peak in the low temperature region (100 to 400 $^\circ\text{C}$), interpreted as the desorption peak of a weak-medium acid. The Cat3 desorption peak area is the largest in this region. In the 400 to 700 $^\circ\text{C}$ region, strong acid desorption peaks are observed and the peak area of Cat3 and Cat4 are much larger than those of the other three materials. The weak-medium acid and strong acid peaks of Cat3 are also much sharper than the peaks of the other catalysts, demonstrating relatively high acidic center density in Cat3.

Table 4 summarizes the acid distributions of these catalysts and shows that the total amount of acid decreases in the order of Cat3 > Cat4 > Cat2 > Cat5 > Cat1 and that Cat3 has the greatest concentration of strong acid (1.050 mmol/g). Catalyst acidity appears to first decrease and then increase with increasing levels of Al_2O_3 , and the most acidic catalyst is associated with an Al_2O_3 content of 60%. The NH_3 -TPD plots, along with the

Fig. 5. NH_3 -TPD profiles for different Pt/ZTA600_x catalysts.

Table 4
Acidity of different catalysts.

Catalyst	Weak-medium acid sites (mmol/g)	Strong acid sites (mmol/g)	Total acid sites (mmol/g)
Cat1	0.058	0.231	0.289
Cat2	0.181	0.463	0.651
Cat3	0.430	1.050	1.480
Cat4	0.303	0.605	0.909
Cat5	0.087	0.429	0.515

above data concerning acid distributions, explain why Cat3 has the greatest surface acidity and the most concentrated acid center density. Reports [34, 35] have stated that C–C bond rupture occurs at strongly acidic sites on the catalyst while hydrogen transfer reactions proceed at different acidic centers. Therefore, increasing the surface acidity of the catalysts increases the ratio of C–C fractures to hydrogen transfer reactions, thus improving the olefin selectivity and reducing carbon deposition. The acidic centers of Cat1, Cat2, and Cat5 are primarily of the strongly acidic types and, while these strongly acidic centers are concentrated, their overall quantity is low. The quantity of strongly acidic sites in Cat4 is larger but diffuse, and this material does not show high acidic center density. In contrast, Cat3 exhibits strong surface acidity, concentrated acid centers and a large quantity of strongly acidic sites, all of which are beneficial to the cracking reaction.

4. Conclusions

We investigated the catalytic cracking of RP-3 kerosene over a series of $\text{Pt/Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ catalysts. The results show that employing these catalysts leads to obvious improvements in the production of gaseous products from the cracking reaction. The total amounts of gaseous products are increased by factors of 2.1 and 1.4 at 650 and 700 $^\circ\text{C}$ compared with thermal cracking. The total amount of gaseous products obtained from Cat1, Cat2, Cat4 and Cat5 catalysts also increased when differing amounts of catalyst were used. However, the Pt/ZTA1000_x catalysts series did not demonstrate suitable catalytic activity. The Cat3 has the highest surface area, pore volume, the greatest degree of surface acidity, the greatest concentration of strongly acidic sites, and change very little after carbon deposits are baked off, and other experimental results verify that Cat3 catalyst is readily regenerated.

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Graphical Abstract

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The performance of Pt/Zr_xTi_xAl_{1-2x}O₂ as Kerosene cracking catalysts

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A series of Pt/Zr_xTi_xAl_{1-2x}O₂ catalysts were prepared and they showed good performance for the kerosene cracking reaction. The quantities of gaseous products obtained from catalytic cracking using ZrO₂:TiO₂:Al₂O₃ (1:1:3)-supported Pt catalyst are increased by factors of 2.1 and 1.4 compared with the quantities generated by thermal cracking at 650 and 700 °C, respectively.

