

Effect of K_2O on Side Chain Alkylation of Toluene with Methanol

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Abstract: The catalysts of $x\%$ K_2O /KLSX ($x = 0, 1, 2, 3, 4$) were prepared by ion exchanging and impregnating method from Low-silica zeolite X (LSX), and superbase of K_2O can be generated from decomposed KNO_3 over KLSX. The effect of superbase on the catalytic performances of $x\%$ K_2O /KLSX for side chain alkylation of toluene with methanol was investigated. The superbase sites of K_2O can polarize the methyl group of toluene better, as well as convert methanol to alkylation intermediate, and even to carbon monoxide and hydrogen. KLSX and 1% K_2O /KLSX exhibited low catalytic activity because of lower alkalinity, 3% K_2O /KLSX and 4% K_2O /KLSX also exhibited low catalytic activity because their excess amount of superbase sites and insufficient amount of weak Lewis acid sites. In contrast, 2% K_2O /KLSX showed high activity due to its adequate Lewis acid sites to adsorb toluene, as well as moderate alkalinity to convert methanol to alkylating agent and activate toluene.

Key words: alkylation; toluene; methanol; KLSX; K_2O

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Styrene is an industrially important chemical that is used for production of plastics and rubbers^[1]. At present styrene is industrially produced by two subsequent reactions: the alkylation of benzene with ethylene to produce ethylbenzene and its high temperature dehydrogenation to styrene^[1]. The side chain alkylation of toluene with methanol for producing a mixture of styrene and ethylbenzene offers economical advantages compared with the conventional homogenous catalytic process^[2].

The catalysts for side chain alkylation of toluene with methanol are mainly composed by basic zeolites, including alkali exchanged zeolites X, Y, L, A and β , etc, as well as non-zeolites alkaline porous materials, including MgO , CaO , MgO/TiO_2 , and Cs_2O/AC , etc^[3-6]. Among them, the activities of basic zeolites are higher, especially alkali exchanged zeolite X^[7-8]. Alkylation of toluene with methanol over alkali exchanged zeolite X yields different products. It has

been observed that ring alkylation of toluene with methanol to give xylene is favored on relatively high acidic zeolite like LiX and NaX, while side chain alkylation to give styrene and ethylbenzene is favored on basic zeolite like RbX and CsX^[9]. For KX, both reactions could be occurred over it. The major products over KX are ethylbenzene and styrene, a spot of xylene could be produced. While KX has important research value compared with RbX and CsX considering of their prices.

Serra J M et al. reported that sufficient base strength to convert methanol to the alkylating agent and polarize methyl group of toluene, as well as enough amounts of weak Lewis acid sites able to stabilize adsorbed toluene are the key requirements for a successful side chain alkylation catalyst^[1, 6]. Previous works show that impregnating alkali hydroxide or oxide particles into zeolite X, Y, L and β promoted this reaction^[1, 4, 10]. Low-silica zeolite X (LSX) has stronger

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base strength and more Lewis acid sites compared to normal zeolite X and other type zeolites because of its low silica alumina ratio, therefore it may be more active for the side chain alkylation of toluene with methanol. By introducing appropriate amount of base precursor KNO_3 into LSX, superbase sites of K_2O can be generated in the zeolite after high temperature calcinations^[11], which is good for side chain alkylation of toluene with methanol.

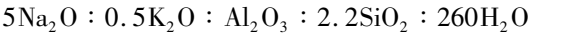
In the present study, we supported different amount of K_2O over KLSX in attempt to improve the catalytic activity. LSX was synthesized by two-step hydrothermal process. KLSX was prepared from LSX by ion exchanging with KNO_3 solution. This further support different amount of KNO_3 to obtain $x\%$ K_2O /KLSX catalysts ($x = 0, 1, 2, 3, 4$). Superbase of K_2O can be generated from decomposed KNO_3 over KLSX. The catalytic performances of the $x\%$ K_2O /KLSX for side chain alkylation of toluene with methanol were investigated. The specific correlations between the activity and the amounts of basic sites and Lewis acid sites of the catalyst for alkylation of toluene with methanol to produce styrene and ethylbenzene were discussed.

1 Experimental

1.1 Catalyst preparation

Reagents: sodium hydroxide (AR), potassium hydroxide (AR), sodium meta-aluminate (AR), sodium silicate (AR), potassium nitrate (AR), active carbon, and distilled water.

