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Investigation of the Isolated Cr(VI) Species in Cr/MCM-41 Catalysts and its Effect on Catalytic Activity for Dehydrogenation of Propane

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Abstract: The modified MCM-41 by Cr with different loadings were prepared and tested for propane dehydrogenation (PDH) reaction. As for Cr/MCM-41 system, the general knowledge was that high Cr loadings resulted in the reduction of silica surface hydroxyl groups, thus leading to the formation of inactive Cr(III) species, as clusters and/or crystalline Cr2O3. However, the difference showed in the present work was the observation of the isolated Cr(VI) states instead of Cr(III) species in the Cr/MCM-41 catalysts, as evidenced by the UV-vis and H2-TPR results. These isolated Cr(VI) species were difficult to be reduced, and causing the decreased activity toward propane conversion and low selectivity of C3H6 for PDH process. On the contrary, a good dispersion of the Cr species was obtained from chromium column adsorption process, and the absence of the isolated state of Cr(VI) species on this sample contributed to high activity toward PDH process. The ivestigation of the isolated Cr(VI) species deserved significant importance for Crbased PDH catalyst system.

Introduction

Recently, growing demand for propene has spurred an increased interest in the dehydrogenation reaction of propane.^[1] Since the product of propene is an important feedstock in the manufacture of many chemicals, such as propylene oxide, polypropylene and acrylonitrile.^[2] In particular, the recent conversion of propane from shale gas has anticipated to decrease the cost of production and made it to be more commercial and attractive, due to the vast amounts and growing shale gas worldwide.[3] production of In general. dehydrogenation reaction can be classified into oxidative and non-oxidative processes. Though the former shows the advantage of reducing coke formation, it is still associated with the problem that the oxidation degree is hard to be controlled during actual industrial application, thus leading to safety issues and low propene yield inevitably.^[4] Consequently, non-oxidative propane dehydrogenation (PDH) process has been gained much attention and realized in commercial applications.^[5]

As far as the PDH catalyst system is concerned, Cr-based

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catalysts are mainly tested in process. On the one hand, various Cr catalysts with supports of Al₂O₃,^[6] ZrO₂,^[7] and SiO₂^[8] have been studied. It is accepted that the type of the support can influence the PDH catalytic activity, and mesoporous silicabased material, MCM-41, with high surface area and uniform pore size is preferentially used as support for a preparation of different kinds of catalysts.^[8] In fact, Cr supported on MCM-41 catalyst has been tested and proved to be a highly active catalyst for oxidative dehydrogenation of propane,^[9] and its application for dehydrogenation of isobutane and ethane has also been reported.^[10] However, to our best knowledge, few works are available in the literatures concerning PDH reaction over Cr/MCM-41 catalyst. On the other hand, understanding the exact nature of active Cr species under PDH condition is critically important and seem to be the fundamental for controlling the catalyst properties.^[8] The present literature results indicate that the redox cycle between active Cr(VI) and Cr(III) species has been proposed to be responsible for the activity of dehydrogenation reaction. Moreover, the presence of oxidized surface Cr species with higher-valence state (e.g. Cr(VI)) seems to be necessary for the production of active Cr sites, and could be generally regarded as active centers.^[7a, 9a, 10, 11]

