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Article

Investigation of the coupled reaction of methyl acetate and *n*-hexane over HZSM-5

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ABSTRACT

The coupled reaction of methyl acetate and *n*-hexane was carried out over a HZSM-5 catalyst. In addition to a thermal coupling effect, systematic variations in the product distribution were also observed in the coupled system. The benzene-toluene-xylene (BTX) selectivity was remarkably improved while the H₂, CO, and CO₂ selectivity decreased. Rapid deactivation of the catalyst was observed, caused by the extremely high reactivity of methyl acetate, which was alleviated after adding *n*-hexane. These results indicated that a coupling effect exists in this system. A detailed pathway for the coupled system is suggested based on the analysis of the surface species, carbonaceous species deposited on the catalyst, as well as the product selectivity changes. The good match between the "hydrogen deficiency" of methyl acetate and the "hydrogen richness" of *n*-hexane is consistent with the observed coupling effect.

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1. Introduction

Steam cracking is one of the most important processes for light olefin production in the petrochemical industry. Light alkanes and naphtha are widely used as raw feeds in steam cracking. After decades of development, steam cracking has become a vastly proven process. However, steam cracking is an endothermic reaction operated at high temperature (>800 °C) and thus, the large energy consumption remains its main drawback [1,2]. A solution to this problem is coupling an exothermic reaction to this highly endothermic process under catalytic conditions to improve the overall energy efficiency.

Nowak et al. [3,4] studied the coupling of C₄ hydrocarbons and methanol over ZSM-5 at 600–700 °C. The results showed that complete thermal neutrality could be achieved at a methanol/*n*-butane molar ratio of 3:1, where the yield of lower olefins was much higher than that with methanol or *n*-butane alone. The coupling cracking of methanol with C₆ hydrocarbons and naphtha also showed high selectivity for lower olefins and became an almost thermoneutral reaction with improved heat control [5]. Shabalina et al. [6] combined methanol to olefin (MTO) with the catalytic cracking of alkanes. The results indicated that the decomposition of methanol over the catalyst in the coupled system was much lower compared to that in the

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individual feed system. Wan et al. [7] investigated the coupled reaction of ethanol and *n*-hexane over HZSM-5. A higher initial conversion rate of *n*-hexane was observed in the coupled system. A systematic investigation on the coupling of methanol and *n*-hexane over a well-designed pulse reaction system showed an increased initial conversion rate and decreased starting reaction temperature [8]. These effects were attributed to the activation of *n*-hexane by interaction with the methoxy species formed on the zeolite.

The exploration of other exothermic reactions that may be coupled to alkane cracking may provide new insight into this important technology. The conversion of methyl acetate (MAc) over a zeolite catalyst is a highly exothermic reaction. MAc, a compound bearing a C=O group with an effective hydrogen index (EHI) of 0.67 [9], has a “hydrogen-deficient” elemental composition and is thus a good candidate for coupled systems. Moreover, MAc can be produced by carbonylation of dimethyl ether with CO over a zeolite in large-scale, which is the core step for the world’s first coal-based ethanol process that has been recently commercialized [10].

However, scarce reports exist on MAc, especially on its conversion over molecular sieves. Romotowski et al. [11] investigated the infrared (IR) spectral features of the interaction of MAc with H/NaZSM-5 under specific experimental conditions and they suggested that the reaction of MAc with zeolites proceeds as follows:

Firstly, MAc interacts with H/NaZSM-5 affording acetic acid and methoxy species. Acetic acid further reacts with H/NaZSM-5 to form acetate and acylium ions. In addition, the hydrolysis of MAc may also lead to the formation of acetic acid [11]. Finally, the reaction of the acylium and acetate species affords acetone and carbon dioxide.

MAc reacts on the ZSM-5 surface to produce a certain amount of hydrocarbon species. However, large amounts of C and O species are released from MAc in the form of CO₂ via decarboxylation; as such, the hydrocarbon yield is lower than that using methanol. Some researchers have managed to combine methanol with MAc; the yield of hydrocarbons was improved as the decarboxylation was transformed into a dehydration process [9,12]. This suggested the existence of some form of synergy when species with EHI < 1 and EHI > 1 react together over ZSM-5. Such an effect may promote the conversion and improve the product distribution [13].

