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Free radical mechanism investigation of the side-chain alkylation of toluene with methanol on basic zeolites X

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ABSTRACT

The side-chain alkylation of toluene represents a novel, environmentally friendly, and low cost route for the production of styrene. However, the yield of styrene produced in this way is currently low, and the mechanism responsible for the side-chain alkylation of toluene is poorly understood. Furthermore, the reason for the higher catalytic efficiency of CsX over NaX and KX remains unclear. In this work, the free radical mechanism of the side-chain alkylation of toluene over basic zeolite X has been elucidated using quantum chemical calculations, together with isotope tracing experiments and the reaction between *p*-nitrotoluene and methanol. The adsorption isotherm of methanol showed that Cs⁺ ions could block methanol from accessing the β -cage, which is where the side-chain alkylation reaction occurred. Furthermore, the H–D exchange results between toluene and deuterated toluene (C₆D₅CD₃) showed that CsX was more efficient as a catalyst than KX for the conversion of toluene to the corresponding benzyl radical (C₆H₅CH₂[•]). These two results therefore explain the higher catalytic activity of CsX towards side-chain alkylation than KX. Based on the free radical mechanism, the selectivity of styrene could be increased from 17.4% to 59.4% using CO₂ as carrier gas instead of N₂.

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1. Introduction

Styrene is an important material that is used for the production of a broad range of polymers, which are themselves used in numerous applications, including medical devices, toys, paper coatings and food packaging [1]. It is noteworthy that the annual worldwide consumption of styrene monomer is currently more than 30 million tons. However, there are many disadvantages associated with the traditional process for the production of styrene, including high costs, as well as high levels of energy consumption and environmental pollution resulting from the high reaction temperature and toxic nature of the raw materials [2]. To address these issues, there has been a recent increase in research directed towards the side-chain alkylation

of toluene because it has the potential to provide a novel route for the production of styrene while avoiding the limitations associated with the traditional production process [3–11].

Yashima et al. [1] and Sidorenko et al. [12] reported that the catalytic activities of X-type zeolites for the side-chain alkylation of toluene with methanol was higher than those of Y-type zeolites. Freeman et al. [13] reported that the catalytic efficiencies of several X-type zeolites increased with the increasing size of the alkali-metal cations used in their reactions (i.e., NaX < KX < CsX). However, the precise reason for the higher catalytic efficiency of CsX compared with NaX and KX remains unclear. Furthermore, the mechanism of the side-chain alkylation of toluene is poorly understood. Rep [14] postulated a mechanism for the side-chain alkylation of toluene. According to this

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mechanism, methanol would be initially dehydrogenated to give formaldehyde (Eq. (1)), which would react with toluene to form styrene via an aldol-type condensation reaction (Eq. (2)). The styrene would then be reduced to ethylbenzene (Eq. (3)).

However, the dehydrogenation of methanol on NaCO_3 [15] and the cracking reaction of propylbenzene to toluene [16,17] is generally considered to proceed via a free radical mechanism, suggesting the possibility that a free radical mechanism could be responsible for the formation of styrene during the side-chain alkylation of toluene. Spin trapping-electron spin resonance (ESR) experiments are normally used to determine whether a reaction proceeds via a radical mechanism. Unfortunately, this technique cannot be used in this particular case because the side-chain alkylation of toluene is conducted at high temperatures (ca. 420 °C), which are too high to use a radical trapping reagent.

With this in mind, isotope tracing experiments have been used in the current study together with the reaction between *p*-nitrotoluene and methanol to confirm the free radical mechanism of the side-chain alkylation of toluene over basic zeolite X. The higher catalytic activity of CsX towards the side-chain alkylation compared with KX has been explained in terms of the adsorption isotherm of methanol and H–D exchange experiments between toluene and deuterated toluene ($\text{C}_6\text{D}_5\text{CD}_3$). The use of CO_2 as carrier gas instead of N_2 led to an increase in the selectivity for styrene.

