

Vapor-phase highly selective *O*-methylation of catechol with methanol over ZnCl₂ modified γ -Al₂O₃ catalysts

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Abstract

It is firstly discovered that ZnCl₂ modified γ -Al₂O₃ solid Lewis acidic catalysts (ZnCl₂/ γ -Al₂O₃), which are prepared by solid-state reaction, are very active and extremely selective for the preparation of guaiacol by the vapor phase *O*-methylation of catechol with methanol in a fixed-bed reactor at 553 K, under the optimum reaction conditions, the conversion of catechol and the selectivity for guaiacol are up to 81.8 and 90.9%, respectively over ZnCl₂ (10%)/ γ -Al₂O₃ and by far better than the reaction results over the solid Brønsted acid catalyst (HY), proposing that the weak coordination of catechol with the Zn²⁺ sites of ZnCl₂/ γ -Al₂O₃ plays a key impact on the high selectivity for guaiacol. The recycling tests indicate that the modification of ZnCl₂ could significantly improve the catalytic stability of γ -Al₂O₃ by it efficiently restraining the catalyst's coking. And the deactivation of ZnCl₂/ γ -Al₂O₃ is mainly caused by its ZnCl₂ leaching and surface coking in the run procedure, therefore its catalytic activity can be only partly recovered by the calcination in air at 773 K for 4 h.

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1. Introduction

Oxy-alkylated benzene derivatives prepared by the *O*-alkylation of phenol derivatives with alkylating agents in the presence of acid or base catalysts are very important fine chemicals. For example, guaiacol, which is synthesized by the liquid or vapor phase *O*-methylation of catechol with methylating agents, is an important synthetic intermediate in the production of flavorings, fragrances and pharmaceuticals. Conventionally, guaiacol is synthesized by *O*-methylation of catechol with corrosive and toxic reagents such as dimethyl sulfate and dimethyl iodide in the presence of stoichiometric quantities of sodium hydroxide as homogeneous catalyst [1,2]. These conventional processes commonly have some defaults like the trouble separation processes, relative low

atom efficiency [3], non-continuity of operation and especially serious environmental pollutions. Currently, increasing attention is drawn on studying and developing an alternative route which is more economical and environmentally friendly in order to overcome the disadvantages of homogeneous catalytic processes, e.g., continuous catalytic processes for methylation of phenol derivatives with methanol or dimethyl carbonate using solid catalysts and fixed bed reactors offer many advantages such as convenient separation of catalyst and product, catalyst reusability, ease of product-work-up and continuity of operation as well as a high atom efficiency [4]. Various solid acid catalysts such as H-ZSM-5 [5], HY [6], AlPO₄/SAPO [7], Al-P-O [8], H₃PO₄/SiO₂ [9], Al₂P₂Ti₂Si₂O [10] and γ -Al₂O₃ [11] or base catalysts such as K/Al₂O₃ [12], basic X-zeolites [13,14] and alkali loaded silica [16,17] have been successfully employed to realize these continuous processes. In general, the solid Brønsted acid catalysts give low oxy-alkylated products because these

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stronger and larger number of acidic sites on the catalyst surface promotes more ring alkylation than side (–O) alkylation reaction [6,17,18]; While the solid base catalysts give the excellent oxy-alkylated products in the alkylation of phenol derivatives [13–17]. For example, Bal and Sivasanker [15] reported that very high conversion (90%) and 100% *O*-methylation selectivity were obtained over Cs-loaded silica for methylation of phenol with methanol, and proposed that the mechanism of the reaction involved the formation of a transient phenolate species on the basic O^{2-} on the surface and the reaction with a $(CH_3)^{\delta+}(OH)^{\delta-}$ species adsorbed on the adjacent alkali ions [4]. However, in the methylation of catechol with methanol, only 75% guaiacol selectivity was obtained over Cs-loaded SiO_2 , this is mainly because this base catalyst could further catalyze the *O*-alkylation of guaiacol to produce about 16% veratrole [17]. Therefore, it is very necessary to find more efficient catalyst for highly selective mono oxy-methylation of catechol with methanol.

