

An improved catalytic cracking of *n*-hexane via methanol coupling reaction over HZSM-5 zeolite catalysts

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Received 6 October 2005; accepted 4 November 2005

The coupling transformation of *n*-hexane and methanol over HZSM-5 has been investigated with a pulse-reaction system. In the temperature range of 400–500 °C, kinetic data was collected and reaction order was determined. Compared with the pure *n*-hexane cracking, the increased rate constant and the lowered apparent activation energy clearly demonstrate an improvement of *n*-hexane activation using methanol as co-reactant and an increased contribution of faster bimolecular mechanism to the *n*-hexane transformation due to methanol introduction. Similarly, the results of coupling transformation performed over HZSM-5 with different Al content further confirm the transition between reaction mechanisms of *n*-hexane on account of the introduction of methanol. Moreover, the further investigation suggests that the enhancement of *n*-hexane activation and the change of reaction mechanism are attributed to the presence of intermediate species evolved from methanol. Thus, a proposed reaction pathway of *n*-hexane activation with methanol as co-reactant was put forward.

KEY WORDS: coupling transformation; mechanism; pulse-reaction; activation energy; Si/Al ratio.

1. Introduction

Hydrocarbon cracking is one of the most important processes for light olefins production in petrochemical industry. The disadvantage of this route is its high endothermicity, which makes it a very energy consuming process. Some researchers have studied on catalyst development for high-efficient transformation and less energy cost, while some efforts are also put on alternative way, such as, introducing some exothermic conversion processes for energy supply into the endothermic hydrocarbon cracking. Considering the energy balance and target products, exothermic MTO/MTG process is a good option for this coupling system.

Lücke and co-workers [1] investigated the coupling transformation of some hydrocarbons with methanol participation. A high olefins yield up to 1000 g kg⁻¹h⁻¹ in the temperature range of 600–700 °C in a nearly thermo-neutral condition was obtained, and the deactivation behavior of different modification HZSM-5 catalyst was also discussed. Gao and co-workers [2] investigated the coupled conversion of methanol and light hydrocarbons over Ga/HZSM-5 catalyst at moderate temperature (< 550 °C), and studied the effect of reaction conditions on the yield of aromatics and lower

alkenes. Shabalina and co-workers [3] also worked in this field of methanol coupled conversion of propane and butane on MFI zeolite, and emphasized on the modification effect of alkaline-earth metals in the formation of light olefins.

In these studies discussed above, besides the consideration of energy supply, most of the study efforts were put on modifying reaction condition and zeolite catalyst for higher light olefins yield. However, for the conversion of methanol and the catalytic cracking of *n*-hexane, they are such reactions catalyzed by acid zeolite catalyst, although both reactions are quite different [4–8]. When two reactions, thermally coupled each other, occur simultaneously, for the reactant and co-reactant, the feed of hydrocarbon and methanol, their transformations may not be independent completely. The chemical mechanism of the coupling transformation of *n*-hexane and methanol, especially the effect from methanol participation on the activation and conversion of hydrocarbon, is still obscure and merit further deep investigation.

In the present study, the transformation of *n*-hexane with and without methanol as co-feed was performed over HZSM-5 in a pulse reactor under the same reaction condition. The initial conversion rates of *n*-hexane at different temperature were tested, from which the rate constants of two reactions were determined, then the apparent activation energies of

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n-hexane in both reactions were calculated. The coupling conversion was also carried out over HZSM-5 with different Al content. By comparing the *n*-hexane alone conversion with methanol coupling *n*-hexane conversion, the change in activation energy of *n*-hexane and the effect of aluminum content on *n*-hexane conversion were discussed. Additionally, the effect of the species from methanol on *n*-hexane conversion was also investigated.

2. Experimental section

2.1. Catalyst preparation

Samples of HZSM-5 (Si/Al $\approx$ 13, 19, 25 and 70) were prepared with ion-exchanged method by exchanging NaZSM-5 (obtained from FuShun Catalyst Plant) with 0.5 M NH_4NO_3 solution at 80 °C for 4 h, and the operation was repeated 4 times, at last the ammonium sample was calcined in air at 550 °C for 4 h. Table 1 lists the physicochemical characteristics of these HZSM-5 samples.

2.2. Catalytic test

A pulse reaction system was used for all conversions. The catalyst (60–80 mesh) of 4.7–20 mg was loaded in the quartz reactor of 3 mm i.d. And quartz sands (60–80 mesh) were filled in the upper part of reactor to get plug flow state of mixture feed. A fresh catalyst was used on each run, and prior to use, the catalyst was pretreated at 550 °C for 1 h in a flow of N_2 .

