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Alkylation of hydroquinone with *tert*-butanol over AlSBA-15 mesoporous molecular sieves

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A series of AlSBA-15 catalysts with different pore size and different Si/Al ratio were prepared and characterized by N_2 adsorption and NH_3-temperature programmed desorption (NH_3-TPD) methods. Their catalytic behaviors for the alkylation of hydroquinone with *tert*-butanol were studied and compared with that of HZSM-5, HY, HAlMCM-41. It is found that the catalytic activity correlates well with the amount of medium-strong acid sites on the surface of the catalysts, and the selectivity towards 2-*tert*-Butylhydroquinone has some connection with the pore size of the catalysts. The reusability of the catalyst depends on its hydrothermal stability, which needs to be improved for the AlSBA-15 catalysts.

KEY WORDS: 2-*tert*-butylhydroquinone; 2,5-di-*tert*-butylhydroquinone; alkylation; mesoporous molecular sieve; AlSBA-15; acidity.

1. Introduction

2-*tert*-Butylhydroquinone (2-TBHQ) is a well-known antioxidant utilized in the food industry because of its excellent antioxidation property and low toxicity. It is also a good stabilizer for plastics or rubbers as well as an important intermediate in the preparation of other chemicals [1]. This compound is conventionally prepared by the alkylation of hydroquinone with *tert*-butanol or isobutylene catalyzed by liquid acids, such as phosphoric acid and sulfuric acid [2,3]. The use of these highly corrosive and polluting liquid acids leads to many serious environmental problems. Solid acids are ideal alternatives, since they are more environmentally benign and have the advantages of easy separation and high reusability.

Various types of solid acids have been employed in the alkylation of hydroquinone or related aromatics. Hojo reported that silica gel was active in the alkylation of hydroquinone, phenol and anisole early in the 1980s [4]. Young and Campbell found Amberlyst-15 was a good catalyst for the alkylation of catechol and other phenols with branched alkenes [5]. Fujita *et al.* discovered ion exchanged layered catalysts could be applied to the alkylation of phenols and naphthols [6]. Yadav *et al.* have investigated the behavior of various K-10 clay supported catalysts in the alkylation of hydroquinone and phenols, and found K-10 supported dodecatungstophosphoric acid had the highest activity [7–10]. They also tried mesoporous material UDCaT-1 as a catalyst for the alkylation of cresol [11]. But the results published were not satisfying due to the low activity, poor selectivity or low stability.

The newly discovered silica mesoporous molecular sieves, synthesized by self-assembly of surfactants or amphiphilic block copolymers, have attracted considerable interest because of their high surface area and uniform hexagonal arrays of cylindrical mesopores, which provide the potential for use as catalysts or catalyst supports for bulky molecules [12,13]. Among them, AlSBA-15 is of particular interest because of its more regular structure, thicker wall and stronger acidity than other types of mesoporous molecular sieves, resulting in much higher catalytic activity and hydrothermal stability [14].

In the present paper, AlSBA-15 with different pore size and different Si/Al ratio were prepared and characterized by N_2 adsorption and NH_3-temperature programmed desorption (NH_3-TPD). The catalytic performance of AlSBA-15 catalysts towards the alkylation of hydroquinone with *tert*-butanol were investigated and compared with that of other solid acid catalysts, such as HZSM-5, HY and HAlMCM-41. The effect of acidity and pore size of the catalysts on the catalytic activity and selectivity is discussed as well.

2. Experimental

2.1. Catalysts preparation

AlSBA-15 was prepared following the procedures in literature [14]. Of 9 ml tetraethyl orthosilicate (TEOS) and the calculated amount of aluminum tri-*sec*-butoxide, to obtain a well-defined Si/Al ratio (5, 10 or 20),

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were added to 10 ml aqueous HCl at pH 1.5. This solution was stirred for over 3 h and then added to 140 ml of aqueous HCl at pH 1.5 containing 4 g triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$, Aldrich) at 313 K. The mixture was stirred for another 1 h and allowed to react at different temperature for 48 h. The solid obtained was filtered, dried at 373 K, and finally calcined in airflow at 823 K or 4 h. These samples are denoted AlSBA$X(T_s)$ where X and T_s represent the Si/Al ratio of reactant gel and the synthesis temperature, respectively.