As we have known, there is little published work on the solid Lewis acid catalysts for this reaction except for $\gamma-Al_2O_3$ [11]. Here, we reported the preparation and characterization of the $ZnCl_2$ modified $\gamma-Al_2O_3$, and firstly explored the basic catalytic properties of these solid Lewis acid materials in the selective synthesis of guaiacol by the *O*-methylation of catechol with methanol in a fixed bed continuous flow micro-reactor.

2. Experimental

The commercial $\gamma-Al_2O_3$ (the content: $\geq 97\%$, the specific surface area: $167\text{ m}^2\text{ g}^{-1}$, the pore volume: $1.58\text{ cm}^3\text{ g}^{-1}$) and NaY (Si/Al: 5.2, Crystal degree: 85.8%) supports were friendly supplied by Changling Petroleum Chemical Engineering Company of Hunan Yueyang of China. $ZnCl_2$ modified $\gamma-Al_2O_3$ catalysts were prepared by using the mechanical mixture method of $\gamma-Al_2O_3$ with 5–15 wt.% of anhydrous $ZnCl_2$ and activated at 823 K for 2 h in air. HY zeolite was prepared by the exchange of NaY with 1 N NH_4NO_3 aqueous at 363 K for 2 h (the ratio of solid to liquid is 1:5, the exchange processes were repeatedly carried out three times), and then filtration, thoroughly washing with deionized water,

drying at 373 K for 2 h, and finally calcination at 723 K for 4 h in air.

The virtual zinc contents of $ZnCl_2/\gamma-Al_2O_3$ samples calcined at high temperature, were measured by Varian CCD SIMULTANEOUS inductive coupled high frequency plasma-atomic emission spectrometry (ICP-AES); The temperature-programmed desorption of ammonia (NH_3 -TPD) of all the samples were measured by use of CHEMDET-3000 instrument (temperature from 393 to 893 K for $\beta = 12\text{ K min}^{-1}$, He flow rate for 32 ml min^{-1}); The specific surface area and pore volume of the samples were measured by MICROMERIPICS ASAP 2400 low temperature N_2 adsorption apparatus on the basis of the china standard GB/T 5816-1995. Thermal gravimetry and differential scanning calorimetry (TG-DSC) was performed on a NETZSCH-STA409PC from 393 to 1273 K with a heating rate of 10 K min^{-1} in air (20 ml min^{-1}).

The vapor phase alkylation reaction was carried out in a standard flow system at atmospheric pressure. A vertical glass reactor of 15 mm inner diameter filled with 10 cm^3 of the catalyst (20–40 mesh) was used. The substrates, solution of an appropriate methanol with catechol in the molar ratio of 4:1, were introduced through the top of the reactor using a micro-pump applying the load of 0.4 h^{-1} . The alkylation reaction was carried out at 513–593 K. However, at pre-chosen temperatures, after stationary equilibrium had set in (after approximately 1 h), the condensed products were collected and analyzed by Agilent 1100 high performance liquid chromatography (SPD-6AV ultraviolet photometric detector $\lambda = 272\text{ nm}$, Eclipse XRB—C₁₈ column ($4.6\text{ mm} \times 250\text{ mm}$, $5\text{ }\mu\text{m}$), eluent: methanol/water 55/45, flow rate: 0.8 ml min^{-1} , 298 K). The identification of products was carried out by GC–MS.

3. Results and discussion

3.1. NH_3 -TPD

The temperature-programmed desorption of ammonia (NH_3 -TPD) was employed to characterize the acidities of all the $ZnCl_2$ -modified $\gamma-Al_2O_3$ samples. The NH_3 -TPD results listed in Table 1 show that the total acidities of all the

Table 1
Zinc contents, acidic amounts, surface area and porous volume of $ZnCl_2/\gamma-Al_2O_3$ catalysts

