ISOMERIZATION OF C5-C7 LINEAR ALKANES OVER WO$_3$-ZRO$_2$ UNDER HELIUM ATMOSPHERE

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Graphical abstract

Abstract

The effect of WO$_3$ on the properties and catalytic isomerization of C5-C7 linear alkanes over ZrO$_2$ was studied under helium atmosphere. The WO$_3$-ZrO$_2$ was prepared by impregnation of Zr(OH)$_4$ with an aqueous (NH$_4$)$_6$[H$_2$W$_{12}$O$_{40}$], followed by calcination at 1093 K for 3 h in air. The amount WO$_3$ was 10 wt%. XRD and BET studies showed that the introduction of WO$_3$ stabilizes the tetragonal phase of ZrO$_2$, leading to larger surface area and stronger acidity of ZrO$_2$. Pyridine FTIR study verified the interaction of WO$_3$ with ZrO$_2$ formed strong Lewis and Bronsted acid sites. The presence of WO$_3$ increased the catalytic isomerization of C5-C7 linear alkanes. The conversion of C5, C6 and C7 reached 1.3, 2.6 and 5.1 %, respectively. While the selectivity of isopentane, isohexane and isoheptane reached 15.6, 20.5 and 19.5 %, respectively. The high activity of WO$_3$-ZrO$_2$ was due to the ability of WO$_3$ to adsorb and dissociate linear alkane to form hydrogen and alkane radical in which the atomic hydrogen underwent to the formation of protonic acid sites and hydride. The presence of protonic acid sites and hydride determined the activity of WO$_3$-ZrO$_2$.

Keywords: WO$_3$-ZrO$_2$, C5-C7 linear alkanes, isomerization, Bronsted acid sites, Lewis acid sites

Abstrak

Kesan WO$_3$ ke atas sifat dan pengisomeran-mangkin C5-C7 alkana lurus pada ZrO$_2$ dikaji dibawah atmosfera helium. WO$_3$-ZrO$_2$ dihasilkan dengan cara pengisitepuan Zr(OH)$_4$ dengan larutan aqous (NH$_4$)$_6$[H$_2$W$_{12}$O$_{40}$], dilanjutkan dengan pengkalsinan pada 1093 K selama 3 jam dalam udara. Jumlah WO$_3$ adalah 10 wt%. Pencirian XRD dan BET menunjukkan bahawa penambahan WO$_3$ menstabilkan fase tetragon ZrO$_2$, yang menyebabkan kepada luas permukaan yang lebih besar dan keasidan lebih kuku pada ZrO$_2$. Kajian Pyridine FTIR menunjukkan interaksi WO$_3$ dengan ZrO$_2$ aing membentuk tapak Lewis dan Bronsted asid yang kuku. Kehadiran WO$_3$ meningkatkan pengisomeran-mangkin C5-C7 alkana lurus. Penukaran C5, C6 dan C7 mencapai 1.3, 2.6 dan 5.1 %. Dan keterpilihan
1.0 INTRODUCTION

In last two decades, the increasing environmental awareness has led to strong restrictions on gasoline contents in aromatic compounds, sulphur and lead. This has caused oil refineries to start and to continuously reformulate their gasoline composition in an attempt to keep their product quality while minimize adverse effects to human and environment. As a result, in regards to the RON of the gasoline, there is a need to maintain the number of available octane, which has recently attracted much interest in isomerization process involving alkanes, particularly lower linear chain alkanes such as n-pentane, n-heptane and n-heptane. Many studies showed that the transition metal or noble metal loaded on metal oxide, mesoporous or microporous materials possesses high activity for the isomerization of lower linear alkanes. Among those supports, zirconia (ZrO$_2$) provides an effective choice for the isomerization process owing to their relatively large surface area, large pore size, high thermal stability, easy to be modified and resistance towards coke formation.

The properties of ZrO$_2$ can be improved by admixtures of oxo-anions of p and d elements such as sulfate, molibdate, chromate and tungstate. They do not form bulk solutions with ZrO$_2$, but they modify the surface properties of ZrO$_2$ in terms of thermal stability, crystallinity, surface area, pore size distribution and acidity of ZrO$_2$. In recent years, SO$_4^{2-}$-ZrO$_2$, MoO$_3$-ZrO$_2$, Cr$_2$O$_3$-ZrO$_2$ and WO$_3$-ZrO$_2$ have been widely explored in acid catalytic reactions such as alkane isomerization and cracking.