As *n*-hexane (the model compound for naphtha) has an EHI of 2.3 and is thus a typical hydrogen-rich alkane, the coupled reaction of MAc and alkanes holds great potential. Herein, the coupled reaction of MAc and *n*-hexane over HZSM-5 was investigated in detail and compared with the individual reactions. The effects of the reaction conditions (such as the temperature, space velocity, and ratio of feed stock) and catalyst Si/Al ratio on the reaction behavior were evaluated. To determine the reaction pathway for such a coupled system, a variety of characterization methods, such as temperature-programmed sur-

face reactions (TPSRs), Fourier transform infrared (FT-IR) spectroscopy, and gas chromatography-mass spectrometry (GC-MS), were applied to analyze the active species deposited on the catalyst surface.

2. Experimental

2.1. Catalyst and reaction conditions

HZSM-5 (Si/Al = 19, 50, and 200) was obtained from the Catalyst Plant of Nankai University (Tianjin, China). The zeolite was pressed into platelets and then sieved to 20–40 mesh. MAc (≥99%) and *n*-hexane (*n*-Hex, ≥99%) as feedstocks were purchased with the highest purity available.

The catalytic reactions were performed in an electrically heated stainless steel fixed bed reactor in the temperature range 300–500 °C under atmospheric pressure. A catalyst sample of 2.5 g was loaded into the reactor in each experiment. The catalyst was first activated at 500 °C under N₂ flow for 1 h before cooling to the desired reaction temperature and then the feedstocks were pumped steadily into the reactor. The reaction effluent was analyzed by online GC (Agilent 7890A) equipped with a FID detector (PONA capillary column) and a TCD detector (TDX-1 packed column). In this work, the conversion and selectivity were calculated based on the carbon content percentage.

2.2. Characterization methods

In-situ FT-IR studies were carried out on a Bruker Tensor 27 FT-IR spectrometer. All spectra were recorded using 32 scans with a resolution of 4 cm⁻¹. The HZSM-5 sample wafer was placed in a high-temperature high-pressure cell fitted with ZnSe windows. The catalyst sample was first activated under He flow at 500 °C for 2 h and then the IR spectra of the activated samples were recorded at different temperatures (denoted Ai). After that, helium was used to carry the vapor of the individual reactants or pre-mixed reactants (W% (MAc/*n*-Hex) = 10%) continuously through the sample, heating the cell at a temperature-programmed heating rate of 10 °C/min. At the same time, the infrared spectra were recorded at different temperature intervals (denoted Bi). At each temperature, the Ai spectrum was subtracted from the Bi spectrum, providing the infrared difference spectrum at that particular temperature.

In the temperature-programmed experiments, a fresh catalyst sample was pretreated in-situ by heating to 500 °C for 2 h under N₂ flow and then cooled to 100 °C. The stream carried by the N₂ was continuously passed through the catalyst bed for 30 min. Then, the reactor was heated from 100 to 500 °C at a heating rate of 4 °C/min. The products were monitored with an online Omnistar mass spectrometer.

The carbon species were analyzed and identified by Guisnetal's methods [14,15]. The extracted oily liquid was analyzed by GC-MS (Agilent 7890A/5975C GC/MSD with an HP-5 chromatographic column). Hexachloroethane was added to dichloromethane as the internal standard and qualified using the NIST11 database.

Table 1Conversion of MAC and *n*-Hex in different reaction systems over different Si/Al HZSM-5 catalysts at 350 °C, TOS = 2.5 min.