The stream with certain amount of *n*-hexane for pulse reaction was generated by passing the carrier gas (He, >99.996%) of an appropriate flow rate through a saturator containing *n*-hexane at proper temperature. This stream was then mixed with the methanol stream with desired pressure generated in the same way, then the mixed stream was introduced into the reactor by the flow of helium. All products were separated and identified on-line by VARIAN CP-3800 gas chromatography equipped with a capillary column of PONA (100 m $\times$ 0.25 mm) and a FID detector. Product analysis was reported by the DHA software. For comparison, the transformation of *n*-hexane alone with the same carbon atoms as co-reactant was carried out under the same condition.

The conversion of *n*-hexane and methanol was calculated based on the GC analysis using the following

equation (where conversion of reactant and concentration of reactant in feed are expressed on molar carbon atom basis):

Transformation was performed with different contact time, which allowed extrapolation of conversion of

$$\begin{aligned} \text{The conversion of reactant } X_i(\text{C}\%) &= \{ \text{concentration of } X_i \text{ in feed}(\%) \\ &\quad - \text{concentration of } X_i \text{ in reactor effluents}(\%) \} / \\ &\quad \text{concentration of } X_i \text{ in feed}(\%) \\ &\quad \times 100\% \end{aligned}$$

n-hexane to zero contact time. As a result, the initial conversion rates of *n*-hexane were estimated from the tangent at zero contact time in the plot of the conversion versus contact time of *n*-hexane [9–11]. The concentration of methanol in feed was fixed at 10% (C%) in most coupling experiments to limit the extent of methanol interconversion reactions.

3. Results and discussion

Varying the flow rate of carry gas with fixed contact time has no influence on the coupling reaction under the work conditions, suggesting no external limitation from diffusion control in the pulse reactor used. Blank test shows that the thermal transformation of *n*-hexane with and without methanol under the operating conditions is negligible.

3.1. Coupling transformation of *n*-hexane and methanol at different temperature

The experiments were carried out in the temperature range of 400–500 °C over HZSM-5 zeolite (Si/Al = 19) with different contact time. The result in figure 1 shows the initial conversion rate of *n*-hexane in *n*-hexane alone cracking and coupling reaction experiments. Compared with the conversion of *n*-hexane alone, a clear increase of initial conversion rate of *n*-hexane is observed in coupling reaction, indicating a conversion enhancement of *n*-hexane by employing a coupling system with methanol as co-feed. It is also very interesting to find that the increase in conversion rate is more pronounced at low temperature than at high temperature compared with the uncoupled *n*-hexane cracking.

It is known that *n*-hexane cracking follows a first order kinetic rate law when the conversion of *n*-hexane is below 30% and the curve of $-\ln(1-x)$, in which x is the conversion of *n*-hexane, is expected to be linear as a function of the contact time [12–16]. For *n*-hexane cracking over HZSM-5, the value of $-\ln(1-x)$ as a function of contact time plotted in figure 2 shows that in the studied temperature range, the conversion of

Table 1
The physicochemical characteristics of the HZSM-5 samples

Sample	Si/Al ratio	Total pore volume (cc/g)	Surface area (m ² /g)
HZSM-5 (13)	14.7	0.227	316.7
HZSM-5 (19)	18.4	0.242	363.2
HZSM-5 (25)	23.7	0.204	317.5
HZSM-5 (70)	70.2	0.215	367.9

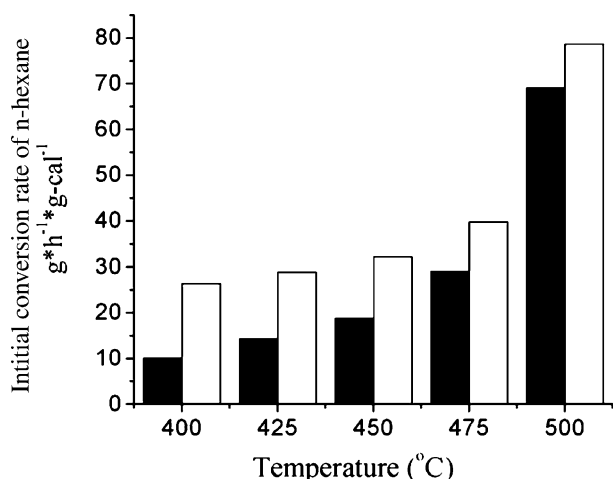


Figure 1. Initial conversion rate of *n*-hexane in the temperature range 400–500 °C for *n*-hexane conversion without methanol coupling (■), and with methanol coupling (□).

n-hexane is a first-order reaction and the value of apparent rate constant can be calculated from equation (1):

$$k = -\ln(1-x)/\tau \quad (1)$$

where k is the apparent rate constant of *n*-hexane conversion, τ is the contact time of *n*-hexane (s).

