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Conversion of methanol with C_5–C_6 hydrocarbons into aromatics in a two-stage fluidized bed reactor

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ABSTRACT

The conversion of methanol mixed with C_5–C_6 hydrocarbons (including pentane, hexane, and cyclohexane) was studied in a two-stage fluidized bed reactor packed with 880 g Zn/ZSM-5 catalyst at 475 °C and 0.4 MPa. The effect of the mixed feed on the methanol conversion, self-decomposition of methanol, coke deposition on the catalyst, aromatic yield, and the aromatic distribution was carefully studied. Methanol conversion was nearly complete and the self-decomposition of methanol can be suppressed significantly. There exhibited a positive heat coupling effect in the feeding of methanol with pentane or with cyclohexane to increase the aromatic yield or to suppress the undesirable side reactions. However, the mixed feed is unfavorable to the transformation of hexane into aromatics. Better aromatic yield in the lower temperature for the mixed feed, as compared to that for the conversion of pure C_5–C_6 hydrocarbons in higher temperature, validated the heat coupling effect. The result confirmed that it is feasible to use the exothermic methanol conversion to enhance the endothermic transformation of some C_5–C_6 hydrocarbons into aromatic, resulting in a great engineering simplification of heat supply or heat removal in high temperature operation.

1. Introduction

As an important catalytic route, methanol to aromatics (MTA) is capable of bridging between the coal or natural gas industry (for supplying the feedstock methanol) and the petroleum industry [1–7]. The latter, however, is originally the only source of aromatics and already had a mature product chain to produce many important polymers using aromatics as raw materials. Technically, bifunctional metal-ZSM-5 catalyst was crucial to the conversion, where metal exhibited a dehydrogenation effect and ZSM-5 provided the acidic site for the dehydration, oligomerization, and ring-closure reactions following a hydrocarbon pool mechanism [8–10]. Tailoring the external surface acidity, the particle size or the lattice orientation of ZSM-5 crystal, it is able to produce the mixture of aromatics (including benzene (B), toluene (T), xylene (X), trimethylbenzene (TriMB)), *Para*-X, or TriMB with high selectivity [11–14], respectively. In addition, operated at around 480 °C, the methanol conversion can be nearly 100%, the yield of aromatics can be 50–60% and the weight ratio of aromatics in organic product is above 90% [15]. Recently, an industrial-scale fluidized bed reaction system with the capacity of 10 kt/a aromatics was successfully run in China, a great breakthrough toward commercial production. In future large-scale production, the heat management of MTA process, however, will became very critical considering this heavily exothermic reaction and high throughput of gases reactants. In addition, the uncontrollable higher temperature in reactor, if any, will result in the yield decrease of aromatics drastically, the coke deposition over the catalyst, as well as the sintering of metal and the de-alumination of ZSM-5 under high partial pressure of water from the decomposition of methanol [16–18]. On the other hand, C_5–C_6 hydrocarbons can also be converted into olefins or aromatics over zinc doped or pure zeolite [19–22]. And the doping of zinc enhanced the formation of aromatics, compared to the pure zeolite, which give the similarity of methanol conversion. But these are all heavily endothermic reactions and operated at a higher temperature condition than that for methanol conversion [19–22]. The heat supply for a high temperature reaction condition is always a tough and energy costive work. From the viewpoint of heat coupling effect [23,24], if methanol and C_5–C_6 hydrocarbons can be simultaneously converted into aromatics in a reactor, the heat supply for C_5–C_6 hydrocarbon conversion and the heat removal for methanol conversion will both not be needed, presenting a great simplification in engineering. Moreover, it is a better way to increase the product value from C_5–C_6 hydrocarbons, which always belong to the

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Table 1
Thermodynamics calculation of methanol or C5–C6 hydrocarbons into xylene, hydrogen, and water (475 °C, 0.4MPa, gaseous state, method: UNIQUAC).

Reaction equation	Heat of reaction ΔH(kJ/mol) HSC	Aspen
CH_3OH (methanol, g) = $\frac{1}{8}C_8H_{10}(p\text{–}X, g) + H_2O(g) + \frac{3}{8}H_2(g)$	−33.571	−32.888
C_5H_{12} (pentane, g) = $\frac{5}{8}C_8H_{10}(p\text{–}X, g) + \frac{23}{8}H_2(g)$	169.524	169.938
C_6H_{12} (cyclohexane, g) = $\frac{3}{4}C_8H_{10}(p\text{–}X, g) + \frac{9}{4}H_2(g)$	148.125	163.322
C_6H_{14} (hexane, g) = $\frac{3}{4}C_8H_{10}(p\text{–}X, g) + \frac{13}{4}H_2(g)$	194.132	192.486

low-cost byproduct in petroleum industry, since it is too heavy as the component of liquefied petroleum gas, but too light as the component of gasoline.

In the present work, we attempted to study the possibility of the conversion of the mixture of methanol with C_5–C_6 hydrocarbons with the current available MTA catalyst (Zn/ZSM-5) in a two-stage fluidized bed reactor (TSFB) [15,25–27], in an operating condition conventionally suitable for the conversion of methanol. Effect of the molar ratio of methanol to C_5–C_6 hydrocarbons on the conversion of reactants, the product profiles and coke deposition on the catalyst was studied carefully. We found that it is capable of achieving a higher conversion of reactants and higher yield of aromatics using certain C_5–C_6 hydrocarbons. The result suggested that it is possible to feed methanol and certain C_5–C_6 hydrocarbons together to solve their heat supply or heat removal problems in large-scale production.

