Catalysis Letters Vol. 104, Nos. 1–2, October 2005 (© 2005)
DOI: 10.1007/s10562-005-7438-x

Spinel-Type cobalt chromites as novel and highly *ortho*-selective catalysts for phenol alkylation

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Received 15 April 2005; accepted 2 July 2005

The gas phase catalytic alkylation of phenol with methanol was investigated over a series of spinel-type cobalt chromite catalysts. The molar ratio of Co/Cr and the calcination temperature have considerable effect on the catalytic performance of the samples. Among them, the Co/Cr = 0.8 sample calcined at 723 K shows the highest activity (97.3% phenol conversion) with a total 94.8% *ortho*-selectivity to *o*-cresol and 2,6-xylenol at the reaction temperature of 693 K.

KEY WORDS: Cobalt chromite; Phenol alkylation; *o*-Cresol; 2,6-Xylenol.

1. Introduction

Alkylation of aromatic substrates is a class of reactions important both academically and industrially [1–8]. Currently, there is a significant interest in the alkylation of phenol with methanol, since several organic compounds (e.g. *o*-cresol and 2,6-xylenol) prepared through the alkylation of phenol are important intermediates for the production of herbicides, polyphenylene oxide (PPO) and special grade paints [5,8]. Many kinds of materials have been investigated as catalysts for the reaction, including various zeolites, pure and mixed metal oxides, hydrotalcites etc. [5–8]. However, most of the tested catalysts show mixed selectivities forming both O- and C-alkylated products, while some others exhibit unsatisfactory stability mainly caused by coking [9,10].

Recently, a few research groups reported independently that a series of ferrospinels containing cations such as Zn, Co, Ni and Cu exhibited very high activity and high selectivity to *ortho*-alkylation for the phenol alkylation [11–13]. It was proposed that the presence appropriate acidity, which depends strongly on the distribution of transition metal cations among the available tetrahedral and octahedral sites in the ferrospinels, plays a dominating role for the phenol methylation [11].

Previously, spinel-type cobalt chromites have showed special catalytic performance in various chemical processes, such as water gas shift reaction, combustion catalysis and the total oxidation of halogenated hydrocarbons [14–18]. In this work, we attempt to use the spinel-type cobalt chromites as novel catalysts for the *ortho*-alkylation of phenol with methanol. The effect of the Co/Cr ratio and the calcination temperature on the catalytic properties was investigated. All the samples were characterized by means of XRD, TEM, N_2-adsorption/desorption and NH_3-TPD in order to build a relationship between the structure, acid–base properties and the catalytic performance.

2. Experimental

2.1. Catalyst preparation

Spinel-type cobalt chromites were synthesized by coprecipitation method following a reference procedure [14]. Typically, a diluted aqueous ammonia (10 wt%) solution was added to a mixed aqueous solution of chromium nitrate and cobalt nitrate under continuous stirring at room temperature until pH 9.3 was achieved. The filtered precipitate was dried and calcined at desired temperature for 5 h. The available powders were ready for the alkylation activity measurements after being crushed and sieved (40–60 mesh).

2.2. Catalyst characterization

XRD patterns were recorded on a Lab XRD-6000 X-ray Diffractometer with nickel-filtered Cu K_α radiation operating at 40 kV and 30 mA in a 2θ range of 10–70 ° TEM images were performed on a Hitachi H-8100 electron microscope operating at 200 kV.

Nitrogen adsorption–desorption isotherms were performed using a Micromeritics ASAP2010N sorptometer. The samples were pre-treated under N_2 stream at 523 K for 6 h prior to measurement. The total pore volume and the mean pore diameter were evaluated from the adsorption branches of the nitrogen isotherm using the BJH model.

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Temperature-programmed desorption of NH_3 (NH_3-TPD) was carried out on the self-made instrument [3]. In a standard procedure, 100 mg of fresh sample was first calcined at 723 K under Ar stream for 1 h, then cooled down to 323 K and exposed to a certain amount of ammonia for 0.5 h. After the system was purged with flowing Ar for 2 h at 323 K, the sample was heated at the rate of 10 K min^{-1} in He (30 ml min^{-1}), the concentration change of the desorbed NH_3 was monitored by using an on-line thermal conductivity detector (TCD).