2. Experimental

2.1. Materials preparation

NaX zeolite was obtained from Tong Xing Corp (Shanghai, China). The CsX and KX zeolites were prepared from NaX following three ion exchange processes with aqueous solutions (1 mol/L) of CsOH and KOH, respectively. The exchanged samples were dried at 85 °C and calcined in air at 520 °C for 3 h before being rehydrated and rinsed with distilled water. Deuterated methanol- d_4 (CD_3OD) and deuterated toluene- d_8 ($\text{C}_6\text{D}_5\text{CD}_3$) were provided by Aladdin Industrial Corporation (Shanghai, China).

2.2. Catalytic reaction

2.2.1. Isotope trace experiments

A specific amount of each catalyst was packed into stainless steel tubular fixed-bed reactors with an inner diameter of 1.5 cm. A mixture of toluene and deuterated methanol- d_4 was then pumped into the reactors at a rate of 10 mL/h. The isotope tracing side-chain alkylation reactions were carried out at 425 °C using a 10:1 (mol/mol) mixture of toluene and CD_3OD under atmospheric pressure with N_2 30 mL/min.

2.2.2. *p*-nitrotoluene side-chain alkylation

CsX catalyst (5.0 g) was packed into a stainless steel tubular fixed-bed reactor with 1.5 cm inner diameter. The reactants were pumped into the reactor at a rate of 10 mL/h. Side-chain alkylation was carried out at 425 °C, 1:1:20 *p*-nitrotoluene: methanol: benzene molar ratio, and atmospheric pressure with N_2 30 mL/min.

2.2.3. H/D exchange experiments

The catalyst (active carbon, CsX, or KX) was packed into a stainless steel tubular fixed-bed reactor with 1.5 cm inner diameter. The mixture of toluene and toluene- d_8 was pumped into the reactor, giving a feed rate (WHSV) of 2 g g^{-1} h $^{-1}$. Side-chain alkylation was carried out at 380 °C, 1:10 toluene: toluene- d_8 molar ratio, and atmospheric pressure with N_2 30 mL/min.

2.2.4. CO_2 effect experiments

CsX catalyst (5.0 g) was packed into a stainless steel tubular fixed-bed reactor with 1.5 cm inner diameter. The mixture of toluene and methanol was pumped into the reactor at a rate of 10 mL/h. Side-chain alkylation was carried out at 420 °C, 1:1 toluene: methanol molar ratio, atmospheric pressure with CO_2 (N_2) 30 mL/min.

3. Results and discussion

3.1. Mechanism verification

The mechanism of the side-chain alkylation of toluene was initially investigated using CD_3OD as an isotope tracer. The crude product was analyzed by GC-MS and ^2H -NMR. The ^2H -NMR spectrum of the reaction mixture (Fig. 1(a)) contained peaks at 2.23 and 1.18 ppm, which were assigned to the deuterated methyl groups of toluene and ethylbenzene, respectively.

Notably, the ion mechanism postulated by Marco Rep (as shown in Eqs. (1–3)) could not be used to explain why most of D atoms were located on toluene, whereas very few were attached to the β -C atoms of ethylbenzene. According to Eqs. (1–3), the β -C atoms of the styrene and ethylbenzene products resulting from the ion mechanism should contain deuterium. However, the results showed that only a small amount of D was incorporated on to the β -C atoms of ethylbenzene and that most of D were observed on the toluene. This result therefore suggested that the H–D exchange reaction between the methyl groups of CD_3OD and toluene was occurring by a free radical reaction (Eqs. (4–7)).

