Investigation of the characteristics and deactivation of catalytic active center of Cr-Al$_2$O$_3$ catalysts for isobutane dehydrogenation

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Abstract

Deactivation mechanism of Cr-Al$_2$O$_3$ catalyst and the interaction of Cr-Al in the dehydrogenation of isobutane, as well as the nature of the catalytic active center, were studied using XRD, SEM, XPS, H$_2$-TPR, isobutane-TPR and TPO techniques. The results revealed that the deactivation of Cr-Al$_2$O$_3$ catalyst was mainly caused by carbon deposition on its surface. The Cr^{3+} ion could not be reduced by hydrogen but could be reduced to Cr^{2+} by hydrocarbons and monoxide carbon. The active center for isobutane dehydrogenation could be Cr^{2+}/Cr^{3+} produced from Cr^{6+} by the on line reduction of hydrocarbon and carbon monoxide. The binding energy of Al^{3+} was strongly affected by the state of chromium cations in the catalysts.

Key words

isobutane dehydrogenation; Cr/Al$_2$O$_3$; deactivation; active center; catalyst

1. Introduction

Isobutylene is a key component for methyl tertbutyl ether (MTBE) and methacrylate synthesis. Considerable research has been undertaken on its synthesis by nonoxidative [1,2], oxidative [3−6], as well as steam cracking [7,8] reaction conditions. Although oxidative dehydrogenation of isobutane is potentially much more economical since it is exothermic and carried out at lower reaction temperature, it has the shortcoming of lower product selectivity owing to that it is easily to be deeply oxidized under the reaction conditions. Currently, isobutylene is produced industrially by the endothermic dehydrogenation of isobutane using a Cr$_2$O$_3$-Al$_2$O$_3$ catalyst at 900 K with a residence time of ∼1 s, and the selectivity to isobutylene is above 90% at an isobutane conversion of 40%–50% [1]. Since higher temperatures used in this reaction are favorable for coke formation, the catalyst needs to be frequently regenerated. A large number of studies have been done with chromium-containing catalysts [9−17] and many useful informations and results have been reported. Al-Zahrani et al. [13,16] suggested that the active center of Cr$_2$O$_3$-Al$_2$O$_3$ catalyst may be Cr^{3+}, but no any direct evidence has been provided. Until now, the knowledge about the deactivation mechanism and the nature of catalytic active

center for the Cr$_2$O$_3$-Al$_2$O$_3$ catalysts used in the isobutane dehydrogenation are still lacking, so systematic research on this reaction is needed.

In this paper, we studied the deactivation mechanism of the Cr-Al$_2$O$_3$ catalyst and its interaction between Cr and Al species, as well as the nature of the catalytic active center using XRD, SEM, XPS, H$_2$-TPR, isobutane-TPR and TPO techniques. Some valuable information was obtained about the carbon deposition on the catalyst, the nature of catalytic active center, and especially the effect of the interaction between Cr and Al species on the state of Al^{3+}. To our best knowledge, this is the first report on the effect of the Cr-Al interaction on the state of Al^{3+}.

2. Experimental

2.1. Sample preparation

All chemicals such as Cr(NO$_3$)$_3$·9H$_2$O and CrO$_3$ were purchased from Shanghai Medical Instrument Limited Company, which were analytical reagents and utilized without further purification.

Chromium oxide supported on Al$_2$O$_3$ catalysts (Cr$_2$O$_3$-Al$_2$O$_3$) were prepared by an impregnation method. A desired

amount of chromium nitrate was dissolved in deionized water, and added to Al_2O_3 support being sieved into $60-80$ mesh granules, dried at $380\,K$, and then treated with flowing air at $873\,K$. The nominal content of Cr_2O_3 in the catalyst was 15 wt%, and the surface area and pore volume of the catalyst were $78\,m^2/g$ and $0.23\,mL/g$, respectively.

2.2. Sample characterization

X-ray powder diffraction (XRD) patterns of the catalyst sample were recorded using a Shimadzu XRD6100 X-ray powder diffractometer (Cu K_α radiation) equipped with a computer system to perform automatic operation and data processing.

X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Fisher Scientific ESCALAB 250 equipped with a standard Mg K_α source and a high performance Al monochromatic source. The binding energies were calibrated by taking the C $1s$ binding energy at 284.6 eV.

Scanning electron microscopy (SEM) micrographs were obtained with a HITACHI 4800 scanning microscope.