Recently, several research groups have extensively focused on the exploration of WO$_3$-ZrO$_2$, as they are more thermally and chemically stable catalyst compared to SO$_4^{2-}$-ZrO$_2$, MoO$_3$-ZrO$_2$ and Cr$_2$O$_3$-ZrO$_2$. WO$_3$-ZrO$_2$ can be operated at relatively high temperatures with higher selectivity and fewer cracking products without suffering from tungsten loss during reaction and undergo significantly less deactivation during the reaction. Scheithauer et al. have reported that Brønsted acid site strength on ZrO$_2$ depend on the WO$_3$ loading in which a higher WO$_3$ loading resulted in a higher concentration of permanent Brønsted acid sites leading to high activity of catalyst. Similarly, Naito et al. have suggested that the permanent Brønsted acid sites on monolayer-dispersed WO$_3$ are active for the isomerization of n-butane. They have concluded that the maximum activity at 6.4 W atoms/nm$^2$ is in good agreement with the maximum Brønsted acidity of the catalyst. Further WO$_3$ loading diminishes the activity of both Lewis and Brønsted acid sites. While, Soultanidis et al. has explored the effect of tungsten surface density in the properties and catalytic activity of n-pentane isomerization. They concluded that the surface Brønsted acidity of W$_2$O$_5$H sample treated at 973 K was constant at ~0.035 sites/W atom below monolayer dispersed W atom and the acidity decreased gradually above monolayer dispersed W atom. However the activity of W$_2$O$_5$H samples demonstrated a volcano-shape dependence on tungsten surface density with maximum activity at 5.2 W/nm$^2$ due to the large population of ZrW$_x$O$_{3-x}$ clusters. We also have reported the influence of WO$_3$ loading on the properties and ability of ZrO$_2$ to form active protonic acid sites from molecular hydrogen. FTIR and n-butane isomerization suggested that 13 wt% WO$_3$ loading on ZrO$_2$ yields the highest amount of isobutene due to the presence of strong Lewis acid sites on monolayer-dispersed WO$_3$ facilitates the formation of protonic acid sites from hydrogen in the gas phase which act as active sites in n-butane isomerization. In addition we also concluded that the permanent Brønsted acid sites could not be directly associated with activity of ZrO$_2$.

Although, large efforts have been undertaken to find an appropriate catalyst and an effective process for the catalytic conversion of low linear alkanes to more valuable hydrocarbon, fundamental study on the ability of catalyst to form active sites is still an interesting subject for developing new type of catalyst. In this study, we have prepared 10 wt% WO$_3$ loaded on ZrO$_2$ by impregnation method for low linear alkanes (C5, C6 and C7) isomerization under helium atmosphere at 623 K. The addition of 10 wt% WO$_3$ on ZrO$_2$ will form a strong interaction between WO$_3$ and ZrO$_2$ support which lead to form a strong acidity of catalyst. The activity of the catalyst was evaluated based on the properties of catalyst and the ability of WO$_3$-ZrO$_2$ to form active protonic active sites from C5, C6 and C7 linear alkanes.
2.0 EXPERIMENTAL

2.1 Preparation of Catalyst

Zirconium hydroxide \([\text{Zr(OH)}_4]\) was prepared from an aqueous solution of \([\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}}\) (99.9%, Wako Pure Chemical) by hydrolysis with 2.8 wt% \(\text{NH}_4\text{OH}\) aqueous solution at 353 K.\(^{15}\) The final pH value of the supernatant was 9.0. The precipitate was aging at 353 K for 3 h followed by aging at room temperature overnight. Then the product was filtered and washed with double deionized water till the final pH value of the supernatant was 7.0. Then the gel obtained was dried at 383 K to form \(\text{Zr(OH)}_4\). The \(\text{WO}_3\)-\(\text{ZrO}_2\) sample was prepared by impregnation of \(\text{Zr(OH)}_4\) with an aqueous \([\text{NH}_4]_6[\text{H}_2\text{Zr}_3\text{O}_4]\) (99.9%, Wako Pure Chemical), followed by calcination at 1093 K for 3 h in air. The amount \(\text{WO}_3\) was 10 wt%.