Si/Al ratio	19		50		200	
Reaction system	Individual	Coupled	Individual	Coupled	Individual	Coupled
Conversion of MAC (%)	100.00	100.00	100.00	100.00	100.00	100.00
Conversion of <i>n</i> -Hex (%)	99.95	99.75	33.95	33.96	1.12	1.03

3. Results and discussion

3.1. Comparison of the coupled reaction with the linear addition of the individual reactions

The initial conversion and product distribution of the co-feeding system were compared to the individual reaction systems at 350 °C. As shown in Table 1, the initial conversion of MAC was 100% in different reaction systems over HZSM-5 at different Si/Al ratios and the conversion of *n*-Hex was also very similar in the different reaction systems.

In Fig. 1, it can be clearly seen that the initial product selectivity by co-feeding shows systematical variations compared to the linear addition of the individual reagents (the linear addition of the individual reaction systems was considered in terms of the mass fraction of the two reactants in the coupled reaction system; the products in the individual systems were multiplied by the mass fraction of the corresponding reactants, and then combined for the overall calculation of the product selectivity).

For example, at Si/Al = 200, the oxygenated species (DME, MeOH, HAc, and acetone) selectivity was 2.3% in the individual system; however, they were not detected in the coupled system. At the same time, the selectivity of CO and CO₂ in the two systems was also quite different. Over HZSM-5 catalysts with different Si/Al ratios, the selectivity for CO + CO₂ in the coupled system was lower than that in the individual system. In particular, at Si/Al = 200, CO and CO₂ occupied a large proportion of the product distribution in the individual reaction system. In the presence of *n*-Hex in the coupled system, the selectivity toward CO and CO₂ decreased by 6.4%. This could be explained

Fig. 1. Selectivity of CO + CO₂ and oxygenated compounds (DME, MeOH, HAc, and acetone) in the coupled and individual systems at the same conversion of Mac. Reaction conditions: *T* = 350 °C, WHSV (*n*-Hex) = 1 h⁻¹, WHSV (MAC) = 0.1 h⁻¹, W% (MAC/ *n*-Hex) = 10%, HZSM-5 catalyst with Si/Al = 19, 50, 200.

by changes in the reaction mechanism of MAC over HZSM-5 upon addition of *n*-Hex. These results suggest a chemical coupling effect in the combined system.

3.2. Effect of the reaction temperature on the coupling behavior

To further understand the observed coupling effects, the combined reaction of *n*-Hex and MAC was carried out at different reaction temperatures (from 300 to 500 °C). HZSM-5 with Si/Al = 200 was used as the catalyst in order to diminish the secondary reactions in the system. The results are shown in Figs. 2 and 3.

The *n*-Hex conversion was relatively lower than that of MAC because the reactivity of MAC is much higher. MAC can react with both the strong and weak acidic sites of HZSM-5, while *n*-Hex can only react with the strong acidic sites. As seen in Fig. 2, the MAC conversion was improved in the coupled system at lower temperatures, where the deactivation was lessened.

Evidently, large amounts of HAc and acetone were formed at lower temperatures in the individual system, as shown in Fig. 3 (the HAc selectivity was 33.8% and acetone selectivity of 6.3% at 300 °C). At the same time, the CO_x selectivity was also very high, especially at 350 °C, while the CO_x selectivity was 24% in the individual systems. These results indicate that the decomposition of MAC over HZSM-5 is favored. Unlike in the individual systems, the coupling of *n*-Hex and MAC significantly reduced the selectivity toward H₂, CO, and CO₂ in the range 300–500 °C; moreover, HAc, MeOH, DME, and acetone were not found in the coupled system. Most importantly, the selectivity toward C₂–C₄ olefins increased remarkably in the coupled system in the range 300–400 °C. These results demonstrate that the addition of *n*-Hex possibly changes the mechanism of MAC conversion over HZSM-5.

At 500 °C, the cracking of *n*-Hex was dominant and produced H₂ and large amounts of alkanes. Upon co-feeding MAC with *n*-Hex, the H₂ and alkane selectivity was significantly reduced, while the C₅+ (heavy aromatic hydrocarbons containing more than five carbons) selectivity was significantly improved. The MAC capacity for “capturing hydrogens” from hydrocarbons was thus confirmed.