Adding amount of $ZnCl_2$ (wt.%)	ICP-AES, Zn content (wt.%)	NH_3 -TPD data ^a		N_2 volumetric adsorption ^b	
		T_m (K)	Total acidity ($\mu\text{mol g}^{-1}$)	S_g ($\text{m}^2\text{ g}^{-1}$)	PV ($\text{cm}^3\text{ g}^{-1}$)
0	0	584	424	167	1.58
5	1.09	601	974	153	1.47
10	1.61	628	1262	142	1.39
15	1.92	632	1237	138	1.35
HY	0	598	1726		

^a The samples were treated at 723 K for 1 h under He atmosphere, and then adsorbed ammonia at 393 K for 0.5 h, finally, the NH_3 -TPD measurement was carried out temperature from 393 to 893 K for $\beta = 12\text{ K min}^{-1}$, He flow rate for 32 ml min^{-1} .

^b Prior to measurement, the samples were degassed at 573 K for 5 h under the vacuum, the N_2 volumetric adsorption was carried out at low temperature (77 K), the special surface area (S_g) and pore volume (PV) were calculated by BET and BJH methods, respectively, on the basis of the N_2 adsorption isotherm.

Table 2
Effects of added amount of ZnCl₂ on the catalytic performances of ZnCl₂/γ-Al₂O₃^a

Added ZnCl ₂ amount (wt.%)	Measured Zn content (wt.%)	Conversion of catechol (%)	Product distribution (%)			Yield of guaiacol (%)
			Guaiacol	Veratrol	C-methylated ^b	
0	0.00	49.0	73.9	2.6	23.5	36.2
5	1.09	73.6	84.0	0.7	15.3	61.8
10	1.61	81.8	90.9	0.1	9.0	67.6
15	1.92	72.5	82.2	4.1	13.7	59.6
FeCl ₂ /γ-Al ₂ O ₃ ^c		56.7	60.6	5.2	34.2	34.4
HY	0.00	11.0	40.4	9.4	50.0	4.4

^a Reaction conditions: 6 g of catalyst pre-treated at 823 K for 4 h in air, m (methanol)/m (catechol) = 4:1; WHSV = 0.4 h⁻¹; reaction temperature: 553 K; reaction time: 4 h.

^b C-methylated products included 3-methyl catechol and 4-methyl catechol.

^c Adding amount of FeCl₂ to γ-Al₂O₃ was 10%, its calcination conditions: at 823 K for 4 h in N₂.

ZnCl₂ modified γ-Al₂O₃ are found to be much more higher than that of unmodified γ-Al₂O₃, their acidic strengths are slightly stronger than that of γ-Al₂O₃. Further compared to the various ZnCl₂/γ-Al₂O₃ samples, may discover that the acidic amounts and strengths of these samples continuously increase as ZnCl₂ loading increases except for ZnCl₂ (15%)/γ-Al₂O₃, which has slightly lower acidic sites than ZnCl₂ (10%)/γ-Al₂O₃.

3.2. ICP-AES

The measured virtual zinc contents of all the ZnCl₂ modified γ-Al₂O₃ samples by ICP-AES are about 1.06–1.92%, and by far lower than the adding quantity of ZnCl₂ in the solid mixture (see Table 1). It is well known that ZnCl₂ has a lower evaporation temperature, and is very easily volatile at the higher temperature. So that a large amount of ZnCl₂ is evaporated and a small amount of ZnCl₂ maintained inside the pore of γ-Al₂O₃ by solid state dispersion and ion exchange in the calcination procedure.

3.3. N₂ volumetric adsorption

The N₂ volumetric adsorption method was employed to measure the specific surface area (*S_g*, m² g⁻¹) and pore volume (PV, cm³ g⁻¹) of γ-Al₂O₃ materials before and after the introduction of ZnCl₂, the measured results are listed in Table 1. It may be clearly discovered that the specific surface area and pore volume of γ-Al₂O₃ continuously decrease as the introducing amount of ZnCl₂ increases, further indicating that the ZnCl₂ has been dispersed inside the pores of γ-Al₂O₃.

