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ARTICLE

Catalyst performance of novel Cr/ZnAlLaO catalyst for oxidative dehydrogenation of isobutane

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The oxidation dehydrogenation of isobutane using a chrome-based catalyst supported on a novel ZnAlLaO mixed oxide support was investigated. The characterization and performance of Cr/ZnAlLaO catalysts were compared with several traditional catalysts. The Cr/ZnAlLaO catalyst showed the best selectivity and conversion rate with highest stability.The performance of Cr/ZnAlLaO catalyst is strongly depends on the Cr content and support properties. The activity peak of isobutane oxidative dehydrogenation occurs at 18 wt% of Cr_2O_3 loading. The selectivity of isobutene and the conversion of isobutene reach to the maximum of 84.07% and 52.44%, respectively. Correlation was observed between coke formation and catalyst deactivation. Moderate alkalinity on the ZnAlLaO support surface is helpful to suppress coke formation as well as improve the catalytic activity and stability. Appropriate water vapour addition to the feed can improve the catalyst stability, while both the selectivity of isobutene and conversion of isobutane decreased.

Introduction

Oxidative dehydrogenation (ODH) of isobutene has received considerable research attention as a route to obtain isobutene (an additive of petrol, used for replacing the lead-containing compounds) in recent years [1]. Due to the development of petroleum and chemical industries, many green technologies were developed for using alkanes. Isobutene is an intermediate mainly from catalytic cracking of petroleum by-products. Chromium supported on alumina was widely employed in this reaction as a catalyst. However it also exhibits several undesired features such as catalysing the side reactions of coking, cracking and finally leading to catalyst deactivation [2].Most of those disadvantages could be avoided in the case of improving the properties of the catalyst. Hence, the most important challenge is to develop a more effective catalytic system which could produce a high yield of the required isobutene products. Supported chromium oxide-based catalysts have been studied for many decades as an active component in many reactions. One of the applications of supported chromium oxide-based catalysts is for the ODH of isobutane to isobutene. Jibril et al. [3] studied the chromium oxide-catalysts activity on different supports surface. The result showed that the order of isobutane conversion rate under 250°C as follow: $Cr_2O_3/Al_2O_3(11.0\%) > Cr_2O_3/SiO_2(8.4\%) \approx Cr_2O_3/TiO_2(8.2\%) > Cr_2O_3/MgO(7.1\%)$. Sloczynski et al. [4] studied the chrome activities on different supports as the following sequence: $Al_2O_3 \approx ZrO_2 > MgO > TiO_2 > SiO_2$. Recently, studies demonstrated that the chromium-oxide based catalysts used for the ODH of isobutane on different supports could be activated at relatively low temperatures 200-300 °C [5, 6]. According to the different system, maximum selectivity of isobutene was between 50-80% and conversion of isobutene was about 10-20%. The Al_2O_3 catalysts exhibit the best performance among these catalysts. However, there action stability and activity of the catalysts are still not satisfactory. Thus, it is necessary to further improve the catalytic performance of Al_2O_3 catalysts in the ODH of isobutane.

Recently, numerous studies have been carried out to measure the modification of the stabilities and activities of the Al_2O_3 catalysts by adding some alkali metal as an active component, such as Pt, Cr, Sn and Ni. Comparison with relatively low Cr surface concentration systems, chromium-oxide-based catalysts with higher concentrations of Cr in industrial plants, is generally supported on alumina with alkali oxides as promoters [7]. After addition of the active component of Cr and additives of K_2O, K-CrO_X/Al_2O_3, the catalyst has exhibited the best performance. McVicker et al. [8] reported the relationship between the acidity and basicity on the support surface as well as the relationship between catalyst reaction performance and resistance to carbon deposition. Moreover, a further attraction of ODH of isobutane is the modification of supports with elements, such as Zn and La [9].

In the present study, various chrome-based catalyst supports and Cr/ZnAlLaO catalyst with different Cr contents were prepared for the isobutane dehydrogenation of isobutane. The object reported here was to study the catalytic and chemical-physical properties in ODH of isobutane. Cr/ZnAlLaO catalysts with different amounts of Cr loading were investigated by several techniques, including XRD, CO_2-TPD and XPS. The reaction conditions such as reaction temperature, alkoxy oxygen ratio and the influence of water vapour were optimized in detail. The catalytic performance was carried out at a relatively lower temperature than that applied industrially. All the results obtained are compared with data from references in an effort to provide us with important information and form a better understand of Cr/ZnAlLaO catalyst on this catalytic system of ODH.

Experimental

Catalyst preparation

Catalysts were prepared according to the procedure described as following [10]. The powder of pseudo boehmite (AlOOH) was originally calcined at 600 °C for 3 h in order to obtain γ-Al_2O_3. The appropriate amount of γ-Al_2O_3 with $Zn(NO_3)_2$•$6H_2O$ (Al/Zn = 8.5-10.5, molar ratio) and $La(NO_3)_3$•$6H_2O$ (La/Al = 0.025, molar ratio) were commixed evenly, and then instilled in the appropriate diluted nitric acid (AR, 99%) aqueous solution (2 wt.%) as adhesive solvent drop by drop until the powder mixture as bonded together to similarly form the dough. Then, it was extruded via a banded extruder (extrusion moulding method) to form original supports. After drying with stoving chest at 50 °C for 12 hours, the supports were cut into cylindrical particles with length about 2 mm to 3 mm. Finally the cylindrical supports were calcined in a muffle furnace at 650 °C for 5 hours.

Subsequently, Cr was introduced into calcined ZnAlLaO by immersing ZnAlLaO support into different concentrations of $Cr(NO_3)_3$•$9H_2O$ aqueous solution. For a typically process, the support was firstly immersing into prepared $Cr(NO_3)_3$•$9H_2O$ solution about 15 min in a stirred vessel and maintained at 60 °C. After drying in a stoving chest at 105 °C for 12 h, the dried catalyst was calcined at 500 °C for 4 h with steam for dechlorination. The heating rate is 2 °C/min. Then the catalyst was heated up to 700 °C and maintained at this temperature for further 5 hours.