3.3. Effect of the ZSM-5 Si/Al ratio on the coupling behavior

To compare the effect of the coupling behavior at different Si/Al ratios, the reactions were also performed over HZSM-5 at Si/Al = 19 and 50. Due to the increased density of acidic sites, the conversion of *n*-Hex over Si/Al = 19 and 50 (Figs. 4 and 6) was evidently higher than at Si/Al = 200. The MAC conversion was also higher than that at Si/Al = 200 and low temperature.

As shown in Fig. 7, at Si/Al = 50, it could be observed that

Fig. 2. Conversion in the different reaction systems over the HZSM-5 catalyst. Reaction conditions: Si/Al = 200, $T = 300\text{--}500\text{ }^{\circ}\text{C}$, WHSV ($n\text{-Hex}$) = 1 h^{-1} , WHSV (MAc) = 0.1 h^{-1} , and atmospheric pressure.

Fig. 3. Initial product selectivity in the coupled system and the linear addition of the individual systems. Reaction conditions: Si/Al = 200, WHSV ($n\text{-Hex}$) = 1 h^{-1} , WHSV (MAc) = 0.1 h^{-1} .

the H_2 selectivity in the coupled system was lower than that in the individual system. This indicated that H atoms from $n\text{-Hex}$ were captured by MAc. By comparing the C_{5+} , $\text{C}_2\text{--C}_4$ olefin, CO, CO_2 , and oxygenated compound selectivity, it can be concluded that MAc captures hydrogens from $n\text{-Hex}$ producing large

amounts of olefins and aromatic hydrocarbons, and that the reaction of MAc over HZSM-5 is thus interrupted. The reaction of MAc over HZSM-5 generates large amounts of heavy aromatics rather than CO, CO_2 , or other oxygenated compounds.

The coupling effect in the product selectivity was more

Fig. 4. Conversion in the different reaction systems over the HZSM-5 catalyst. Reaction conditions: Si/Al = 19, $T = 300\text{--}500\text{ }^{\circ}\text{C}$, atmospheric pressure, WHSV ($n\text{-Hex}$) = 1 h^{-1} , WHSV (MAC) = 0.1 h^{-1} .

pronounced over HZSM-5 at low Si/Al ratios. For instance, at Si/Al = 19 (Fig. 5), the H_2 and $\text{C}_1\text{--C}_4$ alkane selectivity in the coupled system was lower than that in the individual system, and the $\text{C}_2\text{--C}_4$ olefin and C_5+ aromatics selectivity was higher. The selectivity of products is consistent with the H atoms from $n\text{-Hex}$ being captured by MAC. The reason might be the high

density of acidic sites. As a result, the intermediates of MAC on HZSM-5 are more prone to interact with $n\text{-Hex}$.

The selectivity of products over HZSM-5 at Si/Al = 200 was similar to that at Si/Al = 50. In summary, the coupling effect of MAC and $n\text{-Hex}$ in the product distribution is mainly reflected in the reduction of the formation of H_2 , CO, CO_2 , and oxygenated

Fig. 5. Initial product selectivity in the coupled system and the linear addition of the individual systems. Reaction conditions: Si/Al = 19, WHSV ($n\text{-Hex}$) = 1 h^{-1} , WHSV (MAC) = 0.1 h^{-1} , W% (MAC/ $n\text{-Hex}$) = 10%.

Fig. 6. Conversion in the different reaction systems over the HZSM-5 catalyst. Reaction conditions: Si/Al = 50, $T = 300\text{--}500\text{ }^{\circ}\text{C}$, W% (MAC/*n*-Hex) = 10%, atmospheric pressure, WHSV (*n*-Hex) = 1 h^{-1} , WHSV (MAC) = 0.1 h^{-1} .

compounds.

3.4. Effect of the feed ratio on the coupling behavior

Different feed ratios were tested in the temperature range $300\text{--}500\text{ }^{\circ}\text{C}$. The mass fraction of MAC in the coupled system

increased to 43%. Compared to the previous experiments (Fig. 6), the inactivation of HZSM-5 became more severe, and the initial conversion of *n*-Hex in the individual reaction system was much higher than that in the coupled system (Fig. 8). This suggests that an excessive amount of MAC would preferentially occupy the acidic sites and result in the rapid inactivation of the

Fig. 7. Initial product selectivity in the coupled system and the linear addition of the individual systems. Reaction conditions: Si/Al = 50, WHSV (*n*-Hex) = 1 h^{-1} , WHSV (MAC) = 0.1 h^{-1} , W% (MAC/*n*-Hex) = 10%.