AlMCM-41 was prepared following the procedure in another literature [15]. An aqueous solution of CTAB and TMAOH were added to a sodium metasilicate solution with vigorous agitation at room temperature, and then the sodium aluminate solution was dropwise added. The resulting gel mixture had a molar composition of SiO_2:0.25CTAB:0.24TMAOH:0.05Al_2O_3:60H_2O. The gel mixture was transferred to a stainless steel autoclave, which was kept in an oven at 373 K. The pH of the gel mixture was adjusted to 11 after heating for 24 h, and this pH adjustment was repeated twice more. The product was filtered, washed, dried in air and calcined in airflow at 813 K for 6 h. The AlMCM-41 samples were ion exchanged with 0.1 mol/l NH_4Cl solution at 368 K several times, and then washed, dried and calcined at 773 K for 12 h to prepare HAlMCM-41 samples.

HZSM-5 zeolite with a Si/Al of 23.4 was supplied by Shanghai No.7 Chemical Dye Factory. NaY zeolite with a Si/Al of 2.6 was supplied by Wenzhou Catalyst Factory. HY was prepared from NaY by ion exchange with NH_4Cl solution and calcined at 573 K.

2.2. Characterization of catalysts

The N_2 adsorption/desorption isotherms were measured on a Micromeritics ASAP2000 instrument at liquid N_2 temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by BET or Langmuir method, and pore size distributions from the adsorption isotherms by BJH method. NH_3-TPD of the samples was carried out in a flow-type fixed-bed reactor at ambient pressure. The catalysts were pretreated at 773 K for 2 h in He flow. The NH_3 adsorption temperature was 393 K, and the temperature was raised at a rate of 10 K/min. The NH_3 desorbed was collected in a liquid N_2 trap and detected by gas chromatography.

2.3. Activity measurement

Alkylation of hydroquinone with *tert*-butanol was carried out in an autoclave equipped with a magnetic stirrer. Typically, 0.5 g hydroquinone, calculated amount *tert*-butanol (according to the *tert*-butanol/hydroquinone molar ratio) and 0.25 g catalyst were added in the autoclave accompanied with 2 g xylene as solvent. The reaction lasts 4 h at 423 K. The products were analyzed with a gas chromatograph equipped with a SE-54 capillary column (30 m × 0.25 mm × 0.3 μm) and a flame ionization detector.

3. Results and discussion

3.1. Textural properties

A series of AlSBA-15 with different pore size and different Si/Al ratio were synthesized using P123 copolymer as template. Their textural properties were characterized by N_2 adsorption/desorption method. The isotherms of all the prepared AlSBA-15 samples look very similar. They are of type IV with a typical H1 hysteresis loop, suggesting that all the AlSBA-15 samples have very regular mesoporous channels despite their different pore size and different Si/Al ratio. Figure 1 shows the N_2 adsorption/desorption isotherm and pore size distribution of the AlSBA10(343) sample, which is selected as the representation. A narrow gaussian pore size distribution can be seen clearly, which is illustrated in figure 1 as well.

The specific surface area, pore volume and the most probable pore diameter of the samples are summarized in table 1 for comparison. The BET surface areas and mesopore volumes of AlSBA-15 are in the range of 534–863 m^2/g and 0.59–1.24 cm^3/g, respectively, which are quite close to that of AlMCM-41 or HAlMCM-41 sample. The pore diameters of AlSBA-15 determined from the pore size distribution curves depend on the preparation temperature. They are in the range of 7.1–12.0 nm, which are much higher than that of the AlMCM-41 or HAlMCM-41 sample. The above results are consistent with those reported before [14].

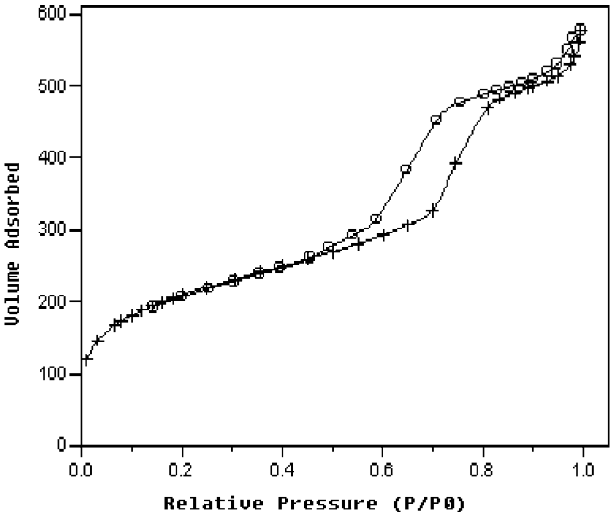

Figure 1. N_2 adsorption/desorption isotherms and pore size distribution (inset) of AlSBA10(343).