It is considered that active Cr(VI) species predominate at low Cr loadings, while high loadings result in the formation of inactive Cr(III) species, as clusters and/or crystalline Cr₂O₃,^[9b, 12] on which not all Cr sites are accessible to the reactants and producing negative effect on the catalytic activity.^[9b] In fact, as for these reported literatures, the general knowledge is that low Cr loadings contribute to good dispersion of Cr species, and as a result, mononuclear Cr(VI) as well as some Cr(III) species with coordinative vacancies are obtained. But high Cr loadings are expected to cause the formation less active polymeric Cr(III) species. The formation of inactive Cr(III) species is attributed to the consumption of silica surface hydroxyl groups, which can provide anchoring sites for the stabilization of Cr(VI) species.[13] Consequently, some of the Cr(VI) species are converted to inactive Cr(III) species, accompanied by the depletion of surface hydroxyl groups at higher Cr loadings.^[14] In our present work, to verify the effect of Cr loadings on the nature of the Cr species, Cr/MCM-41 catalysts with different weight of Cr loadings (5, 10, and 15wt%) were prepared. Surprisingly, it is found that at high Cr loading, not all the Cr(VI) species are expectantly converted to inactive Cr(III) species. Instead, some of the inactive Cr(VI) species regarded as isolated Cr(VI) species are observed on 15%Cr/MCM-41 catalyst. Furthermore, these isolated Cr(VI) species, which exhibits difficulty to be reduced, cuase the decreased activity for PDH process. However, as far as we know, few reports are focued on investigating the presence of isolated Cr(VI) species and their effects on the catalytic activity of PDH reaction. Thus, our current work is mainly to study the isolated Cr(VI) species in the Cr/MCM-41 catalysts and analyzing its effect on catalytic activity for dehydrogenation of

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propane, which deserves significant importance for Cr-based PDH catalyst system.

Results and Discussion

Figure 1 shows the catalytic activity for PDH over Cr/MCM-41 catalysts. As a result, all the samples exhibit a similar trend as a function of time in terms of propane conversion and propene selectivity. The decrease in the activity within initial 40 min of running time could be attributed to the coversion of part of the active Cr(VI) sites and the formation of coke during the PDH reaction,^[4b,15] as revealed in the followings. Sample 10Cr/MCM-41 obtains the best catalytic performance with a propane conversion of 40% and a propene selectivity of 80% after 1 h of reaction, whereas sample 15Cr/MCM-41 shows the poorest catalytic performance with regard to propane conversion and propene selectivity. To explain the above results, further characterization studies are carried out and given.



Figure 1. Catalytic activity of Cr/MCM-41 catalysts for (A) propane conversion, and (B) propene selectivity.

The XRD patterns of the Cr/MCM-41 catalysts with different Cr contents are given in Figure 2A. It is observed that the diffraction lines of Cr₂O₃ are clearly found in the XRD patterns of all the tested samples,^[16] and the peak intensity increases with increasing the Cr content from 5% to 15%, suggesting the good crystallinity of Cr₂O₃ at high Cr loadings. Despite this, catalytic

experiments are carried out using mechanical mixtures of Cr₂O₃ with MCM-41 support, and almost no catalytic activity is seen in the PDH reaction, as shown in Figure S1 in Electronic Supplementary Information (ESI). Therefore, a detailed analysis towards the effect of bulk Cr₂O₃ phase on the activity of PDH process will not be discussed further. The UV-vis spectra of the Cr/MCM-41 samples are compared in Figure 2B. From Figure 2B, UV bands at about 270 and 360 nm express O-Cr(VI) charge transfer transitions of chromates species.^[17] Specifically, the intense peak centered at about 360 nm, which is characteristic for isolated Cr(VI) oxide,[11c] is more pronounced in the 15Cr/MCM-41 catalyst, indicating more isolated Cr(VI) species are presented in the case of the samples with a high Cr content. Additionally, two bands at about 460 and 600 nm assigned to octahedral Cr(III) in CrOx clusters or Cr₂O₃ are mainly found for all samples.^[9a] Actually, the band located at around 600 nm could be assigned to the presence of crystalline Cr₂O₃.^[17] Thus, the obtained UV-vis results is in accordance with the XRD data.



Figure 2. (A) XRD patterns, (B) UV-vis spectra, and (C) $\rm H_2\text{-}TPR$ profiles of Cr/MCM-41 catalysts.

