Supported Al–Ti bimetallic catalysts for 1-decene oligomerization: Activity, stability and deactivation mechanism

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A B S T R A C T

A variety of supported bimetallic catalysts were prepared through immobilization of AlCl3 and TiCl4 on different porous materials and used for the oligomerization of 1-decene in a fixed-bed reactor. The supported catalysts were characterized by various techniques including X-ray photoelectron spectroscopy (XPS), 27Al MAS NMR, N2 adsorption, adsorbed pyridine infrared (Py-IR), thermogravimetry and differential scanning calorimetry (TG–DSC), energy-dispersive spectrometry (EDS), and content measurement of active species. Their catalytic activity was examined and the underlying deactivation mechanism was explored. The initial catalytic activity was observed to be a linear function of the chlorine content of the supported catalyst. A catalyst using a coal-derived activated carbon support has the highest loading capacity and exhibits the highest yield of polyalphaolefin (PAO), while a γ-Al2O3-supported catalyst gives higher stability. In addition, thermal treatment of the γ-Al2O3-supported catalyst results in reduced initial activity but enhanced stability. Both the loss of active species and the blockage and coverage of the pore structure by oligomers account for the deactivation of the supported catalyst.

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1. Introduction

With a variety of excellent performance features including good thermal and oxidative stability, high viscosity index, good low-temperature fluidity, low volatility, low corrosiveness, and high biodegradability, synthetic lubricants find increasingly wide applications under extreme conditions [1–4]. Polyalphaolefin (PAO)-based synthetic lubricants are proven to offer high activity and ability to achieve well-controlled molecular weight and stereochemistry of oligomers. However, their highly corrosive and hazardous features and disposal problem lead to researchers’ incessant attempts to devise green processes in order to circumvent such drawbacks. Anchoring homogeneous complexes on various supports is considered a very promising method for minimizing the costs and environmental impact of metal complexes [27–29]. Extensive investigations on loading of active species are being carried out to screen supports and immobilization conditions. Moreover, although the deactivation of the resulting catalysts is realized to be a fundamentally important issue for optimizing performances and applications, it has not been understood very well, and the underlying mechanism is not clear.

In this work, we performed the catalytic oligomerization of 1-decene on supported Al–Ti bimetallic catalysts in a fixed-bed reactor. Catalysts were prepared by immobilization of AlCl3 and TiCl4 on a variety of porous supports. This study presents a quantitative relationship between the catalytic activity and chlorine content of supported catalysts and provides insight into the deactivation mechanism of supported Al–Ti bimetallic catalysts.
2. Experimental

2.1. Materials

1-Decene (Dowpol Chemical International Corporation, China) is of >96.2% purity. Titanium tetrachloride, anhydrous ethanol, and diethyl ether (Shanghai Lingfeng Chemical Reagent Co., Ltd., China) and aluminum trichloride, benzene, toluene, acetone, and nitric acid (Sinopharm Chemical Reagent Co., Ltd., China) are analytical grade. All chemicals were used as obtained. However, if the reagents have been uncovered for a long time, they should be purified with dehydration and deoxygenation reagents prior to being used again in order to prevent water contamination. Coal-derived activated carbon (CDAC) (Shanghai Activated Carbon Co., Ltd., China), coconut shell activated carbon (CSAC) (Shanghai Xinhui Activated Carbon Co., Ltd., China), γ-Al2O3-1 and silica gel (Sinopharm Chemical Reagent Co., Ltd., China), γ-Al2O3-2 (China Research Institute of Daily Chemical Industry, China), and zeolites HZSM-5-1 (Si/Al = 50) and HZSM-5-2 (Si/Al = 360) (the Catalyst Plant of Nankai University, China) were employed as supports.

2.2. Preparation of immobilized AlCl3–TiCl4 catalysts

Catalysts were prepared by loading the active species AlCl3 and TiCl4 onto various supports including γ-Al2O3-1, γ-Al2O3-2, CDAC, CSAC, silica gel, and zeolites HZSM-5-1 and HZSM-5-2. The corresponding supported catalysts were labeled A1, A2, C1, C2, S, Z1, and Z2 (see Table 1). Various organic solvents including benzene, toluene, ethanol, diethyl ether, acetone, and carbon tetrachloride were used during the immobilization procedure.