Gels of the following oxide molar composition were prepared for the synthesis of LSX:



First, 7.20 g NaOH, 2.80 g KOH and 8.20 g NaAlO_2 were dissolved in 110.00 g H_2O together, and 31.25 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 106.50 g H_2O at 50 °C. Then, two kinds of solutions above were mixed at 50 °C and made into gels in the synthesis reactor. The LSX was synthesized by two step hydrothermal process of aging at 50 °C for 24 h and crystallizing at 100 °C for 6 h using homogeneous synthesis reactors with stirring at 30 rpm. After cooling the reactors, the samples were centrifuged at 3 000 rpm, the recovered LSX product was washed with distilled water until $\text{pH} = 7$ and dried at 100 °C for 12 h.

KLSX was prepared from LSX (50 g) by ion exchanging with potassium nitrate solution (1 L, 2 mol/L) for two times at 80 °C and washed with distilled water (400 mL). Next different amount of potassium nitrate were supported on the KLSX to prepare the catalysts of $x\%$ K_2O /KLSX. For the catalyst of $y\%$ K_2O /AC, it was produced by supporting different amount of potassium nitrate over active carbon (AC). Before the alkylating reaction, the supported potassium nitrate would be decomposed to K_2O directly under nitrogen atmosphere in the reactor. This can prevent the supported K_2O reacting with carbon dioxide in the air.

In the catalysts of $x\%$ K_2O /KLSX and $y\%$ K_2O /AC, the parameter x and y are refer to mass ratio of K_2O to KLSX and AC respectively (Table 1).

Table 1 Composition of the catalysts

Catalyst	KLSX/g	KNO_3/g	Catalyst	AC/g	KNO_3/g
KLSX	10	0	AC	10	0
1% K_2O /KLSX	10	0.2147	2% K_2O /AC	10	0.4293
2% K_2O /KLSX	10	0.4293	4% K_2O /AC	10	0.8587
3% K_2O /KLSX	10	0.6440	6% K_2O /AC	10	1.2880
4% K_2O /KLSX	10	0.8587	8% K_2O /AC	10	1.7173

1.2 Catalyst characterization

X-ray powder diffraction (XRD) (Cu $\text{K}\alpha$ radiation, D8 Advance, Bruker) was carried out to deter-

mine crystallinity of the catalysts. The scanning range of 2θ was set between 5° and 50° with a step size of 0.02°.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo iCAP 6300) was performed to determine the elements content of the catalysts.

The surface areas and pore volumes of the catalysts were determined by N_2 physisorption at $-196\text{ }^\circ\text{C}$ using a Micromeritics ASAP 2020 physical adsorption analyzer system. The samples were degassed under a 10^{-6} mmHg vacuum at $120\text{ }^\circ\text{C}$ for 6 h prior to measurement. Specific surface areas and pore volumes were calculated using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method separately.

The infrared spectra of adsorbed pyridine (Py-IR) were tested on Bruker Vector 22. Prior to pyridine adsorption, the catalysts were evacuated for 1 h at $400\text{ }^\circ\text{C}$ under high vacuum (1.33×10^{-3} Pa) to eliminate the absorbed impurities. Pyridine adsorption was carried out at room temperature until saturation (equilibration time 0.5 h), then the excess of physical adsorbed pyridine was removed under vacuum (1.33 Pa) at $200\text{ }^\circ\text{C}$ for 1 h. After this, the corresponding spectrum was recorded.

Temperature programmed desorption of NH_3 (NH_3 -TPD) were used to determine the acid strength and amounts of the catalysts. The samples (0.1 g) were activated at $500\text{ }^\circ\text{C}$ for 1 h under nitrogen flow, then cooled down to $50\text{ }^\circ\text{C}$ to adsorb NH_3 for 15 min. Next physically adsorbed NH_3 was removed by nitrogen flow at $50\text{ }^\circ\text{C}$ for 3 h. NH_3 desorption measurements were achieved in the temperature range of $50\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

For infrared spectra of coadsorption experiment, the stainless steel cell with catalyst was evacuated to pressure below 0.01 Pa to eliminate the absorbed impurities. Then the catalyst was equilibrated with toluene at $80\text{ }^\circ\text{C}$. Subsequently the load catalyst was exposed to methanol for 0.5 Pa until the adsorption/desorption equilibrium was reached. After this, the corresponding spectrum was recorded.