Catalyst testing

The catalytic activities measurements were carried out in a continuous flow reaction system consisting of stainless steel single pipe fixed-bed reactors(Φ9×2 mm, 500 mm in length) with a gas chromatograph for on-line product analysis 2 g of catalysts were used each time. The reactant gases were fed through mass flow controllers (MFC), which was used to deliver a defined flow of each gas. The ratio of i-C_4H_{10}/O_2 was 3.5 (molar ratio) at space velocity (SV) of 200 mL/g•h. The feed compositions were obtained by mixing 6.67 mL/min of isobutane, 1.67 mL/min of oxygen and 0.05mL/min of water vapour at normal condition. For the tests without water vapour, the feed compositions were calculated by keeping the same ratio of i-C_4H_{10}/O_2 and SV. The activity measurements were carried out at 560–600 °C under atmospheric pressure. The reaction temperature was measured by three thermocouples, one at the top, the other at middle, and another at the bottom, which placed near the catalyst bed and was maintained constant at 580 °C for 10 h at normal conditions. The Fig.1 displays the flow diagram of ODH.

Reactants and products were analysed online using a gas chromatography reactants and products were analysed online using a gas chromatograph-mass spectrometer (SP2100) equipped with a three sample loops and 13-port sampling valve. One sample loop was injected into an Alumina PLOT column, and then eluting products were detected by a flame ionization detector (FID). The second sample loop was injected into a second Alumina Plot column (Φ1/8in×3 m) and analysed by the mass spectrometry. The contents of the third sample loop were injected into a Hayesep N column (Φ1/8in.×2 m) using to adsorb CO_2, H_2O and heavy hydrocarbons connected in series with a Mol Sieve 5A packed column. The products eluting from this column were detected by a thermal conductivity detector (TCD). Analytical conditions: Nitrogen was used as carrier gas, column temperature at 50°C, temperature of TCD detector at 100 °C, the sample amount is 5 μL. The catalyst behaviour was evaluated according to the following formulas, where F is the molar flow rate:

Conversation of isobutane:

$$X_{isobutane} = \frac{F_{\text{isobutane, in}} - F_{\text{isobutane, out}}}{F_{\text{isobutane, in}}}$$

Selectivity to isobutene:

$$S_{\text{isobutene}} = \frac{F_{\text{isobutene}}}{F_{\text{isobutane, in}} - F_{\text{isobutane, out}}}$$

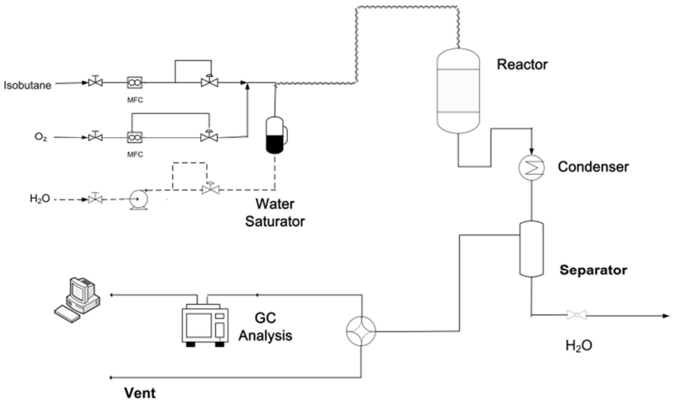

Fig.1. Flow diagram of dehydrogenation of isobutene

The X-ray diffraction (XRD) of the catalysts was collected on a D8 Advance (Bruker, German) instrument using Cu Kα radiation (40 kV and 30 mA). XRD data were collected in the 2θ range of10° to 90 ° using a scan speed of 12 °/min and a step size of 0.02 °.

Temperature-programmed desorption (TPD) characterization of catalysts was performed by a quadrupole mass spectrometer (AMETEK HQ 200M, USA) in a quartz fixed bed reactor with the inner diameter of 6 mm. Catalysts (0.4 g) were placed in the TPD reactor and reduced under 10 % (v/v) H_2/Ar flow at 600 °C for 0.5 h. Then the temperature was dropped to 400°C for 10 min and Ar (30 mL/min) gas was start purged into reactor for removing H_2 and steam. After naturally cool down to room temperature, the temperature of the reactor was adjusted by a cooling machine. CO_2 or isobutene was adsorbed on the catalyst at -5 to -8 °C for 1 h. After the reactor purged under Ar flow (30 mL/min) for 1 h, the adsorbate was desorbed by heating at 15 °C/min under Ar flow.

X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra DLD (delay-line detector) spectrometer (ThermoScientific, USA), using a focused monochromatized AlKα radiation (1486.6 eV) with CAE mode. The material was introduced into the treatment chamber using double-sided tape. The sample was maintained under high vacuum at 5.0×10^{-9} mbar. It was reported that the high resolution XPS region scan spectra were obtained within a short period of time (ca. 12 min) at 20 eV pass energy to minimize the photo-reduction of surface chromium species that may be induced by X-rays [11-13].The compositions of different chemical states of surface chromium in the samples were obtained by XPS spectra using Vision 2.0 software.

Results and discussion

XRD and CO_2-TPD characterization of different support catalysts

Pic.1. Pictures of different supports used for loading Cr. (a) Cr/CaAlLaO; (b) Cr/CrAlLaO; (c) Cr/MgAlLaO; (d) Cr/ZnAlLaO. Cr loading: 18 wt%