At first, all as-received porous materials were pretreated to obtain different supports. Specifically, γ-Al2O3-1, γ-Al2O3-2, zeolites HZSM-5-1 and HZSM-5-2, and silica gel were heated at 400 °C in a SXC-1.5/10 muffle furnace (Hangzhou Lantian Instrument Co., Ltd., China) for 4 h and then cooled to room temperature in a desiccator. Activated carbon supports CDAC and CSAC were treated in 1 M nitric acid aqueous solution at room temperature for 8 h and then thoroughly washed with deionized water until the washing water reached neutral pH. After that, the resulting supports were air-dried overnight at 110 °C and then conserved in the desiccator. Subsequently, active components AlCl3 and TiCl4 were immobilized onto different supports using a reflux apparatus under dry N2. The quantities 16 g of AlCl3 and 4.5 g of TiCl4 were dissolved in 150 mL solvent. The molar ratio n(Al)/n(Ti) and the mass ratio of AlCl3 to support were fixed at 5 and 0.4 for every immobilization. The solution was transferred into a 250 mL flask containing 40 g support under high-purity nitrogen flow (80 mL min⁻¹), followed by heating of the mixture at the desired temperature for 12 h with a magnetic stirrer. The as-prepared fresh catalyst slurry with solvent was divided into two parts. A small part of it was heated in a glass tube under N2 flow (80 °C) for the removal of the solvent. The solvent-free sample was kept in a desiccator for further characterization. The rest was loaded into a fixed-bed reactor for the oligomerization reaction and then thoroughly swept (for at least 6 h) using hot N2 flow (80 °C and 120 mL min⁻¹) in order to repel residual solvent in catalyst. The slurry containing solvent was used while filling the column in order to prevent the catalyst from being exposed to atmosphere.

A sample of catalyst using γ-Al2O3-1 support underwent special heating treatment at 400 °C in a muffle furnace under nitrogen flow (100 mL min⁻¹) for 4 h, labeled as A1-2 (see Table 1).

2.3. Oligomerization procedure

The oligomerization of 1-decene was performed in a custom-built fixed-bed reactor (Fig. 1) with an inner diameter of 15 mm. A plate formed of 10–20 mesh silica sand was fixed at the bottom of the reactor in order to hold the catalyst, and acted as flow distributor. The reactor was filled with around 60 mL catalyst and its temperature was raised to 80 °C under the high-purity nitrogen flow (120 mL min⁻¹). 1-Decene was introduced into the bottom of the reactor using a 2PB-00C plunger pump (Beijing Xingda Technology Development Corporation, China). Liquid hourly space velocity (LHSV) was fixed at 0.5 h⁻¹ for the oligomerization of 1-decene. The product mixture was separated through vacuum distillation. Only the >280 °C fraction was collected as the PAO product and used for further analyses.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Supported catalysts using various supports or preparation conditions.</th>
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<tbody>
<tr>
<td>Catalyst</td>
<td>Support</td>
</tr>
<tr>
<td>A1-1</td>
<td>γ-Al2O3-1</td>
</tr>
<tr>
<td>A1-2</td>
<td>γ-Al2O3-1</td>
</tr>
<tr>
<td>A2</td>
<td>γ-Al2O3-2</td>
</tr>
<tr>
<td>C1-1</td>
<td>CDAC</td>
</tr>
<tr>
<td>C1-2</td>
<td>CDAC</td>
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<td>CDAC</td>
</tr>
<tr>
<td>C2</td>
<td>CSAC</td>
</tr>
<tr>
<td>S</td>
<td>Silica gel</td>
</tr>
<tr>
<td>Z1</td>
<td>Zeolite HZSM-5-1</td>
</tr>
<tr>
<td>Z2</td>
<td>Zeolite HZSM-5-2</td>
</tr>
</tbody>
</table>

¹ Coal-derived activated carbon.
² Coconut shell activated carbon.
³ Immobilization time.
⁴ Immobilization temperature.
⁵ Heating treatment temperature.
The magic angle spinning (MAS) $^{27}$Al NMR spectra were recorded using an Avance III 400 MHz spectrometer (Bruker, Germany) operating at 78.2 MHz and spun at 5 kHz.