Temperature-programmed reduction with hydrogen (H_2-TPR) was carried out using a TP5000 multifunction absorber equipped with a computer system to perform automatic operation and data recording. The effluent gas was passed through a dryer tube to remove water before detection. The catalyst weight was 20 mg, and the particle size was $60-80$ mesh. The inside diameter of the quartz reactor was 3 mm with a built-in thermocouple used to monitor the temperature. A mixture of 10% H_2/90% N_2 was used as the reduction gas and the heating rate was 10 °C/min.

Temperature-programmed oxidation (TPO) of carbon deposited samples was carried out using a equipment of TP5000 multifunction absorber. The effluent of reaction was analyzed using gas chromatography on-line by a TCD with a Porapark-QS packed column. Typically, 100 mg catalyst with the particle size ranging between 60–80 mesh and a mixture of 5% O_2/95% He was used as the oxidation gas at a heating rate of 5 °C/min during TPO experiment.

Temperature-programmed reduction with isobutane (isobutane-TPR) of the catalyst samples was carried out using a TP5000 multifunction absorber equipment. The effluent was analyzed using an on-line gas chromatograph by a TCD with a Porapark-QS packed column. The catalyst weight was 100 mg, and the particle size was 60–80 mesh. Pure isobutane (99.5%) was used as the reduction gas and the heating rate was 5 °C/min during isobutane-TPR experiment.

The activity of Cr-Al_2O_3 catalyst for isobutane dehydrogenation was evaluated using a 28 mm×3 mm×100 mm stainless steel reactor with an inner diameter of 22 mm. The height of catalyst bed was 10 mm. The isobutane was added into the reactor from the reactor bottom and the reaction was operated under isothermal condition and atmospheric pressure with the temperature of 600 °C±5 °C. The effluent from the reactor was analyzed using on-line gas chromatography by a FID with an Al_2O_3 capillary column.

3. Results and discussion

3.1. Catalytic activity

Figure 1 shows the graph of isobutane conversion and products selectivity as a function of reaction time. It is clear from the results that the conversion of isobutane decreased as reaction time increased, while the selectivity of isobutylene maintained at 90% before running the reaction for 750 min, and then it was declined continuously with the increase of reaction time. The productivity of lower molecular weight hydrocarbons such as methane, propane, and especially propylene also increased after 750 min. After carbon deposition on the surface of the catalyst, the conversion of isobutane decreased as reaction time increased. Generally speaking, the selectivity of isobutylene should increase as reaction time increased, because some acid centers, which are responsible for the hydrocarbons cracking, were covered by deposited carbon. At the beginning of the reaction, the selectivity of isobutylene remained in the 90%–93% range, after about 750 min, the selectivity of isobutylene decreased continuously. This may be explained as follows: in the beginning of the reaction the active centers of the catalyst were exposed to the isobutane and favored the reactant dehydrogenation. As the carbon deposition increased on the catalyst surface, the active centers of the catalyst were covered by the carbon species and the number of active centers decreased, which don't favor the dehydrogenation of isobutane. The reaction results also demonstrated that the cracking reaction of isobutane was not selective.
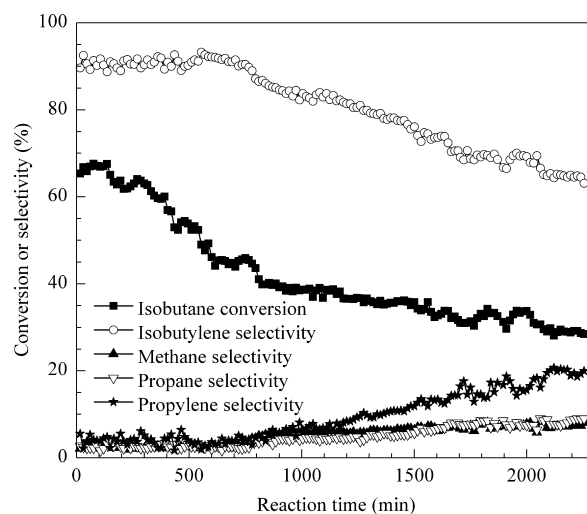

Figure 1. Variations of isobutane conversion and isobutylene and other lower hydrocarbons selectivities with reaction time

3.2. Carbon deposition

The amount of carbon deposited on used catalysts was detected using the temperature-programmed oxidation (TPO) of carbon deposits method. Figure 2 illustrates the results of TPO of different used catalysts after running the reaction for