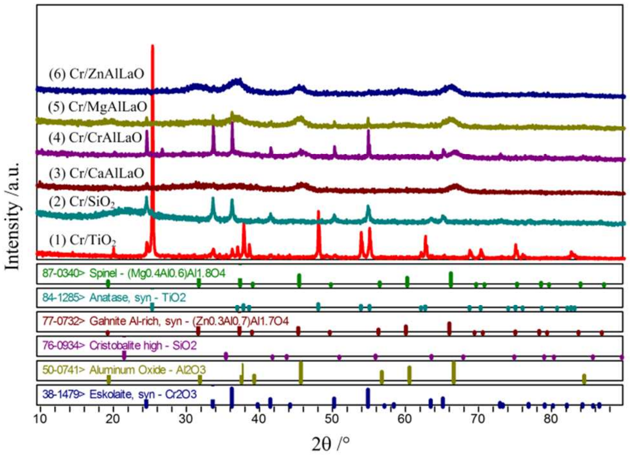

Fig.2. XRD patterns of different types of supports

Fig.2 shows the XRD patterns of the same Cr active component on different types of supports. The diffraction peaks of different supports indicate that the Cr in the samples is a partially amorphous phase or small crystalline particles due to the difficulties of interaction between Cr with TiO_2 and SiO_2 [14]. As shown in both XRD patterns of Cr/TiO_2 and Cr/SiO_2, it can deduce that the bulk Cr_2O_3 were gathered on the supports surface and the active component was dispersed unevenly. From Pic.1, it can be seen from the pictures, the active component Cr over CaAlLaO support is caked on the external surface, indicating uneven dispersity. The Cr on the CaAlLaO catalyst showed the agglomeration, active component cannot be fully utilized on the surface. For CrAlLaO catalyst, due to the self-containing of Cr element, the CrAlLaO interacted with the active component and exhibits strong syn-Cr_2O_3 diffraction peaks. It can be observed that the active component not only existed on the external surface of the catalyst, also penetrated into the interior. Hence, the utilization rate of active component Cr on the catalyst external surface should be lower than that of the MgAlLaO and ZnAlLaO catalysts. The reaction performance of various catalysts also proved this speculation (Fig.3). From the XRD pattern of MgAlLaO catalyst, magnesium aluminate spinel structure has been formed on the catalyst surface. The peaks at 37.904°, 46.102° and 67.275° can be indexed as $(Mg_{0.4}Al_{0.6})Al_{1.8}O_4$. From XRD pattern of ZnAlLaO catalyst, the diffraction peaks are assigned to the zinc-aluminum spinel phase $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$, which are slightly stronger than diffraction peaks of MgAlLaO. It probably due to the stronger interaction of active component Cr with ZnAlLaO support than that of MgAlLaO support, which further enhancing the diffraction peak intensity of Al_2O_3. Furthermore, there is no obvious diffraction peaks of Cr_2O_3 were observed for both Cr/MgAlLaO and Cr/ZnAlLaO catalysts. It implies the active component dispersed evenly on the support surface. However, from the Pic.1, it can be seen clearly that penetrated thickness of the active component in ZnAlLaO catalyst is lower than that of MgAlLaO catalyst. The active component of ZnAlLaO catalyst is mainly distributed on the external surface, suggesting that the Cr utilization rate of ZnAlLaO catalyst on the outside layer is higher that of MgAlLaO catalyst [15, 16].

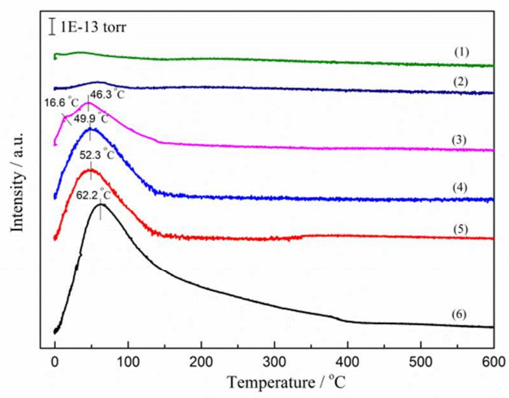

Fig.3. CO_2-TPD profile of different supports:(1) TiO_2; (2) SiO_2; (3) Cr/ZnAlLaO; (4) Cr/MgAlLaO; (5) Cr/CrAlLaO; (6) Cr/CaAlLaO

In order to further study the influence of different supports on catalytic properties, CO_2-TPD experiments were carried out. Fig.3 shows the CO_2-TPD profiles of the different samples. It can be observed that, for SiO_2 and TiO_2 catalysts, there are no obvious desorption peaks observed, indicating almost no alkalinity on supports surface of SiO_2 and TiO_2. The CO_2-TPD profile of CaAlLaO support shows the highest intensity with desorption temperature at 62.2 °C. However, CO_2 desorption peak areas of CrAlLaO, MgAlLaO and ZnAlLaO supports are relatively smaller than CaAlLaO support, which indicating that those three supports have weaker alkaline than that on the CaAlLaO support surface. Moreover, ZnAlLaO support emerged two CO_2 desorption peaks. The first peak located at 16.6 °C is assigned to weak physical desorption peak. Another peak is weak alkaline desorption centre appear at temperature of 46.3 °C.

Generally, appropriate alkaline sites can significantly improve the catalyst ability of carbon elimination as well as enhance the catalyst stability [17, 18]. The acidic sites are carbon ions activation centre, and easily lead to catalyst carbon deposition. It is an important factor for causing the decrease of catalyst activity and stability. Thus, the appropriate alkalinity on the catalyst surface can improve the selectivity of isobutene and the ability of resistance of carbon deposition. Weak acid sites are much easier to adsorb isobutene and then form tertiary carbonium ion. Then the intermediates leave the catalyst surface to produce isobutene product [19, 20]. If the isobutane isadsorbed on the acid sites, its intermediates cannot desorption of catalysts surface timely or immediately adsorption again after desorption. This process could lead to deep oxidation of isobutane and then produce carbon deposition. The carbon deposition can cause catalyst deactivation and decreasing the selectivity of isobutene [21]. However, the alkaline centre can activate oxygen element effectively on the ZnAlLaO support surface, promoting ODH reaction. We believe that the selectivity is associated with the lattice oxygen of the catalyst surface. The number of lattice oxygen can improve the conversion rate of the catalyst and reduce the selectivity of the catalyst [22, 23]. In addition, when the deep oxidation happened on the catalyst surface and produced carbon deposition, the adjacent weak alkalinity site can activate oxygen of ZnAlLaO support, in which can elimination of carbon deposition. Consequently improve the stability and activity of the Cr/ZnAlLaO catalysts. It has also been proved by the Fig.3, the selectivity and conversion rate of ZnAlLaO catalyst is much higher than that of other catalysts. Therefore we believe that the moderate alkalinity and acidity are important factors for catalytic activity and stability.