1.3 Catalyst evaluation

Catalyst tests for side chain alkylation of toluene with methanol were carried out in a fixed-bed reactor. Catalyst powders were pressed, crushed, and sieved to

particle size $0.450 \sim 0.280\text{ mm}$. The catalyst sample (6.0 g) was placed in a quartz tube with an inner diameter of 10 mm. Reaction was conducted at atmospheric pressure. The obtained products were analyzed by a gas chromatography (SP3420) with Innowax capillary column. The yields of the products were defined as follows:

$$\text{Conversion(Methanol)} = \frac{\text{The mole number of the consumed methanol}}{\text{The mole number of the feed methanol}}$$

$$\text{Yield(i)} = \frac{\text{The mole number of the product i}}{\text{The mole number of the feed methanol}}$$

$$\text{Selectivity(i)} = \frac{\text{The mole number of the product i}}{\text{The mole number of the consumed methanol}}$$

2 Results and discussion

2.1 Physical characterization of Catalyst

Fig. 1 shows the XRD patterns of zeolite product synthesized. The peaks at 6.1° , 10.0° , 15.4° , 23.3° , 26.6° and 30.9° assigned to the characteristic peaks of zeolite with a FAU structure^[12] are observed on the XRD patterns. Combined the silica alumina molar ratio ($n(\text{Si})/n(\text{Al})$) in Table 2, it can be concluded that the zeolite product synthesized was relatively pure LSX.

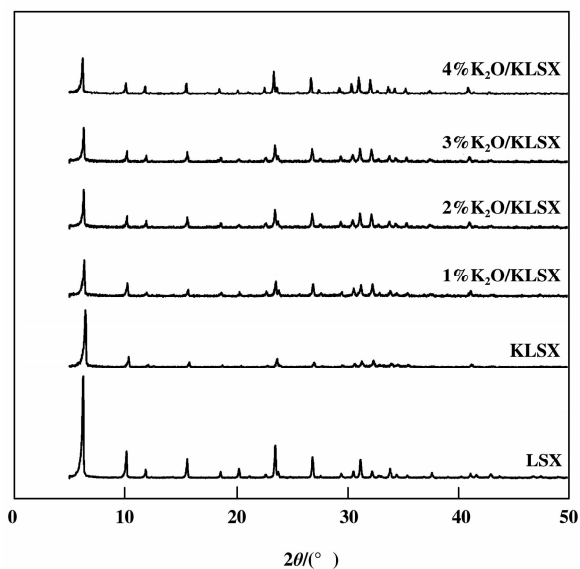


Fig. 1 XRD patterns of the catalysts

Besides, from Fig. 1 we can see that the relative diffraction line intensity of LSX decreased slightly after ion exchanging process and supported K_2O . This indi-

cates that the framework of LSX damaged slightly and the crystallinity of LSX decreased after ion exchanging process and supported K₂O. It suggests that the framework stability of LSX is poor; this is due to that the silica alumina molar ratio of LSX tends to theoretical limit value 1. The molar ratio $n(\text{K})/[n(\text{Na})+n(\text{K})]$ of KLSX is reached 92.1% after ion exchange, as can be seen in Table 2, it indicates that its ion exchange degree is higher.

The surface areas and pore volumes of KLSX could be affected by the supported K₂O, which is most likely present as metal oxide clusters supported inside

the zeolite cages. As can be seen in Table 3, the surface areas and pore volumes of the catalysts decreased with the increasing amount of supported K₂O. This is due to part of zeolite pores were blocked by supported K₂O, as well as the K₂O occupies some fraction of the intrazeolitic void space and contributes a certain amount of fraction to the total weight of the sample. While the surface areas are still higher, among which 4% K₂O/KLSX has the lowest surface area of 428 m²/g, and the surface area of KLSX are highly reached 554 m²/g. Besides, the pores of all catalysts are mainly microporous.

Table 2 Elements content of LSX and KLSX

Sample	Na/(wt%)	K/(wt%)	Si/(wt%)	Al/(wt%)	$n(\text{Si})/n(\text{Al})$	$n(\text{K})/[n(\text{Na})+n(\text{K})]$
LSX	10.68	2.04	16.65	14.09	1.14	0.098
KLSX	0.97	18.41	16.60	14.03	1.14	0.921

Table 3 Surface areas and pore volumes of the catalyst

	KLSX	1% K ₂ O/KLSX	2% K ₂ O/KLSX	3% K ₂ O/KLSX	4% K ₂ O/KLSX
Total Surface Area/(m ² · g ⁻¹)	554	522	496	454	428
Micropore Area/(m ² · g ⁻¹)	540	494	485	436	392
Total Pore Volume/(cm ³ · g ⁻¹)	0.263	0.255	0.242	0.219	0.216
Micropore Volume/(cm ³ · g ⁻¹)	0.251	0.229	0.218	0.202	0.182

Volume adsorbed at P/P₀=0.99

2.2 Acid characterization of Catalyst

IR spectra of pyridine adsorbed onto acid sites of the catalysts are shown in Fig. 2. The peaks at 1 440 cm⁻¹, 1 450 cm⁻¹ and 1 540 cm⁻¹ of Py-IR spectra are assigned to Lewis acid sites from alkali ions, Lewis acid sites from framework, and Bronsted acid sites, respectively^[7, 13]. Py-IR results show that adsorption peaks of pyridine adsorbed on Lewis acid sites (from alkali ions) can be found from all catalysts, and no adsorption peaks of pyridine adsorbed on Bronsted acid sites can be observed from all catalysts. This indicates that all *x*% K₂O/KLSX catalysts contain Lewis acid only, without any Bronsted acid sites.