As indicated in the above equations, the toluene would be cracked to give $\text{C}_6\text{H}_5\text{CH}_2\cdot$ and $\text{H}\cdot$ and CD_3OD would dissociate to give $\cdot\text{CD}_2\text{OD}$ and a deuterium radical ($\text{D}\cdot$). The $\text{C}_6\text{H}_5\text{CH}_2\cdot$ and $\text{D}\cdot$ radicals would then combine to form deuterated toluene- d_1 ($\text{C}_6\text{H}_5\text{CH}_2\text{D}$), whilst $\cdot\text{CD}_2\text{OD}$ would react with $\text{H}\cdot$ to give trideu-

Fig. 1. (a) ^2H -NMR spectrum of the reaction mixture; (b) Representation of the faujasite structure showing only the tetrahedral atoms (SI, SI', SII, SII', SIII, and SIII' are the positions of the cationic sites); (c) Adsorption isotherms of methanol; (d) Deuterium distribution density.

teromethanol (CHD_2OD).

Seemingly, H–D exchange between methyl group of CD_3OD and toluene also could proceed by ion reaction (Eqs. (8–11)).

Quantum chemical calculations were performed at the B3LYP/6-31+G level using the Gaussian 09 program system to verify the route of the H–D exchange reaction. Scheme 1 provides a visual insight into the energies associated with the different reactants, as well as the energies of the transition states and products. The transition state of the radical mechanism was found to be about 0.149 Hartree higher than that of methanol. In contrast, the transition state of the ion mechanism was about 0.657 Hartree. The energy barrier associated with the radical route was therefore shown to be much lower than that of the ion route, which provided a strong indication that the H–D exchange reaction between the methyl group of CD_3OD and toluene would have proceeded via the radical route.

Although the results of the H–D exchange reaction can be used to confirm the presence of free radicals during the reaction, they cannot be used to demonstrate that the side-chain alkylation of toluene proceeds via a free radical reaction. To examine whether the side-chain alkylation of toluene is a free radical reaction, we investigated the reaction of *p*-nitrotoluene ($\text{NO}_2\text{-Ph-CH}_3$) with methanol instead of toluene. Aromatic nitro-groups generally behave as strong electron acceptors, as

evidenced by the fact that the methyl hydrogen of $\text{NO}_2\text{-Ph-CH}_3$ ($\text{p}K_a = 20.4$) dissociates much more readily to give H^+ than that of toluene ($\text{p}K_a = 43$), with the resulting *p*-nitro-benzyl anion ($\text{NO}_2\text{-Ph-CH}_2^-$) being much more stable than the benzyl anion (Ph-CH_2^-). If the side-chain alkylation of toluene did proceed via an ionic mechanism, then the yield of the product resulting from the side-chain alkylation of *p*-nitrotoluene would increase compared with that of toluene. Furthermore, nitrobenzene compounds generally behave as radical free radical scavenger because aromatic nitro groups can react with active radicals to form more stable radicals (Eq. (12)).

However, if the side-chain alkylation did proceed via a free radical reaction mechanism, then the methyl side-chain of *p*-nitrotoluene would not be alkylated. In practice, the results of this experiment revealed that there was no product resulting from the side-chain alkylation of *p*-nitrotoluene, which indicated that the side-chain alkylation of toluene proceeded via a free radical reaction.

Overall, the isotope trace experiments demonstrated that a D atom from the methyl group of CD_3OD was exchanged with a hydrogen atom from the methyl group of toluene. Furthermore, the results of the quantum chemical calculations showed that the energy barrier for the H–D exchange reaction was 0.148640 Hartree for the radical route and 0.656555 Hartree for the ionic route. Taken together, these results provided strong evidence in support of the H–D exchange reaction between the methyl

Scheme 1. (a) Relative energies of H/D exchange between toluene and methanol (Hartree) in radical mechanism; (b) Relative energies of H/D exchange between toluene and methanol (Hartree) in radical mechanism.