The H₂-TPR profiles of the synthesized Cr/MCM-41 samples are displayed in Figure 2C. Over the 5Cr/MCM-41 and 10Cr/MCM-41 catalysts, one broad reduction peak at about 420 °C considered as a result of the reduction of Cr(VI) species interacted with the support can be seen.^[17] Furthermore, an additional reduction band centered at about 280 °C appears clearly from the 15Cr/MCM-41 sample, which is given account for the reduction of Cr(VI) species dispersed on crystalline α -Cr₂O₃.^[12, 17] This result is in line with the XRD and UV-vis data that suggest the presence of crystalline Cr₂O₃ for the tested sample. In particular, one high temperature reduction peak

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located at about 540 °C can be detected in the case of the 15Cr/MCM-41 sample, supposedly caused by the reduction of the isolated Cr(VI) species, which is reported to be difficult to be reduced.^[11c] Thus, the H₂-TPR data combined with the UV-vis results confirm part of Cr(VI) species exists as the isolated state in the sample of 15Cr/MCM-41. Besides, mechanical mixtures of CrO₃ with MCM-41 solid (with Cr content of 1, 5 and 15%) are designed to shed some further light on the nature of active Cr species in the Cr/MCM-41 system, since no interaction between active Cr(VI) species and MCM-41 support is obtained from this mechanical mixing process, and consequently, the isolated state of Cr(VI) species are likely to appear. From the characterization results of UV-vis and H₂-TPR as demonstrated in Figure S2 in ESI, it is shown that the isolated Cr(VI) species, as marked in Figure S2A, lead to the reduction peak divide into two parts (Figure S2B), thus further confirming our current conclusion.

Figure 3 illustrates the presence of both Cr(VI) and Cr(III) states in the synthesized samples, and peak fitting of the Cr2p BE region of the 10Cr/MCM-41 and 15Cr/MCM-41 samples shows that a higher relative percent of Cr(VI) are presented on the 15Cr/MCM-41 catalyst. Actually, an actual Cr(VI) content over the 10Cr/MCM-41 and 15Cr/MCM-41 catalysts are calculated, and it seems that H₂ comsumption (regarded as the peak area from H₂ reduction process) is positively related to the actual Cr(VI) content. However, the H₂ comsumption over the 15Cr/MCM-41 sample is lower than it deserves (as shown in Figure 3C), possibly resulted from the existence of isolated state of Cr(VI) species, and causing an inhibition of reduction process.



Figure 3. (A) and (B) Cr 2p XP spectra of Cr/MCM-41 catalysts; (C) $\rm H_2$ consumption and actual Cr(VI) content over Cr/MCM-41 catalysts.

Figure S3 in ESI shows the Si 2p, O 1s and Cr 2p XPS curves of the Cr/MCM-41 catalysts. From Figure S3B, the intense O 1s XP spectra of the 15Cr/MCM-41 sample located at low binding energy (BE) arises from the contribution of lattice oxygen,^[18] which symbolizes the possible generation of crystalline Cr₂O₃ form,^[10a] as illustrated by the XRD, UV-vis and H₂-TPR results. Moreover, as seen in Figure S3A and Figure S3B, the shift in the Si 2p and O 1s BE of the 15Cr/MCM-41 sample is likely caused by the fact the local environment in CrO_x domain is different,^[19] as revealed that some unexpected isolated state of Cr(VI) species are presented. Besides, the increase in the intensity of the Cr 2p XP spectra in Figure S3C confirms the increase in the Cr loadings. In addition, an examination of Cr2p XP spectra in





Figure 4 is the FT-IR results for the Cr/MCM-41 samples. From Figure 4A, a typical band at about 640 cm⁻¹, which is absent in the MCM-41 support, is observed over the 10Cr/MCM-41 and 15Cr/MCM-41 catalysts, indicating the formation of Cr₂O₃ phase. ^[16] Moreover, a weak IR band around 905 cm⁻¹, attributed to a Cr(VI)-O vibration,^[20] is seen in the tested Cr/MCM-41 samples, which is in accordance with the UV-vis and XPS results. Besides, a FT-IR band around 960 cm⁻¹ is correlated with the superficial hydroxyl groups from Si-O bond vibration.^[21] The shift of this band to the low wavelength location, when Cr content increases to 15wt%, is related to the replacement of OH groups.^[20] Furthermore, it is noted that the high-frequency region from 3200 to 3700 cm⁻¹ can be assigned to the stretching vibration of SiO-H bond.^[22] The decrease in the intensity of this band in the