Catalytic performance of different support catalyst

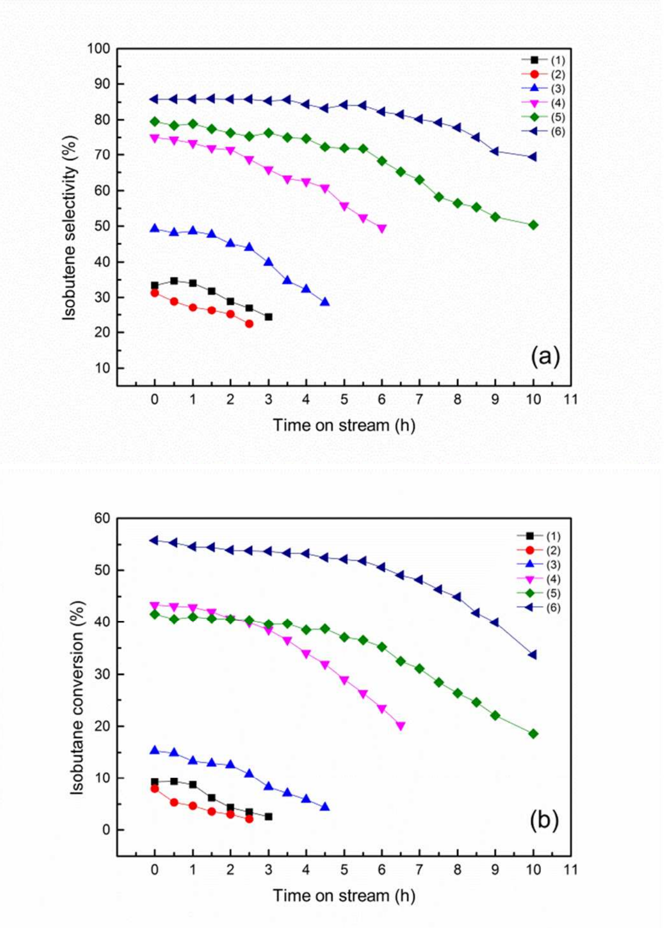

Fig.4.(a) selectivity and (b) Conversion as functions of time for the different support catalysts:
(1) Cr(18%)/TiO_2; (2) Cr(18%)/SiO_2; (3) Cr(18%)/CaAlLaO; (4) Cr(18%)/CrAlLaO; (5) Cr(18%)/MgAlLaO; (6) Cr(18%)/ZnAlLaO.
Reaction condition: temperature580 °C, 1 atm, 2 g catalysts, $i\text{-}C_4H_{10}/O_2$ = 3.5(molar ratio), SV = 200 mL/g·h

Catalytic performances of the different support catalysts are presented in Fig.4. All catalysts showed the decreasing of catalytic activity along with the reaction time. The initial selectivity of isobutene catalyzed by Cr(18%)/MgAlLaO and Cr(18%)/ZnAlLaO are 78.87% and84.07%, respectively. In our experiments, the Cr(18%)/ZnAlLaO catalyst exhibits the best catalytic performance and highest selectivity conversion compared with other five catalysts. This result is superior to that of previously reported 10% Cr/Al_2O_3 catalysts (63.1%) selectivity and 10.7% conversion when using $Cr(NO_3)_3$•$9H_2O$ as precursor. 100% selectivity and 0.1% conversion when using $CrK(SO_4)_2$•$12H_2O$ as precursor. However, the Cr(18%)/ZnAlLaO catalyst also showed relatively unsatisfactory stability after 6 h reaction.

In order to obtain better catalytic performance, we further study the influence of the Cr content and water vapour.

XRD and CO_2-TPD characterization of different loading ZnAlLaO catalyst

Pic.2. Pictures of different supports loading Cr. (1)Cr(8.56%)/ZaAlLaO; (2)Cr(18.12%)/ZnAlLaO; (3)Cr(32.03%)/ZnAlLaO

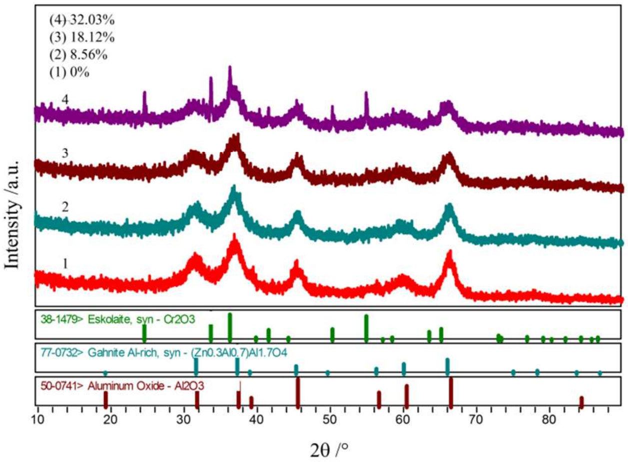

Fig.5. XRD patterns of the catalysts with different Cr addition

Several studies have proved that the addition of Cr to ZnAlLaO catalyst could enhance the catalytic performance and the reaction stability [24]. The loading amount of Cr in this case act as a promoter in ODH. As the loading amount of active component Cr increasing, the loading thickness on the external surface is also increased, which can be easily observed on the digital pictures (Pic.2). From Fig.4, the samples with Cr loading of 8.56% and 18.12% did not obviously appear diffraction peaks associated with Cr_2O_3 crystalline structure. The results suggest that the Cr_2O_3 is highly dispersed in the loading range of 8% to 18%. The XRD patterns of the 8.56% and 18.12% Cr loading is appearance of $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$ aluminium rich zinc spinel lattice structure. It has been reported that the Cr can diffuse into the oxygen vacancies in the $ZnAl_2O_4$ spinel lattice [25]. It can be observed that $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$spinel structure of Cr(32.03%)/ZnAlLaO catalyst is damaged by the loading amount of Cr up to 32% on the catalyst surface. The diffraction peaks of Cr_2O_3 are significantly strengthened and the appearance of Cr_2O_3 crystalline phase on the catalyst surface.

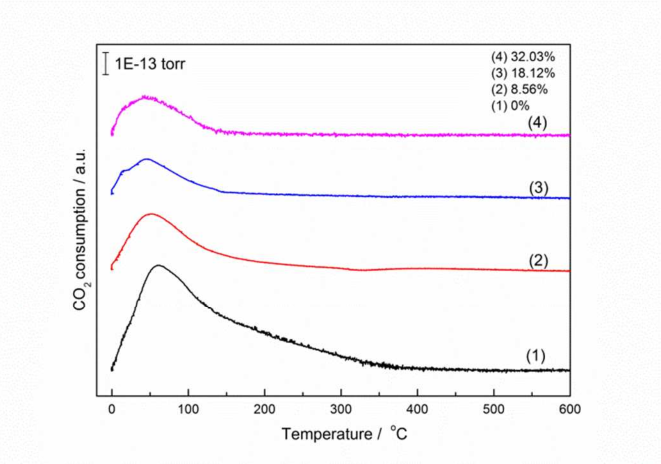

Fig.6. CO_2-TPD profile of the catalysts with different Cr loading
(1) Cr (0%)/ZnAlLaO; (2) Cr(8.56%)/ZnAlLaO; (3) Cr(18.12%)/ZnAlLaO; (4) Cr(32.03%)/ZnAlLaO

The Fig. 6 displays the CO_2-TPD profiles of the different Cr loading samples. Generally, various catalysts appear the CO_2 weak alkalinity peak range from 48 °C to 62 °C, low temperature desorption peaks are assigned toCO_2 on Cr_2O_3 [26]. It can be observed that the alkalinity of ZnAlLaO catalyst without active component Cr loading showed strongest alkalinity comparing with other catalysts. However, the ZnAlLaO catalyst without active component has the lowest active performance. Consequently, higher alkalinity has disadvantages for the ODH reaction. As the increase of active component Cr loading, the area of CO_2 desorption peak area decrease generally. The addition of active component Cr can lead to the formation of weak alkaline sites. Also, the weak alkaline sites can effectively activate oxygen element in ZnAlLaO support [26], inhibiting the production of coke deposition. Whereas the overloading of Cr results the blocking effect of a worse Cr particle distribution on the catalyst surface, which has been proved by the XRD pattern in Fig.5.