groups of CD_3OD and toluene proceeding via a radical mechanism. Further proof of this process occurring via a radical mechanism came from the observation that the side chain of *p*-nitrotoluene was not alkylated with methanol. Instead, the $\text{C}_6\text{H}_5\text{CH}_3/\text{C}_6\text{H}_5\text{CH}_2 \cdot$ reacted with $\text{CH}_3 \cdot/\text{CH}_3\text{OH}$ to generate 2-phenyl-ethanol ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$), which underwent a dehydration to produce styrene (Eqs. (13) and (14)). Furthermore, the reaction of $\text{C}_6\text{H}_5\text{CH}_2 \cdot$ with CH_3OH and the reaction of $\text{CH}_3 \cdot$ with $\text{C}_6\text{H}_5\text{CH}_3$ would give ethylbenzene (Eqs. (15) and (16)). Ethylbenzene was also produced by the hydrogenation of styrene with $\text{H} \cdot$ (Eq. (17)).

Toluene could also react with $\text{CH}_3 \cdot$ to generate ethylbenzene (Eq. (16)), and the $\text{CH}_3 \cdot$ radical could react with CH_3OH to generate CH_4 (Eq. (20)), CO (Eq. (21)), and several other by-products. The radical mechanism could also be used to explain the formation of CO and CH_4 (Eqs. (20) and (21)). The enthalpy changes associated with Eqs. (16), (20), and (21) were 50.6, -27.9, and -27.0 kJ/mol, respectively, and therefore very different. Based on the theory of thermodynamics, $\text{CH}_3 \cdot$ would be better suited to form CH_4 and CO than styrene and ethylbenzene. To improve the usage of CH_3OH , it would therefore be necessary to reduce the probability of a collision between $\text{CH}_3 \cdot$ and CH_3OH /formaldehyde (CH_2O), while improving the probability of a collision between $\text{CH}_3 \cdot$ and $\text{C}_6\text{H}_5\text{CH}_3$ (or $\text{C}_6\text{H}_5\text{CH}_2 \cdot$).

3.2. β cages constraint on methanol

X-type zeolites are composed of faujasite and β cages (Fig. 1(b)). The diameters of the 12- and 6-ring orifices of the

faujasite and β cage structures are around 0.74 and 0.25 nm, respectively. The diameter of toluene is about 0.65 nm, which is much bigger than the diameter of the 6-ring orifice of the β cage structure of the NaX. With this in mind, toluene should be able to go inside the faujasite cages, but not inside the β cages. Basler et al. [18] demonstrated that NH_3 can enter the β cages of NaX. Given that the diameter of CH_3OH is similar to that of NH_3 , it was envisaged that CH_3OH would also be able to access to the β cages of NaX.

The adsorption isotherms of CH_3OH were measured to determine the validity of this hypothesis and the results are shown in Fig. 1(c). The results revealed that NaX had a similar adsorption capacity (ca. 8500 molecules per unit cell) to KX. The adsorption capacity of NaX was found to be much greater than that of CsX (ca. 6300 molecules per unit cell). This result indicated that the β cages would be blocked when SII and SII' were occupied by Cs^+ instead of K^+ because the radius of Cs^+ is larger than that of K^+ and CH_3OH would therefore be prevented from entering the β cages. In this case, the $\text{CH}_3 \cdot$ radical would only be able to react with $\text{CH}_3\text{OH}/\text{CH}_2\text{O}$ to form side-products in the β cages. Furthermore, the $\text{CH}_3 \cdot$ radicals would collide with toluene molecules to generate styrene and ethylbenzene in the faujasite cages. The blocking of the β cages with Cs^+ ions would therefore improve the probability of collisions between the $\text{CH}_3 \cdot$ radicals and toluene (or $\text{C}_6\text{H}_5\text{CH}_2 \cdot$). Taken together, these results show that CsX is more efficient than KX for catalyzing the reaction of CH_3OH with toluene to give styrene and ethylbenzene.