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of the 15Cr/MCM-41 sample further case reflects the consumption OH groups during Cr impregnation process. As mentioned above, high Cr loadings may cause the depletion of surface hydroxyl groups. This effect, as evident from the FT-IR analysis, decreases the stabilization of the Cr(VI) species on the support.[13] Consequently, some of the Cr(VI) species are converted to inactive Cr(III) species, accompanied by the depletion of surface hydroxyl groups. As a result, inactive Cr(III) species as well as some unexpected isolated Cr(VI) states are found. The diagram for the formation of isolated state of Cr(VI) species on Cr/MCM-41 is exhibited in Figure 5, on which not all the Cr(VI) species are converted to inactive Cr(III) species, while some of the inactive Cr(VI) species regarded as isolated Cr(VI) species are observed on 15Cr/MCM-41 catalyst. The isolated Cr can be located on the support, interface, steps and edges, et.al. On the other hand, the high amount of OH groups allows us to expect a better stability of the catalyst by suppressing the coke deposition during the reaction.[2b,10b] Thus, a decrease in the activity for PDH process over the 15Cr/MCM-41 catalyst with low intensity of OH groups is obtained.



Figure 5. The diagram for the formation of isolated state of Cr(VI) species on Cr/MCM-41.

The STEM/Mapping images as well as SEM/ampping analysis $\overset{\Xi}{\odot}$ are respectively shown in Figure 6, Figure S4 and Figure S5 in ESI, which indicates the difference in the dispersion of Cr between 10Cr/MCM-41 and 15Cr/MCM-41 samples. From Figure 6, it is clearly found that the introduced Cr species are agglomerated on the MCM-41 support. Thus, it could be concluded that the poor dispersion of Cr species over the 15Cr/MCM-41 catalyst gives rise to the formation of isolated Cr(VI) states. In fact, it's worth mentioning that another method for the synthesis of Cr/MCM-41 catalyst, called as Chromium Column Adsorption process and reported in our previous work,^[13c] shows a better dispersion of Cr species over the Cr/MCM-41 sample, as displayed in Figure S6 in ESI (according to the XRF data, the Cr content from this method is close to 15%wt, restuls are not shown). Surprisingly, no characterization of the isolated state of Cr(VI) species are seen from the H2-TPR profile (as shown in Figure S7B in ESI), and meanwhile, its activity towards PDH reaction is higher than that over the 15Cr/MCM-41 sample, as exhibited in Figure S7A in ESI). The observation of the reduction band at about 280 °C evidences the formation of crystalline α -Cr₂O₃ over the sample from the Chromium Column Adsorption process, which indicates a high content of Cr contains on this catalyst. But to our surprise, the high activity towards PDH process over this sample is mainly

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Figure 6. STEM/Mapping images of the 15Cr/MCM-41 catalysts.



Figure 7. (A) CH₄, (B) C₂H₆ and (C) C₂H₄ selectivity of Cr/MCM-41 catalysts.