Table 1
Composition and properties of the catalysts

Catalyst	Si/Al	Synthesis temperature (K)	Surface area (m^2 /g)	Pore volume (cm^3 /g)	Pore diameter (nm)
AlSBA5(373)	5^{a}	373	534^{c}	0.854	11.7
AlSBA10(373)	10^{a}	373	816^{c}	1.24	12.0
AlSBA20(373)	20^{a}	373	863^{c}	1.23	10.4
AlSBA10(343)	10^{a}	343	721^{c}	0.821	8.3
AlSBA10(323)	10^{a}	323	611^{c}	0.586	7.1
AlMCM-41	10^{a}	373	754^{c}	0.693	3.3
HAlMCM-41	10^{a}	373	525^{c}	0.576	2.9
HY	2.6^{b}	–	912^{d}	0.368	0.74
HZSM-5	23.4^{b}	–	508^{d}	0.188	0.55

[a] Si/Al ratio of reactant gel.
[b] Si/Al ratio determined by NMR.
[c] calculated by BET method.
[d] calculated by Langmuir method.

3.2. *Acidity measurement*

The acidity of the AlSBA-15 samples was measured by NH_3-TPD method. The TPD profiles are given in figure 2. The desorption temperatures and the NH_3 uptakes are listed in table 2, together with the data of AlMCM-41, HAlMCM-41, HY and HZSM-5 for comparison. Since the AlMCM-41 sample was synthesized from a reaction mixture with excess Na^+, ion exchange with $NH_4{}^+$ is carried out to forms HAlMCM-41 sample. Similar to HAlMCM-41, there is only one asymmetric broad peak on the TPD profiles of the AlSBA-15 samples. The peak temperatures are in the range of 560–583 K, about 30–50 K higher than HAlMCM-41, showing that the acid strengths of the AlSBA-15 samples are stronger than those of HAlMCM-41. Nevertheless, the acid strength of AlSBA-15 samples is still lower than zeolites, such as HY and HZSM-5, which may be due to their amorphous silica-alumina framework. However, there are fewer acid sites on the AlSBA-15 samples than on the HAlMCM-41 sample. The number of acid sites on AlSBA-15 increases with a decrease in Si/Al ratio. The AlSBA5(373) sample is an exception, since a great number of aluminum may be not incorporated into the framework at such a low Si/Al ratio.

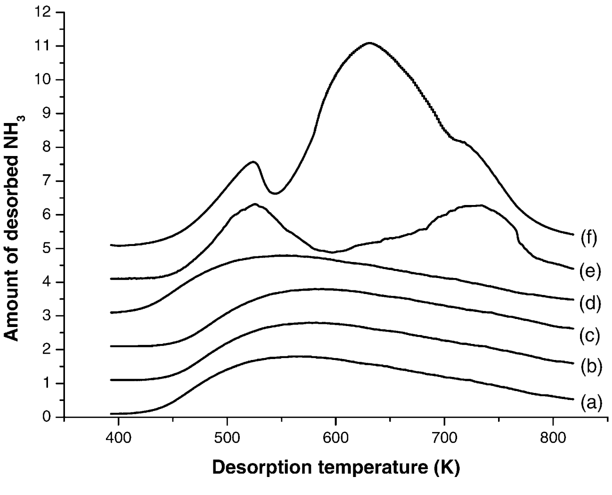

Figure 2. NH_3-TPD profiles of (a) AlSBA5(373); (b) AlSBA10(373); (c) AlSBA20(373); (d) HAlMCM-41; (e) HZSM-5; and (f) HY.

3.3. *Catalytic performance*

The activities of various AlSBA-15 samples for the alkylation of hydroquinone were tested, and the results were listed in Table 3, together with those of AlMCM-41, HAlMCM-41, HY and HZSM-5 for comparison. 2-*tert*-butylhydroquinone and 2,5-di-*tert*-butylhydroquinone are the only two products found after the reactions. No other by-products such as ether or paraffin are formed during the reaction.