While in the plot of methanol coupled *n*-hexane cracking, even the conversion has been improved in the whole temperature range, it can be still observed that the curve of $-\ln(1-x)$ is liner as the function of contact time as shown in figure 3. The apparent rate constants of *n*-hexane conversion listed in table 2 show that the first-order reaction rate constant k increases with reaction temperature, while in the whole temperature range, k from coupled reaction is always higher than that from the reaction of *n*-hexane without methanol introduction.

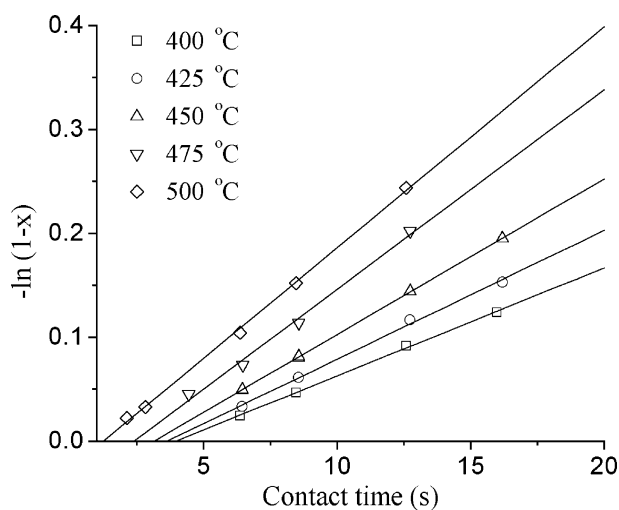


Figure 2. First-order kinetics plot for *n*-hexane cracking over HZSM-5 in the temperature range 400–500 °C.

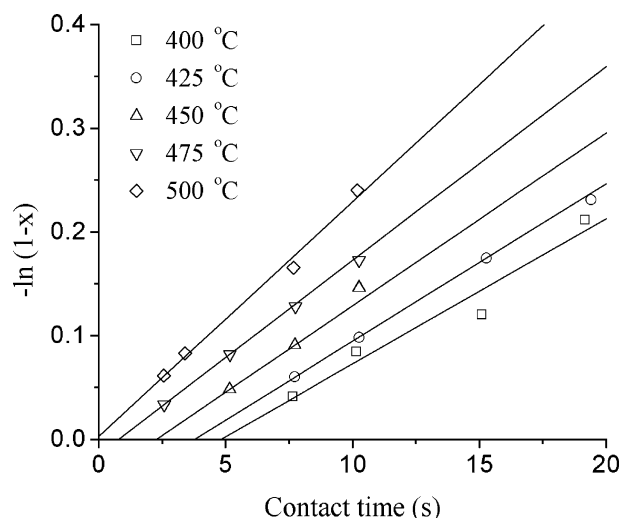


Figure 3. First-order kinetics plot of *n*-hexane in coupling reaction of *n*-hexane and methanol over HZSM-5 zeolite in the temperature range 400–500 °C.

Arrhenius plot given in figure 4 and the apparent activation energy data listed in table 2 show that apparent activation energies showing the conversion of *n*-hexane increase with increasing temperature in both cases, such as for pure *n*-hexane cracking, activation energy of 38.12 kJ/mol at 500 °C and 18.65 kJ/mol at 400 °C, while for coupling conversion of *n*-hexane and methanol, the value is 34.39 kJ/mol at 500 °C and 6.33 kJ/mol at 400 °C, respectively.