2.3. Catalytic tests

The vapor phase alkylation of phenol with methanol was carried out in a fixed bed continuous down-flow reactor at atmospheric pressure. Before the start of the reaction, 0.8 g of catalyst was activated at 693 K for 1 h in nitrogen in a glass-tube reactor (I.D. = 0.8 cm and Length = 40 cm). A pre-mixed phenol–methanol mixture was then fed from the top of the reactor using a SY-04 syringe pump along with N_2 gas (3.2 ml min^{-1}). The reaction conditions are as follows: phenol/methanol = 1/5 (mole ratio), reaction temperature = 693 K, weight hourly space velocity (WHSV) = 0.897 h^{-1}. The products were analysed by a gas chromatograph equipped with a HP-5 capillary column and identified with known standards and GC-MS.

3. Results and discussion

3.1. Characterization results

The XRD patterns of various cobalt chromite samples are displayed in figure 1. All the samples with different Co/Cr ratios show the characteristic diffraction peaks of the spinel phase (see figure 1a). For the Cr rich samples (Co/Cr = 0.2, 0.5), additional diffraction peaks corresponding to Cr_2O_3 phase can also be observed. With the increase of Co contents (Co/Cr > 0.5), the crystallinity of the spinel phase increase. This result might be explained by the formation of a more uniform structure, like $Co^{2+}\,Co^{3+}{}_{x}Cr^{3+}{}_{2\text{-}x}O_4$ solid solutions, as suggested by Castiglioni *et al.* [19]. For the Co/Cr = 0.8 samples calcined at different temperatures (see figure 1b), an increase in the calcination temperature leads to a considerable increase in the peak intensity of the sample. Meanwhile, the widths of the diffraction peaks become narrower with the increase of calcination temperature, indicating that the size of particles increases, which can be further confirmed by the TEM images (see figure 2).

Moreover, the textural properties of various cobalt chromite samples measured from N_2-adsorption isotherms are presented in table 1. It can be seen that three samples with the Co/Cr ratios of 0.5, 0.8 and 1.0 exhibit higher BET surface areas than others. Additionally, for the samples with Co/Cr ratio of 0.8, the BET surface area decreases notably with the increase of calcination temperature.

Figure 3a shows the NH_3-TPD profiles of cobalt chromites with different Co/Cr ratios. For the Co/Cr = 0.2 sample, two desorption peaks appeared at around 430 and 543 K can be assigned to weak and intermediate acidic sites, respectively. As the ratio of Co/Cr increases from 0.2 to 0.8, the areas of the two desorbed peaks increase, and the position of the low-temperature desorption peak (T_{max}) shifts slightly to higher temperatures. Especially, a new high-temperature desoption peak at around 670 K appears in the TPD profile of Co/Cr = 0.8 sample, indicating that the existence of relatively strong acidic sites in this sample. With further increase in the ratio of Co/Cr, the total acidic amount decreases gradually and reaches to the lowest level when the Co/Cr ratio is 2.5.

For a stoichiometric $CoCr_2O_4$ with normal spinel structure, it is known that Cr^{3+} is generally located at octahedral sites (O_h), and Co^{2+} is in tetrahedral sites. Previously, Jacobs *et al.* [20] have revealed that mainly O_h sites cations are exposed on the surface of spinels, thus O_h cations play a dominating role in determining the surface acidity. Besides, it is also known that the acid–base properties of spinel-type compound depend strongly on the extent of polarity of the metal cation and

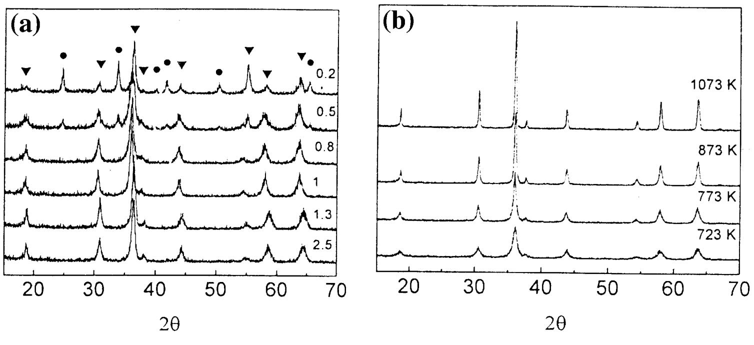

Figure 1. Powder XRD patterns for (a) cobalt chromite samples with different Co/Cr ratios calcined at 723 K, and (b) Co/Cr = 0.8 samples calcined at different temperatures. Characteristic diffraction peaks of spinel phase (▼) and Cr_2O_3 (●) are indicated.