3.3.1. *Effect of acidity of the catalysts*

Alkylation of hydroquinone with *tert*-butanol is a typical Friedel–Crafts reaction catalyzed by acid, so the acidity of the catalysts must play an important role in this reaction. From table 3 we can see that high selectivity towards 2-*tert*-butylhydroquinone is obtained over the all AlSBA-15 catalysts. Especially on the AlSBA10(323) catalyst, no by-product was formed in the reaction and 100% selectivity is achieved with 2-TBHQ

Table 2
NH_3-TPD data of the catalysts

Catalyst	Peak temperature (K)	NH_3 desorbed (mmol/g)
AlSBA5(373)	566	0.53
AlSBA10(373)	580	0.59
AlSBA20(373)	583	0.48
AlSBA10(343)	574	0.79
AlSBA10(323)	560	0.70
AlMCM-41	498	0.48
HAlMCM-41	533	0.95
HY	524/631	3.45
HZSM-5	526/734	0.75

Table 3
Activity for alkylation of phenol over various catalysts

Catalyst	Conversion (%)	Selectivity (%)		Yield (%)
		2-TBHQ	2,5-DTBHQ	
AlSBA5(373)	51.0	83.3	16.7	42.5
AlSBA10(373)	64.2	74.7	25.3	47.9
AlSBA20(373)	53.7	75.9	24.1	40.7
AlSBA10(343)	64.5	80.5	19.5	52.0
AlSBA10(323)	40.2	100	0	40.2
AlSBA10(323)[a]	62.0	92.1	7.9	57.1
AlMCM-41	0	0	0	0
HAlMCM-41	17.9	100	0	17.9
HY	25.2	100	0	25.2
HZSM-5	20.0	100	0	20.0

[a] The catalyst loading is 0.3 g.

yield of 40.2%. Since the product 2-TBHQ and the by-product 2,5-DTBHQ are very difficult to separate owing to their close boiling points, this result is inspiring, which will lead to a easy way to produce 2-TBHQ with high purity.

The conversion of hydroquinone over AlSBA-15 catalysts is much higher than that of HAlMCM-41 catalysts though the amount of acid sites on HAlMCM-41 is larger than that on AlSBA-15 samples. The marked difference in catalytic activity between the two types of catalysts may be due to their different acid strength, as revealed by the NH_3-TPD results. The stronger the acid sites present on the catalysts, the higher the activity reaches. This is why no activity is found over AlMCM-41 catalyst while a conversion of 53.7% was reached over AlSBA20(373) catalyst, though there was almost the same amount of acid sites on the two catalysts. The above results imply that the alkylation of hydroquinone with *tert*-butanol takes place on the medium-strong acid sites, the acid sites of weak strength are inactive for this reaction. The increased activity of AlSBA-15 catalysts is associated with the increased amount of the medium-strong acid sites not the increased total amount of the acid sites on the surface of the catalysts. This can also explain the difference in catalytic activities among the AlSBA-15 catalysts with the closed acid strength, for example, the more amount of the acid sites is found on the AlSBA10(373) catalyst than that on AlSBA20(373), the higher activity was reached on AlSBA10(373).

3.3.2. *Effect of pore size of the catalysts*

It can be seen clearly that zeolites including HY and HZSM-5 exhibit relatively low activity compared with the AlSBA-15 catalysts though they have more medium-strong acid sites than the AlSBA-15 catalysts. The possible explanation may come from the marked difference in pore structure between the two types of the catalysts. The pore size of HY and HZSM-5 zeolites, which is 0.74 and 0.55 nm, respectively, is relatively too small compared with the bulky reactant and product molecules (~1 nm of kinetic diameter). In that case, the mass transfer resistance becomes very seriously and the accessibility of the active sites inside the pores is highly restricted during the liquid-phase reaction. The alkylation would take place mainly on the external surface of the catalyst and only the acid sites on the external surface could act as the active sites for the reaction. This may account for the poor activity of zeolite catalysts. On the contrary, the pore size of AlSBA-15 catalysts is large enough for the bulky reactant molecules to come into and out of the pore channel freely. No evident mass transfer resistance could be observed then.

The pore size of the catalysts has also some effect on the selectivity of the catalysts besides the acidity. The selectivity to 2-TBHQ increases from 74.7% to 92.1% at comparable conversion with decreasing of the pore size of the catalysts. This is because the by-product 2,5-DTBHQ molecule is larger than the product 2-TBHQ molecule, relatively small pore size of the catalysts will lead to larger difference of the diffusion between 2-TBHQ and 2,5-DTBHQ, resulting a high selectivity to 2-TBHQ. A similar result was observed in the catalytic alkylation of 4-*tert*-butylphenol with styrene [16].