10 h, 20 h, and 30 h, respectively. It can be seen from Figure 2 that as the reaction time increases, the amount of carbon deposit increased and the oxidation temperature of carbon species shifted to a higher temperature. This demonstrates that the state of carbon species changed to the stable one and its degree of polymerization increased. Using the general method of carbon determination with burning it in air at 1073 K and CO_x adsorption with alkali asbestos, the amounts of deposited carbon on the catalyst after running the reaction for 10 h, 20 h and 30 h were 2.5%, 4.2% and 5.3%, respectively. These results illustrated that as the reaction time increased the amounts of deposited carbon increased, but the formation rate of carbon deposition decreased. That is to say, as the reaction proceeded, the surface of the catalysts was covered by deposited carbon which retarded the deposition of more carbon.
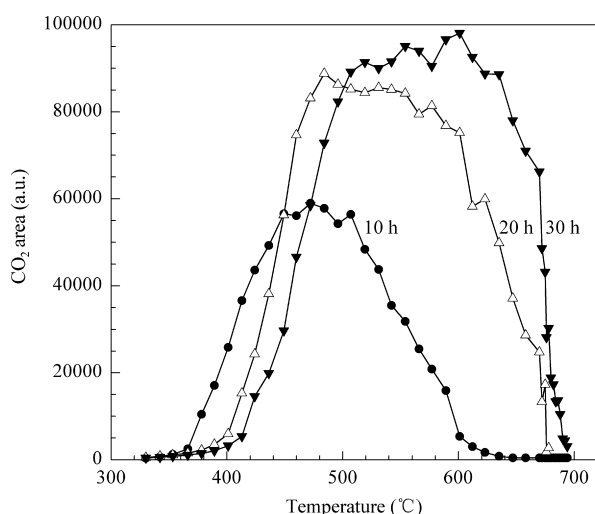

Figure 2. TPR profiles of used catalysts

3.3. Phase characterization

The XRD patterns of a fresh catalyst, a used catalyst for running the reaction for 30 h, and its regenerated catalyst at 873 K with air are showed in Figure 3. It can be seen from the pattern that the major state of all the catalysts is amorphous Al_2O_3, and no crystalline Cr_2O_3 phase could be detected, indicating that in all of the tested catalyst samples the chromium was in well dispersion state. The reaction of dehydrogenation of isobutane and the regeneration with air on the sample have no effect on the phase state of the chromium oxide. This result also demonstrates that the phase state of the catalyst was not altered in the reaction and regeneration, so the change of the catalytic activity and selectivity has no relation with the change of phase state of the catalyst.

SEM micrographs of the catalysts are illustrated in Figure 4. One can see from the image that no phase change occurred after the use and regeneration. Especially, there was no fibrous carbon formed in the used catalyst. This result was in well accordance with the mechanism proposed in Refs.

[18,19], i.e., fibrous carbon formation should need the presence of metal particles. For the Cr/Al_2O_3 catalyst no metal particles could be formed either in the preparation procedure or in the reaction. It is also demonstrated that the deposited carbon was in amorphous form and none of detectable amount of crystalline graphic carbon could be formed. This result also agrees with the results of TPO, because the crystalline graphic carbon should be oxidized at least as high as 1073 K [17], yet in our tests all of the deposited carbon was burned off before 973 K.
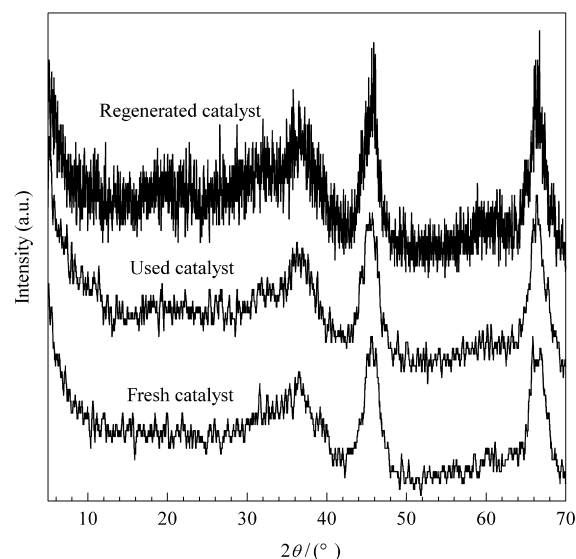