Catalytic performance of different Cr loading ZnAlLaO catalyst

Fig.7 shows the effect of Cr content on the catalytic performance of isobutane ODH over 10 h. The Cr(18.12%)/ZnAlLaO catalyst achieves the maximum of isobutene selectivity (84.07% after reaction for 6 h). It has been studied that Cr has become a key ingredient in oxidative dehydrogenation catalysts because of its high activity for Cr-O-Al bond formation [25]. That is reason why an intrinsic high selectivity of unprompted Cr toward isobutene ODH. On the other hand, it has been proved by XRD pattern (Fig.5), these results obtained at a better performance level confirm the increase of dehydrogenation activity partly due to a better particle distribution prompted by suitable loading of Cr on ZnAlLaO catalyst. However, the continuous addition of Cr leads to the decreasing in the catalytic activity due to the blocking effect of a worse Cr particle distribution on the catalyst surface [27]. The reactant gas can easily interact with the active sites due to over-loading of Cr species and then enhanced active component dispersion unevenly on catalyst surface. This behaviour causes the occurrence of side reaction during this process, and then leads to the decrease of the selectivity eventually. Hence, the active component disperses evenly and appropriate Cr loading (about 18%) on the catalyst surface are the reasons for the enhancement of the catalytic activity and stability.

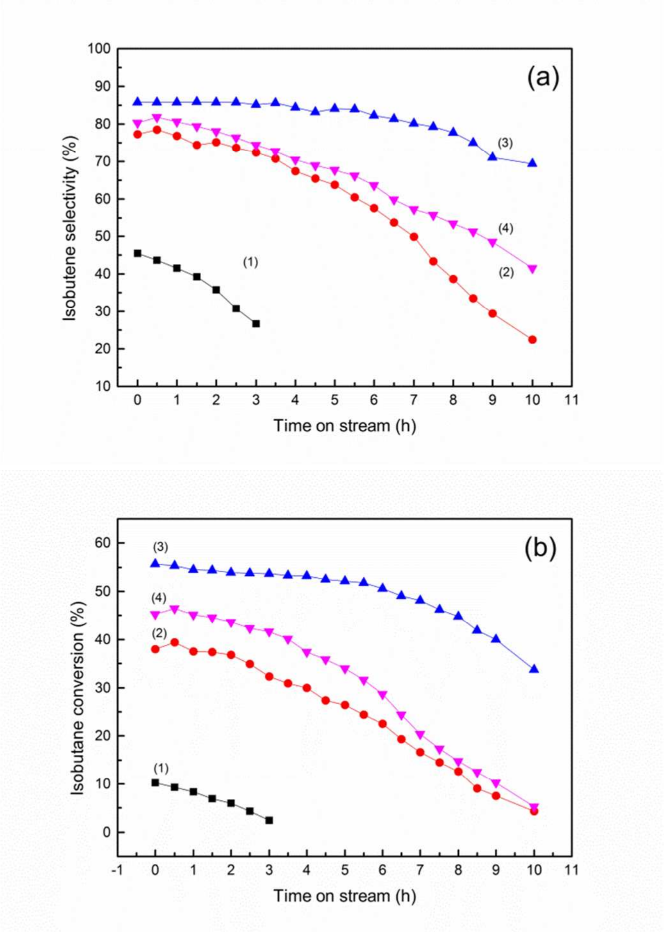

Fig.7.(a) selectivity and (b) Conversion as functions of time for the different loading catalysts:
(1) Cr(0%)/ZnAlLaO; (2) Cr(8.56%)/ZnAlLaO; (3) Cr(18.12%)/ZnAlLaO; (4) Cr(32.03%)/ZnAlLaO. Reaction condition: Al/Zn = 8.5-10.5, temperature 580 °C, 1 atm,2 g catalysts, i-C_4H_{10}/O_2 = 3.5(molar ratio),SV = 200 mL/g·h

According to the literatures [28, 29], the formation of CO_X and CH_X species from readsorption of isobutane and isobutene is one of the significant factors for coke deposition on the catalyst surface, in this case, the carbon depositions on the catalyst surface may act as a reason to decrease the catalysis activity by deactivating the active sites [30, 31]. Therefore, minimizing the readsorption and the dissociation of the C—C bond will effectively eliminate the formation of carbon deposition on the catalyst surface [32]. Subsequently we did some experiments about the addition of water vapour and influence as one part of feed gas for ODH.

The effects of water vapour

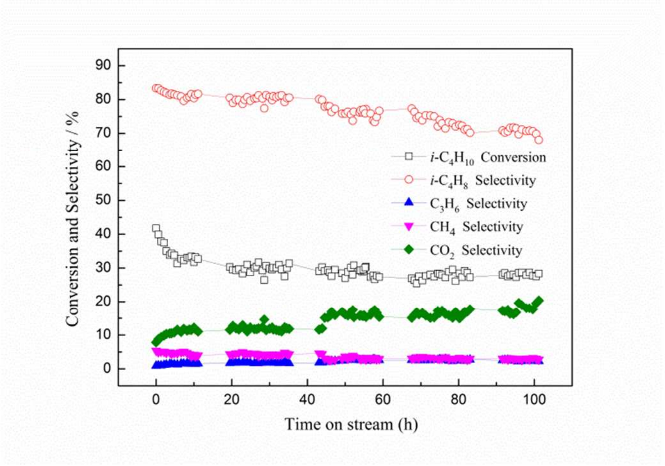

Fig.8.100 h test of Cr(18%)/ZnAlLaO catalyst with steam as diluent. Reaction condition: temperature 580 °C, 1 atm, 2 g catalysts, i-C_4H_{10}/O_2 = 3.5(molar ratio),SV = 200 mL/g·h