Fig. 3 shows the NH₃-TPD spectra of the investigated catalysts. All the samples exhibit two peaks.

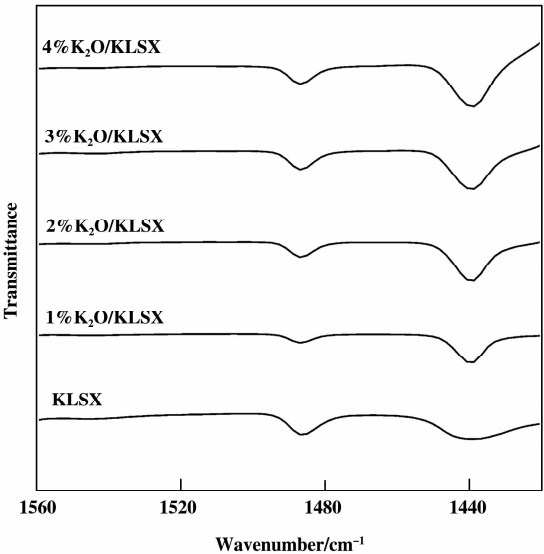


Fig. 2 Py-IR spectra of the catalysts

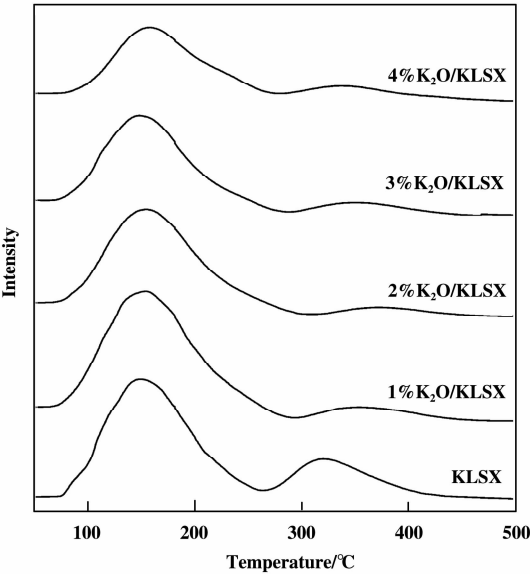


Fig. 3 NH₃-TPD curves of the catalysts

One is at low temperature (about 150 °C), corresponding to desorption of adsorbed NH₃ on weak acid sites, and the other is at high temperature (about 320 °C), which can be assigned to the desorption of adsorbed NH₃ on strong acid sites. These two peaks are probably results from alkali ions located at different site in zeolite^[14]. The acid amount of catalysts calculated from the peak areas of NH₃ desorbed are shown in Table 4, from which we can see that the amounts of the Lewis acid sites decreased with the increased amount of supported K₂O over KLSX. This could be that amounts of the zeolite channels were blocked by supported K₂O, which can be confirmed by the decrease of pore volumes of the catalysts. This implies that the available

Table 4 Results of NH₃-TPD characterization of the catalysts

Sample	Weak acid /(mmol·g ⁻¹)	Strong acid /(mmol·g ⁻¹)	Total acid /(mmol·g ⁻¹)
KLSX	2.170	0.556	2.726
1% K ₂ O/KLSX	2.110	0.180	2.290
2% K ₂ O/KLSX	1.867	0.116	1.983
3% K ₂ O/KLSX	1.546	0.111	1.657
4% K ₂ O/KLSX	1.144	0.105	1.249

mmol/g; (mmol NH₃)/ (g catalyst)

Lewis acid sites for reaction decreased with the increased amount of supported K₂O over KLSX. Besides, the amount of weak Lewis acid sites decreased rapidly from 2% K₂O/KLSX (1.867 mmol/g) to 3% K₂O/KLSX (1.546 mmol/g).

2.3 IR spectra after coadsorption of toluene and methanol

The IR spectra recorded after coadsorption of toluene and methanol over KLSX is shown in Fig. 4. The peaks at 2 910 cm⁻¹ and 3 045 cm⁻¹ assigned to the CH stretching vibrations of the methyl group and the aromatic ring of toluene separately^[15]. A sharp at 3 258 cm⁻¹ assigned to the methanol OH stretching vibration was observed. The asymmetric shape indicates that the band consists of two components^[16] with maxima at 3 413 cm⁻¹ and 3 235 cm⁻¹. The band with higher wavenumber is attributed to methanol molecules that experience lateral hydrogen bonding of their OH group with lattice oxygen of zeolite, the second band is attributed to the interaction hydrogen bonded between some additional methanol adsorption to other absorbed methanol molecules^[16].