Figure 7 exhibits the selectivity of the produced CH₄, C_2H_6 and C_2H_4 over these Cr/MCM-41 catalysts. From Figure 7, it is

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clearly seen that higher amounts of CH₄ and C₂H₄ are shown on the 15Cr/MCM-41 sample, possibly resulted from the side reaction of $C_3H_8(g) \rightleftharpoons CH_4(g) + C_2H_4(g)$ ($\Delta r H^{\circ}_{298K} = 81.7 \text{ kJ/mol}$), instead of the occurrence of the main reaction of $C_3H_8(g) \rightleftharpoons$ $C_{3}H_{6}(g) + H_{2}(g) (\Delta r H^{\circ}_{298K} = 123.8 \text{ kJ/mol})$. From this point, it is deduced that the isolated state of Cr(VI) species function as the inactive one during PDH process. Besides, from Figure S1, it is known that catalyst of mechanical mixing of Cr₂O₃ with MCM-41 shows no catalytic activity towards PDH, but an improved activity is observed for its oxidized phase (by oxidizing the sample with air at 600 °C, as shown in Figure 8). However, from Figure 8B and Figure 8C, the existence of the isolated Cr(VI) state results in the lower selectivity of C₃H₆ during the reaction. Thus, these results claerly show that the generated isolated Cr(VI) species lead to the decreased activity toward propane conversion and low selectivity of C₃H₆ for PDH process, due to the low catalytic activity of the generated isolated Cr(VI) species.

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Cr species,[12a] present simultaneously at the 15Cr/MCM-41 sample, which indicates that high Cr loading leads to polymeric Cr species. As a matter of fact, from the above analysis, these polymeric Cr not only contains the inactive Cr(III) species, but also includes the formed isolated Cr(VI) species, which shows low catalytic activity for PDH. Meanwhile, Raman spectra toward the spent 15Cr/MCM-41 catalysts are shown in Figure 9B. It is seen that Raman signals at about 1380 and 1610 cm⁻¹, representing for the accumulation of coke deposit over the spent catalyst,^[23] are found in the spent 15Cr/MCM-41 sample. From Figure 9B, it is noted that the existence of coke deposit has affected the expression of Cr signals. Hence, further analysis for the spent 15Cr/MCM-41 sample is not given. Additionally, C₃H₈-TPD tests of the 10Cr/MCM-41 and 15Cr/MCM-41 samples are carried out. From Figure 9C, it is observed that 10Cr/MCM-41 sample shows a more intense C₃H₈ desorption peak, which suggests the better catalytic activity of this sample. Moreover, the intensity of the C3H6 (desorption product) over the 10Cr/MCM-41 sample is higher than that of the 15Cr/MCM-41 sample, which can be applied to explain the poor selectivity of C₃H₆ over the 10Cr/MCM-41.



Figure 8. (A) C_3H_8 conversion, (B) selectivity of the produced hydrocarbons of over Cr_2O_3 -MCM-41 catalyst (mechanical mixing), and (C) UV-vis of the Cr_2O_3 -MCM-41 catalyst (mechanical mixing) and oxidized Cr_2O_3 -MCM-41 catalyst (mechanical mixing).

To further clarify the type of the formed Cr species, Figure 9A displays the Raman spectra obtained for the 10Cr/MCM-41 and 15Cr/MCM-41 samples. As seen in Figure 9A, 10Cr/MCM-41 and 15Cr/MCM-41 show an intense band at about 982 cm⁻¹, which is attributed to the symmetric stretching of surface monochromate species.^[12a] Furthermore, the bands located at about 400, 545 and 600 cm⁻¹, respectively characteristic of the bending mode of CrO₂ units, the symmetric stretching mode of Cr₂O₃ crystals as well as the symmetric stretching of polymeric



Figure 9. Raman spectra of (A) Cr/MCM-41 catalysts; (B) spent 15Cr/MCM-41 catalysts; (C) and (D) $C_3H_8\text{-}TPD$ and $C_3H_6\text{-}TPD$ profiles of Cr/MCM-41 catalysts.

Conclusions

To summarize, Cr/MCM-41 catalysts with different Cr loadings were prepared and tested for the PDH reaction. It was shown that some inactive Cr(VI) states regarded as the isolated Cr(VI) species were found over the high Cr content Cr/MCM-41 catalyst, accompanied by the reduction of silica surface hydroxyl

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groups. Instead, the previous general knowledge is that high Cr loadings can cause the generation of inactive Cr(III) species, as clusters and/or crystalline Cr₂O₃. Therefore, understanding and investigating the characters of the formed isolated Cr(VI) species in Cr/MCM-41 catalysts can be used to realize its negative effect on catalytic activity for PDH process, which deserved significant importance for Cr-based PDH catalyst system.