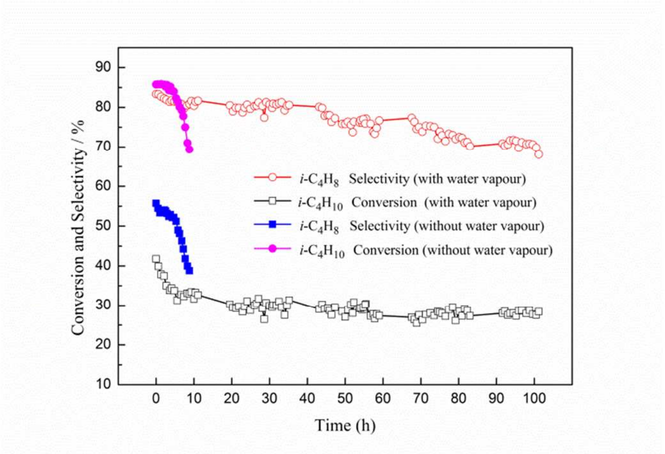

Fig.9.100 h test comparison of Cr(18%)/ZnAlLaO catalyst with and without water vapour. Reaction condition: temperature 580 °C, 1 atm, 2 g catalysts, i-C_4H_{10}/O_2 = 3.5(molar ratio), SV = 200 mL/g·h

Water vapour is effective method used as a diluent and oxidant in many dehydrogenation reactions in order to eliminate carbon deposition [33, 34]. However the studies of using water vapour as a feed gas for the ODH reaction are not many have been reported yet. The Fig.8 shows the 100 h reaction of Cr/ZnAlLaO catalyst with steam as diluent, it can be observed that the conversion of isobutene declined significantly (32.74%) after 6 h, and CO_2 selectivity (10.92%) obviously increased after addition of water vapour. On the condition of without water vapour, a small amount of dehydrogenation products, such as unsaturated olefin, will be polymerized on strong acid centre of the catalyst surface. Then the deep dehydrogenation occurs and eventually results in formation of carbon deposition precursors. The water vapour could act as a diluent to reduce the partial pressure of oxygen in the reaction gas and promote the ODH reaction equilibrium towards the right. On the other hand, water vapour is responsible to reduce the acidity of the support surface and interact with some carbon deposition to make carbon deposition gasification. Thus the CO_2 selectivity increased and side reactions occur, such as steam reforming. It also can delay the coverage rate of carbon formation on the catalyst surface [35]. Due to adsorption of water molecules on the Cr_2O_3surface, the adsorption and desorption capacity of oxygen species are decreased on support surface. The interaction between active component and support can be weakened gradually [36]. Thereby, the addition of appropriate water vapour to the feed can continuously enhance the catalyst stability, while both the isobutane conversion and isobutene selectivity decreased at the same time.

XPS analysis

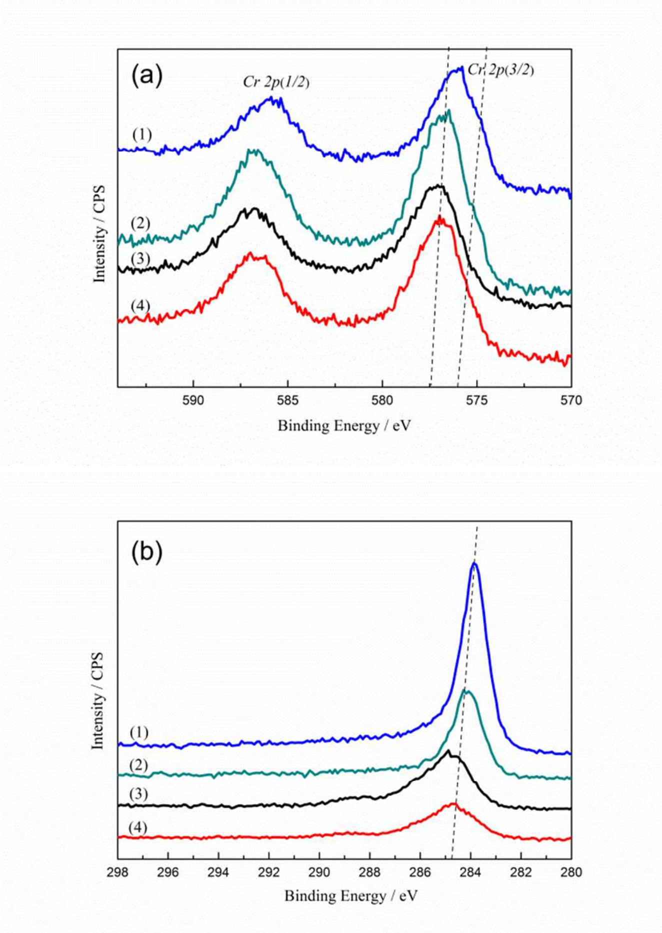

Fig.10. (a) XPS spectra of chrome over various catalysts surface; (b) XPS spectra of carbon over various catalysts surface.
(1) Cr(18%)/ZnAlLaO catalyst after 100 h test with water vapour (with H_2O-100h); (2) Cr(18%)/ZnAlLaO catalyst after 8 h test without water vapour (without H_2O-8h); (3) Cr(18%)/ZnAlLaOfreshcatalyst (fresh catalyst); (4) Cr(18%)/ZnAlLaO catalyst after 30 h test with water vapour. (with H_2O-30h).