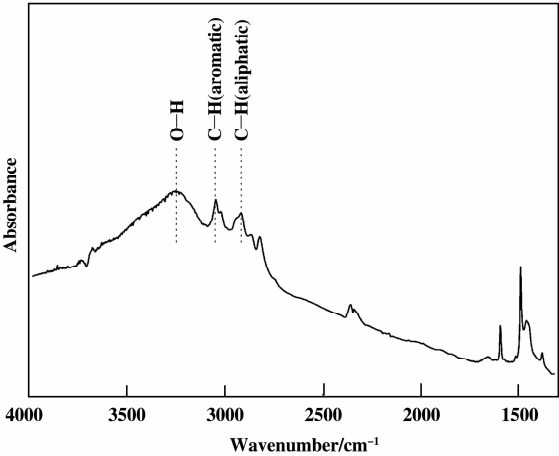


Fig. 4 IR spectra after coadsorption of toluene and methanol over KLSX

2.4 Optimization of Reaction Conditions

The effect of reaction temperature on the side chain alkylation of toluene with methanol over KLSX catalyst is shown in Fig. 5 (a). The yields of styrene and ethylbenzene increased first and then decreased with the increased of reaction temperature. The results

show that the optimum reaction temperature is 420 °C. It can be explained that side chain alkylation of toluene with methanol is an endothermic reaction, thus low temperature is unfavorable for the reaction. While methanol could be fast decomposed to carbon monoxide and hydrogen when the reaction temperature is too higher, this decreased the methanol utilization ratio. The yield of styrene rapidly decreased and the yield of ethylbenzene slowly decreased when the reaction temperature exceeded 420 °C, this is because styrene could be converted to ethylbenzene through the subsequent hydrogenation.

Fig. 5(b) shows the effect of weight hourly space velocity (WHSV) on the side chain reaction. The yields of styrene and ethylbenzene increased first and then decreased with the increased of WHSV. As can be seen in Fig. 5(b), the optimum WHSV is 1 h⁻¹. Lower WHSV prolonged the contact time between reactants, products and catalyst, which leads excessive

methanol decomposed to carbon monoxide and hydrogen, meanwhile styrene could be converted to ethylbenzene through hydrogenation. While higher WHSV shortened the contact time, which decreased the conversion of raw materials.

The effect of toluene methanol molar ratio on the side chain alkylation of toluene with methanol over KLSX catalyst is shown in Fig. 5(c). The results show that the yields of styrene and ethylbenzene increased first and then kept constant with the increased of toluene methanol molar ratio. The optimum toluene methanol molar ratio is 5. Because methanol could be absorbed, activated, and decomposed to carbon monoxide and hydrogen easily during the reaction process, excessive toluene should be added to increase the utilization ratio of methanol. The yields of styrene and ethylbenzene would be kept constant when the toluene methanol molar ratio exceeded 5, which could decrease the toluene utilization ratio.

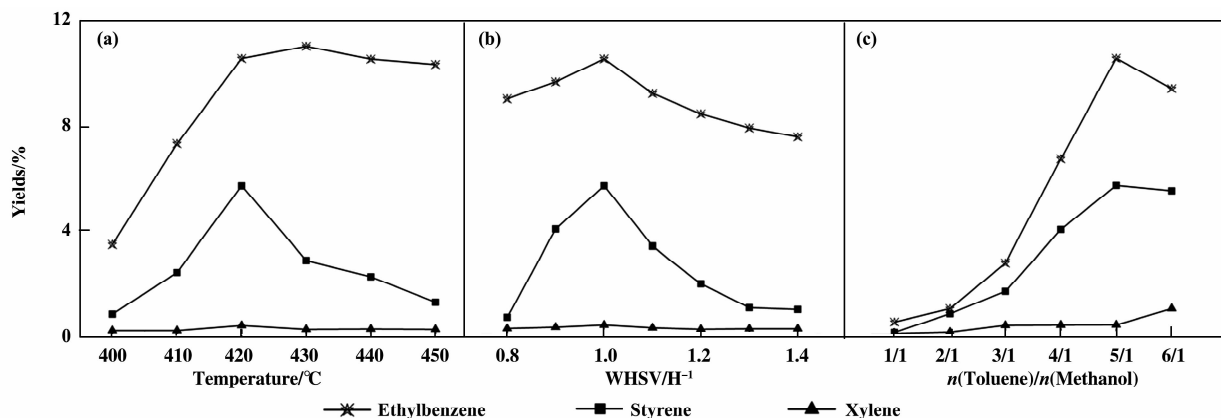


Fig. 5 Reaction condition investigation of KLSX

a: WHSV = 1 h⁻¹, $n(\text{Toluene})/n(\text{Methanol}) = 5/1$; b: $T = 420\text{ °C}$, $n(\text{Toluene})/n(\text{Methanol}) = 5/1$;

c: $T = 420\text{ °C}$, WHSV = 1 h⁻¹.