Figure 3. XRD patterns of fresh, used, and regenerated catalysts

The XPS spectra of Cr $2p$ (Figure 5a) demonstrate that, in the case of a fresh catalyst, the Cr $2p_{3/2}$ has two peaks at 577.6 eV and 579.6 eV, respectively, which correspond to the binding energy of Cr^{3+} and Cr^{6+} [20,21]. In the regenerated catalyst, the Cr $2p_{3/2}$ also has two peaks at 577eV and 579.4 eV, respectively, demonstrating that the chromium species existed in the form of Cr^{3+} and Cr^{6+} in fresh and regenerated catalysts. However, the difference between the fresh catalyst and the regenerated one was also clear, that is, in the case of a fresh catalyst, the Cr^{6+} species was the main form of chromium, while in the latter, the amount of Cr^{3+} species was greater than that of Cr^{6+}. This difference will be explained in the section on TPR. The Cr $2p_{3/2}$ recorded on the used catalyst had only one peak at 577 eV, corresponding to Cr^{3+} species, indicating that the chromium existed in the form of Cr^{3+} under the reaction conditions. In other words, the active center of the catalyst was Cr^{3+} species, which is in agreement with the results reported in Refs. [13,16]. It is very difficult to distinguish the difference between Cr^{3+} and Cr^{2+} using XPS spectra, so the nature of the active center will be discussed in the section on TPR and isobutane TPR. The binding energies of Cr $2p_{1/2}$ of a fresh catalyst, used catalyst and regenerated catalyst were 588 eV, 587 eV and 587.7 eV, respectively. These results also illustrate the existance of Cr^{6+} in the fresh catalyst and regenerated catalyst.
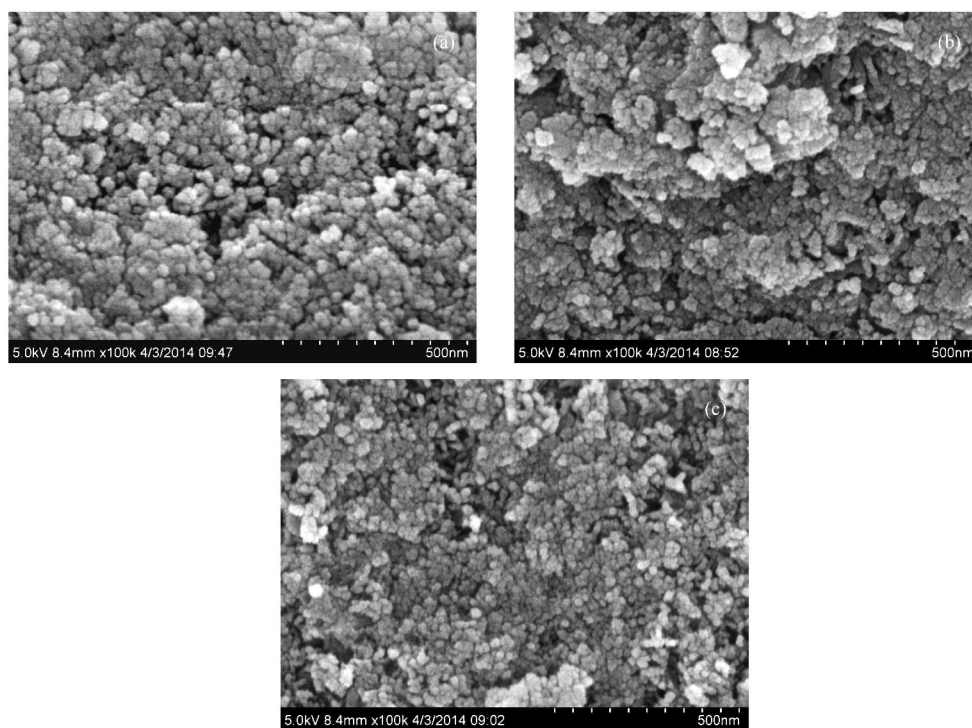
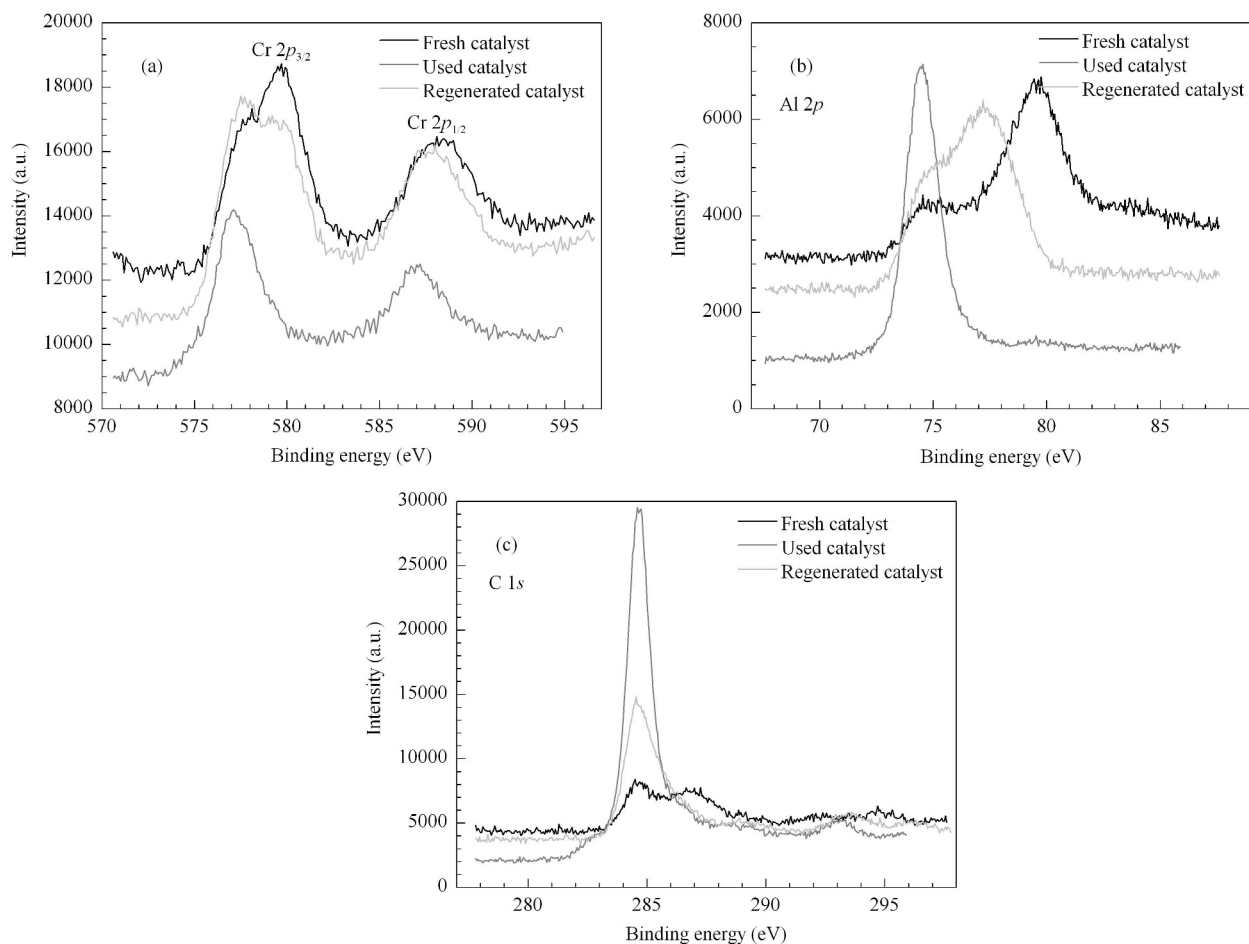**Figure 4.** SEM micrographs of fresh (a), used (b), and regenerated (c) catalysts