The figure 10(a) shows the XPS spectra in the Cr 2*p* region for various catalysts. The quantitative data of binding energies are illustrated in Table.1. Curve fitting of the experimental data showed the presence of two distinct chromium species. The oxidation states species have been totally assigned to Cr(III) and Cr(VI) at the binding peak of 577 and 579 eV, respectively. It has been reported by reference [37] that the oxidation states of chromium were determined by the binding energy of the Cr 2*p*(3/2) peak and the value of spin-orbit splitting Cr 2*p*(1/2)-Cr 2*p*(3/2). The binding energy fall in the range from 576.4 eV to 576.9 eV for Cr(III). Due to the intrinsic complexity of the Cr(III), it is quite hard to ascertain the contribution of intermediate chromium stated in the Cr 2*p*3/2 region. Studies have shown that both Cr(VI) and Cr(III) are the catalytic activity centres of ODH , however, the Cr(VI) is usually unstable and easy to be reduced [25]. It can be observed that the fresh catalyst and with H_2O-30h catalyst mainly appear the binging energy of Cr(III) at 577.08 eV and 577.28 eV (2*p*3/2) [37, 38]. At the same time, the catalysts without H_2O-8h and with H_2O-100h displayed the Cr (closed to zero valent state) at the binging energy of 576.88 eV and 576.28 eV. The relative amount of Cr(III) increased in the used sample comparing with fresh catalyst, indicating the reduction of Cr(VI) to Cr(III) and the result is in agreement with the conclusions reported in recent literatures [15, 39]. The binding energy of Cr(III) declined along with the reaction time increasing, meanwhile close to zero valent state of Cr generally formed, leading the decrease of the catalytic activity on the catalyst surface, and eventually the catalytic performance dropped. Furthermore, the decrease of interaction between oxygen adsorption and the active component is probably due to the adsorption of water molecules on the active component surface. Thereby, the addition of water vapour is beneficial to inhibit the formation of carbon deposition and deep oxidation on the catalyst surface. Due to the coke formation is the main factor of deactivation process of ODH, we characterized the basic coke information of the catalyst before and after catalytic reaction. Fig.10 shows the XPS of C1s of the fresh and used 18% Cr/ZnAlLaO catalysts. One main peak and some broad peaks are observed in each case. The area percentages and quantitative data of binding energies are summarized in Table.2. The C1s region spectra display the features corresponding to the various chemical nature of carbon: pregraphite-like, aromatic, aliphatic, partially oxidized, and the binding energies were identified according to the previous reports [9]. As for the fresh catalyst, two main peaks at binding energy of 284.88 and 288.76 eV are detected, which assign to the adventitious hydrocarbon (C-C/C-H) and oxidized carbon species (O-C=O), respectively. They probably from residues after the calcination of the synthesized catalyst or the interaction of feed gas on catalyst surface. The value of C-C/C-H is generally shifted toward the lower binding energy with reaction time increasing. In contract, the C1s spectrum also displays the asymmetric peaks shape on the used catalysts (without H_2O-8h and with H_2O-100h) at binding energy of 284.28 eV and 283.88 eV. It is obviously that the catalyst of with H_2O-100h achieves the maximum peak intensity (the binding energy at 283.88eV), and the coke deposits possibly comprise of the sp^2 hybridized carbon and this type of coke probably consists of the aromatic rings according to the previous references [40-42]. Furthermore, the produced coke deposits of used catalysts of without H_2O-8h and with H_2O-100h are assigned to pregraphite-like carbon, which was present in study [43]. It has a lower binding energy than graphitic carbon, suggesting the high electron density related to its structure [42]. Moreover, compared to the catalyst of without H_2O-8h, the coke deposit of pregraphite-like carbon has not determined in the catalyst of with H_2O-30h, which suggests that the presence of water vapour, can decrease the amount of coke on the catalyst surface and improve the stability of ODH reaction. It also has been proved by the consequence of catalytic performance shown in Fig.9 and 10. The C1s spectrum of the catalyst with H_2O-30h looks similarly to that of fresh catalyst. However, the main peak at 283.88 eV in the catalyst with H_2O-100h has a lower binding energy than that of the C1s spectra in the catalyst without H_2O-30h. This indicates the coke structure formed over the catalyst with H_2O-100h has a higher electron density than that over the catalyst without H_2O-30h.

Apparently, coke deposit was an important factor for the activity and stability of catalysts. The possible regeneration routes of the catalysts was reported in the literature [33, 44] that several sequential regeneration cycles of various catalysts, it can be carried out through the method of burning the formed coke [38] under some controlled conditions. For instance, the temperature of reactor is cooled to about 250°C, simultaneously, using the an inert steam such as Ar as only feeding gas. After reaching this temperature, inert steam Ar was replaced by an air flow and then generally rising up to about 550 °C. During this process, formed coke on the surface of catalyst was burn through interacting with oxygen gas. Approximately 1 h later, the catalysts were cooled to the room temperature and remaining that way overnight. By this measure, the samples are ready to be used in a new cycle.

Table.1. Curve-fitting parameters for Cr 2p region XPS of the spent and fresh catalysts

catalysts	Cr 2p3/2 B.E. (eV)		Cr 2p1/2 B.E. (eV)	
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
with H_2O-100h	-	575.96	586.88	585.90
without H_2O-8h	577.02	576.71	-	586.69
fresh catalyst	577.56	577.13	588.17	586.77
with H_2O-30h	578.47	576.87	586.97	586.69

Table.2. Curve-fitting parameters for C1s XPS of the spent and fresh catalysts

catalysts	C1s B.E. (eV)				
	Pregraphite -like	C-C /C-H	CxHy	-C=O	O-C=O
with H_2O-100h					
BE (eV)	283.88	-	-	287.38	-
Area (%)	84.05	-	-	0.33	-
without H_2O-8h					
BE (eV)	284.28	-	285.88	-	-
Area (%)	19.80	-	0.02	-	-
fresh					
BE (eV)	-	284.88	-	-	288.76
Area (%)	-	77.67	-	-	5.07
with H_2O-30h					
BE (eV)	-	284.68	-	-	288.88
Area (%)	-	68.18	-	-	3.25

Optimization of reaction temperature

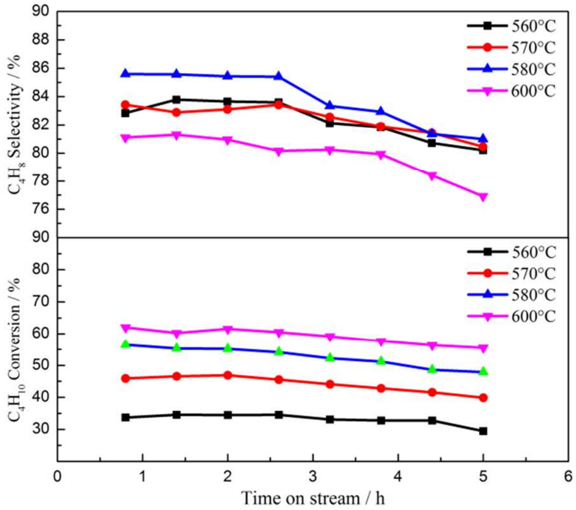

Fig.11. TheC_4H_{10} conversion and C_4H_8 selectivity at differenttemperature. **R**eaction condition: 1 atm, 2 g catalysts, *i*-C_4H_{10}/O_2 = 3.5(molar ratio), SV = 200 mL/g·h, without water vapour

The Fig.11 shows the catalytic activities of C_4H_{10} and C_4H_8 under various temperatures. It can be seen that the catalytic activity and isobutane conversion is relatively low at temperature between 560 °C and 570 °C. With the reaction temperature increasing, the conversion rate significantly increases. The isobutene selectivity reaches the maximum and stabilizes at about 85% between 570 °C to 585 °C. As the reaction time prolonging, the conversion and selectivity are both generally decline. When the temperature reaches too high (600 °C), not only the cracking reaction rate and coke deposition increase, also the catalyst specific surface area and active catalysts decrease [45, 46]. As shown in the Fig.12, as the temperature increasing, cracking reaction generally occurs, which results increasing of selectivity of CH_4 and C_3H_6, and the selectivity of CO_2 decreases. Hence, the optimal reaction temperature is in the range from 575 °C to 580 °C. Optimal temperature of fixed bed is in the range from 580 °C to 590 °C. The conversion of isobutane (52.44%) and selectivity of isobutene (84.07%) achieve the optimum at 577°C.

