

Promoting the Selectivity of Light Olefins in Methanol-to-Olefins Processes through the Low-temperature Air Regeneration

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Highlights

- Low-temperature air regeneration strategy is proposed in MTO process.
- The improvement in ethene selectivity is obtained.
- The more available space and advantageous diffusion diffusivity are confirmed.

1. Introduction

The SAPO-34 catalyst used in methanol-to-olefins (MTO) processes exhibits very high selectivity for light olefins due to the cylindrical cage structure and small-pore openings, while also rapidly deactivating because of the accumulation of coke inside the cage. The previous studies have shown that coke not only affects catalyst activity but is also closely bound up the selectivity of light olefins, making the regulation of coke in cages extremely important [1]. According to the dual-cycle mechanism, the species of the active hydrocarbon pool confined within zeolite cage are conducive to production of light olefins. These can be either pre-added or converted from other inactive components, corresponding to two regulatory methods: precoking and partial regeneration. For instance, a facile 1-butene precoking strategy was proposed by Zhou et al for enhancing the ethene selectivity by controlling “coke” spatial siting to the extension of the reaction zone inward in the crystal [2]. Also, recently, Wang et al demonstrated a strategy combining ethene precoking and subsequent steaming for construction of active naphthalenic species within SAPO-34 crystals, which promotes the olefin selectivity and prolongs the catalyst lifetime in the MTO conversion [3]. Regeneration is the elimination of coke in deactivated catalysts to restore their activity, while partial regeneration, retaining a portion of “coke”, is commonly explored in industry for boosting ethene selectivity. Zhou et al. developed a steam regeneration approach to directionally transform deactivating coke species to active naphthalenic species that not only impetus ethylene formation in MTO conversion, but also yields valuable synthesis gas [4]. In this work we propose a low-temperature air regeneration strategy and compare the differences with the conventional high temperature of 873 K from microfluidized bed reactor experiments, *in situ* infrared spectroscopy, Gas chromatography-mass spectrometry (GC-MS) and structured illumination microscopy (SIM).

2. Methods

The commercial shaped catalyst is loaded into a microfluidized bed reactor for MTO reaction (atmospheric pressure, $WHSV = 2 \text{ g}_{\text{MeOH}} \text{ g}_{\text{CAT}}^{-1} \text{ h}^{-1}$, 748 K), and the effluent products are analyzed by online gas chromatograph equipped with capillary column and FID detector. When the methanol conversion is lower than 80 %, it is considered that catalyst is deactivated, and then it is raised to 743 and 873 K under N₂ purge, and then switched to air with $WHSV$ of $1 \text{ g}_{\text{air}} \text{ g}_{\text{CAT}}^{-1} \text{ h}^{-1}$ for regeneration for different times. GC-MS is used to identify the retained species liberated by HF dissolution-solvent extraction method in deactivated samples. The recovery of acid sites of deactivated catalysts during the regeneration is obtained through in-situ infrared (IR) spectroscopy at 3590 and 3610 cm^{-1} . The spatiotemporal distribution of the soluble coke species located in zeolite crystals was obtained by SIM.

3. Results and discussion

The MTO reaction performance represented as the maximum ethylene selectivity here is compared firstly at the same residual coke content after different regeneration times at 743 K and 873 K (Figure 1 a). Compared to high-temperature regeneration at 873 K, the SAPO-34 catalyst regenerated at 743 K

can increase ethylene selectivity by up to 5.5 %, but the difference gradually decreases to zero as the amount of residual carbon decreases. The investigation in Figure 1 b) reveals that the samples regenerated at low temperature have a larger specific surface area, thus providing more sufficient reaction space. Low temperature reduces the oxidation ability of oxygen molecules, causing soluble carbon deposits in the deactivated zeolite cage to be quickly cleared (Figure 1 h), while the insoluble species slowly decrease (Figure 1 g). Oxygen molecules at 873 K make no difference in their capacity to oxidize insoluble and soluble carbon, resulting in a synchronous decrease in their content (Figure 1 d and e). Accordingly, the removal of soluble carbon with more uniform distribution will restore more available space and increase the number of acid sites, leading to the better reaction performance. The improvement of ethylene selectivity may also originate from the diffusion differences caused by different species spatial arrangements, as low-temperature regeneration leaves bulk carbon deposits adsorbed on acid sites (Figure 1 c), but this still needs further exploration. To recap briefly, the difference between high and low temperature regeneration may lie in their decoking mode, with the former tending towards a shrinking mode (as shown in Figure 1 f, where coke gradually disappear from the outside to the inside), while the latter resembles a uniform model (Figure 1 i).

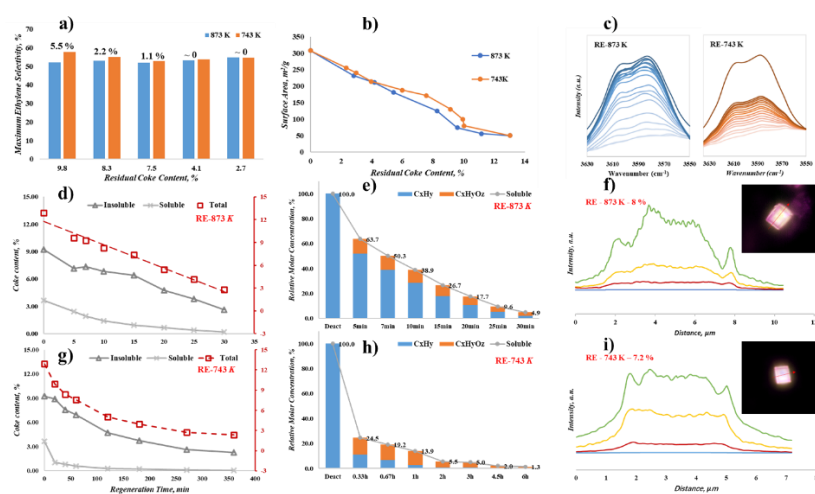


Figure 1. **a** the maximum ethylene selectivity of the reactivated catalyst at the same residual coke content after different regeneration times at 743 K and 873 K; **b** surface area of samples regenerated at 873 K and 743 K with different residual coke contents ; **c** *in situ* IR spectra of the deactivated samples treated by air at 873 K and 743 K with different time; **d**, **g** changes in overall carbon content under different regeneration times; **e**, **h** changes in soluble carbon content under different regeneration times; **f**, **i** the spatiotemporal distribution of carbonaceous species (blue: benzenic, green: naphthalenic, yellow: phenanthrenic, red: pyrenic carbocations) obtained from the SIM images of regenerated materials, at 873 K and 743 K, respectively.

4. Conclusions

In this study, we propose a low-temperature air regeneration strategy in MTO process and explore the possible reasons for the increase in ethylene selectivity compared to high-temperature regeneration through various characterization methods. The weak oxidation ability of oxygen at low temperatures first removes the more evenly distributed soluble carbon, resulting in a larger nanoconfinement space. Meanwhile, the residual bulk carbon may also bring advantages in the diffusion of ethylene. The low-temperature regeneration strategy proposed by the author has higher economic efficiency and can be used as a process intensification method for MTO industry.

References

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Keywords

Methanol-to-Olefin; Air Regeneration; Coke Spatial Distribution; Process Intensification