Figure 5. XPS spectra for (a) Cr 2p, (b) Al 2p and (c) C 1s recorded on fresh, used, and regenerated catalysts

The XPS spectra of Al $2p$ (Figure 5b) revealed that in the three samples there was a peak at 74.5 eV, which corresponds to the binding energy of Al_2O_3. It is especially significant to note in the sample of used catalyst that the aluminum existed only in the form of Al_2O_3. The sample of the fresh catalyst has another XPS peak at 79.5 eV, which may indicate that the inner electron of Al^{3+} was affected by the cations of Cr^{6+}. This result was confirmed by the XPS spectra of Cr $2p$; in the fresh catalyst, Cr^{6+} was the major species. A second peak at 77.2 eV for the regenerated catalyst showed the existance of Cr^{6+} and in an amount smaller than that for the fresh catalyst.

The XPS spectra of C $1s$ (Figure 5c) indicated all the samples have one XPS peak located at 284.6 eV which should be attributed to graphitic carbon [22,23], and their intensities vary as follows: fresh catalyst<regenerated catalyst<used catalyst. These results agree with the TPO results. It should be noted that in the sample of regenerated catalyst the deposited carbon was not burned off completely. The carbon deposited on the catalyst could be mainly in the form of amorphous graphitic carbon.

3.4. H_2-TPR and isobutane-TPR results

H_2-TPR and isobutane-TPR of a fresh catalyst were performed in order to determine the chromium state under the reaction conditions. The TPR curve for the fresh catalyst is shown in Figure 6(a). There is a single reduction peak at 372 °C (645 K). In order to compare this result with that of the reduction of CrO_3 and Cr_2O_3, two samples were prepared by physical mixing of CrO_3/Al_2O_3 and Cr_2O_3/Al_2O_3 with a weight ratio of about 1 : 2, without any other pretreatment. Their TPR curves are also illustrated in Figure 6(a). It is clear that CrO_3 could be reduced by hydrogen and its reduction peak temperature was 372 °C (645 K), while the sample of Cr_2O_3/Al_2O_3 has no TPR peaks in the tested reduction temperature range. The results demonstrate that the TPR peak for the fresh catalyst could be attributed to the reaction of Cr^{6+} to Cr^{3+}, i.e., $CrO_3 + H_2 \rightarrow Cr_2O_3 + H_2O$ and Cr^{3+} cannot be reduced by hydrogen to a lower valence state.

The TPR profiles for a fresh catalyst and regenerated catalyst are illustrated in Figure 6(b). It can be seen that the two samples have the same reduction temperatures and the amount of hydrogen consumption of the fresh catalyst was greater than that of the regenerated one. That is to say, in the fresh catalyst the amount of CrO_3 was larger. The effect of regeneration time on the state of chromium with air is shown in Figure 6(c), where the treatment temperature was 650 °C and the regeneration times were 20 min and 60 min, respectively. When the treatment time increased, the amount of CrO_3 increased, but only increased a little as the treatment time was prolonged from 20 min to 60 min. This may imply that after the reaction part of Cr_2O_3 could not be oxidized to CrO_3. The
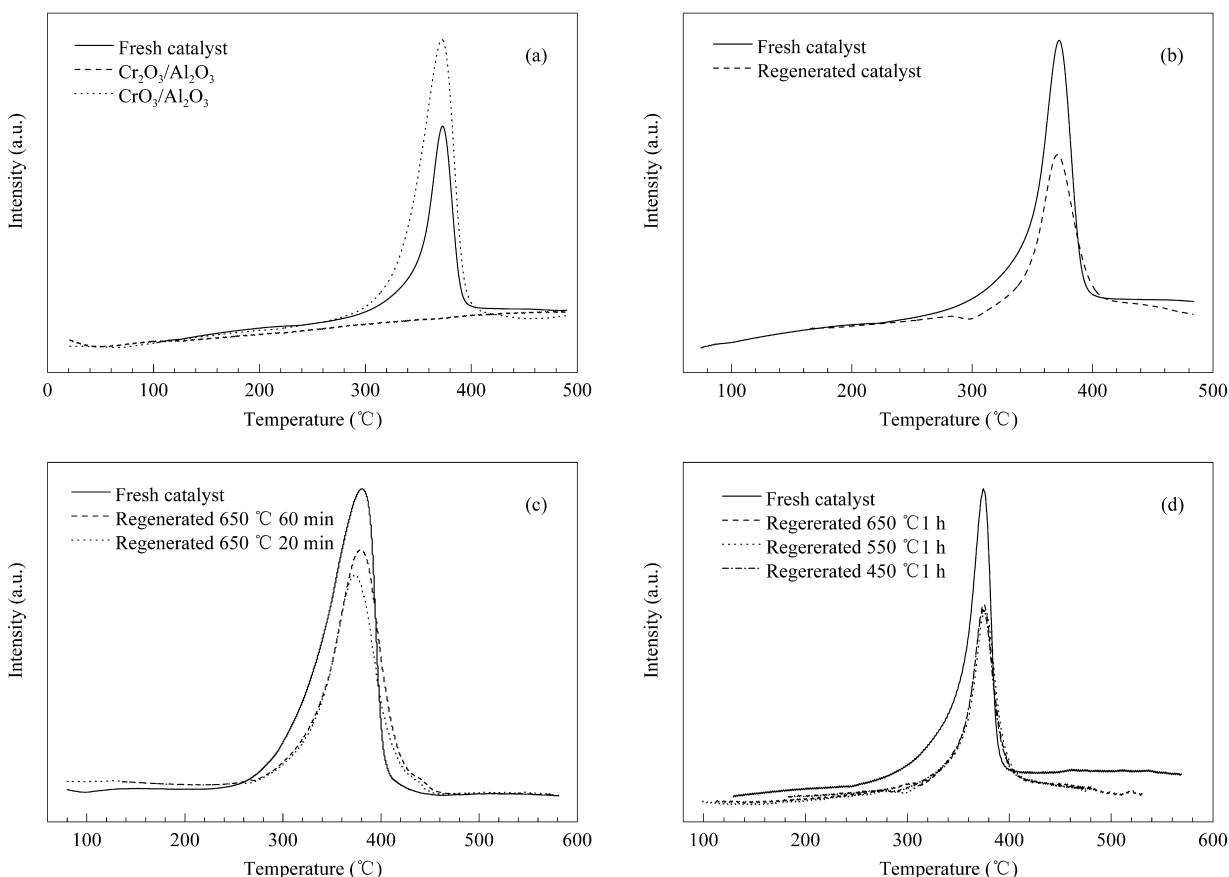