2. Experimental

Methanol, C_5–C_6 hydrocarbons including pentane, hexane, and cyclohexane with high purity was purchased commercially. The Zn/ZSM-5 catalyst, reported elsewhere [15], had a Zn content of 3%. Stainless steel TSFB reactor with a diameter of 100 mm (similar to that in ref. 14) was divided into two sections with a perforated plate of hole ratio of 0.5%. A total of 550 and 330 g catalyst were packed into the lower and upper stage of the reactor separately, which did not mix in the reaction due to the use of perforated plate with small hole ratio. The molar ratio of methanol to C_5–C_6 hydrocarbons was controlled to 1:1 to 3:1. In operation, mixture of reactants was fed into the reactor from its bottom and was catalytically converted over the catalyst at 475 °C, 0.4 MPa, and a space velocity of methanol to be 0.4 h^{-1}. Gas product was analyzed by using an online gas chromatography after 30 min stable operation. Coke deposited over the catalyst was determined by the thermal gravimetric analyzer, after 3 hrs reaction.

Methanol conversion, conversion of C_5–C_6 hydrocarbons, yield of hydrocarbons, and selectivity of hydrocarbons were calculated following above equations. Yield of hydrogen and coke was calculated based on the hydrocarbon base [15].

$$\text{Methanol conversion} = \frac{\text{methanol in feedstock} - \text{unreacted methanol}}{\text{methanol in feedstock}}$$

$$\text{Hydrocarbon conversion} = \frac{\text{hydrocarbon in feedstock} - \text{hydrocarbon methanol}}{\text{hydrocarbon in feedstock}}$$

$$\text{Yield} = \frac{CH_2\ \text{in product}}{\text{total}\ \ CH_2\ \text{in feedstock}}$$

$$\text{Selectivity} = \frac{CH_2\ \text{weight in product}}{\text{total}\ \ \text{reacted}\ \ CH_2\ \text{weight}}$$

3. Result and discussions

3.1. Thermodynamics of the mixed feed for the consideration of heat balance

Firstly, the reaction heat of methanol or C_5–C_6 hydrocarbons converted into aromatics were calculated by using the HSC method or the data in ASPEN data using UNIQUAC equation. The conversion of methanol to X is an exothermic reaction releasing reaction heat of 33 kJ/mol (Table 1). The conversions of pentane, hexane, or cyclohexane into X were all endothermic reaction absorbing the heat of 150–193 KJ/mol. Data calculated by two methods closely matched. From the consideration of heat supply balance, it needs 6 mol methanol with 1 mol hydrocarbons in the feedstock to ensure their complete conversion to produce a pure X product. However, these reactants exhibited different activities to give a different conversion rate over the same catalyst. In addition, the product of aromatics by the single-pass conversion is not a pure X, but a mixture of aromatics (B, T, X, and TriMB) and gaseous C_1–C_5 hydrocarbons, as well as the water and H_2 [1–15]. As follows, we calculate the reaction heat of conversion of methanol, C_5–C_6 hydrocarbons by using the similar product components reported elsewhere [15]. Clearly, the formation of aromatics and olefins are highly endothermic, but the formation of light paraffins is highly exothermic. In this case, the formation of mixed hydrocarbons from C_5–C_6 hydrocarbons above absorbed the heat of 60–106 KJ/mol (Table 2), far lower than that absorbed to produce a pure aromatic product. In addition, the reaction heat released by methanol conversion is increased from 33 KJ/mol based on the pure X product to 46.6 KJ/mol based on the practical product distribution. In this case, the thermal balance between exothermic and endothermic reaction did not need the addition of methanol in large amount above. The molar ratio of methanol to pentane, hexane, and cyclohexane is 2.1:1, 1.3:1, and 2.3:1, respectively. As follows, we mainly focused on the study using the molar ratio of methanol to C_5–C_6 hydrocarbons in the range of 1:1 to 3: 1.

3.2. Effect of the mixed feed on the conversion of methanol

Firstly, we studied the effect of the mixed feed of methanol with C_5–C_6 hydrocarbons on the conversion of methanol. In the molar ratio range of methanol to C_5–C_6 hydrocarbons of 1:1 to 3:1, we observed the conversion of methanol was nearly complete and approached to 100% (>99.995%) (Fig. 1a). Approaching to the measurement limits of GC, the conversion of methanol increased a little bit with the increased addition of methanol. It suggested that the presence of C_5–C_6 hydrocarbons did not influence the conversion of methanol or methanol is relatively easily converted with this catalyst. The result is in agreement with the previous investigation of the sole methanol conversion in TSFB [15]. In previous study, we found that methanol can be completely converted in the exit of the lower stage and other light C_3–C_6 hydrocarbons can be further converted into aromatics in the upper stage [15]. In the present work, hydrogen yield is not decreased in the aromatization using the mixed feed (Fig. 1b) and it increased with the increased addition of methanol, in agreement with the result in Fig. 1a. The result also