Therefore, the optimum reaction conditions for side chain alkylation of toluene with methanol over KLSX were obtained as follows: $T = 420\text{ °C}$, $n(\text{Tol})/n(\text{MeOH}) = 5/1$, WHSV = 1 h⁻¹.

2.5 Catalytic reaction

Fig. 6 shows the reaction results of alkylation of toluene with methanol over $x\%$ K₂O/KLSX catalysts. The results of liquid phase analysis show that the main products are styrene and ethylbenzene, micro amount

of xylene is produced over all catalysts, especially KLSX. The yields of styrene, ethylbenzene, and xylene kept constant in 10 h for all catalysts. The yield of styrene decreased gradually with the increased amount of supported K₂O over KLSX. For 1% K₂O/KLSX and 2% K₂O/KLSX, which the amounts of supported K₂O are lower, the yield of styrene decreased slightly compared with KLSX. The yield of styrene decreased sharply when the amounts of supported K₂O exceeded

2% . For 4% $\text{K}_2\text{O}/\text{KLSX}$, there is micro amount of styrene being produced. The yield of ethylbenzene increased first with the increased amount of supported K_2O from 0% to 2% over KLSX, and then decreased gradually with the amount of supported K_2O exceeded

2% . The highest yield of ethylbenzene can be found over 2% $\text{K}_2\text{O}/\text{KLSX}$. The yield of xylene decreased gradually with the increased amount of supported K_2O over KLSX, though the highest yield over KLSX is only 0.28% .

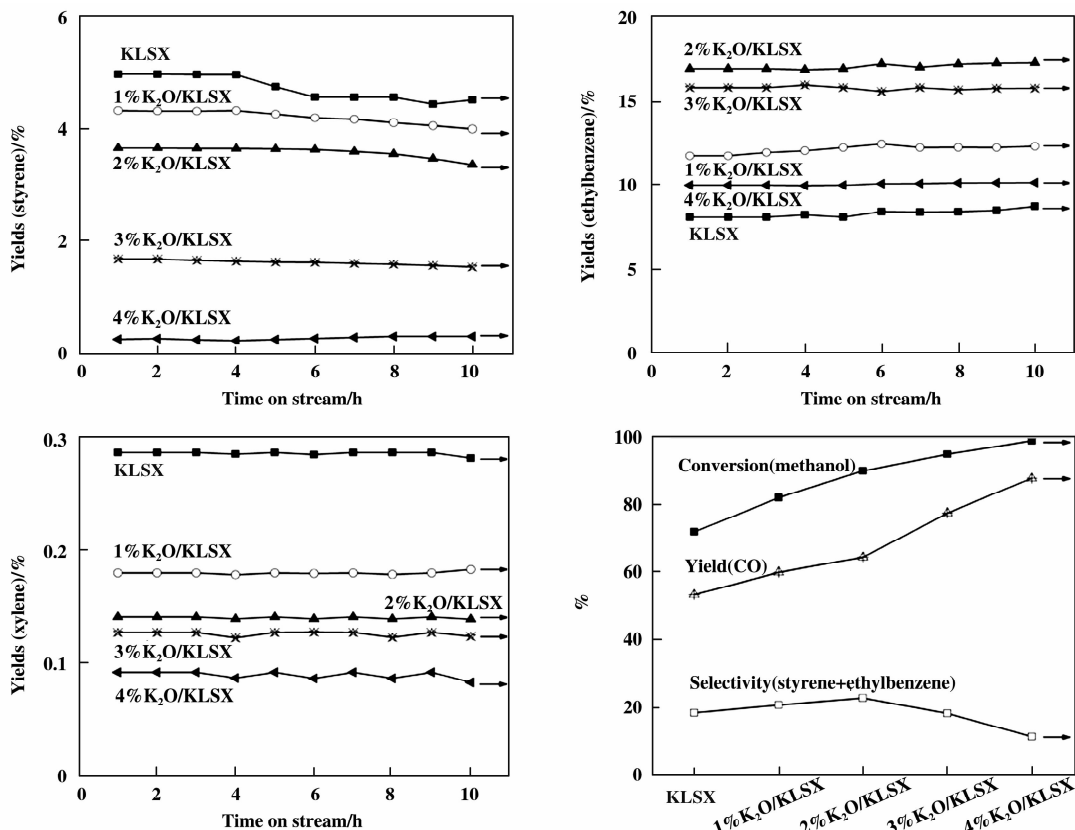


Fig. 6 Results of the alkylation of toluene with methanol over $x\% \text{K}_2\text{O}/\text{KLSX}$ catalysts
($T=420\text{ }^\circ\text{C}$, $n(\text{Toluene})/n(\text{Methanol})=5/1$, $\text{WHSV}=1\text{ h}^{-1}$)