3.3. Activation ability of toluene on different X zeolites

As mentioned above, the side-chain alkylation of toluene occurs via a free radical mechanism. With this in mind, the process responsible for the formation of the free radicals represents an important step in this reaction. The activation of $\text{C}_6\text{H}_5\text{CH}_3$ to give the corresponding radical species $\text{C}_6\text{H}_5\text{CH}_2 \cdot$ was evaluated with a variety of different catalysts based on the H/D exchange reaction of a 10:1 (mol/mol) mixture of $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_6\text{D}_5\text{CD}_3$. The resulting distribution of D in the products

was analyzed by GC-MAS and the results are shown in Fig. 1(d).

The deuterium distribution density results (Fig. 1(d)) showed that $C_6D_5CD_3$ existed as the major species in the reaction mixture when the catalytic process was conducted with active carbon. This result indicated that it was difficult to convert $C_6H_5CH_3$ to the corresponding $C_6H_5CH_2^\bullet$ radical using activated carbon as a catalyst. Furthermore, the experiments involving the side-chain alkylation of toluene showed that the conversion of toluene was about 0.1% when the reaction was conducted over active carbon (Table 1). Taken together, these results show that the catalytic effect of activated carbon towards the side-chain alkylation of $C_6H_5CH_3$ was in agreement its catalytic effect towards the conversion of $C_6H_5CH_3$ to $C_6H_5CH_2^\bullet$. In contrast, when the reaction was conducted in the presence of a X-type zeolite (KX or CsX), the amount of $C_6D_5CD_3$ decreased sharply, whereas the amount deuterated toluene- d_1 increased considerably. This result demonstrates that the zeolite was having a significant effect on activating toluene towards free radicals. The effect of the zeolite could be attributed to a captodative effect involving the synergistic effect of electron-withdrawing (captor) and electron-releasing (donor) groups attached to the radical center, which could make the radical much more stable [19]. As the toluene molecules entered the cavities of the zeolite, the cations would form complexes with the aromatic rings, and the resulting complexes would attract electrons. At the same time, the anions within the zeolite framework would donate an electron to the methyl group of toluene (Fig. 2). Based on these interactions, the zeolite would be able to stabilize the $C_6H_5CH_2^\bullet$ radical.

Compared with the KX catalyst, more of the deuterium atoms present in the mixture existed as toluene- d_1 following the CsX-catalyzed process. The fact that more deuterium atoms were exchanged from deuterated toluene to toluene using the CsX catalyst demonstrated that the H/D exchange process occurred to a much greater extent over the CsX catalyst than it did over the KX catalyst and that the $C_6H_5CH_2^\bullet$ radical was much more stable over CsX. Cs can lose an electron more readily than K, which means that the CsX zeolite has a weaker Cs^+ cation (electron-withdrawing) and stronger framework anion (electron-releasing) than the KX zeolite. The cooperativity of the acceptor and donor moieties of the CsX zeolite therefore possesses better captodative effects to increase the stability of the $C_6H_5CH_2^\bullet$ radical. Furthermore, CsX exhibited higher catalytic activity towards the side-chain alkylation of toluene than KX. The levels of toluene conversion using the CsX and KX zeolites were found to be 16.6% and 3.6% (Table 1), respectively. This result therefore demonstrates that the higher catalytic activity

Fig. 2. The captodative effect of metal cation and anion on the framework.

of CsX towards the conversion of $C_6H_5CH_3$ to $C_6H_5CH_2^\bullet$ was critical to its higher catalytic activity towards the side-chain alkylation of toluene compared with KX.