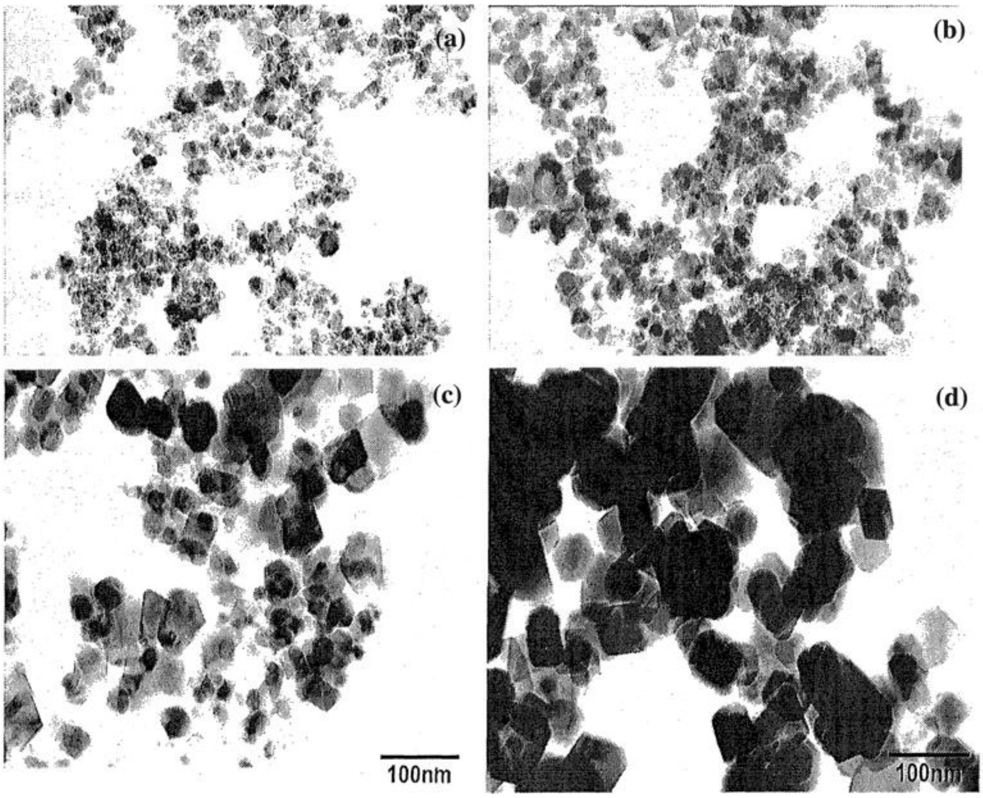

Figure 2. Representative TEM images of Co/Cr = 0.8 samples calcined at different temperatures: (a) 723 K, (b) 773 K, (c) 873 K, (d) 1073 K.

Table 1
Selected physical data for various cobalt chromite samples

Samples	Co/Cr (mol)	Calcination temp. (K)	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
1	0.2	723	35	0.12
2	0.5	723	66	0.28
3	0.8	723	67	0.31
4	1.0	723	63	0.24
5	1.3	723	49	0.23
6	2.5	723	29	0.18
7	0.8	773	50	0.24
8	0.8	873	25	0.17
9	0.8	1073	7	0.03

the oxygen anion respectively [11]. Therefore, we suppose that the decrease of the acidic amount with the Co/Cr ratio (above 0.5 should be mainly caused by the partial substitution of Cr^{3+} ions by Co^{3+} ions in the O_h sites of the spinel-type cobalt chromites.

For the Co/Cr = 0.8 samples calcined at various temperatures (see figure 3b), the amount of NH_3 desorption decreases obviously with the increase of calcination temperature. The desorption peak corresponded to the strong acid sites is nearly undetectable when the calcination temperature reaches to 1073 K. These results suggest that both the acidic amount and acidic strength of the cobalt chromites can be also considerably influenced by calcined temperature.

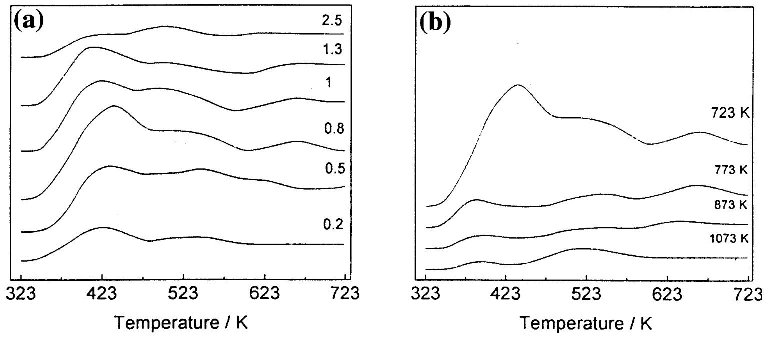

Figure 3. NH_3-TPD profile of (a) cobalt chromite samples with different Co/Cr ratios calcined at 723 K and (b) Co/Cr = 0.8 samples calcined at different temperatures.