Fig. 8. Conversion in the different reaction systems over the HZSM-5 catalyst. Reaction conditions: Si/Al = 50, $T = 300\text{--}500\text{ }^{\circ}\text{C}$, W% (MAC/*n*-Hex) = 43%, atmospheric pressure, WHSV (*n*-Hex) = 5 h^{-1} , WHSV (MAC) = 2.16 h^{-1} .

catalyst. In other words, the presence of excess MAC results in competition with *n*-Hex over the catalytic sites.

3.5. Coke species on ZSM-5 in the different reaction systems

Compared to those in Fig. 9(B) and (C), a small amount of heavy aromatic compounds is observed in Fig. 9(A), which is consistent with the slower inactivation of the catalytic reaction in the individual *n*-Hex system. The reaction systems in Fig. 9(B) and (C) produce a particularly large number of heavy aromatic species. The acidic sites are covered and the pores are blocked by these heavy aromatic species, which is the main reason for the rapid deactivation of the catalyst. Comparing the two spectra (Fig. 9(B) and (C)), the compound peak position is basically the same, except those at 250 and 300 °C. At 250 °C, 4,6-dimethyl-2*H*-pyran-2-one(α -pyrone) is only found in the individual MAC system. With the increase in temperature, the amount of α -pyrone decreases and only a small amount is observed at 300 °C. In view of the catalyst deactivation trends, the addition of *n*-Hex to the coupled system interrupts the path for α -pyrone and the catalyst deactivation is correspondingly mitigated compared to the case of the individual MAC system. This phenomenon implies a possible process of carbon deposition

and catalyst deactivation by MAC; that is, the formation of α -pyrone firstly on the catalyst, followed by its further conversion to other oxygen-containing heavy aromatics compounds and, finally, decomposition into aromatics and polycyclic aromatics containing large amounts of side chains.

3.6. TPSR with on-line mass analysis under continuous flow

As shown in Fig. 4, a remarkable difference can be observed at 300 °C: in the coupled system, the initial *n*-Hex conversion is 100% while, in the individual system, it is only ~60%. The online mass was determined to clarify this observation. The evolution of the signal intensity at $m/e = 86$, i.e., the molecular ion peak of *n*-Hex, is shown in Fig. 10. Compared to that of the individual *n*-Hex system, the starting temperature of the *n*-Hex cracking reaction decreases from 208 to 174 °C due to a coupling effect. In the range of 300 to 400 °C, several increases are observed in curve (b). This indicates that isomerization reactions of *n*-Hex possibly occur in the coupled system.

3.7. FT-IR spectroscopic studies

The infrared difference spectra of HZSM-5 in the $\nu(\text{OH})$ re-

Fig. 9. Deposited carbon species in the three different reaction systems. (A) Individual *n*-Hex system; (B) Individual MAC system; (C) Coupled reaction system. Reaction conditions: $T = 250\text{--}500\text{ }^{\circ}\text{C}$, WHSV (*n*-Hex) = 5 h^{-1} , WHSV (MAC) = 2.16 h^{-1} , TOS = 110 min.