Experimental Section

The mesoporous MCM-41 was prepared in our laboratory as previously reported.^[13c] The Cr modified MCM-41 catalysts with different weight of Cr loadings (5, 10, and 15wt%) were synthesized by the wet impregnation method, due to its superiority of low cost and operational easy. Appropriate amounts of (NH₄)₂CrO₄ in aqueous solution were mixed with 2 g of MCM-41 samples and vigorously stirred for 1 h. After impregnation, the resulting mixtures were dried at 90 oC for 6 h and subsequently calcined at 550 °C for 6 h. All of the prepared catalysts were pressed, crushed and sieved before the activity test.

X-ray diffraction (XRD) were obtained using Rigaku D/max-1200 diffractometer, with Cu-K α radiation (λ =1.5406 Å) at 40 kV and 30 mA, to determine the crystal structure of the obtained catalyst samples. X-ray photoelectron spectroscopy (XPS) were recorded on a PHI 5000 Versa Probe II spectrometer to study the surface atomic states of chromium species, and carbon calibration was done by referring C1 s peak at 284.6 eV. Ultraviolet-visible spectra (UV-vis) in absorbance mode were measured with a Cary 500 spectrometer at room temperature, and the spectra were recorded within the wavelength range of 200-850 nm. Fourier-transform infrared spectroscopy (FT-IR) were collected on a Nicolet 560 IR spectrometer, using KBr plate in the range of 500-4000 cm-1. H2-temperature programmed reduction (H2-TPR) were performed on a apparatus equipped with a thermal conductivity (TCD) detector. 50 mg of catalyst was pretreated in pure Ar flow at 400 °C for 1 h, and reduced from 100 to 700 °C (at a ramping rate of 10 °C/min) with H₂ (10%)/Ar flow. Scanning electron microscopy (SEM) were observed using an S-4800 SEM (Hitachi S-4800, Japan), and elemental mapping of catalysts were carried out. The STEM images coupled with the EDX elemental mapping were also conducted.

The PDH reaction was operated in a fixed-bed micro-reactor under atmospheric pressure, and the reaction temperature was fixed at 630 °C. Prior to reaction, 0.4 g of the catalyst was preheated at 630 °C in a stream of N₂ flow for 0.5 h. Afterwards, the feed gas consisted of C₃H₈(14%)/N₂ was introduced into the reactor, with the total flow rate of 29 mL/min. Products of PDH were analyzed by an online gas chromatograph (GC) equipped with TCD, and FID (flame ionization detector). The conversion of propane and selectivity of propene were defined based on follows:

C₃H₀ Conversion =	$\frac{C_{[C_3H_8]m} - C_{[C_3H_8]m}}{C_{[C_3H_8]m}} \times 100\%$
C ₃ H ₆ Selectivity =	$C_{[C_{3H6}]_{out}}$ $\sim 100\%$
	$\overline{C_{[C_{2}H_{6}]out} + (2/3)C_{[C_{2}H_{6}]out} + (2/3)C_{[C_{2}H_{4}]out} + (1/3)C_{[CH_{4}]out}} \times 100\%$

where $C_{[C3H8]in}$ is the initial concentration of C_3H_8 before the reaction, and $C_{[CxHy]out}$ is the output concentration of hydrocarbons during the reaction.

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The observation of the isolated Cr(VI) states instead of Cr(III) species in the Cr/MCM-41 catalysts, caused the decreased activity toward propane conversion and low selectivity of C_3H_6 for PDH process.



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Investigation of the Isolated Cr(VI) Species in Cr/MCM-41 Catalysts and its Effect on Catalytic Activity for Dehydrogenation of Propane