The major reaction during toluene alkylation with methanol over solid bases is usually the formation of carbon monoxide by methanol decomposition^[17]. From Fig. 6, we can see that significant amount of carbon monoxide was produced over all catalysts. The conversion of methanol and the yield of carbon monoxide increased with the increasing amount of supported K_2O over KLSX. The selectivity of side chain alkylation products (styrene and ethylbenzene) increased first with the increased amount of supported K_2O from 0% to 2% over KLSX, and then decreased gradually with the amount of supported K_2O exceeded 2% . Meanwhile the yield of carbon monoxide increased sharply when the amounts of supported K_2O exceeded 2% , and methanol

consumed completely over 4% $\text{K}_2\text{O}/\text{KLSX}$.

Fig. 7 shows the reaction results of alkylation of toluene with methanol over $y\% \text{K}_2\text{O}/\text{AC}$ catalysts. The activities for alkylation of toluene with methanol are very low compared with the catalysts of $x\% \text{K}_2\text{O}/\text{KLSX}$. The yield of ethylbenzene increased with the increased amount of supported K_2O over AC from 0% to 6% , and then decreased because of the too strong base strength of the catalyst. There is almost no styrene and xylene being detected over all $y\% \text{K}_2\text{O}/\text{AC}$ catalysts.

2. 6 Discussion

Upon adsorbed toluene, the CH stretching vibration of the methyl group shifts to lower wavenumbers

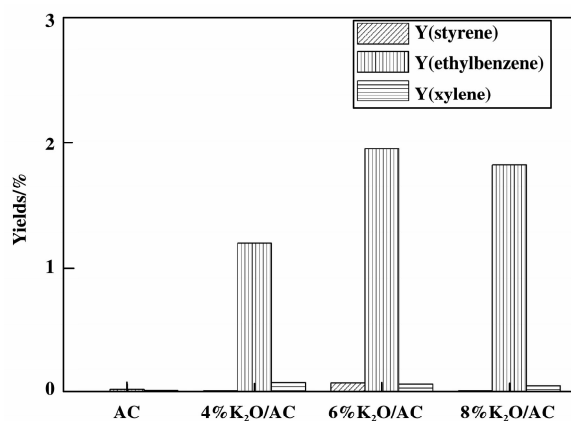


Fig. 7 Results of the alkylation of toluene with methanol over γ % K₂O/AC catalysts

($T=420\text{ }^{\circ}\text{C}$, $n(\text{Toluene})/n(\text{Methanol})=5/1$, $\text{WHSV}=1\text{ h}^{-1}$).

compared with free toluene (2925 cm^{-1} ^[18]) indicated that the hydrogen of methyl group bonded to lattice oxygen of KLSX. The adsorbed toluene also bounded via its π -electron of aromatic ring to the Lewis acid sites^[15] (alkali ions). This multipoint adsorption leads to a low mobility of the adsorbed aromatic molecules on the KSLX. It suggests that the catalyst needs adequate amount of weak Lewis sites to absorb toluene and amount of base sites to activate toluene. As to adsorbed methanol, the catalyst needs optimum base strength sites to catalyze it converted to alkylating agent formaldehyde^[15].

Furthermore, Itoh H *et al.* studied the side chain of toluene with methanol by quantum chemical calculation and proposed that specific configurations of acidic and basic sites with steric restrictions are required for this reaction^[19]. In order to prove this, the reaction was tested on active carbon and supported K₂O. In theory, it has basic sites (O^{2-}) and Lewis acidic sites (K^{+}) to activate methanol and toluene over γ % K₂O/AC catalysts. However, the yields of styrene and ethylbenzene are very low, as seen in Fig. 7.

Considering that ring alkylation of toluene with methanol to give xylene is favored on relatively high acidic zeolite and the reaction results over x % K₂O/KLSX above, it can be confirmed that the side chain alkylation of toluene with methanol would require proper acid-base pair sites for activating both toluene and

methanol. Specifically, the base sites of O^{2-} are needed for activating dehydrogenation of methanol to formaldehyde and activating the methyl group of adsorbed toluene, the Lewis acid sites needed to adsorb and stabilize toluene. Besides, the acid-base pair configuration must be needed to facilitate the reaction.