2.2 Characterization of Catalyst

The crystalline structure of catalysts was determined with XRD recorded on a Bruker AXS D8 Automatic Powder Diffractometer using Cu Ka radiation with \(\lambda = 1.5418 \, \text{Å}\) at 40 kV and 40 mA, over the range of \(2\theta = 20-40^\circ\). The fraction of tetragonal and monoclinic phases of \(\text{ZrO}_2\) in the catalyst was determined based on Toraya formula.\(^{16}\) The BET specific surface area and BJH pore size distribution of the catalyst were determined with a Beckman Coulter 3100SA at 77 K. The amount of adsorbed water or organic contaminants. Then, the activated catalyst was exposed to 0.13 kPa of pyridine at 423 K, followed by purging with helium flow at 373 K for 30 min to remove the physical adsorption of ammonia. The TPD was run at a heating rate of 10 K/min from room temperature to 900 K under the helium flow, and the desorbed ammonia was detected by mass spectrometry.

In the measurement of IR spectra, a self-supported wafer placed in an in situ stainless steel IR cell with CaF2 windows was activated with oxygen flow at 623 K for 30 min and hydrogen flow at 623 K for 3 h, followed by outgassing at 623 K for 1 h.\(^{17,18}\) The sample was exposed to 0.13 kPa of pyridine at 423 K, followed by outgassing at 573 K to remove gas phase or physical adsorption of pyridine on the catalyst surface. In the alkane-exposure process, the sample pretreated at 623 K was exposed to 0.13 kPa of pyridine at 423 K for 15 min, followed by outgassing at 623 K for 15 min. Then the sample was exposed to 20 kPa of alkane \(\text{C}_5\), \(\text{C}_6\) or \(\text{C}_7\) linear alkane) at room temperature. The sample was heated stepwise from room temperature in 50 K increments. All spectra were recorded on an Agilent Cary 640 IR spectrometer at room temperature.

2.3 Reaction Procedure

Isomerization of \(\text{C}_5\), \(\text{C}_6\) or \(\text{C}_7\) linear alkane was carried out employing a microcatalytic pulse reactor according to the method described in the literatures.\(^4\) Catalyst sample of 0.2 g set in the reactor was pretreated with flowing oxygen at 673 for 1 h and flowing hydrogen at 673 K for 3 h, followed by a flowing helium at 623 K for 1 h. A dose of \(\text{C}_5\), \(\text{C}_6\) or \(\text{C}_7\) linear alkane [43 μmol] was passed over the activated catalyst in a carrier helium flowing at 50 mL/min, and the products were trapped at 77 K before being flash-evaporated into an online 6090N Agilent gas chromatograph equipped with HP-5 Capillary Column and FID detector. The interval between doses was kept constant at 30 min. The reaction reached steady state at pulse number three (90 min). The conversion and selectivity were calculated based on the assumption that the retention time for alkanes passing through the catalyst bed is negligibly small. Thus the rate of conversion can be calculated by multiplying with reaction rate constant at 623 K.

3.0 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for \(\text{ZrO}_2\) and \(\text{WO}_3\)-\(\text{ZrO}_2\) samples. Both showed similar peaks in which the peak at about \(2\theta = 30^\circ\) is assigned to tetragonal phase of \(\text{ZrO}_2\) and the peaks at about 28° and 32° to monoclinic phase of \(\text{ZrO}_2\). The peak ascribed to tetragonal phase of \(\text{ZrO}_2\) was predominant on \(\text{WO}_3\)-\(\text{ZrO}_2\). The introduction of \(\text{WO}_3\) partially eliminated and broadened the peaks assigned to the monoclinic phase of \(\text{ZrO}_2\) and intensified the peak corresponding to the tetragonal phase of \(\text{ZrO}_2\). The ratio of monoclinic to tetragonal phase of \(\text{ZrO}_2\) altered from 93/17 to 19/81 showing that the addition of \(\text{WO}_3\) inhibits the sintering of \(\text{ZrO}_2\) crystallites and stabilizes the tetragonal phase of \(\text{ZrO}_2\).\(^{19}\) No cubic phase and bulk crystalline of \(\text{ZrO}_2\) was observed in this samples. In fact the addition of 10 wt% \(\text{WO}_3\) formed 87% \(\text{WO}_3\) coverage on \(\text{ZrO}_2\) with the \(\text{WO}_3\) surface density of 5.9 \(\text{WO}_3/\text{nm}^2\) (Table 1).