This behavior of temperature dependency should be attributed to two different mechanisms of *n*-hexane cracking: monomolecular and bimolecular [4–6, 12–17]. Usually, under conditions of low conversion and high temperature, the initial reaction occurs by a monomolecular attack by the Brønsted acid site on C–H or C–C bonds. This attack results in an adsorbed high-energy

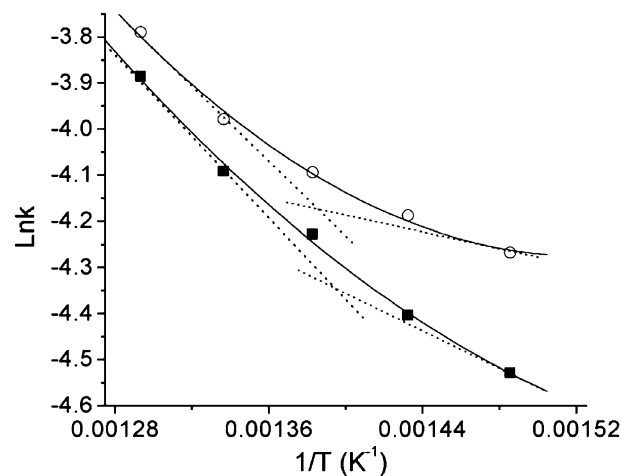


Figure 4. Arrhenius plot showing the rate of conversion of *n*-hexane in the temperature range 400–500 °C over HZSM-5 zeolite for *n*-hexane transformation without methanol coupling (■) and with methanol coupling (○).

Table 2

The apparent rate constant and activation energy of *n*-hexane conversion in the transformation of *n*-hexane with and without methanol coupling in the temperature range of 400–500 °C

Temperature (°C)	<i>n</i> -hexane alone cracking		Coupling conversion	
	k (10^{-2} s^{-1})	E_a (kJ/mol)	k (10^{-2} s^{-1})	E_a (kJ/mol)
400	1.08	18.65	1.40	6.33
425	1.22	23.41	1.52	13.91
450	1.46	28.58	1.67	21.49
475	1.67	32.55	1.87	27.33
500	2.05	38.12	2.26	34.9

pentacoordinate carbonium ion, which decomposes to a smaller alkane (or H_2) and an adsorbed carbenium ion. The high-energy transition state determines the high activation energy in this mechanism route. At higher conversions and low temperature, the bimolecular mechanism becomes the prevailing pathway involving the transfer of a hydride ion between the reactant alkane and an adsorbed carbenium ion derived from decompose of carbonium ion or the adsorption of an alkene on a Brønsted acid site. These adsorbed species then undergo isomerization, β -scission, and alkylation of alkenes.

It is worthy to point out that in the whole temperature range, the introduction of methanol lowers the activation energy of *n*-hexane cracking, especially at low temperature, suggesting that methanol may play an important role in activation step of *n*-hexane and accelerate the formation of intermediate or transition state of *n*-hexane cracking reaction. Furthermore, considering the different mechanism of paraffin cracking at low and high temperature, more pronounced decline of activation energy at low temperature (400 °C) indicates that methanol introduction may increase more contribution of the bimolecular reaction to the overall reaction rate at low reaction temperature than at high temperature. The reports given by Haag and by Williams have suggested that the bimolecular reaction occurs faster than the monomolecular initiation step [15–17]. It seems that the prevailing faster bimolecular route can account for the acceleration of initial conversion rate of *n*-hexane due to methanol introduction.

3.2. The effect of aluminum contents on coupling transformation of *n*-hexane and methanol

The initial conversions rates for *n*-hexane cracking with and without methanol as co-reactant have been determined at 500 °C over the series of HZSM-5 zeolites with different aluminum contents ($\text{Si}/\text{Al} \approx 13, 19, 25$ and 70, respectively) and the results are depicted in figure 5.

The highest initial conversion rate can be observed in *n*-hexane cracking over HZSM-5 with the lowest Si/Al ratio of 13. With the increase of Si/Al ratio from 13 to 19, 25 and 70, the initial conversion rate gradually decreases. The lowest value is obtained over HZSM-5

with the highest Si/Al ratio of 70. This change is also observed for the coupling transformation. It seems that the conversions of *n*-hexane in both cases need more active sites and these active sites can be supplied by HZSM-5 with high Al content. Comparing the *n*-hexane alone conversion with methanol coupling *n*-hexane conversion, a clear and pronounced increase in initial conversion rate of *n*-hexane is observed in coupling reaction over HZSM-5 with low Si/Al ratio. While with the increase of Si/Al ratio, the initial conversion rate improvement caused by methanol coupling gradually is decreased. For the sample with Si/Al ratio of 70, a slight decrease of initial conversion rate is found due to the methanol introduction.

To further investigate and understand the effect of aluminum contents, the first-order rate constant for the transformation of *n*-hexane with and without methanol as co-reactant has been determined as a function of aluminum content. The result is displayed in figure 6. It can be seen that the slope of the straight line obtained upon plotting $\log k_0$ versus $\log [\text{Al}/(\text{Al} + \text{Si})]$ is about 1.4 for the pure *n*-hexane cracking and 2.03 for the conversion of *n*-hexane with methanol as co-feed, indicating that the apparent order in the aluminum content increases from 1.4 to 2.03 using methanol as co-reactant.