3.4. CO_2 effect on the selectivity of styrene

Several experiments were designed to improve the selectivity of the side-chain alkylation reaction of toluene based on the radical reaction mechanism. Notably, CO_2 was used as a carrier gas instead of N_2 . Under an atmosphere of N_2 , there are three possible reaction routes for $H^\bullet$ (Fig. 3(a)), including: (1) the reaction of $H^\bullet$ with CH_3OH following route S to generate $\bullet CH_2OH$, which would be subsequently converted to styrene; (2) the reaction of $H^\bullet$ with CH_3OH according to route E_1 to generate $CH_3^\bullet$, which would subsequently react with toluene to give $C_6H_5CH_2CH_3$; and (3) the reaction of $H^\bullet$ with $C_6H_5CH=CH_2$ following route E_2 to give $C_6H_5CH_2CH_3$. Under an atmosphere of CO_2 , $H^\bullet$ would react with CO_2 to form $\bullet COOH$. The high bonding energy of the C–H bond in formic acid (ca. 468 kJ/mol) indicates that the $\bullet COOH$ radical could readily abstract a H atom from the methyl group of CH_3OH to form $HCOOH$ as an intermediate, which could decompose to give H_2 and CO_2 at the end of the reaction (Fig. 3(b)). It would be much more difficult for the $\bullet COOH$ radical to obtain an OH moiety from CH_3OH to form H_2CO_3 because of the low bonding energy of the C–OH bond in H_2CO_3 . CH_3OH would therefore be more inclined to form styrene following route S because the reaction of CH_3OH with $\bullet COOH$ would be relative facile and energetically favorable. The presence of CO_2 would lead to a decrease in the concentration of $H^\bullet$, which would lead to a further decrease in the production of $C_6H_5CH_2CH_3$ from the reaction between styrene and $H^\bullet$. Thus, the selectivity of the reaction for styrene would be increased. Pleasingly, the experimental results of this study were found to be consistent with the design strategy, as shown in Table 1, with the conversion of toluene decreasing slightly and the selectivity for styrene increasing from 17.4% to 59.4% when the reaction was conducted under CO_2 .

Table 1
Toluene side-chain alkylation data.

Catalyst	Conversion of toluene (%)	Yield of styrene (%)	Yield of EB (%)	Selectivity of styrene (%)	Conversion of methanol (%)	Yield of methane (%)	Yield of CO (%)
C	0.75	0.15	0.15	—	—	—	—
KX	3.60	1.32	1.37	—	99.4	43.5	49.3
CsX	16.60	2.89	12.67	17.4	98.2	34.2	48.2
CsX (CO_2 atmosphere)	13.80	8.20	7.80	59.4	—	—	—

$Y_{CO} = N_{CO, out} / N_{MeOH, in}$, $Y_{methane} = N_{methane, out} / N_{MeOH, in}$, where N_i is calculated from the GC response signal (area of the FID or TCD peak) using the response factors for individual components and converted into mols.

Fig. 3. (a) Reaction in atmosphere of N_2 ; (b) Reaction in atmosphere of CO_2 .

4. Conclusions

The reaction mechanism of the side-chain alkylation of toluene has been fully elucidated using isotope tracing experiments, as well as investigative reactions between *p*-nitrotoluene and methanol. H/D exchange reactions between CD_3OD and $C_6H_5CH_3$ provided experimental proof of the presence of free radicals in the reaction process. The results for the reaction between *p*-nitrotoluene and methanol further validated the idea that the side-chain alkylation of toluene proceeded via a free radical reaction mechanism. Cs^+ ions blocked CH_3OH from going inside the β cages, which consequently reduced the occurrence of side reaction. Furthermore, CsX was found to be more effective than KX for activating toluene towards free radicals, which was in agreement with the results of our experiments for the catalytic side-chain alkylation of toluene. In light

of the strong interaction between CO_2 and $H\cdot$, the use of CO_2 as carrier gas led to significant improvements in the selectivity for styrene.

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Graphical Abstract

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Free radical mechanism investigation of the side-chain alkylation of toluene with methanol on basic zeolites X

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Cs^+ complexes with the aromatic ring and attracts the electron, simultaneously, the anion on the framework of zeolite donates the electron to methyl group of toluene. The synergistic effect makes the radical much more stable.