3.4. Catalytic performances

The alkylation of catechol with methanol was carried out at 553 K over γ-Al₂O₃, ZnCl₂ or FeCl₂-modified γ-Al₂O₃, and HY, the results shown in Table 2 indicates that γ-Al₂O₃ with lower Lewis acidic sites, itself exhibits the definite catalytic activity (49% of catechol conversion) and selectivity for guaiacol (73.9%). After the modification by ZnCl₂, it be-

comes very active and extremely selective for this reaction, e.g., the high catechol conversion (81.8%), excellent guaiacol selectivity (90.9%) and low C-methylated products (9.0%) can be obtained over ZnCl₂ (10%)/γ-Al₂O₃. This should be relative to the more and stronger Lewis acidic sites on ZnCl₂ modified γ-Al₂O₃. Further compared to the ZnCl₂/γ-Al₂O₃ catalysts with different ZnCl₂ loading may discover that catechol conversion and guaiacol selectivity increase with the ZnCl₂ loading increasing from 5.0 to 10.0%. However, the excess of ZnCl₂ loading (15%) inversely results in the slight decrease in the conversion and selectivity. Hence, ZnCl₂/γ-Al₂O₃ with 10% of ZnCl₂ loading is the optimum catalyst, which is consistent with its large number of acidic sites (see Table 1).

Noteworthy, FeCl₂ modified γ-Al₂O₃ with similar Lewis acidities to ZnCl₂ modified γ-Al₂O₃, does not show expectant excellent catalytic performances, inversely, lower activity (56.7% of conversion), abnormal poor selectivity for guaiacol (only 60.6%) and with a concomitant significant increase in the C-methylated products (34.2%) are observed over it.

In compared to the Lewis acid catalysts, HY, which mainly possesses the Brønsted acidic sites, gives very low catalytic activity and poor O-methylated selectivity (catechol conversion and guaiacol selectivity are only 11.0 and 40.4%, respectively) with a concomitant high selectivity of C-methylated products (50%). some available literatures [5,6,17–19] on the vapor phase alkylation of phenol derivatives over solid acid catalysts suggest that the stronger and larger number of Brønsted acidic sites of the catalysts is more efficient for C-alkylation than O-alkylation of phenol derivatives, our experimental result strongly supports this suggestion.

3.5. Process parameters

More experiments were carried out at different reaction temperature, feed ratio (molar ratio of methanol to catechol) and weight hourly space velocity (WHSV) over ZnCl₂ (10%)/γ-Al₂O₃ catalyst. These data are presented in Tables 3 and 4 and Fig. 1. A general trend of increasing activity with temperature and feed ratio is noticed. For example,

Table 3
Effects of reaction temperature on the catalytic performances of (10%) ZnCl₂/γ-Al₂O₃^a

Temperature (K)	Conversion of catechol (%)	Product distribution (%)			Yield of guaiacol (%)
		Guaiacol	Veratrol	C-methylated	
513	44.2	99.2	0.8	0.0	43.8
533	71.8	90.9	0	9.1	65.3
553	81.8	90.9	0.5	8.6	74.4
573	90.3	70.4	0	29.6	63.6
593	100	51.5	0	48.5	51.5

^a Reaction conditions were the same as Table 2, except for reaction temperature.

Table 4
Effects of the substrate ratios on the catalytic reaction over (10%) ZnCl₂/Al₂O₃^a

M(methanol): m(catechol)	Conversion of catechol (%)	Selectivity of guaiacol (%)
2:1	35.6	90.4
3:1	68.1	91.1
4:1	81.8	90.9
5:1	80.5	91.3
6:1	82.4	92.0

^a Reaction conditions were the same as Table 2, except for m(methanol)/m(catechol).

the increase in catechol conversion is about 1.2-fold to 1.3-fold, when the temperature is increased from 513 to 593 K or the feed ratio is increased from 2:1 to 4:1. With increasing space velocity, there is a continuous decrease in activity; the drop is about 23% when the space velocity is increased 5-fold (from 0.12 to 0.6 h⁻¹). However, the selectivity for guaiacol continuously decreases with concomitant continuous increases in the selectivities of subsequent *O*-methylated product (veratrole) and especially *C*-methylated products as the reaction temperature increasing or the space velocity decreasing. As a result, there are the optimum process parameters (temperature for 553 K, feed ratio for 4:1 and WHSV