Adsorbed pyridine infrared (Py-IR) analyses were performed on a Tensor 27 FTIR spectrometer (Bruker, Germany). At first, the samples were evacuated in situ in an IR cell. Pyridine was adsorbed and then desorbed at 25 °C for 30 min and then at 150 °C for 60 min.

The yield of PAO product, $Y$, was defined as $Y = m_c/m_0 \times 100\%$, where $m_c$ and $m_0$ are the mass of the >280 °C fraction in the synthesized mixture and the raw material 1-decene, respectively. $Y$ is calculated according to collected product within the first 2 h time on stream to determine the catalytic performance of various freshly prepared catalysts. Meanwhile, a series of oligomerizations were performed continuously in the same fixed-bed reactor in order to evaluate the catalyst stability.

3. Results and discussion

3.1. Catalytic performance of AlCl$_3$–TiCl$_4$ on various supports

The nature and pore structure of the support can largely determine the immobilization of the active species and therefore can have an extremely significant effect on catalytic performance. In order to evaluate such influences, various porous materials including γ-Al$_2$O$_3$ with distinct pore size, different types of activated carbon, silica gel, and zeolites HZSM-5 with different Si/Al molar ratios were used as the supports in the preparation of immobilized catalysts. Their chlorine content, $x_{Cl}$, and yield of PAO, $Y$, are presented in Fig. 2a. In addition, the micropore analysis results for different supports are listed in Table 2. The chlorine content is found in the following order: CDAC > γ-Al$_2$O$_3$-1 > γ-Al$_2$O$_3$-2 > CSAC > HZSM-5–2 > HZSM-5–1 > silica gel. Overall, the yield of PAO in ranks almost the same order, except for CSAC and HZSM-5, which have reversed yields. This indicates that CDAC and γ-Al$_2$O$_3$ with small pore size are promising candidates for immobilization of AlCl$_3$–TiCl$_4$ involved in catalytic synthesis of PAO. In the case of CDAC, the highest $x_{Cl}$ and the largest $Y$ are observed as 14.2% and 90.81%, respectively. In contrast, silica gel has a low chlorine content ($x_{Cl}$ equals 0.6%), although possessing relatively high specific surface area (730 m$^2$/g; see Table 2); hence, it fails to catalyze the oligomerization of 1-decene efficiently (with $Y$ of only 3.10%). Taking all the supports used here into consideration, it seems that there is no strong dependence of $x_{Cl}$ on the specific surface area. It has been proven that γ-Al$_2$O$_3$ can be an excellent medium for binding AlCl$_3$, owing to its inherently abundant OH groups, which have a strong bonding affinity for the active species [30]. The present results support this conclusion by providing both γ-Al$_2$O$_3$–supported catalysts with around 88% PAO yield.

The formation and distribution of Al and Ti on the surfaces of various supports are revealed by XPS, $^{27}$Al MAS NMR, and SEM/EDS mapping analyses (Fig. 3). In Fig. 3a, all samples display the Al$_2$P$_{1/2}$ (74 eV) and Ti$_2$P$_{1/2}$ (465 eV) and Ti$_2$P$_{3/2}$ (460 eV) doublet, associated with the binding energy of the oxygenated states of Al and Ti, respectively. Catalyst $S$ displays a bonding energy of 73 eV, corresponding to Al$_2$P$_{1/2}$. The $^{27}$Al MAS NMR results (Fig. 3c) indicate that AlCl$_3$ species can be 4-, 5, and 6-coordinated by binding oxygen groups from the support surface, which agrees with previous studies [31–33]. From SEM/EDS mapping analysis (Fig. 3d), the Al and Ti species are found to be highly dispersed on the surface of the support. Using oxygen as a reference, the relative values of the molar ratio Ti/O for different samples, therefore, can be estimated from their corresponding XPS peaks in order to evaluate the relative content of active species on catalyst surface. In Fig. 3b, Ti/O presents an order generally consistent with the chlorine content for various supports. Among all the fresh catalyst

![Image](https://via.placeholder.com/150)

1. N$_2$ cylinder, 2 - dryer, 3 - flowmeter; 4 - fixed-bed reactor, 5 - raw material tank; 6 - pump, 7 - product tank, 8 - temperature controller

Fig. 1. Flowchart for oligomerization.