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碱性X分子筛催化甲苯与甲醇侧链烷基化自由基机理研究

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摘要: 苯乙烯是重要的工业原料, 年消耗量约3000万吨。传统工艺中, 苯乙烯由乙苯催化脱氢得到。由于传统工艺高能耗, 高污染, 甲苯与甲醇侧链烷基化合成苯乙烯引起了人们广泛关注, 但是目前该路线进入工业化还有很多问题需要解决, 甚至催化机理仍不明确。本文对甲苯侧链烷基化机理及提高反应选择性等方面进行了研究。

采用离子交换法制备CsX分子筛, 在固定床反应器上进行甲苯与氘代甲醇的同位素示踪实验和硝基甲苯的侧链烷基化实验, 结合量子计算明确反应机理。采用IGA-002系统测定甲醇在CsX, KX和NaX上的等温吸附线, 考察甲醇在分子筛不同笼结构中的吸附情况。将氘代甲苯与甲苯在CsX, KX和活性炭催化下进行氢氘交换实验, 检验自由基在不同催化剂上的稳定性。以CO₂为载体进行甲苯与甲醇侧链烷基化实验, 考察CO₂对反应的影响。

甲苯与氘代甲醇进行侧链烷基化反应时, 大多数氘出现在甲苯上, 仅少数氘存在于苯乙烯及乙苯上, 表明甲苯氢与甲醇的甲基氢进行了氢氘交换。量子化学计算表明, 甲苯与甲醇的氢氘交换沿自由基路径的能垒远小于沿离子路径的。氘代实验和量子计算结果表明, 甲苯侧链烷基化过程中存在自由基, 但不能证明侧链烷基化是自由基反应。为了验证甲苯侧链烷基化反应是否为自由基机理, 以4-硝基甲苯(NO₂-Ph-CH₃)代替甲苯与甲醇进行侧链烷基化反应。硝基是强吸电子基团, 能稳定苄基负离子, 如果甲苯侧链烷基化是离子反应, 硝基甲苯侧链烷基化产物收率会升高。另外, 硝基又能与活泼自由基生成稳定自由基, 若反应为自由基机理, 则硝基甲苯不发生侧链烷基化反应。分析结果表明, 反应液中不存在侧链烷基化产物, 确定了甲苯侧链烷基化反应为自由基机理, 而不是离子机理。

热力学上甲醇更容易进行生成CO和H₂等的副反应, 从而减少CH₃·与H·碰撞甲醇的几率。甲醇等温吸附线显示甲醇在NaX和KX上的吸附容量相近且远大于CsX上的, 表明Cs⁺阻碍了甲醇进入X分子筛的β-笼。由于甲苯不能进入β-笼, NaX和KX的β-笼内甲醇与甲基自由基接触发生副反应。CsX催化时Cs⁺阻碍甲醇进入β-笼而抑制了副反应的发生, 提高了甲醇利用率。

甲苯与氘代甲苯在CsX, KX和活性炭上进行氢氘交换, 反应物用GC-MS分析。结果表明, 在CsX上氢氘交换进行得更彻底, 在活性炭上几乎没有氢氘交换。X分子筛活化甲苯为自由基的效果优于活性炭, 这可能是推拉效应造成的。当甲苯进入分子筛后, Lewis酸性阳离子与苯环络合并吸引电子, 催化剂阴离子骨架与甲苯的甲基作用并供给电子, 推电子与吸电子共同作用使甲苯更容易生成苄基自由基, 并使其更稳定。CsX对甲苯的活化作用强于KX, 表明CsX的酸碱搭配更有助于甲苯生成自由基。这也是CsX催化甲苯与甲醇侧链烷基化效果优于KX的原因。

以CO₂替代N₂作为载气能显著提高苯乙烯的选择性, 这是由于CO₂的存在降低了H·和CH₃·的浓度, 提高了·CH₂OH的浓度。·CH₂OH与甲苯生成苯乙烯, H·的减少降低了苯乙烯加氢生成乙苯。

关键词: 甲苯; 侧链烷基化; 自由基机理; X分子筛; 苯乙烯; 同位素示踪

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