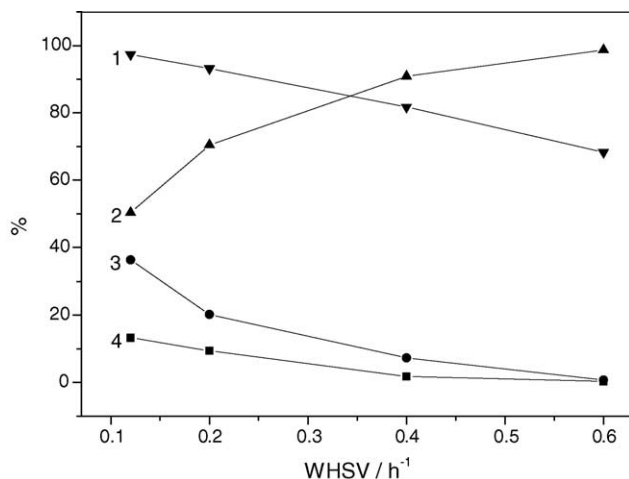


Fig. 1. Effects of space velocity on methylation of catechol with methanol over ZnCl₂ (10%)/γ-Al₂O₃. (1) Conversion of catechol; (2) selectivity for guaiacol; (3) selectivity for *C*-methylated products; (4) selectivity for veratrol.

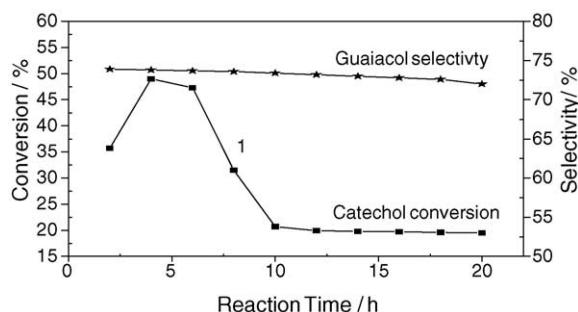


Fig. 2. Effects of reaction time on catechol conversion and guaiacol selectivity over γ-Al₂O₃.

for 0.4 h⁻¹) for obtaining the highest yield of guaiacol over ZnCl₂ (10%)/γ-Al₂O₃.

3.6. Stability of catalyst

The used lifetime of the catalyst is a very key factor in the continuous flow reaction run, and we checked the effects of time on stream on the catalytic properties of γ-Al₂O₃ and ZnCl₂ (10%)/γ-Al₂O₃ catalysts for the methylation of catechol with methanol under the optimum reaction conditions. The results are presented in Figs. 2 and 3. A similar change trend of catechol conversion with the time on stream is observed over two catalysts, namely, high catechol conversion can steadily remain about 7 h over γ-Al₂O₃ and 30 h over ZnCl₂ (10%)/γ-Al₂O₃ in the early periodic run, then conversion dramatically decrease in the medium-stage run (from 47.5 to 20.5% in 7–10 h over γ-Al₂O₃ and from 81 to 35%

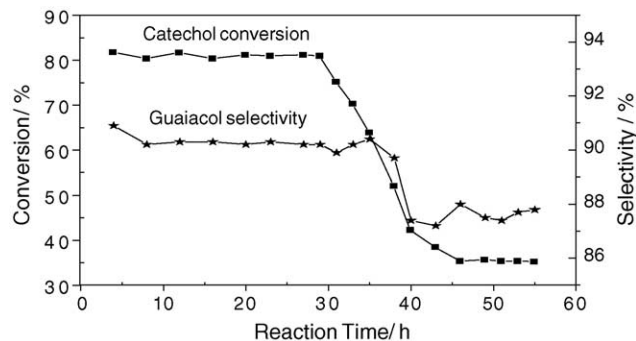


Fig. 3. Effects of reaction time on catechol conversion and guaiacol selectivity over ZnCl₂/γ-Al₂O₃.