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国产航空煤油裂解催化剂Pt/Zr_xTi_xAl_{1-2x}O₂的性能

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摘要: 采用共沉淀法制备了一系列Zr_xTi_xAl_{1-2x}O₂复合氧化物载体材料, 考察了其作为裂解催化剂载体对航空煤油裂解反应的影响。采用全自动吸附仪、X射线衍射、扫描电镜/能谱仪联用、NH₃-程序升温脱附等手段对催化剂进行了表征。结果表明, 当ZrO₂:TiO₂:Al₂O₃质量比为1:1:3时催化剂具有最大的比表面积和孔容; 具有最强的表面酸性和最集中的强酸中心密度, 且具有良好的再生功能。实验结果表明, 载体ZrO₂:TiO₂:Al₂O₃质量比为1:1:3时催化剂上650 °C裂解产气量较热裂解提高了2.1倍, 700 °C时提高1.4倍。另外, 该系列载体材料经1000 °C焙烧5 h后, 所制得的催化剂几乎失去了催化活性。

关键词: Zr_xTi_xAl_{1-2x}O₂复合氧化物; 管式涂层; 催化裂解; 吸热燃料; 酸性

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1. 前言

当飞行器以高超声速飞行时,与空气摩擦产生的热量急剧增加,飞行器表面及动力设备温度迅速升高,对飞行器造成极大损害^[1,2],成为超高音速飞行器的主要难题.吸热型碳氢燃料是近年来崛起的一类新型燃料,它既可作为性能优良的燃料,为高超音速飞行提供推进动力;又可作为良好的冷却剂来达到为高超音速飞行器冷却的目的^[3–5].飞行器的冷却过程主要是利用吸热型碳氢燃料的裂解反应热来吸收热能,包括热裂解和催化裂解.热裂解的反应所需温度较高且易结焦,所以催化裂解成为研究的热点.催化剂的加入既可降低初始反应温度,提高催化剂的催化活性,又可提高发生吸热反应的选择性,生成大量烯烃,提高燃料的吸热能力,使得催化裂解成为吸热型碳氢燃料具有吸引力的反应之一^[6,7].

上世纪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.美国率先开展了对吸热型碳氢燃料在催化裂解方面的研究.裂解催化剂主要包括贵金属催化剂、沸石催化剂和复合氧化物催化剂等.贵金属催化剂早先被用于催化脱氢,因为反应简单,所以产物稳定,但是贵金属催化剂容易中毒,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,但沸石催化剂高温下会出现孔结构坍塌,高温稳定性较差.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,失活较快. HZSM-5的失活速率较慢,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.

对于负载型催化剂,载体对催化剂性能的影响很大. ZrO_2 和 TiO_2 具有特殊的性能,作为催化剂载体已得到广泛关注^[10,11].单一的 ZrO_2 和 TiO_2 的比表面积较小,热稳定性较差,且在使用过程中易发生晶相变化,从而影响催化剂的反应性能.复合氧化物则具有更大的比表面积、更好的热稳定性和机械强度以及更强的表面酸碱性,作为载体往往表现出以更好的催化性能^[12–14].将 ZrO_2 和 TiO_2 制成 ZrO_2 - TiO_2 复合氧化物,不但可以保持 ZrO_2 和 TiO_2 原有的特殊性能,而且可以克服二者各自的缺点. ZrO_2 - TiO_2 复合氧化物近年来已引起人们极大的关注,已广泛用于乙酸与正丁醇的酯化反应^[15],水杨酸的光致氧化和Cr(VI)的光致还原^[16],柴油车尾气中颗粒物的氧化

净化^[17], NSR催化剂的抗S中毒载体^[18]等.研究发现^[19,20],可以通过加入助剂 La_2O_3 或 Y_2O_3 对其进行改性,以及引入 SiO_2 制成 ZrO_2 - TiO_2 - SiO_2 三元复合氧化物等方法,得到物化性质更优异的、对特定反应有更高催化活性的 ZrO_2 - TiO_2 - MO_x 复合氧化物载体. Al_2O_3 具有大比表面积,热稳定性较好,高温下不易结晶的优点,所以将 Al_2O_3 引入 ZrO_2 - TiO_2 复合氧化物载体中有利于催化剂的高温稳定性.有研究表明^[21],用 Al_2O_3 和 Zr_2 - TiO_2 作为双组分载体对水汽变换反应有较好的催化性能.但将 ZrO_2 - TiO_2 - Al_2O_3 载体用于煤油裂解和石油化工却鲜为报道.本课题组长期研究Pt/CA(CeO_2 - Al_2O_3)催化剂上煤油裂解反应,已取得一些有意义的结果^[22],本文采用共沉淀法制备了一系列不同 Al_2O_3 添加量的 ZrO_2 - TiO_2 - Al_2O_3 (ZTA)复合氧化物,以调节其结构、织构性能、表面酸性和高温稳定性,并将其作为载体制备了Pt/ZTA催化剂,考察了该系列催化剂上国产航空煤油(RP-3)裂解反应的性能,结果表明,该催化剂具有优异的催化效果.

