Phenol etherification with methanol to anisol on supported Cs catalysts

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Abstract: The effect of acid and basic sites, support, cesium precursor and cesium loading on the performance of supported Cs catalysts in the etherification of phenol with methanol to anisole was investigated. The results show that the cation of basic site plays an important role in the selective conversion of phenol to anisole. Moreover, the support has an influence on the cesium site, which leads to different activity and selectivity. Cs/SiO_2 prepared with various precursors are different in the amount of surface Cs species, as a result of different activity on them.

Keywords: phenol, anisol, etherification.

1. Introduction

Medium- and Low-temperature coal tar contains a lot of phenols, especially phenol and methylphenol. These phenols are easily deoxygenated in hydrogenation process, leading to value reduction and increase of hydrogen consumption [1, 2].The traditional way is to cut out the phenol oil from coal tar, and then extract the value-added phenols [2, 3].However, this process generates a large amount of acid and alkali waste liquid [2,4]. In the light of abundant phenols in phenol oil with boiling point below 200 ^{o}C and high octane number of anisol and methylanisol, direct conversion of phenol oil with methanol to gasoline blend oil is a promising clean way.

This work studied the effect of different acid and basic sites, support, Cs precusors and Cs loading on the catalyst performance in the etherification of phenol with methanol to anisole, in order to provide some guidance to the phenol oil etherification with methanol to high octane oil.

2. Experimental (or Theoretical)

The catalysts were prepared by wet-impregnation method. They were first dried at room temperature and then at 120 ^{o}C. After that, they were calcinated at 600 ^{o}C for 6 h with a temperature rising rate of 5 ^{o}C/h.

XRD, CO_2-TPD, Raman, XPS and TG analysis were done to characterized these catalysts.

The reaction was carried out on a fix-bed. A mixture of phenol and methanol was pumped into the reactor with N_2 as the carrier gas. The reactant and products were analyzed by GC.

3. Results and discussion

Different kinds of SiO_2 supported catalysts were examined, as shown in Table 1. Both acid and basic sites improves the phenol conversion. However, basic sites has better anisol selectivity than acid sites. Moreover, the anisol selectivites on K/SiO_2 and Cs/SiO_2 are larger than that on Ba/SiO_2, which indicates not only the alkalinity but also the cation influences the selectivity.

Table 1. Phenol conversion and product selectivity on different SiO_2 supported catalysts

Catalyst	Conversion	Selectivity *s*/%						
	x/%	Anisol	2-MA①	3/4-MA①	o-cresol	m/p-cresol	Xylenol	others
$H_4Si(W_3O_{10})_4/SiO_2$	9.0	22.7	1.2	0.6	36.7	8.4	5.7	24.7
$AlCl_3/SiO_2$	71.9	33.9	6.9	2.9	20.0	4.2	16.2	15.9
K/SiO_2	6.3	95.4	0.7	0.3	1.5	0.3	0.2	1.6

Cs/SiO$_2$	36.0	98.7	0.2	~0.0	0.3	0.1	~0.0	0.7
Ba/SiO$_2$	15.0	88.0	0.5	0.3	7.0	1.6	0.4	2.2
SiO$_2$	1.4	63.6	4.0	2.0	13.7	3.8	5.1	7.8

①: 2-methylanisol(2-MA), 3-methylanisol(3-MA), 4-methylanisol(4-MA).

note: 400 °C, LHSV=1.0 h^{-1}, N$_2$ 20 mL/min, TOS~5 h, H, Al, Ba, Cs, Rb, K, Na loading~0.5 mmol/g (CH$_3$COOCs as the precusor).

With the same Cs loading of 0.5 mmol/g, Cs/SiO$_2$ prepared by different cesium precusors of CH$_3$COOCs, CsNO$_3$ and Cs$_2$CO$_3$ have different activities (Figure 1). The catalyst prepared by Cs$_2$CO$_3$ has high phenol conversion of 53.1%, closely followed by the catalyst prepared with CsNO$_3$ of 50.7% conversion. However, the phenol conversion on the catalyst prepared by CH$_3$COOCs is as low as 36%. This differency was related to the amount of surface Cs species.

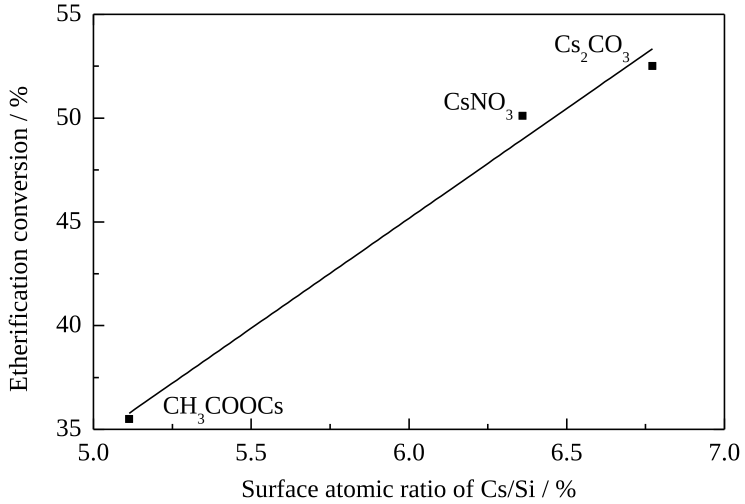

Figure 1. Relationship between phenol etherification conversion and the surface atomic ratio of Cs/Si. Reaction conditions:400 °C, LHSV=1.0h^{-1},N$_2$ flow of 20 mL/min,TOS =5 h,Cs loading of 0.5mmol/g.

4. Conclusions

Phenol etherification reaction on some different acid and basic catalysts were studied. It shows that basic catalyst has better anisol selectivity than acid catalyst. The cation ion of the basic site also influences anisol selectivity. The cesium catalysts with various supports have different activities. Compared with HY, SiO$_2$-Al$_2$O$_3$, Al$_2$O$_3$, MgO-Al$_2$O$_3$(3/7) and MgO-Al$_2$O$_3$(7/3), SiO$_2$ supported cesium catalyst has the highest phenol etherification activity and the best anisol selectivity. It seems that there is electron interaction between the support and cesium species. Cs^{x+} species with higher electron binding energy shows better activity. Differently, the anisol selectivities on these different supports were mainly related to the basicity. The etherification is favorite on the weak basic sites, but the side reaction is easy to occur on the stong basic sites. The differency of activity on Cs/SiO$_2$ prepared by various cesium precursors is more likely due to the different amount of surface cesium species. Cs/SiO$_2$ with a single layer dispersal of nearly 1.0 mmol/g has the best activity.

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