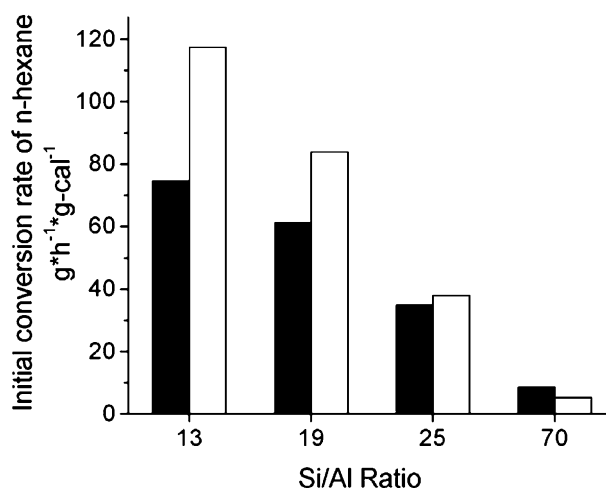


Figure 5. Initial conversion rate of *n*-hexane at 500 °C over HZSM-5 zeolite with different Si/Al ratio for *n*-hexane conversion without methanol coupling (■), and with methanol coupling (□).

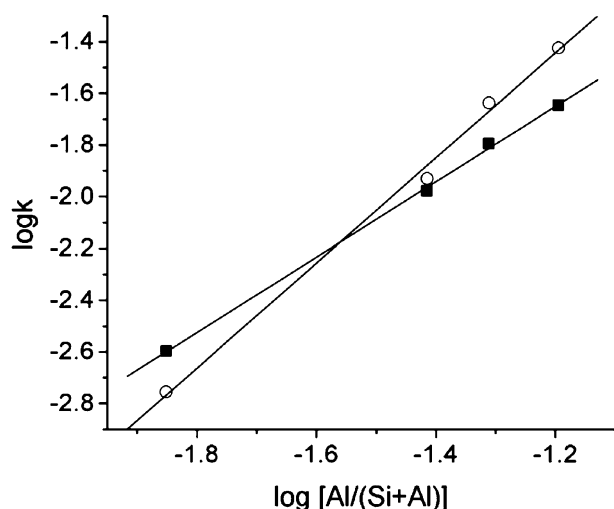


Figure 6. Reaction activity of *n*-hexane as a function of aluminum content for HZSM-5 zeolite with different Si/Al ratio at 500 °C for *n*-hexane transformation without methanol coupling (■) and with methanol coupling (○).

The results reported by Jolly et al. [12] and Wielers et al. [13] have suggested that the aluminum content dependency of the overall rate constant most probably reflected the change in the reaction mechanism, and they also claim that bimolecular H-transfer is favored by the presence of two adjacent acid sites, and the value of 1 is related to the occurrence of the monomolecular mechanism, whereas the value of 2 is attributed to the occurrence of the bimolecular mechanism reaction of hydride transfer. Therefore, the value of 1.4 in our study may imply that both monomolecular and bimolecular pathway occur in parallel in pure hexane cracking, whereas the value of 2.03 may indicate that the bimolecular H-hydride will be dominant pathway when methanol is fed to feed of *n*-hexane, in good accordance with the result from the Arrhenius plot constructed in present work. As a result, with the aluminum content increased, the increased contribution of faster bimolecular route results in the enhancement of initial conversion rate of *n*-hexane due to methanol introduction.

3.3. The effect of species from methanol on *n*-hexane activation

The effect of species from methanol on *n*-hexane activation can be probed by varying the partial pressure of methanol in the range of 3.4–62 kPa and keeping constant partial pressure of *n*-hexane at 14 kPa in an experiment, which was carried out at 400 °C over 14.1 mg HZSM-5 zeolite (Si/Al=19) with a constant total gas flow of 200 ml/min. The result is shown in figure 7. It can be seen that the conversion of *n*-hexane reaches the maximal value at the methanol partial pressure of 9.5 kPa. Meanwhile, methanol always shows the highest conversion of 100% (no shown in figure 7), which indicates that methanol is the first

molecule to achieve the active sites to be transformed into intermediate species, this can be readily understood in term of the 89 kJ/mol difference between the proton affinities of *n*-hexane and methanol as listed in table 3 [18–19]. The maximum value of the *n*-hexane conversion suggests that it is a function of the nature of the adsorbed-species from the methanol conversion. At lower partial pressure of methanol, a minor proportion of ad-species decrease; it induces a diminution in *n*-hexane conversion. At higher partial pressure of methanol, the intermediate species react between them, which reduce the interaction of *n*-hexane and ad-species from methanol. From these results, it is possible to suppose that the intermediate species evolved from methanol will activate the *n*-hexane molecule to affect the reaction route of *n*-hexane.