2. 实验部分

2.1. $\text{Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ 复合氧化物和催化剂的制备

采用共沉淀法制备系列不同 Al_2O_3 含量 $\text{Zr}_x\text{Ti}_x\text{Al}_{1-2x}\text{O}_2$ 复合氧化物^[23,24].将一定量 $\text{Zr}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ (AR, 山东鱼台清达精细化工厂), $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ (CP, 丹东化学试剂厂), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (CP, 成都化学试剂厂)溶于高纯水中,按相应的质量比配成稀溶液(ZrO_2 : TiO_2 : $\text{Al}_2\text{O}_3 = 1:1:x$, $x = 1, 2, 3, 4, 5$),以氨水和碳酸铵混合溶液作为沉淀剂,调节pH值至10,进行共沉淀,将沉淀进行陈化处理,抽滤,洗涤,120 °C干燥2 h, 600 °C焙烧3 h,得到系列催化剂载体材料,记为ZTA600_x; 1000 °C焙烧3 h后,得到ZTA1000_x样品.

催化剂采用浸渍法制备.用一定浓度的氯铂酸溶液浸渍ZTA600_x和ZTA1000_x系列载体(Pt 0.7wt%),再经120 °C干燥, 500 °C焙烧2 h,得到Pt/ZTA系列催化剂粉末.然后将所得催化剂粉末和少量水混合,球磨,制成浆液.取处理好的15 cm, $\phi 3$ mm $\times$ 0.5 mm不锈钢管(孔体积为0.471 cm³)进行涂覆,110 °C干燥, 500 °C焙烧2 h后得系列催化剂, ZTA600_x负载的催化剂记为Cat1, Cat2, Cat3, Cat4, Cat5. ZTA1000_x制得的催化剂记为Cat6, Cat7, Cat8, Cat9, Cat10.催化剂上载量均为0.035 g/15 cm.

2.2. 催化剂评价

以航空煤油RP-3为原料,在自制的一台常压煤油裂

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,反应装置,冷凝装置,分析系统等六个子系统。如图1所示,反应管是15 cm长的 $\phi 3$ mm $\times$ 0.5 mm的不锈钢管,其中预热段长250 mm,反应段长150 mm。这两段均采用温控装置控制温度,其中预热段控制在300 °C恒温,反应段分别控制在600, 650, 700和750 °C。质量流量计精确控制流量,反应段停留时间0.3 s。对裂解的气相产物用六通阀直接进入气相色谱仪(GC2000 III上海技术计算研究所),选用50 m HP-AL/S毛细管分离柱和FID检测器检测有机小分子烃类;用实验室自己装配的2 m填充柱(固定相TDX-101)和TCD检测器检测H₂,外标法定量。

2.3. 催化剂表征

催化剂的织构性能用Quadrascorb SI全自动比表面测定仪(美国康塔公司)测定。样品首先在300 °C下抽真空处理1 h,以N₂作为吸附质,−196 °C下进行测量。

采用日本Hitachi-S-4800型扫描电镜(SEM)观察催化剂涂层的微形貌特征,采用英国Oxford-IE-250型能量弥散谱仪(EDS)对催化剂粉料的微观区域的元素分布进行定性定量分析。

催化剂的结构性能采用DX-2500旋转阳极X射线衍射(XRD)仪(中国丹东方圆仪器有限公司)进行分析。采用Cu K α 辐射,石墨单色器,Ni滤波片,管电压为40 kV,管电流为25 mA,扫描速率0.03°/s,扫描范围 $2\theta = 10^\circ$ – 80° 。

采用TP-5076型程序升温脱附(TPD)动态吸附仪(天津先权公司)测试材料的表面酸性。样品的用量为100 mg,首先样品在N₂ (30 ml/min)中以8 °C/min升到400 °C,恒温45 min后降温,然后切换为NH₃ (2%) + N₂ (98%)混合气吸附60 min,流速为20 ml/min,待降至室温后,以8 °C/min升至900 °C,TCD检测器检测。