2.4. Analysis and characterization

Kinematic viscosities of PAO products were measured using a SYD–265C capillary viscosity meter (Shanghai Geological Instrument Factory, China) according to ASTM D445. The viscosities of PAO were tested at 40 and 100 °C, denoted as $\nu_{40}$ and $\nu_{100}$, respectively. The viscosity index (VI), which can reflect the temperature dependence of viscosity of the PAO product, can be derived from $\nu_{40}$ and $\nu_{100}$ according to ASTM D2270. The freezing point (FP) was measured on a SYP1022-2 freezing point analyzer (Shanghai Boli Instrument Co., Ltd., China).

Chlorine content of the catalysts was determined using a ZWC-2001 salt content analyzer (Jiangsu Jierui Instrument and Equipment Co., Ltd., China). First, a catalyst sample weighing around 1 g was treated with 40 mL 0.5 M nitric acid aqueous solution for 8 h and washed at least three times with deionized water. The solution was separated through centrifugation and collected. The treating solution for each catalyst was diluted to 250 mL with deionized water. The mass fraction of chlorine in fresh and deactivated catalysts, $x_{Cl}$, could be simply calculated according to $x_{Cl} = 250c_{Cl}/m_0$, where $c_0$ is the chlorine content in solution, g mL$^{-1}$, and $m_0$ is the mass of the catalyst sample, g. In addition, chlorine content in synthetic PAO product was determined using a WK-Boli Instrument Co., Ltd., China).

The formation and distribution of Al and Ti on the surfaces of various supports are revealed by XPS, $^{27}$Al MAS NMR, and SEM/EDS mapping analyses (Fig. 3). In Fig. 3a, all samples display the Al$_2$P$_{1/2}$ (74 eV) and Ti$_2$P$_{1/2}$ (465 eV) and Ti$_2$P$_{3/2}$ (460 eV) doublet, associated with the binding energy of the oxygenated states of Al and Ti, respectively. Catalyst $S$ displays a bonding energy of 73 eV, corresponding to Al$_2$P$_{1/2}$. The $^{27}$Al MAS NMR results (Fig. 3c) indicate that AlCl$_3$ species can be 4-, 5, and 6-coordinated by binding oxygen groups from the support surface, which agrees with previous studies [31–33]. From SEM/EDS mapping analysis (Fig. 3d), the Al and Ti species are found to be highly dispersed on the surface of the support. Using oxygen as a reference, the relative values of the molar ratio Ti/O for different samples, therefore, can be estimated from their corresponding XPS peaks in order to evaluate the relative content of active species on catalyst surface. In Fig. 3b, Ti/O presents an order generally consistent with the chlorine content for various supports. Among all the fresh catalyst
samples, C1-6 has the highest value, while S has the lowest one. As compared with the sample A1-1, sample A1-2 (with heating treatment at 400 °C) has lower Ti/O due to the escape of active species from the support during heating. Next, the acidity of samples was characterized by Py-IR analysis. A characteristic band with respect to coordination of pyridine molecules to Lewis acid sites can be clearly identified at ~1450 cm⁻¹ for all tested samples (Fig. 3e). However, almost no pyridinium ions can be detected (note the absence of the ~1540 cm⁻¹ band), suggesting that the catalysts have no Brønsted acidity. Again, sample A1-2 shows fewer Lewis acidic sites than A1-1 resulting from the impact of thermal treatment on A1-2. A previous study indicated that supported catalysts have increasing catalytic activity and stability with increasing average pore size of γ-Al₂O₃ supports because of less pore blockage and less diffusion resistance of oligomer molecules within larger pores of the catalysts [34]. However, this conclusion cannot be drawn from our results. Instead, the catalysts using two γ-Al₂O₃ supports possessing different average pore diameters (6.25 nm for γ-Al₂O₃-1 and 19.52 nm for γ-Al₂O₃-2) seem to display comparable catalytic activity (PAO yields of 88.4% vs. 87.9%). A reasonable explanation is that the accessible acidic sites are highly dispersed on the surfaces of supports and therefore contribute equally to the catalytic activity. This can be supported by our characterizations presented above. From XPS analysis, similar content of active species is found on the surfaces of both catalysts.