The stabilization effect of tungstate in the tetragonal phase of \(\text{ZrO}_2\) is consistent with previous reports on oxo-species such as sulfate, chromate, molybdate supported on \(\text{ZrO}_2\).\(^{11-12}\) In addition, the effect of \(\text{WO}_3\) on \(\text{ZrO}_2\) has been reported by several research groups. Scheithauer et al. reported that the monoclinic phase of \(\text{ZrO}_2\) dominated at low \(\text{WO}_3\) content and was lower when the catalyst was calcined at 1098 K.\(^{19}\) An increase in \(\text{WO}_3\) loading up to 19 wt% \(\text{WO}_3\) increased the fraction of the tetragonal phase of \(\text{ZrO}_2\). Vaudagna et al. reported that bulk crystalline \(\text{WO}_3\) was formed by calcination of the catalysts at 1103 K regardless of the degree of \(\text{WO}_3\) loading\(^{20}\), while Scheithauer et al. concluded that crystalline \(\text{WO}_3\) was formed only for 19 wt% \(\text{WO}_3\) loading on \(\text{ZrO}_2\) with calcination temperatures of 1023.
K and above.\textsuperscript{\textasteriskcentered} We have also reported the effect of WO\textsubscript{3} on the properties of ZrO\textsubscript{2} which the specific surface area and total pore volume passed through a maximum of WO\textsubscript{3} loading at 13 wt\%; this loading corresponds to 5.9 WO\textsubscript{3}/nm\textsuperscript{2} and is near the theoretical monolayer-dispersed limit of WO\textsubscript{3} on ZrO\textsubscript{2}.\textsuperscript{9}

Nitrogen physisorption showed that the introduction of WO\textsubscript{3} on ZrO\textsubscript{2} increases the BET specific surface area and total pore volume by about 96\% and 196\%, respectively (Table 1). Figure 2 shows the BJH pore size distribution of the catalysts where ZrO\textsubscript{2} has smaller number of pores size centered at pore diameter of 7.8 nm. The presence of WO\textsubscript{3} markedly increased the number of pores in the range of 4-10 nm in diameter in which this change may be related to the altering of monoclinic to tetragonal phase of ZrO\textsubscript{2}. In fact the specific surface area of bare WO\textsubscript{3} was about 3 m\textsuperscript{2}/g. Increase in the number of pore led to increase the BET specific surface area and total pore volume.

![Figure 1 XRD patterns of ZrO\textsubscript{2} and WO\textsubscript{3}-ZrO\textsubscript{2}](image)

![Figure 2 BJH pore size distribution of ZrO\textsubscript{2} and WO\textsubscript{3}-ZrO\textsubscript{2}](image)

**Table 1** The properties of ZrO\textsubscript{2} and WO\textsubscript{3}-ZrO\textsubscript{2}

<table>
<thead>
<tr>
<th>Terms</th>
<th>ZrO\textsubscript{2}</th>
<th>WO\textsubscript{3}-ZrO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO\textsubscript{3} content [wt%]</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>BET surface area [m\textsuperscript{2}/g]</td>
<td>25</td>
<td>49</td>
</tr>
<tr>
<td>Total pore volume [mL/g]</td>
<td>0.029</td>
<td>0.086</td>
</tr>
<tr>
<td>Surface density [WO\textsubscript{3}/nm\textsuperscript{2}]</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>WO\textsubscript{3} coverage [%]</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>Monoclinic/Tetragonal [vol%/vol%]</td>
<td>93/17</td>
<td>19/81</td>
</tr>
</tbody>
</table>