3. 结果与讨论

3.1. 催化剂活性

表1为650和700 °C时热裂解与催化裂解总产气量。由表可知,Cat1–Cat5的加入降低了裂解反应的温度,提高了裂解反应的速率,各种小分子的生成量也相应的增加,产气量远高于热裂解。其中以Cat3催化活性最好,650和700 °C时产气量分别可达到10.41和17.43 mmol/g (消耗1 g油产生x mmol气体),分别较热裂解产气量(3.31和7.24 mmol/g)增加了2.1倍和1.4倍。Pt/ZTA600_x系列催化剂具有较大的比表面积,有利于催化裂解反应的发生,

其中Cat3表现出最高的催化活性和它有最大的比表面积有一定的关系,比表面积大有利于催化剂与反应物分子的接触,从而增加了反应物与活性组分碰撞机率,提高了催化剂的催化效率。700 °C时Pt/ZTA1000_x系列催化剂催化活性较低,产气量小于热裂解,其中产气量最大的Cat8最接近于热裂解,这是由于经过1000 °C的ZTA1000_x焙烧后比表面积和酸性急剧减少所致。然而不锈钢管也有一定的催化作用,Cat6–Cat10系列催化剂涂覆在钢管内表面,阻止了反应物分子与不锈钢管的接触。对积碳后的Cat3进行富氧焙烧后,测试其裂解性能,650和700 °C的产气量分别可达到10.47和17.38 mmol/g,与新鲜Cat3样品相同,可见,该催化剂具有良好的再生功能。

图2为Cat3在不同温度时裂解气相产物分布图。气相产物主要是甲烷、乙烷、乙烯、丙烷、丙烯、丁烯、丁烷和丁二烯等。低于650 °C时,裂解反应较慢;随温度的升高,反应物分子运动加速,碰撞增加,裂解反应速率加快,产气量增加。甲烷、乙烯和丙烯在裂解过程中产生量比乙烷、丙烷、丁烷和丁烯等大得多。反应物分子先吸附在催化剂表面,再发生反应,其中部分C₄发生了二次裂解反应,因而C₁和C₂小分子的生成量增加^[25]。

3.2. 催化剂的织构性能

表2为ZTA600_x和ZTA1000_x系列样品的比表面积、孔容和平均孔径。可以看出,随着样品中Al₂O₃含量的增加,催化剂的比表面积先增加后减少,至60%时达最大,比表面积和孔容分别为336.8 m²/g和0.73 ml/g。经1000 °C焙烧而制的Cat8和Cat10比表面积分别仅为38.1 m²/g和33.5 m²/g。比表面积大有利于活性组分的均匀分散,可降低活性中心的尺寸和防止活性组分烧结团聚。相反,比表面积小,则活性组分分散度可能会下降,易引起活性中心的团聚,影响催化剂活性。Cat3的高活性与其大比表面积有一定的关系。N₂物理吸附实验结果表明,ZTA600_x和ZTA1000_x系列样品的吸附等温线属于IV型,滞后回线为H2型(IUPAC分类法),表明其孔结构为狭缝型和墨水瓶型,由BJH法计算得到的孔径分布结果显示,仅存在孔径<6 nm的小孔^[26,27]。

3.3. SEM/EDS结果

图3(a)为高温热氧化后的管道内部形貌,由于高温焙烧后管壁被氧化,出现4–6 μ m大小的颗粒,此时的管道内壁比较粗糙,有利于催化剂在管壁上生长。图3(b)为催化剂涂覆后的管道内壁的SEM图片。可见催化剂很均匀地平铺在管壁内侧,催化剂颗粒为2–4 μ m。图

3(c)为裂解反应积碳后管道内壁的图片. 由图可知, 积碳覆盖了催化剂表面甚至堵塞了催化剂孔道. 图3(d)为将积碳管道经过富氧焙烧后管内壁催化剂形貌. 由图可见, 积碳被氧化后催化剂重新暴露出来, 其结构并没有被破坏. 为了更清楚地了解积碳前后催化剂的变化情况, 对图3(b)–(d)进行EDS能谱测试(表3). 结果表明, 经富氧焙烧后, Cat3样品的原子百分比没有变化, 结合SEM图片说明, 催化剂的结构和成分并未变化, 反应结果表明该催化剂具有良好的再生功能. 对积碳后的反应管内表面扫描可知, 来源于积碳的C原子含量已达63.9%, 积碳阻碍了裂解反应的进行, 是裂解催化剂失活的最主要原因之一^[28].