### 3.2. Effect of immobilization solvents

During the immobilization process, the solvent can play a critical role in impregnating active species into a porous support and endowing a catalyst with high catalytic activity [32,35]. Various solvents including benzene, toluene, ethanol, diethyl ether, acetone, and carbon tetrachloride were used for immobilization of AlCl₃ and TiCl₄ on CDAC support. Both XCl and Y are observed to be fairly distinct for various supports (Fig. 2b). Catalyst C1-6 (using carbon tetrachloride) exhibits the highest XCl and Y, which is in good accordance with the results in an early investigation on the immobilization of AlCl₃ using benzene and various chloroalkane solvents. In contrast, samples C1-3, C1-4, and C1-5 give very low XCl and Y. AlCl₃ and TiCl₄ can be immobilized on CDAC through strong bonding with oxygen groups or weak electrostatic interaction with the surface. In general, both interactions play changeable roles in helping activated carbon supports hold the guest active species. Meanwhile, the solvent can also have strong bonding interactions with AlCl₃ or TiCl₄. In the cases of diethyl ether and acetone with respect to catalysts C1-4 and C1-5, the coordination bonding interactions between AlCl₃ and solvent molecules become significant [36,37]. Specifically, diethyl ether (corresponding to catalyst C1-4) can chelate AlCl₃ and TiCl₄ to form stable complexes AlCl₃·Et₂O and TiCl₄·Et₂O, respectively [38]. The interactions of active components with solvent molecules are stronger than those between active components and support, and therefore reduce the latter interactions. Consequently, the resulting catalysts have low XCl and Y. The C1-3 sample has a moderate content of active species but almost no activity for 1-decene oligomerization. This can be attributed to two reasons. First, alcoholysis can be involved in immobilization processes when using ethanol solvent. Also, AlCl₃ and ethanol can act as a Lewis acid and a Lewis base, respectively. As a result, the tin salt, which fails to catalyze the oligomerization

![Fig. 2. Chlorine content (xCl) and PAO yield (Y) of catalysts (a) using different supports, (b) using different immobilization solvents, and (c) at different immobilization times; (d) relationship of chlorine content (xCl) to PAO yield (Y).](image-url)
reaction, can be formed from the acid–base neutralization reaction and deposits onto the support. In contrast, carbon tetrachloride, benzene, and toluene, which have moderate solubility of AlCl₃ and TiCl₄ and weak active component–solvent interactions, impart high loading and catalytic activity to catalysts C1-1, C1-2, and C1-6.

3.3. Effect of immobilization time

The effect of reflux time on immobilization of AlCl₃ and TiCl₄ onto CDAC was also examined using carbon tetrachloride as solvent. The chlorine content of the supported catalysts initially increases with immobilization time and reaches a plateau at
3.4. Effect of immobilization temperature

The corresponding results with respect to various catalysts prepared at different temperature for 12 h immobilization in carbon tetrachloride are presented in Table 3, indicating the considerable influence of temperature on the loading of active species as well as on the catalytic performance of the resulting catalysts. As temperature increases from 50 to 80 °C, $x_{Cl}$ and Y increase from 9.8% to 14.2% and from 60.37% to 90.81%, respectively. Moreover, the viscosity of the PAO product also rises with increasing immobilization temperature. In addition to immobilization time, immobilization temperature can largely determine the diffusion rate of active species in both liquid solvent and porous support and thus affects the interaction between the active species and the support, which leads to distinct chlorine content and PAO yield. Furthermore, higher loading can provide higher catalytic activity for oligomerization of 1-decene, and therefore, the PAO product with a higher degree of oligomerization and a higher kinetic viscosity can be obtained (see Table 3). However, all oligomerization cases using different catalysts show comparable viscosity indices (in the range 154–161). This can be explained by the $^1$H NMR analysis results, which indicate that all PAO products have a very consistent branch ratio (the ratio of methyl to methylene groups in the oligomer [39]) of around 0.19.

3.5. Relationship of chlorine content ($x_{Cl}$) to yield of PAO (Y)

The chlorine content of supported catalysts prepared under various conditions was plotted against their corresponding yields of PAO products (see Fig. 2d). It is clearly shown that there is a linear relationship between $x_{Cl}$ and Y, suggesting that the content of active species on the supported catalysts determines the catalytic oligomerization of 1-decene. However, the yields of PAO for catalysts C1-3, C1-4, and C1-5 deviate from this linear trend. It also can be ascribed to the strong interactions of active components with ethanol (for C1-3), diethyl ether (for C1-4), and acetone (for C1-5).