Figure 6. H_2-TPR profiles for fresh and regenerated catalysts and physical mixture samples

effect of regeneration temperature on the state of chromium was also investigated. The results are illustrated in Figure 6(d). The regeneration time was 60 min for all the samples but the treatment temperature were 450 °C, 550 °C and 650 °C, respectively. It can be seen that if the treatment time is long enough, the regeneration temperature has no effect on the state of the chromium at least in the tested temperature region. We also tested the influence of regeneration temperature at lower temperature and found that if the regeneration temperature was lower than 100 °C, no reoxidized species could be detected by H_2-TPR.

The isobutane-TPR experiments of a fresh catalyst and physical mixture of Cr_2O_3/Al_2O_3 were performed in order to determine the chromium state under the reaction conditions. The results are illustrated in Figure 7(a) and 7(b), respectively. For Cr_2O_3/Al_2O_3 mixture there were H_2O, CO, and CO_2 could be detected with the corresponding peaks centered at 248 °C, 630 °C and 565 °C, respectively, indicating that the Cr^{3+} cations could be reduced with C_4H_{10} to Cr^{2+} as expressed in the following reaction:

$$C_4H_{10}+Cr_2O_3 \rightarrow H_2O+CO_2+CO+Cr^{2+}$$
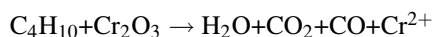
While for the fresh catalyst, H_2O, CO, and CO_2 could be detected but with the corresponding peaks centered at 275 °C, 538 °C and 340−400 °C, respectively. This indicates that the CrO_3 in the catalyst reacted with isobutane as follows:

$$C_4H_{10}+CrO_3 \rightarrow H_2O+CO_2+CO+Cr^{2+}$$

Obviously, the corresponding peak temperatures of CO and CO_2 appeared in the profiles of isobutane-TPR on the fresh catalyst and Cr_2O_3/Al_2O_3 mixture are different. It is understandable that in the fresh catalyst, the chromium mainly existed in the form of Cr^{6+}, which has higher oxidation capability than Cr^{3+}, so the reaction temperature was lower. To further explore the state of chromium under the reaction conditions, CO-TPR was also performed with a reduction gas of 10% CO/90% N_2 on the fresh catalyst and Cr_2O_3/Al_2O_3, the results are illustrated in Figure 7(c). It can be seen from Figure 7(c) that in both cases CO_2 was produced, but the peak temperatures and areas were quite different. In the case of the fresh catalyst, the amount of CO_2 was greater than that for Cr_2O_3/Al_2O_3 and peak temperature was located in the range of 350−430 °C which is similar to the results obtained in isobutane-TPR experiment. While in the case of Cr_2O_3/Al_2O_3, the peak area of CO_2 was less than for the fresh catalyst and the peak temperature was in the range of 545−594 °C, i.e., shifted to the higher temperature, which was similar to the result obtained in isobutane-TPR over Cr_2O_3/Al_2O_3. In the former case, the reaction may be expressed as follows:
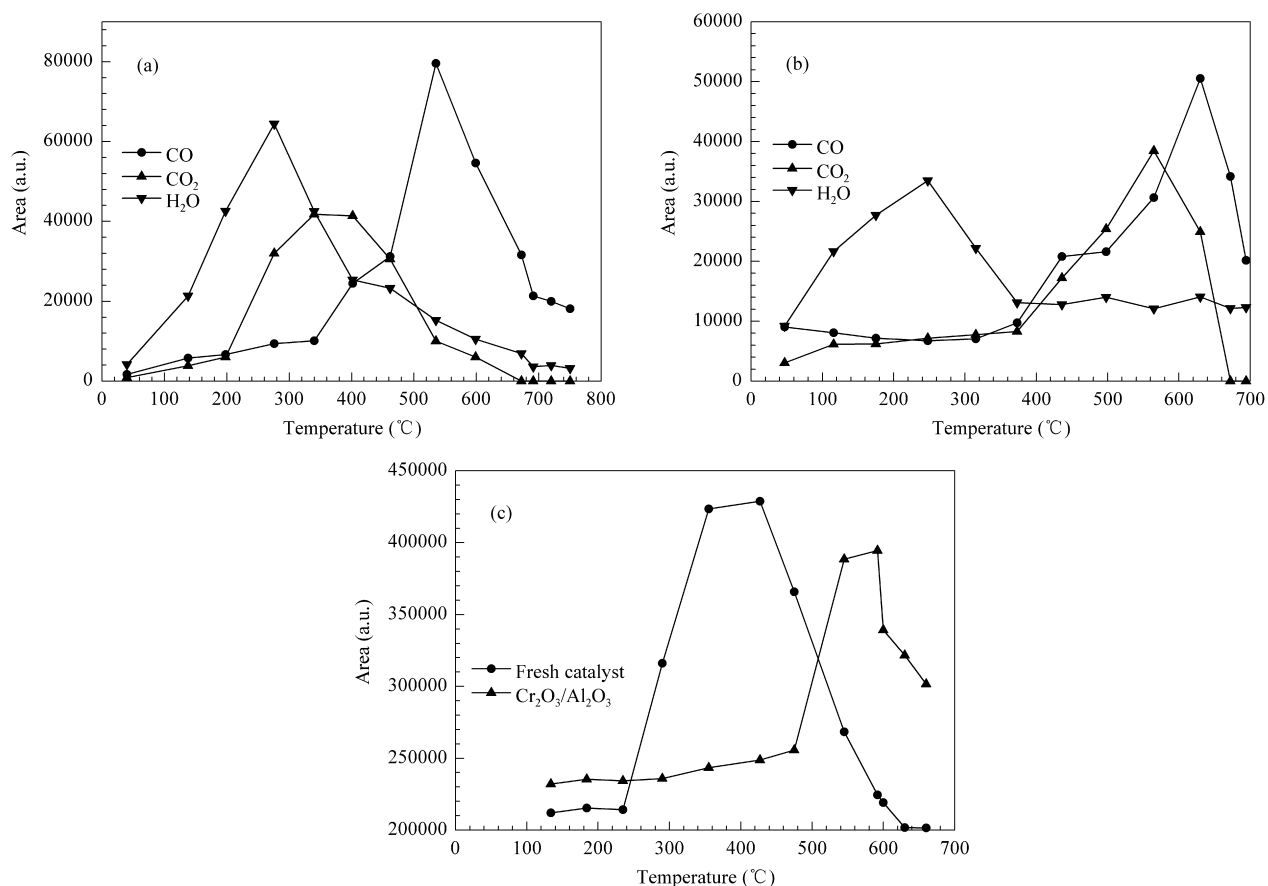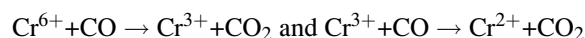
$$Cr^{6+}+CO \rightarrow Cr^{3+}+CO_2 \text{ and } Cr^{3+}+CO \rightarrow Cr^{2+}+CO_2$$

Figure 7. Isobutane-TPR profiles of fresh catalyst (a) and Cr_2O_3/Al_2O_3 mixture (b) and corresponding CO-TPR profiles (c)

while in the case of Cr_2O_3/Al_2O_3, the reaction should be expressed in the form of $Cr^{3+}+CO\rightarrow Cr^{2+}+CO_2$.

Because under industrial conditions, the catalyst is frequently suffered from the regeneration with air, so there is a large amount of Cr^{6+}, which may be reduced by the reactant isobutane to Cr^{3+} or Cr^{2+}. Meanwhile, the reduction of Cr^{6+} with isobutane will produce CO which will further react with Cr^{3+} to produce Cr^{2+}. Therefore, the ratio of Cr^{3+} and Cr^{2+} in the catalyst should be closely dependent upon the composition of reactants as well as the regeneration condition.

4. Conclusions

The $Cr-Al_2O_3$ catalyst for the dehydrogenation of isobutane has been studied with various techniques and some significant information was obtained. The catalyst deactivation was mainly caused by the carbon deposition on the catalyst surface, and the deposited carbon existed in the form of amorphous lower polymer and amorphous graphic carbon. In the fresh and regenerated catalysts there were two kinds of chromium species, Cr^{6+} and Cr^{3+}, while in the used catalyst the main forms of chromium were Cr^{2+} and Cr^{3+}. The state of chromium affects the inner electron distribution of Al^{3+}. When the main form of chromium was Cr^{6+} in the catalyst, the binding energy of Al^{3+} shifted to the higher value. The Cr^{3+} could not be reduced by H_2, but can be reduced by hydrocarbons and CO to Cr^{2+}. The catalytic active center for the isobutane dehydrogenation was Cr^{2+} and Cr^{3+}. Hence, we conclude that, under the reaction conditions, the catalytic active center should be Cr^{2+} and Cr^{3+}, and Cr^{2+} should be the major active center.

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