3.4. XRD结果

图4是各Pt催化剂的XRD谱. 由图4(a)可知, Cat1–Cat5基本以无定型结构存在, 没有出现锐钛矿的TiO₂晶相和ZrTiO₄, 这可能由于Al³⁺的添加导致在沉淀过程中把一部分Ti⁴⁺和Zr⁴⁺包裹到内部所致^[29]. 复合氧化物晶化后, 比表面积下降和表面酸性减弱, 均使得催化剂活性下降. Al₂O₃的加入提高了锐钛矿TiO₂和ZrTiO₄的晶化温度, 抑制了催化剂比表面积和酸性的下降, 从而有利于提高催化剂的活性. 由图4(b)可知, Cat6–Cat10晶型已经基本形成, 均在30.5°出现的ZrTiO₄ (PDF = 07-0290)晶相的衍射主峰^[30]; 25.7°, 35.3°, 37.9°, 43.5°, 57.7°, 66.5°和68.4°等处出现 α -Al₂O₃ (PDF = 05-0712)晶相的衍射峰^[31]; 27.5°, 36.3°, 54.3°和63.8°等处出现锐钛矿的TiO₂ (PDF = 65-0190)晶相的衍射峰^[32]. 并且随着Al₂O₃含量的增加, α -Al₂O₃的衍射峰强度增强, ZrTiO₄衍射峰强度减弱.

3.5. NH₃-TPD结果

图5是Cat1–Cat5样品的NH₃-TPD图. 由图可见, 各样品表面吸附的NH₃呈连续脱附状态, 表明其表面酸中

心强度呈非均一化连续分布, 且表面的酸性位种类较多^[33]. 各催化剂都在100–400°C出现一个肩峰, 对应于弱酸和中强酸位, 其中以Cat3峰面积最大. 400–700°C的高温脱附峰对应于强酸位, 其中Cat3和Cat4峰面积比Cat1, Cat2和Cat5的大得多. Cat3的弱酸峰和强酸峰峰形相对尖锐, 酸中心密度相对集中. 表4为Cat1–Cat5样品的酸量分布. 由表可知, 总体上各催化剂的总酸量顺序为Cat3 > Cat4 > Cat2 > Cat5 > Cat1, 其中Cat3的强酸酸量最大, 为1.050 mmol/g. 随着Al₂O₃含量的增加, 催化剂的酸性先增加后减少, 至60%时酸性最强. 由此可见, Cat3具有最强的表面酸性和最集中强酸中心密度. 研究表明^[34,35], C–C键的断裂需在催化剂的强酸中心上进行, 而其最主要的竞争反应氢转移反应则在不同的酸性位都可以进行, 且主要生成烷烃和大分子芳烃, 易积碳, 堵塞催化剂的孔道, 导致催化剂失活. 因此, 增强催化剂表面酸性和提高强酸中心密度有助于提高烯烃的选择性, 减少积碳量. Cat1, Cat2和Cat5的样品酸性中心以强酸为主且分布较集中, 但酸量较小; Cat4强酸峰峰面积较大, 但比较弥散, 强酸中心密度分布不集中, 而Cat3则具有较强的表面酸性和集中的强酸中心密度以及较大的强酸量, 从而有利于裂解反应的进行.

4. 结论

考察了负载型Pt/Zr_xTi_xAl_{1-2x}O₂系列催化剂上煤油RP-3常压裂解反应性能. 结果表明, 催化剂的加入明显的提高了裂解反应产气量, 其中650°C时Cat3催化剂上产气量较热裂解提高了2.1倍, 700°C时提高了1.4倍. 1000°C焙烧后制得的Cat6–Cat10催化剂活性较低. 结果表明, Cat3具有最大的比表面积和孔容, 最强的表面酸性和最集中的强酸中心密度, 经富氧焙烧后其组成和结构变化不大, 因而具有良好的再生功能.