3.6. Stability of supported AlCl₃–TiCl₄ catalysts

The lifetime test was carried out to evaluate the stability of supported catalysts. The oligomerization of 1-decene in a fixed-bed reactor filled with supported AlCl₃–TiCl₄ catalysts was performed continuously. The yields of PAO with respect to different catalysts were plotted against time on stream (see Fig. 4). The catalytic activity of catalysts A1-1 and A2 displays very similar decreasing trends with increasing time on stream, suggesting the negligible influence of pore size on catalytic stability. As compared with the three $\gamma$-Al₂O₃-supported catalysts, C1-6 has higher initial activity, whereas it undergoes faster deactivation after 10 h, which indicates that $\gamma$-Al₂O₃ can provide supported catalysts with higher stability. In addition, a remarkable difference in initial activity and stability can be observed between catalysts A1-1 and A1-2. After 26 h, A1-1 and A1-2 still have yields of 34.3% and 38.7%, which account for 38.83% and 54.86% of their respective initial activity (88.36% for A1-1 and 70.54% for A1-2). AlCl₃ is located on the support in four forms: (-Al–O)–AlCl₂, (-Al–O)₂–AlCl, (-Al–O)₃–Al, and free AlCl₃ [30,40]. Correspondingly, TiCl₄ is also immobilized in both bonded and free forms [41,42]. As for the free active species, their nonbonding interaction with the support is weak. Considering the sublimation temperature of 178 °C for AlCl₃ and the boiling point of 136 °C for TiCl₄, heating postsynthesized catalysts accelerates the release of free active species from support, leading to low loading and therefore low initial catalytic activity. On the other hand, thermal treatment or high-temperature vapor deposition methods can benefit bonding between active species and support, which enhances the stability and life of catalysts [30,31,34].

### Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_1$ (°C)</th>
<th>$x_{Cl}$ (%)</th>
<th>Y (%)</th>
<th>$\nu_{im}$ (mm²/s)</th>
<th>$\nu_{fin}$ (mm²/s)</th>
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3.7. Mechanism of deactivation of supported AlCl₃–TiCl₄ catalysts

To figure out the deactivation mechanism of the supported catalysts, used samples were characterized carefully and compared with fresh ones. The SEM images for $\gamma$-Al₂O₃ support and fresh and used A1-1 catalysts are presented in Fig. 5a, b, and c. It is clearly shown that the support and fresh catalysts possess porous structures. Meanwhile, uniformly distributed active species can be observed on the surface of the fresh catalyst (see Fig. 5b). Results of $N₂$ adsorption (see Fig. 5d and e) indicate that the same fresh catalyst has a much smaller specific surface area (132.30 m²/g) and larger average pore diameter (11.31 nm) than the parent support, which has a specific surface area of 281.38 m²/g and an average pore diameter of 6.25 nm. Both the decrease of surface area and the increase of pore size are caused by partial pore blocking resulting from the immobilization of active species on the porous support. The morphology analysis also suggests the evolution in the pore structure of the deactivated catalyst. It seems that the porous structure almost disappears for the used catalyst sample (see Fig. 5c). Micropore analysis supports this view by providing a very small specific surface area of 29.95 m²/g. In addition, the pore size distribution for the used catalyst shifts to larger values; as a result, the average pore diameter increases to 17.62 nm. Such changes in pore structure can be attributed to pore blockage and surface coverage. Oligomerization reactions can form oversized oligomer molecules that cannot diffuse out of the internal space through the size-limited channels of the catalyst, resulting in deactivation.
In order to evaluate the content of oligomers trapped in the pores of the catalyst, TG–DSC analyses were carried out under oxygen flow. The used A1-1 has its main mass loss in the temperature range between 200 and 500 °C (accounting for 74.9% of total mass loss) and shows 6.52% higher overall mass loss than the corresponding fresh catalyst sample (Fig. 6a). When oxygen is during the TG–DSC analyses, both the mass loss with respect to over 300 °C in the TG trace (Fig. 6a) and the corresponding exothermic peaks (Fig. 6b) in the DSC curve denote the oxidation removal of the oligomers from the catalyst sample. For Fig. 6b, (used – fresh) A1-1 displays the corrected DSC signal of the used catalyst by subtracting a baseline, the signal of the fresh sample. Similar mass changes resulting from the oxidative removal of organic compounds have also been observed on heating coked zeolite 5A under oxygen flow [43].