Fig. 10. Signal evolution under a flow of the reactant mixture and individual *n*-Hex passing through the HZSM-5 zeolite (Si/Al = 19, functional temperature: $m/e = 86$); (a) individual *n*-Hex, (b) mixture of reactants).

gion is shown in Fig. 11(A). In the individual *n*-Hex reaction system, two types of hydroxyl groups are observed from the negative nature of the bands at 3750 and 3610 cm^{-1} , which correspond to terminal hydroxyl Si(OH) and bridge hydroxyl Si(OH)Al groups [16–20]. With the increase in temperature, the intensity of these negative features gradually decreased. A broad band at 3480 cm^{-1} was observed at 200 °C, attributed to the interaction of the bridge hydroxyls of the zeolite with hydrocarbon compounds and the corresponding formation of H-bonds [18,19], which disappeared at temperatures above 300 °C. In the individual MAC system, the band at 3480 cm^{-1} is not observed, and the bands at 3610 and 3750 cm^{-1} do not change significantly with the temperature variation. Furthermore, in the coupled system, the spectrum is similar to that for the individual MAC reaction system. These observations suggest that, in the coupled system, MAC is adsorbed on the acidic sites before *n*-Hex.

In the individual *n*-Hex reaction system, the bands at 2964, 2935, and 2874 cm^{-1} are attributed to the physical adsorption of *n*-Hex and other hydrocarbons over the zeolite [21]. Compared to that in the individual *n*-Hex reaction system, the appearance of a new band at 2850 cm^{-1} in the coupled system

Scheme 1. Formation of methoxy species on HZSM-5.

could be assigned to the symmetric stretching vibration of the $-\text{CH}_3$ group of adsorbed MAC. In the individual MAC reaction system, the band at 3013 cm^{-1} can be assigned to the OH vibrations of the methylcarboxonium ion (CH_3OH_2^+), formed by attraction of a skeletal proton [22]. At 200 °C, a small shoulder at 2980 cm^{-1} appears next to the 2964 cm^{-1} band, which could be assigned to surface methoxy groups formed at Brönsted acid sites [16]. With the increase in temperature, the intensity of the 3013 cm^{-1} band gradually weakens, while that of the 2980 cm^{-1} band gradually increases in the temperature range 200–400 °C. At 500 °C, the intensity of the 2980 cm^{-1} band slightly decreased. These observations suggest that the methylcarboxonium ion is gradually converted into surface methoxy species with the increase in temperature. In view of the decreasing trend of the band at 2850 cm^{-1} , it can be inferred that the C–O bond of MAC has been cleaved. The IR difference spectrum of the coupled system is similar to that of the individual *n*-Hex system. This suggests that MAC first forms an intermediate with HZSM-5, which then rapidly interacts with *n*-Hex to generate other hydrocarbons.

In the coupled system, the initial hydride transfer reaction starts with the attack of *n*-Hex to the surface methoxy species formed from the MAC reaction. The possible process is shown in Scheme 1.

3.8. Proposed reaction pathway for the coupled *n*-Hex and MAC reaction

Fig. 12 shows the changes in the initial product distribution for the different reaction systems in the temperature range 125–500 °C. At low temperatures, MAC is mainly decomposed into HAC, DME, and MeOH. Above 200 °C, the decarboxylation reaction of HAC is dominant, the CO and CO_2 selectivity is

Fig. 11. IR difference spectra recorded for the HZSM-5 zeolite (Si/Al = 50) under continuous flow of a stream of *n*-Hex, MAC, and a mixture of *n*-Hex and MAC.

Fig. 12. Changes in the product distribution over HZSM-5 for the individual MAc reaction system (A), individual *n*-Hex reaction system (B), and coupled system (C) ($T = 125$ – 500 °C).

Scheme 2. Transformation of *n*-Hex and MAc in the coupled system over HZSM-5.

proved, and the HAc selectivity decreases. By comparing B and C, the addition of MAc changes the product distribution of *n*-Hex, especially at low temperatures; the selectivity of alkanes in the coupled system significantly decreases, while the C_{5+} aromatics selectivity increases.

We propose a series of possible reaction routes for this coupled reaction system (Scheme 2). MAc is preferentially absorbed on the catalyst. At 150 °C, the reaction consists mainly of the reverse carbonylation of DME. At 250 °C, MAc reacts with the catalyst to form 4,6-dimethyl-2*H*-pyran-2-one, which is then mainly decomposed to CO, CO₂, and C₆₊. At 300 °C, MAc interacts with HZSM-5 producing mainly methoxy species and acetic acid. With the increase in temperature, the methoxy route predominates.

