Tungsten dispersion and coke reduction on metathesis catalyst for propene production

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Abstract: The modifications of WO_3/SiO_2 catalyst were investigated in the metathesis of ethene and 2-butene for propene production. Sol-gel processes, non-hydrolytic and aerosol-assisted sol-gel, display outstanding textural properties and feature high tungsten dispersion. Nano extra support addition with WO_3/SiO_2 catalyst shows the better tungsten dispersion by thermal spreading during thermal treatment. Second metal addition with WO_3/SiO_2 catalyst, such as Lanthanum, Cerium and Yttrium, improved the tungsten dispersion. These modifications enhanced the metathesis activities. Moreover, the coke formation on the metathesis catalyst was investigated. NaOH ion-exchange method and Lanthanum as second metal modified WO_3/SiO_2 catalyst reduced the coke formation.

Keywords: tungsten dispersion, metathesis, coke formation.

1. Introduction

Due to the rising demand for propene in the petrochemical industry, the metathesis of ethene and 2-butene is now used for on purpose propene production by WO_3 catalyst[1]. It has been confirmed that crystalline WO_3 is not active for metathesis. Only amorphous tungsten oxide species exhibit metathesis activity and high dispersion is a prerequisite for high metathesis activity[2]. In this paper, we conclude the various methods to gain more the tungsten dispersion. Non-hydrolytic and aerosol-assisted sol-gel catalysts were prepared as the elaborate catalysts involving an active oxide phase dispersed at the surface of a mixed oxide support. Nano extra support addition with WO_3/SiO_2 catalyst was evaluate for thermal spreading concept to obtain the well-dispersed tungsten oxide. The last presented technique is second metal addition with WO_3/SiO_2 catalyst such Lanthanum, Cerium and Yttrium. These techniques aim to develop the metathesis catalyst with the high dispersion. Generally, tungsten oxide catalysts are active at higher reaction temperatures (300–500 °C). The formation of coke is expected to cause deactivation. The mechanism of coke formation is promoted by acidity on the catalyst[3,4]. So, we also focused on poisoning the acid sites with small amounts of NaOH by ion-exchange method to mitigate the acidity with unchanged in metathesis activity.

2. Experimental

The catalysts were tested in the gas-phase metathesis reaction between ethene and 2-butene within a fixed-bed tubular flow reactor under atmospheric pressure. Firstly, the catalyst was pretreated under a nitrogen flow at a temperature not greater than 600 °C for 1 h. Then, the system was cooled down to the reaction temperature at 400-500 °C under a nitrogen flow. The reactant feed was admitted in the reactor. An online gas chromatograph and a flame ionization detector using nitrogen as the carrier gas were used to monitor both reactants and products.

3. Results and discussion

In this paper, three powerful techniques for improving tungsten dispersion were concluded. A new one-pot preparation route based on non-hydrolytic sol-gel is presented as a powerful new method to prepare highly active WO_3-SiO_2 and WO_3-SiO_2-Al_2O_3 metathesis catalysts. These new catalysts reach high propene yields in the industrially relevant metathesis conditions. The method offers a good control on the final catalyst composition and provides mixed oxides with excellent textures (large mesopores, high surface area). Decisively, non-hydrolytic sol-gel catalysts feature high W dispersion, which correlates with lower reducibility, higher acidity and higher metathesis activity. Another one-step preparation is aerosol-assisted sol-gel process to prepare WO_3-based metathesis catalyst with well controlled composition, excellent texture and high catalytic performance. The metathesis activity of WO_3-SiO_2 catalysts increases with increasing WO_3 loading. The catalyst loading can be increased relatively high (up to 15 wt.%), while keeping an excellent W dispersion. Characterization indeed reveals that no crystallites are formed on aerosol made catalysts and surface W content is high. The best aerosol catalysts outperformed markedly reference impregnated catalyst for which poor WO_3 dispersion appears to be the main limitation.

The concept which drives the migration of tungsten oxide to its high dispersion is adding the nano-sized extra support with WO_3/SiO_2 catalysts. ZrO_2 and TiO_2 as an additional support to the catalyst were carried out to help improving dispersion of tungsten oxide species via thermal spreading. Evidences from FT-Raman, ICP-OES, and H_2-TPR results of the separated ZrO_2 and TiO_2 additional support indicated that thermal spreading occurred and using the ZrO_2 support, which have higher surface energies than the TiO_2, could result in a more dispersed tungsten oxide species sites. Better dispersion of catalysts mixed with the nano-sized additional supports could enhance trans-2-butene conversion and propene selectivity. Accordingly, the higher surface energies of the ZrO_2 chosen as an additional support, as compared to the TiO_2, provided for the spreading was the differentiating source to leading to the distinctive catalytic performances.

The last presented technique is second metal addition with WO_3/SiO_2 catalyst. Lanthanum, cerium, and yttrium were added as a second metal on the WO_3/SiO_2 catalysts by the incipient wetness impregnation method. As revealed by various characterization results, the dispersions of tungsten and adsorption properties were significantly improved by adding of the second metals, especially the adsorption of the mixed cis/trans-2-butene isomers. Hence, their catalytic performances were higher than the non-modified one when mixed cis/trans-2 butene isomers were used as the feeds.

Moreover, the deactivation by coking on the metathesis catalyst was expected to reduce by NaOH treatment. The mechanism of coke formation is promoted by acidity on the catalyst. The metathesis activity of the WO_3/SiO_2 catalysts with NaOH treatment remained almost unchanged while the Lewis acidic sites were poisoned by sodium. This suggested that the remaining acidity on the catalyst was enough to ensure the efficient formation of the metal-carbene. TGA analysis was used for determining coke formation on the spent catalysts. In the present work, the coke contents on WO_3/SiO_2 catalyst with NaOH treatment were quite low. Two mass loss peaks were observed at 280 and 460 °C, which corresponded to aliphatic hydrocarbons (soft coke) and polyaromatics (hard coke), respectively. In addition, the presence of La as the second metal on WO_3/SiO_2 catalyst could also reduce coke formation on the catalysts probably by decreasing the ensemble site effect.

4. Conclusions

Non-hydrolytic and aerosol-assisted sol-gel processes could well control the composition of WO_3-based metathesis catalyst with the high tungsten dispersion. Nano extra support addition was used as the one of techniques which easily applies to the commercial process to enhance the dispersion of tungsten active phases. Furthermore, second metal addition with WO_3/SiO_2 catalyst promoted the metathesis activity by also increasing the tungsten dispersion. These various modifications led to the good improvement of tungsten oxide dispersion, resulting in the high metathesis activity. In addition, the coke formations on the catalyst were reduced by NaOH treatment and Lanthanum as second metal modified WO_3/SiO_2 catalyst.

References

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