3.3.3. *Effect of reaction conditions*

The effect of molar ratio of *tert*-butanol to hydroquinone on the alkylation reaction over AlSBA10(343) has been investigated and shown in Figure 3. With the increasing of the molar ratio of *tert*-butanol to hydroquinone, the conversion of hydroquinone increases while the selectivity to 2-TBHQ decreases. The reason is that the alkylation of hydroquinone with *tert*-butanol is a consecutive reaction, including the alkylation of hydroquinone with *tert*-butanol to form 2-TBHQ and the alkylation of 2-TBHQ with *tert*-butanol to form 2,5-DTBHQ, more *tert*-butanol favors the both alkylation reactions, leading to consumption more *tert*-butanol and formation more by-products 2,5-DTBHQ.

The effect of reaction temperature on the alkylation of hydroquinone over AlSBA10(343) catalyst was also

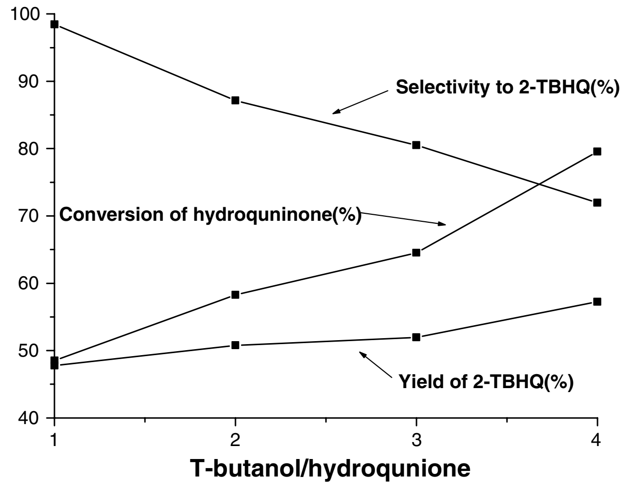

Figure 3. Effect of *tert*-butanol to hydroquinone molar ratio on the alkylation reaction over AlSBA10(343).

studied and the results were shown in table 4. An increase in conversion of hydroquinone can be observed with the increase in temperature, especially from 403 to 423 K. But the selectivity towards 2-TBHQ decreases, due to an increased rate of reaction towards formation of 2,5-DTBHQ. The optimum yield can be obtained at the reaction temperature of 423 K.

3.3.4. Reusability of the catalyst

The reusability of AlSBA(343) catalyst was also tested. After reaction, the catalyst was filtered off, washed with ethanol, dried and calcined in air at 723 K for 3 h. Table 5 shows the reusability of the catalyst for three runs. The catalyst deactivates rapidly after each run, the conversion of hydroquinone decreases from 64.5% to 18.3% during the three runs. To understand the reason of this poor stability, the textural property and the acidity of the catalyst after each run were characterized. The results listed in table 6 shows that the specific surface area and the pore volume of the catalyst decreases markedly after reaction, indicating that some of the mesoporous structure collapsed during the reaction, leading to a rapid decrease in the number of active sites. This was due to the poor hydrothermal stability of the catalyst under relatively high temperature and pressure, as reported before [12,14,17].

4. Conclusions

The alkylation of hydroquinone with *tert*-butanol over AlSBA-15 mesoporous molecular sieves has been studied systematically and compared with HAlMCM-41, HY and HZSM-5. AlSBA10(343) catalyst is found to be the most active catalyst for this reaction. The

Table 4
Effect of reaction temperature on the alkylation reaction over AlSBA10(343)[a]

Temperature (K)	Conversion (%)	Selectivity (%)		Yield (%)
		2-TBHQ	2,5-DTBHQ	
403	34.6	94.3	5.7	32.6
423	64.5	80.5	19.5	52.0
443	73.1	66.6	33.4	48.6

[a]The *tert*-butanol to hydroquinone molar ratio is 3 in the reaction.

Table 5
Effect of reusability of AlSBA10(343) on alkylation reaction

Run	Conversion (%)	Selectivity (%)		Yield (%)
		2-TBHQ	2,5-DTBHQ	
1	64.5	80.5	19.5	52.0
2	28.7	100	0	28.7
3	18.3	100	0	18.3

Table 6
Properties of fresh and used catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Peak temperature (K)	NH_3 desorbed (mmol/g)
Fresh	721	0.821	8.3	574	0.79
First use	430	0.664	9.5	540	0.61
Second use	384	0.640	9.6	520	0.52

conversion of hydroquinone and the yield of 2-TBHQ at 423 K are 64.5% and 52.0%, respectively. The activity of the mesoporous molecular sieves correlates well with the amount of medium-strong acid sites on the surface, and the selectivity towards 2-TBHQ has some connection with the pore size of the catalysts. The reusability of the catalysts depends on the hydrothermal stability, which needs to be improved for the AlSBA-15 catalysts.

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