Acid site distribution and strength for WO\textsubscript{3}-ZrO\textsubscript{2} catalysts were studied by ammonia TPD and pyridine adsorbed IR spectroscopy (Figure 3 and 4). Figure 3 shows ammonia TPD plots for ZrO\textsubscript{2} and WO\textsubscript{3}-ZrO\textsubscript{2}. The TPD plots for WO\textsubscript{3}-ZrO\textsubscript{2} consisted of two peaks: one main peak appearing at about 460 K and the shoulder peak at about 650 K. The shoulder peak which emerged when the catalysts were heated to 900 K reveals that the surface acid strength was widely distributed on the catalysts. While ZrO\textsubscript{2} possessed small single peak at 460 K and almost no-peak was observed at 500 K and above. These results indicated that ZrO\textsubscript{2} has almost no-acidity at all temperature experiments. Contrarily, WO\textsubscript{3}-ZrO\textsubscript{2} possessed wide distribution of acid sites ranging from low to relatively strong acid sites in which the ammonium probe molecule desorbed at 850 K and below.

![Figure 3 Ammonia TPD plots of ZrO\textsubscript{2} and WO\textsubscript{3}-ZrO\textsubscript{2}](image)

Figure 4 shows the IR spectra of pyridine adsorbed on ZrO\textsubscript{2} and WO\textsubscript{3}-ZrO\textsubscript{2} to distinguish the type acidic sites. The IR bands at 1540 and 1450 cm\textsuperscript{-1} assigned to pyridinium ions adsorbed on Brønsted acid sites and pyridine coordinated to Lewis acid sites appeared on both catalysts, respectively. The bare ZrO\textsubscript{2} possessed strong Lewis acid sites at 1445 cm\textsuperscript{-1} due to the presence of cus Zr\textsuperscript{4+}, while the broad band in the range of 1515-1570 cm\textsuperscript{-1} may be an artifact produced during preparation of the sample.\textsuperscript{11} The introduction of WO\textsubscript{3} altered the acidity of the catalyst significantly. Particularly, the Brønsted acid sites was observed clearly at 1540 cm\textsuperscript{-1} and the peak assigned to Lewis acid sites shifted from 1445 to 1450 cm\textsuperscript{-1}. The shift of the peak must be due to the interaction of WO\textsubscript{3} with cus Zr\textsuperscript{4+} through O atom. The formation of the Brønsted acid sites due to the presence of WO\textsubscript{3} was also observed in the altering of the peak at 1490 cm\textsuperscript{-1} attributed to the combination of Lewis and Brønsted acid sites. Only small peak corresponds to Lewis acid sites at 1490 cm\textsuperscript{-1} was observed on bare ZrO\textsubscript{2}, however the peak obviously intensified with the presence of WO\textsubscript{3} indicating that interaction between WO\textsubscript{3} and ZrO\textsubscript{2} surface formed acidic hydroxyl groups on the surface catalyst.
Based on our previous IR assignment, WO$_3$-ZrO$_2$ possessed two IR bands in the W=O stretching region indicates two different types of W=O species are on the surface. The IR band at 1021 cm$^{-1}$ is assigned to the stretching of the W=O which is connected to the other W through O. The band at 1014 cm$^{-1}$, which is connected to the stretching of the W=O which is connected to the other W through O. No-dioxo (O=W=O) tungsten oxide species were present in the sample, due to the different relative intensities and wavenumbers of those two bands (symmetric and antisymmetric stretching modes of the O=W=O) is less than 30 cm$^{-1}$. Scheme shows the proposed model and structure of WO$_3$-ZrO$_2$.

Scheme 1: Proposed model and structure of WO$_3$-ZrO$_2$.