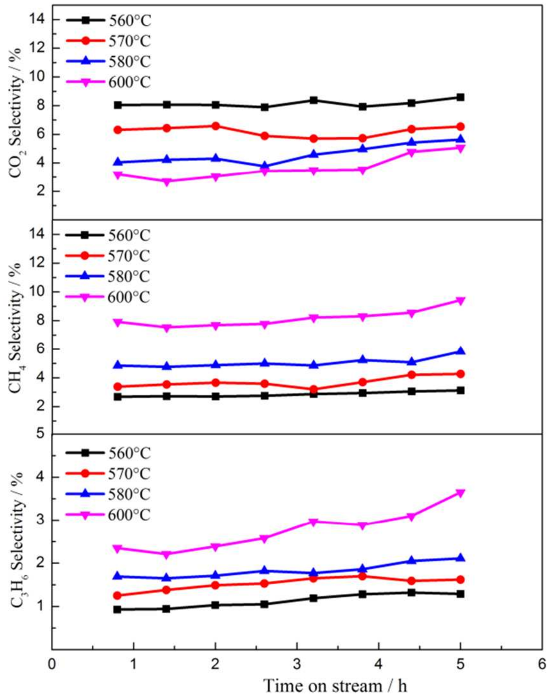

Fig.12. The selectivity of CH_4, CO_2 and C_3H_6at different temperature Reaction condition: 1 atm, 2 g catalysts, i-C_4H_{10}/O_2 = 3.5(molar ratio), SV = 200 mL/g·h, without water vapour.

Optimization ofalkoxyoxygen ratio

Table.3 Cr/ZnAlLaO catalytic performance as a function of alkane oxygen ratio

i-C_4H_{10}/O_2	Conversion / %	Selectivity / %				
	i-C_4H_{10}	i-C_4H_8	C_3H_6	CH_4	CO	CO_2
1.0	43.72	63.71	6.00	8.43	3.78	13.99
2.0	46.27	72.41	5.82	6.03	4.55	7.22
3.0	52.79	80.89	3.45	5.45	3.96	4.17
3.5	52.44	84.07	3.37	4.31	3.53	3.27
4.0	57.04	83.05	3.12	4.56	3.03	2.98
5.0	60.39	72.49	4.81	8.48	3.89	2.54
6.0	60.39	72.49	4.81	8.48	3.89	2.54

Reaction condition: temperature 580 °C, 1 atm, amount of catalyst = 2 g, i-C_4H_{10}/O_2 = 3.5(molar ratio), SV = 200 mL/g·h, without water vapour.

Table 3 shows the Cr/ZnAlLaO catalytic performances of different alkane oxygen ratio. It can be observed that the isobutene selectivity achieves the maximum when alkoxy ratio is 3.5. When alkoxy ratio is relatively low (range from 1 to 3), the intermediates and products are easy for generating by-products of C_3H_6, CH_4 and CO_2 in the oxygen-enriched environment. Also, the oxygen-enriched environment can make competitive adsorption of isobutane at disadvantage situation. It leads to the decrease of selectivity of isobutene and the raw material waste. As the alkoxy ratio increasing to 3.5, the catalytic activity reaches maximum. We continue to increase the content of isobutane, it can be seen that the isobutane conversion increase continuously while both isobutene and CO_2 selectivity declining. It because the formation of the oxycarbide in the oxygen-poor environment. Isobutane from relatively excessive content reach at the C_4H_{10}/O_2 ratio of 6, it causes an increase of side reactions and isobutane cracking. In conclusion, we believe that the optimum of alkoxy ratio for isobutane ODH range from 3 to 4.

Conclusions

In summary, different supports of chrome-based catalysts have obvious impact on the catalytic activity of isobutane dehydrogenation. Novel ZnAlLaO support shows the best selectivity of isobutene and conversion of isobutene comparing with the other supports. Both the distribution of Cr_2O_3 active component evenly as well as the moderate alkalinity over the ZnAlLaO catalyst surface are beneficial for the activity and stability of catalyst. The addition of appropriate water vapour as one part of feed gas can effectively inhibit formation of carbon deposition on the catalyst surface and enhance the catalyst stability, whereas both the selectivity and conversion are declined. In this case, the optimum reaction temperature is in the range from 575°C to 580°C.The alkoxy ratio has been chose in the range of 3 to 4.From this present study, the catalytic activity of Cr/ZnAlLaO catalyst has obtained a significant improvement in order to compete with the commercial catalyst.

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Notes and references

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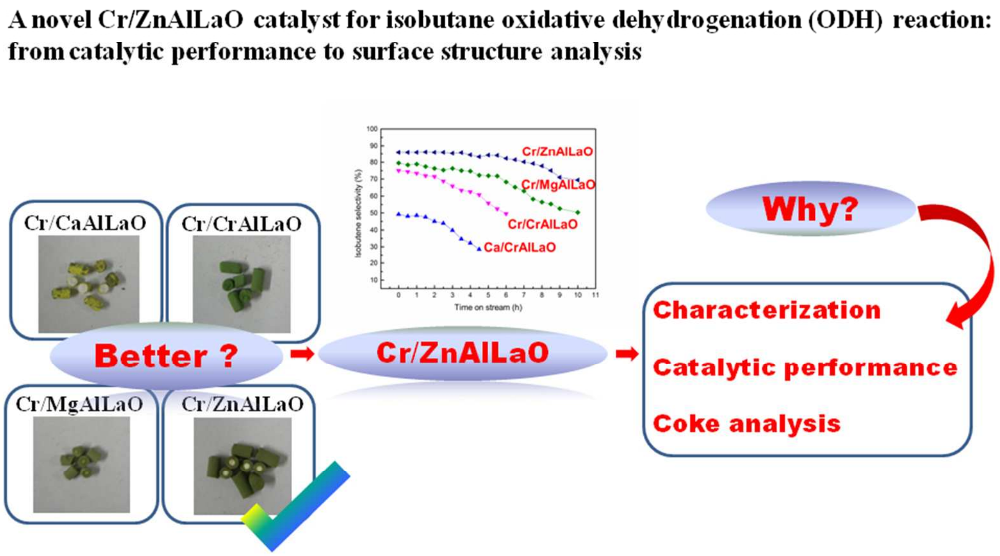

A novel Cr/ZnAlLaO catalyst for isobutane oxidative dehydrogenation (ODH) reaction: from catalytic performance to surface structure analysis

254x190mm (96 x 96 DPI)