Table 5
Measured surface area, porous volume and coking amounts of γ -Al₂O₃ and ZnCl₂/ γ -Al₂O₃

Reaction time (h)	Parameter	ZnCl ₂ loading in γ -Al ₂ O ₃ (%)			
		0	5	10	15
Fresh	S_g (m ² g ⁻¹)	167	153	142	138
	PV (cm ³ g ⁻¹)	1.58	1.47	1.39	1.36
	Coking (wt.%)	–	–	–	–
60	S_g (m ² g ⁻¹)	123	148	133	110
	PV (cm ³ g ⁻¹)	1.30	1.42	1.26	1.05
	Coking (wt.%)	34.77	10.11	27.58	32.43
Average rate of coke deposit (%/h)		0.60	0.16	0.45	0.53

in 30–45 h over ZnCl₂ (10%)/ γ -Al₂O₃, finally, remains at a lower level. The selectivity of guaiacol over the two catalysts slightly decreases with the reaction time going on, but can be basically maintained at a higher level about 73–75% over γ -Al₂O₃ and 87–90% over ZnCl₂ (10%)/ γ -Al₂O₃. The dramatic deactivation of two catalysts all occurred in the medium-stage run, perhaps indicates that gradually accumulating cokes on the catalysts seriously covers the catalyst's active sites and leads to the dramatic drop on the catalyst's activity in this stage. Although two catalysts all exist the deactivation, the deactivation rate of ZnCl₂ modified γ -Al₂O₃ is obviously slower than that of γ -Al₂O₃, this clearly shows that the modification of ZnCl₂ can not only enhance the catalytic activity and selectivity of γ -Al₂O₃, but also improve the stability of γ -Al₂O₃.

3.7. Characterization of coked catalysts

In order to investigate the reasons to result in the deactivation of the catalysts in the run, the specific surface area, pore volume and surface coke deposits of the recovered γ -Al₂O₃ and ZnCl₂ modified γ -Al₂O₃ catalysts after running 60 h were measured by low N₂ volumetric adsorption and TG-DSC methods, and compared to these of their fresh catalysts, the measured results listed in Table 5 make known that the specific surface area and pore volume of the used catalysts all decrease with a concomitant serious coking on them in the different extent, but, the coking amounts on the modified γ -Al₂O₃ samples with a different amounts

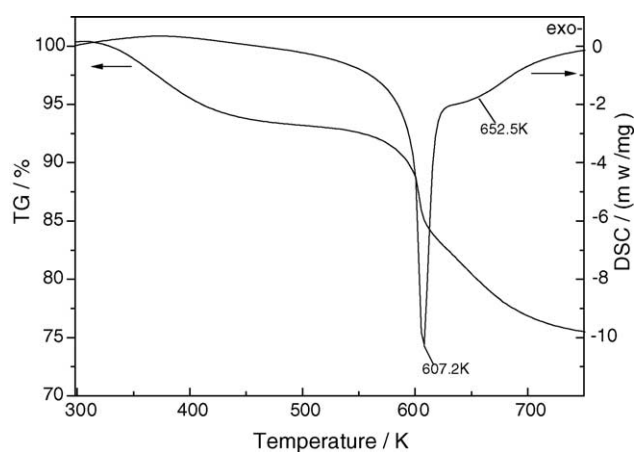


Fig. 4. TG-DSC curves of the coked ZnCl₂/ γ -Al₂O₃.

of ZnCl₂ are obviously lower than that of the unmodified γ -Al₂O₃, indicating that the modification of ZnCl₂ can enhance the resistant-coking capacity of γ -Al₂O₃. A typical TG-DSC curves of the coked ZnCl₂/ γ -Al₂O₃ is presented in Fig. 4. Two exothermic peaks near 607 K (very strong and sharp) and 653 K (very weak and broad) were observed in its DSC curve. The peak at 607 K is attributed to the soluble cokes, which consists of diphenyl ether and its derivatives and can be eliminated by calcinations at lower temperature; while the peak at 653 K is attributed to the insoluble cokes, which consists of polymers of aromatic hydrocarbons with hydrogen-deficiency or graphite-like car-