Figure 4: IR spectra of ZrO$_2$ and WO$_3$-ZrO$_2$ catalysts

Figure 5 shows the isomerization of C5, C6 and C7 linear alkanes over ZrO$_2$ and WO$_3$-ZrO$_2$ under helium atmosphere at 623 K in a microcatalytic pulse reactor. In general, the outlet was composed of isoproduct, C1-C3 cracking-products and unreacted linear alkanes. The absence of hydrogen in this experiment markedly suppressed the yield of the reaction for both ZrO$_2$ and WO$_3$-ZrO$_2$ due to the inability of catalysts to form active protonic acid sites and also hydride from molecular hydrogen. In addition, the catalytic activity was very low for ZrO$_2$ due to the absence of WO$_3$ which act as active site in the adsorption and dissociation of linear alkanes to form hydrogen and alkane radical. Then the hydrogen spillover into the surface of ZrO$_2$ and finally formed an active protonic acid sites by releasing an electron to the adjacent Lewis acid sites. The WO$_3$-ZrO$_2$ also showed good stability at 623 K, in which the activity did not decrease after 3 h of reaction. Small deactivation after 3 h may be due to the formation of coke deposits on catalyst. In addition, both ZrO$_2$ and WO$_3$-ZrO$_2$ did not active for isomerization of C5, C6 and C7 linear alkanes at 523 K and below. This may be due to the inability of WO$_3$ to adsorb and to dissociate linear alkanes to form hydrogen and alkane radical at relatively lower temperature (at and below 523 K).

We have reported the acid catalytic activity of WO$_3$-ZrO$_2$ in the isomerization of n-butane at 573 K in a closed recirculation batch reactor with a mixture of H$_2$ (40 kPa) or N$_2$ (40 kPa) and n-butane (6.67 kPa). In the presence of hydrogen gas, the product consisted of only isobutane and residual n-butane. It is interesting to note that neither lower nor higher linear alkanes were observed, indicating that dimerization, hydrogenolysis or cracking did not take place over WO$_3$-ZrO$_2$ in the temperature range of reaction. In addition, it has also been concluded that the activity of WO$_3$-ZrO$_2$ in n-butane isomerization was strongly determined by the amount of WO$_3$ loading. Increasing WO$_3$ loading improved the yield of isobutane and reached a maximum for 13wt% WO$_3$ loaded on ZrO$_2$.

Figure 6 shows the changes of IR spectrum in the region 1600-1400 cm$^{-1}$ when the pyridine-preadsorbed WO$_3$-ZrO$_2$ was heated in the presence of A) n-pentane, B) n-hexane and C) n-heptane vapour up to 473 K. The peak at 1450 cm$^{-1}$ is ascribed to pyridine adsorbed on Lewis acid sites, and the peak at 1540 cm$^{-1}$ is ascribed to pyridine adsorbed on protonic acid sites as pyridinium ions. Figure 6A shows the spectra when pyridine-preadsorbed WO$_3$-ZrO$_2$ was heated from 298 to 473 K in n-pentane vapour. As the temperature was raised, the intensity of the peak at 1450 cm$^{-1}$ decreased, with concomitant increased in the intensity of the peak at 1540 cm$^{-1}$. These results indicated that Lewis acid sites converted into protonic acid sites when the sample was heated in n-pentane vapour. Similar results were observed when WO$_3$-ZrO$_2$ was heated in the presence of n-hexane or n-heptane (Figure 6B-C), the intensity of Lewis acid sites decreased in tandem with the increase in the intensity of protonic acid sites. Contrarily, heating of ZrO$_2$ catalyst in the presence of n-pentane, n-hexane or n-heptane did not show any changes in the Lewis and protonic acid sites indicating there is no interchange between Lewis and protonic acid sites by contacting with linear alkanes.
4.0 CONCLUSION

The generation of protonic acid sites from \( n \)-pentane, \( n \)-hexane and \( n \)-heptane molecules was observed by IR study of adsorbed pyridine over the surfaces of \( \text{WO}_3\text{ZrO}_2 \). The protonic acid sites are generated through dissociation of alkane molecules to form hydrogen atoms and alkane radicals followed by spillover of the hydrogen atoms onto the support and migration to reach Lewis acid site where the hydrogen atoms donates electrons to adjacent Lewis acid site and becomes protonic acid sites. The other hydrogen atoms may interact with electrons to form hydrides on the catalyst surface. Then the formed protonic acid sites and hydrides involved in the isomerization to form isoproduts with the selective range of 15-20 \%. While the conversion of \( C_5 \), \( C_6 \) and \( C_7 \) linear alkanes did not exceed 5 \%. This result suggested the protonic acid sites formed from the reactant over \( \text{WO}_3\text{ZrO}_2 \) is able isomerize the reactant itself, however they did not satisfy to improve the catalytic isomerization of \( C_5 \), \( C_6 \) and \( C_7 \) linear alkanes significantly.

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