Two types of reaction routes exist for *n*-Hex in the coupled system. One fraction of *n*-Hex interacts directly with HZSM-5 undergoing a single molecular mechanism to generate alkanes and H₂, while the other larger fraction interacts with the methoxy species via a bimolecular mechanism to generate alkanes, olefins, and BTX.

4. Conclusions

Coupling the reactions of *n*-Hex and MAc over a zeolite catalyst was found to improve the *n*-Hex conversion. The initial cracking temperature of *n*-Hex was reduced upon addition of MAc, as proven by TPSR measurements. Under most reaction conditions, the selectivity for alkanes and H₂ decreased and the selectivity toward olefins and heavy aromatics increased in the coupled reaction system. These results suggested that the hydrogen atoms in *n*-Hex are captured by MAc. Based on the GC-MS analysis of carbon species, we suggested that α -pyrone

might be the main active intermediate species in the catalyst deactivation induced by MAc. Methoxy species, the active intermediates, were detected by in situ FT-IR spectroscopy and were presumed to serve as the active sites for *n*-Hex conversion. A mechanism was also proposed to explain the possible reaction routes present in this coupled system.

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Graphical Abstract

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The coupling of methyl acetate (hydrogen-deficient) and *n*-hexane (hydrogen-rich) not only exhibits thermal coupling but also chemical coupling, whereby the product distribution is improved compared to the catalytic cracking of individual *n*-hexane.

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乙酸甲酯和正己烷在HZSM-5上耦合反应的研究

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摘要: 蒸汽裂解是石油化工行业生产低碳烯烃和芳烃的一种非常重要的手段。石脑油和一些低碳烷烃在蒸汽裂解中被广泛用作原料。经过长时间的发展和改进, 蒸汽裂解技术已经有了长足的进步, 但它作为一个强吸热的反应过程, 需要非常高的温度才能进行, 巨大的能耗是蒸汽裂解技术所要面临的重大问题。虽然催化裂解能够显著降低裂解温度到650 °C左右, 但若将强吸热的反应和强放热的反应进行耦合, 这将是一种全新的解决能源利用率问题的途径。我们将强放热的乙酸甲酯在HZSM-5上的反应和强吸热的正己烷的裂解反应结合, 使得热量得到耦合。其次, 乙酸甲酯拥有碳氧双键, 是一种“缺氢化合物”, 而正己烷作为一种“富氢”化合物, 其元素组成上具有大量的氢元素。两种反应物的共同反应, 除了热量耦合效应外, 必将具有某种形式的元素耦合效应。

在固定床反应器上考察了不同条件下乙酸甲酯和石脑油模型化合物正己烷在HZSM-5上的反应, 发现耦合体系中产物分布的系统性变化是显而易见的。在多数反应条件下, 耦合体系中烯烃和C₅以上芳烃的选择性升高, 而烷烃, H₂, CO和CO₂的选择性则明显降低, 表明元素耦合效应存在于耦合体系中, 且契合了“缺氢”的乙酸甲酯能够夺取“富氢”的正己烷中氢元素的特性。

在Si/Al=19的HZSM-5分子筛上, 反应温度为300 °C时, 耦合体系的正己烷初始转化率达到100%, 而此时正己烷单独

进料体系的初始转化率只有58.9%。我们通过TPSR对两种体系的正己烷变化趋势进行考察,发现乙酸甲酯的加入会显著降低正己烷的初始裂解温度,进而促进正己烷的转化,同时加剧了正己烷的芳构化。

乙酸甲酯非常高的活性导致催化剂的迅速失活,但随着正己烷的加入而得到缓解。通过GC-MS对积碳物种的分析发现,正己烷的加入改变了乙酸甲酯在分子筛上形成的积碳物种前驱体,这也为我们研究耦合体系的反应机理提供了证据。结合低温乙酸甲酯的产物分布和原位红外对三种反应体系的研究,我们提出了一种正己烷和乙酸甲酯耦合体系的反应机理。

关键词: 乙酸甲酯; 正己烷; 耦合反应; HZSM-5

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