Table 6
Recycling experiments of γ -Al₂O₃ and ZnCl₂ modified γ -Al₂O₃ catalysts for methylation of catechol with methanol^a

Catalyst	Recycling no.	Zn content (wt.%)	Conversion of catechol (%)	Selectivity of products (%)	
				Guaiacol	C-methylated
γ -Al ₂ O ₃	Fresh	0	49.9	73.5	22.9
	1	0	49.3	72.8	23.7
	2	0	49.7	73.0	22.8
	3	0	49.1	73.2	23.0
ZnCl ₂ / γ -Al ₂ O ₃	Fresh	1.37	79.0	91.9	9.0
	1	0.92	68.5	84.6	14.8
	2	0.58	57.4	77.3	21.7
	3	0.17	48.5	72.8	29.5

^a Measured the average conversion and selectivities of guaiacol and C-methylated products within 7 h over γ -Al₂O₃ and 30 h over ZnCl₂ (10%)/ γ -Al₂O₃.

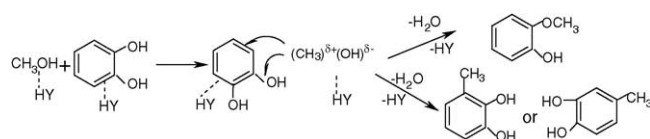
bons and their removal needs a higher calcined temperature [20].

3.8. Recycling tests

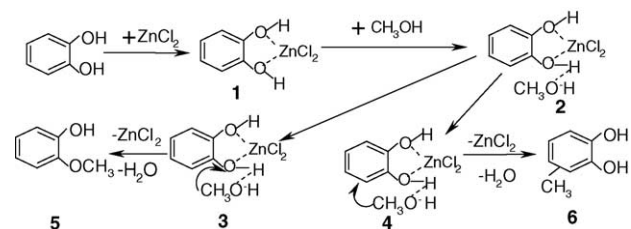
Following recycling experiments of γ -Al₂O₃ and ZnCl₂ (10%)/ γ -Al₂O₃ carried out under the optimum reaction conditions, further prove that the deactivated γ -Al₂O₃ could be recovered and reused many times without any loss of activity by the calcination in air at 773 K for 4 h (see Table 6), indicating that the coking on γ -Al₂O₃ is the only reason to result in its deactivation. However, as for ZnCl₂ (10%)/ γ -Al₂O₃, the measured zinc content, catechol conversion and guaiacol selectivity over the regenerated catalyst each time obviously decrease continuously with recycling times, finally, to near to the reaction results of γ -Al₂O₃. This moment, the total zinc leaching (87.6%) and the drop in catechol conversion (62.9%) after recycling the third times were very serious. This indicates that, except the coking deposits on the surface, the ZnCl₂ leaching on ZnCl₂/ γ -Al₂O₃ in the run should be a more serious factor to lead to its deactivation, therefore, its activity is only partly recovered by the calcination at high temperature in air by removing the coking on its surface. The high leaching of the active component ZnCl₂ may imply that ZnCl₂ is mainly dispersed inside the pores of γ -Al₂O₃ that is lack of the cationic exchange sites, and this dispersed ZnCl₂ is very easily leached by the water vapor liberated by alkylation. A continuous and significant increase in *C*-methylated products with recycling times is most likely that HCl produced by ZnCl₂ leaching could play a significant role in *C*-alkylation.