In the catalysts of x % K₂O/KLSX, there are two different oxide sites that can function as base sites: the oxygen atoms of KLSX frameworks and occluded K₂O supported in the KLSX pores. By introducing base precursor KNO_3 , superbase sites of K₂O can be generated in the zeolites^[11, 20]. While very strong base sites are also good catalyst for decomposing methanol to carbon monoxide and hydrogen^[4]. The reaction results indicate that superbase sites could catalyze the alkylating reaction between toluene and methanol, while methanol decomposed to carbon monoxide and hydrogen would compete with this reaction throughout.

The catalytic activity of KLSX increased after supported K₂O, the total yields of styrene and ethylbenzene increased from 13.3% (over KLSX) to 21% (over 2% K₂O/KLSX). This is due to the base strength of KLSX increased after supported K₂O, this promoted more methanol convert to formaldehyde, which is the alkylating agent. Besides, the superbase sites of oxygen in occluded K₂O may polarize the methyl group of toluene better. Therefore, supported amounts of K₂O over KLSX can increased the base strength of the catalyst, which enhanced the catalytic activity of the catalyst. This indicated that the optimum base strength which side chain alkylation of toluene with methanol needs cannot be reached over KLSX, although its ion exchange degree was higher (ICP-AES result). While the yields of styrene and ethylbenzene decreased after the supported amount of K₂O over KLSX exceeded 2%, this is due to the catalysts contain more amount of K₂O to catalyze excess amount of methanol decomposed to carbon monoxide and hydrogen, as well as insufficient weak Lewis acid sites to adsorb and stabilize toluene. This effect becomes more obvious with the further increased supported amount of K₂O over KLSX. In contrast, 2% K₂O/KLSX shows high activity due to the presence of adequate amount of

weak Lewis acid sites to adsorb and stabilize toluene, as well as moderate alkalinity and reasonable amount of basic sites to catalyze methanol converted to alkylation intermediate and activate the methyl group of toluene.

3 Conclusion

The catalysts of $x\%$ K₂O/KLSX ($x = 0, 1, 2, 3, 4$) were prepared and their catalytic performances for side chain alkylation of toluene with methanol were investigated. Superbase sites of K₂O can be generated from the decomposed KNO₃ over KLSX. All $x\%$ K₂O/KLSX catalysts contain Lewis acid sites only, without any Bronsted acid sites. The amount of available Lewis acid sites for reaction decreased with the increased amount of supported K₂O over KLSX, which is caused by the zeolite channels were blocked after supported K₂O.

The superbase sites of K₂O can polarize the methyl group of toluene better, and convert methanol to alkylation intermediate, which favors the side chain reaction. On the contrary, the superbase sites also decompose excess amount of methanol to carbon monoxide and hydrogen, which shows an unfavorable influence on this reaction.

The total yields of styrene and ethylbenzene increased first and then decreased with the increased amount of supported K₂O over KLSX. KLSX and 1% K₂O/KLSX exhibited low catalytic activity because of lower alkalinity, while 3% K₂O/KLSX and 4% K₂O/KLSX also exhibited low catalytic activity because of their excess amounts of superbase sites and insufficient amounts of weak Lewis acid. In contrast, 2% K₂O/KLSX shows high activity due to the presence of adequate amount of weak Lewis acid sites to adsorb and stabilize toluene, as well as moderate alkalinity and reasonable amount of basic sites to catalyze methanol convert to alkylation intermediate and activate the methyl group of toluene.

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超强碱 K_2O 对甲苯甲醇侧链烷基化反应的影响

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摘要: 采用离子交换法、浸渍法和焙烧分解法制备了 $x\% K_2O/KLSX$ ($x = 0, 1, 2, 3, 4$) 催化剂, KLSX 上的超强碱性位 K_2O 通过 KNO_3 分解制得. 考察了 $x\% K_2O/KLSX$ 的甲苯甲醇侧链烷基化反应催化性能及超强碱性位 K_2O 对反应的影响. 超强碱性位 K_2O 可以更好的极化甲苯甲基, 以及催化甲醇转化为烷基化中间体, 甚至完全分解为 CO 和 H_2 . KLSX 和 $1\% K_2O/KLSX$ 因碱性较弱所以活性较低, $3\% K_2O/KLSX$ 和 $4\% K_2O/KLSX$ 因含超强碱性位太多和可利用 L 酸性位太少, 其活性也很低. 相比之下, $2\% K_2O/KLSX$ 具有足够量的弱 L 酸位来吸附甲苯, 以及适当强度的碱性位来转化甲醇和活化甲苯甲基, 因此具有较高的催化甲苯甲醇侧链烷基化反应活性.

关键词: 烷基化; 甲苯; 甲醇; KLSX; K_2O