In case of the γ-Al₂O₃ support, the mass decreases slowly on heating from room temperature to 800 °C. In the range from room temperature to 200 °C, the mass loss can be assigned to the dehydration of the support with an increase in temperature: hydroxyl water on the surface can be extracted. As for fresh catalyst A1-1, the mass loss was found to be 8.97% higher than that of A1 support. That can be attributed to the loss of active species. Furthermore, the DTA results support our aforementioned conclusion, that the catalyst A1-2 (with thermal treatment at 400 °C) has lower initial catalytic activity than A1-1 because of the release of free active species with heating. Reconsidering the sublimation temperature of AlCl₃ and boiling point of TiCl₄, fresh A1-1 undergoes considerable mass decrease during heating, resulting from the escape of free active species. Moreover, a small part of the active species bonded with the support can be stripped at higher heating temperatures (i.e., higher than 600 °C). All of these results mean that the loss of active species should be considered to be an important aspect to explain the deactivation mechanism of supported AlCl₃–TiCl₄ catalyst.

The elemental analyses for fresh and used catalysts were done to confirm the changes in active species content of supported catalysts during the oligomerization process. For the sake of comparison between fresh and used catalyst, the atomic fraction of oxygen was selected as the reference. The EDS results (see Fig. 6c) agree with our previous analysis very well. The atom ratios C/O, Al/O, and Ti/O are found to be 0.247, 0.698, and 0.130 for fresh A1-1 and 1.423, 0.585, and 0.020 for used A1-1, respectively. The deactivated catalyst has a higher C/O ratio because of the deposition of oligomer compounds, and lower Al/O and Ti/O ratios owing to the loss of active species. Ti/O for the surface of used A1-1 derived from XPS analysis can also agree with that by displaying a lower value than for the fresh catalyst (Fig. 3b). Consequently, the acidity of the deactivated catalyst is greatly reduced (Fig. 3e), and thus provides decreasing catalytic activity.

Chlorine content of used catalysts was determined and illustrated in Fig. 6d. The chlorine content in synthesized PAO products was also analyzed. As it can be seen, both chlorine contents exhibit damped decrease with increasing time on stream. In addition, the content of Al and Ti in the PAO product collected in the initial
reaction stage were measured. The observed concentrations of Al and Ti are 1100 and 320 mg/L, respectively. Such results clearly indicate active species transfer from catalyst bulk to liquid stream.

The loss of active species is also confirmed to be the main reason for the deactivation of CDAC-supported catalyst. From our ICP analysis results, the content of Al, Ti, and Cl species contained in the product stream is around 600, 193, and 2810 mg/L at 6 h time on stream. It was also supported by our SEM/EDS analysis (results not given).

To sum up, all results presented here lead to the conclusion that the deactivation of supported catalysts results from two main aspects: the blockage and coverage of the pore structure of the support by deposited oligomers, and the loss of active species during the oligomerization process. The decreasing number of active sites and increasing diffusion resistance jointly cause the supported catalyst to lose catalytic activity, resulting in a declining yield of PAO product.

4. Conclusions

Oligomerization of 1-decene was studied in a fixed-bed reactor with a series of Al–Ti bimetallic catalysts prepared by anchoring AlCl₃ and TiCl₄ onto different supports under varying preparation conditions. The active species are highly dispersed on the surfaces of the supports. Their catalytic activities and stabilities were evaluated and the deactivation mechanism was revealed in terms of catalyst characterizations and active species determination. There is a linear relationship between PAO yield and chlorine content of supported catalysts. For CDAC-supported catalyst, the highest chlorine content and PAO yield are found to be 14.2% and 90.81%, respectively. However, γ-Al₂O₃ enables the supported catalyst to achieve a higher stability than others. Deactivation of supported catalysts can be attributed mainly to the blockage and coverage of the pore structure by deposited oligomers and the loss of active species.

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