3.9. Proposed reaction mechanism

Traditionally, liquid or solid Brønsted acid catalysts are active in *C*-alkylation of phenol or its derivatives, An S_N1 type reaction mechanism, which involves that a transient alkyl carbocation species is firstly formed on the H⁺ sites and then attacks the ring *C*-atom of phenol or its derivatives to produce alkyl phenol derivatives, is usually suitable for alkylation of phenol derivatives with isobutyl alcohol [21]; But, Vehi and Swamy [18] reported that the reaction of phenol with 1-propanol proceeded without skeletal isomerization of the propyl moiety over solid acid, suggesting an S_N2 type mechanism, which involves that formation of a transition (C₃H₇)^{δ+}(OH)^{δ-} on the H⁺ sites of catalyst and reacts with phenol derivatives adsorbed the adjacent H⁺ sites. This S_N2 type mechanism, which should be more suitable for methylation over HY than an S_N1 type mechanism because formation of a transient carbocation species by methylating agents is highly unstable, is presented in Scheme 1. As for L-acids catalyze alkylation of phenol derivatives, earlier literatures reported that aluminium phenolate [22,23] and zinc aluminate spinel [24] are active and highly selective for *ortho-C*-methylation of phenol, suggesting that the *ortho*-directing effect of the OH groups by formation of a transient complex with Lewis acid plays a key importance,



Scheme 1. Proposed the reaction mechanism over solid Brønsted acidic catalyst.



Scheme 2. Proposed the reaction mechanism over ZnCl₂ modified solid Lewis acidic catalysts.

but there are little successful reports about *O*-alkylation of mono-hydroxyl benzene derivatives. Why is ZnCl₂ modified γ -Al₂O₃ (included γ -Al₂O₃ itself) Lewis acid very suitable for *O*-alkylation of catechol? We propose that the catechol coordinates with ZnCl₂ on γ -Al₂O₃ giving the donor-acceptor complex **1** which is a strong Brønsted acid [22,23,25]. Following, it is reasonable to suppose that hydrogen bonding between **1** and methanol gives rise to the complex **2**. This interaction has two effects: the simultaneous activation of both the methanol (by H-bonding) and the catechol (by loosening the O–H bond). Finally, whether the activated methanol selects to attack the hydroxyl O atom of the catechol to form a transition complex **3** or the ring C atom of catechol to form a transition complex **4**, should be dependant on the stability of the complex **1**. As it is well known, the coordination ability between the Zn²⁺ ion and the catechol is weak, this weak coordination is more advantageous of the activated methanol further attacking its hydroxyl O atom to obtain guaiacol **5** rather than its ring C atom to obtain *C*-methylated products **6**, and realizing the catalytic cycle of the Zn²⁺ sites. As a result, the high conversion and extremely excellent mono-*oxy*-methylated selectivity can be realized at the same time over the Zn²⁺ sites (see Scheme 2). Our proposed this S_N2 type mechanism may give a reasonable explanation to the results over FeCl₂/ γ -Al₂O₃. Because a transition complex formed by the stronger coordination of Fe²⁺ with catechol has the better stability and the activated methanol may prefer attacking its ring C atom to its hydroxyl O atom. So that the high *C*-methylated selectivity is obtained over it.

4. Conclusion

ZnCl₂ modified γ -Al₂O₃ by the solid state reaction, is very efficient solid L acid catalyst for highly selective preparing guaiacol from vapor phase *O*-methylated of catechol with methanol, under the optimized reaction conditions, 81.8% of

catechol conversion and 90.9% of guaiacol selectivity can be obtained over ZnCl_2 (10%)/ $\gamma\text{-Al}_2\text{O}_3$, which is by far better than that over the solid B acid catalyst (HY). This is a reasonable to suppose that the weak coordination of catechol with the Zn^{2+} sites of $\text{ZnCl}_2/\gamma\text{-Al}_2\text{O}_3$ plays a key impact on the high selectivity for guaiacol. In addition, the modification of ZnCl_2 to $\gamma\text{-Al}_2\text{O}_3$ can not only enhance its catalytic activity and selectivity for guaiacol, but also improve its stability through restraining its surface coking. And the high ZnCl_2 leaching and surface coking deposits of the catalyst in its run are two main reasons to result in its deactivation, this perhaps implies that ZnCl_2 is mainly dispersed inside the pores of $\gamma\text{-Al}_2\text{O}_3$ and this dispersed ZnCl_2 is very easily washed away in the reaction process.

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