3.4. Proposed reaction pathway of *n*-hexane activation with methanol as co-reactant

As discussed above, the lowered apparent activation energy indicates that the introduction of methanol may decrease greatly the activation barrier of *n*-hexane, which make the transition state more easily formed. In term of the ionic mechanism of paraffin cracking [4–6, 12–17], this behavior means that methanol introduction increases greatly contribution of the bimolecular reaction to the overall reaction rate. Moreover, considering the apparent order in the aluminum content, the value of 2.03 in coupling reaction may further confirm the dominant behavior of bimolecular mechanism. In addition, the way involving the bimolecular route is probably the bimolecular hydride transfer reaction [12–13]. The further investigation in section 3.3 has shown that it is the surface intermediate species evolved from

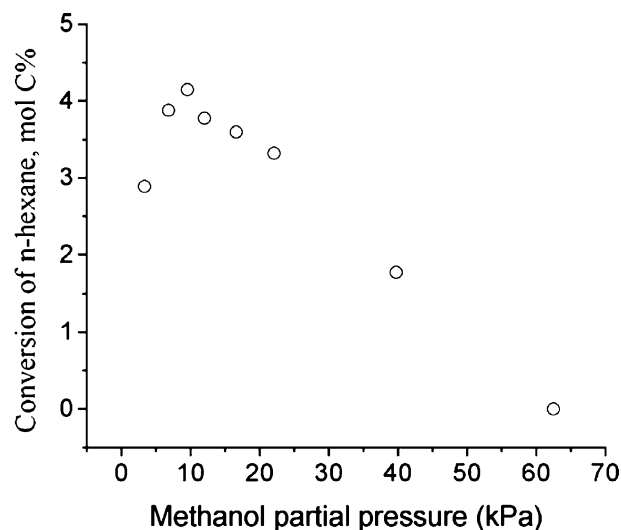


Figure 7. Rate of *n*-hexane conversion versus methanol partial pressure: 14 kPa *n*-hexane coupling reaction with 3.4–62 kPa methanol; reaction temperature = 400 °C; total gas flow = 200 ml/min.

Table 3
Proton affinities of two kinds of feed

Compound	<i>n</i> -hexane	Methanol
Proton affinity (kJ/mol)	665	754

methanol that affect the route of *n*-hexane activation. Indeed, many mechanism studies of methanol conversion over zeolite have suggested that the possible intermediate species, such as methoxy groups or carbenium ion, display ionic character to some extent [7–8, 20–30]. It seems that the intermediate species can more easily attack *n*-hexane molecules than Brønsted site of the zeolite surface.

Thus, we tentatively put forward that the initiation step of *n*-hexane is dominated by bimolecular hydride transfer between the intermediate species from methanol and *n*-hexane molecule instead of the direct monomolecular protonation of *n*-hexane on Brønsted acid site of zeolite. As a result, the faster bimolecular initiation step will result in the enhancement of initial conversion rate of *n*-hexane in the coupling transformation of *n*-hexane and methanol. Further studies on the intermediate species and the detail mechanism for the coupling system will be summarized in our next study.

4. Conclusions

The coupling transformations of *n*-hexane and methanol over HZSM-5 zeolite catalysts, as well as the conversion of the hexane alone under the same conditions, have been investigated with a pulse reaction system. Comparing with the conversion of *n*-hexane alone, the increased rate constant and lowered apparent activation energy of *n*-hexane clearly show an improvement of *n*-hexane activation using methanol as co-reactant, and the increase of *n*-hexane conversion can be favored by the highly acid sites density and lower reaction temperature, which may be attributed to the presence of intermediate species evolved from methanol. Therefore, it can be allowed to propose a reaction pathway, where the initiation step of *n*-hexane is dominated by faster bimolecular hydride transfer between the species from methanol and *n*-hexane molecule instead of the direct monomolecular protonation of *n*-hexane on Brønsted acid site of zeolite. As a result, the bimolecular progress

will become a prevailing pathway in the coupling transformation of *n*-hexane and methanol.

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