Table 2
Catalytic properties of cobalt chromite samples with different Co/Cr ratios calcined at 723 K

Samples	Co/Cr (mol)	Conv. (%)	Product selectivity (%)				Yield (%)	
			o-cresol	2,6-xylenol	anisole	Others[a]	*o*-cresol	2,6-xylenol
1	0.2	73.2	70.4	22.6	1.6	5.4	51.5	16.5
2	0.5	90.5	48.6	43.1	1.6	6.7	44.0	39.0
3	0.8	97.3	42.2	52.6	0.6	4.6	41.1	51.2
4	1.0	89.9	65.3	30.1	0.5	4.1	58.7	27.0
5	1.3	82.3	75.6	21.2	0.5	2.7	62.2	17.4
6	2.5	43.7	81.1	12.0	1.1	5.8	35.4	5.2

Reaction conditions, m_{cat} = 0.8 g; phenol/methanol = 1/5 mol; WHSV = 0.897 h^{-1}; reaction temperature = 693 K; reaction time = 3–4 h; nitrogen flow rate 3.2 ml min^{-1}.

[a] Other side products include alkyl phenols.

3.2. Catalytic performance

Some representative catalytic data for the alkylation of phenol with methanol over various cobalt chromites are presented in table 2. It is seen that all the catalysts are active and highly selective for methylating phenol in the *ortho* position leading to *o*-cresol and 2,6-xylenol as the major products. For the Co/Cr = 0.2 sample, the phenol conversion is 73.2%, with a 70.4% selectivity to *o*-cresol and a 22.6% selectivity to 2,6-xylenol. As the ratio of Co/Cr increases from 0.2 to 0.8, the conversion of phenol increases and reaches to a maximum of 97.3%, while the selectivity to 2,6-xylenol increases to 52.6% accompanied with the decrease of *o*-cresol selectivity. With further increase the ratio of Co/Cr, the phenol conversion and the selectivity to 2,6-xylenol decrease, while the selectivity to *o*-cresol increases gradually. However, the total *ortho*-selectivity is nearly no change, kept up at a very high level (>91%) regardless of the composition of the samples.

The effect of calcination temperature on the catalytic performance was investigated over Co/Cr = 0.8 samples (figure 4). Obviously, the phenol conversion decreases rapidly with the increase of calcination temperature. When the calcination temperature increases from 723 K to 1023 K, the selectivity towards *o*-cresol increases from 42.2% to 87.5%, accompanied with a decrease in 2,6-xylenol selectivity from 52.6% to 9.9%. By comparing with the characterization results, it can be seen that the change of catalytic activity of cobalt chromites has a similar trend, to the BET surface and acid amount. Such as the Co/Cr = 0.8 sample calcined at 723 K, bearing the highest BET surface and acidic amount, exhibits the highest catalytic activity for the alkylation of phenol. It should be pointed out that no obvious carbon deposition can be observed on all the cobalt chromite catalysts after the catalytic tests, and the catalytic activity is maintained with only a slight decrease during the whole reaction process. These results suggest that the cobalt chromites exhibit good stability for the reaction of phenol alkylation.

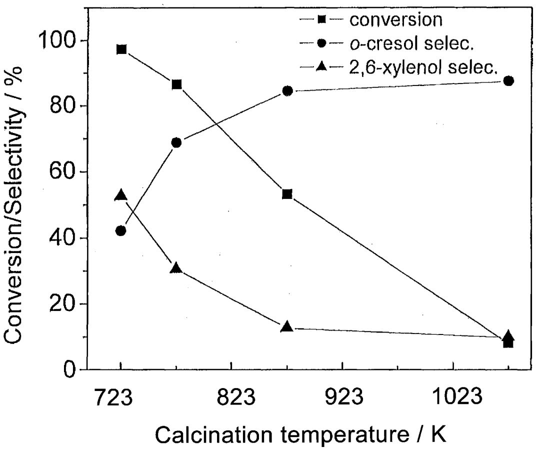

Figure 4. Catalytic properties over Co/Cr = 0.8 samples calcined at different temperatures.

Previously, it is well known that the alkylation of phenol is very sensitive to the acidic and basic properties of the catalysts, while strong acidity favors the C-alkylation and basic catalysts are found to promote O-alkylation [5]. Recently, Sreekumar and Sugunan proposed that the stronger acid sites are responsible for the formation of 2,6-xylenol, whereas the weaker acid sites are in favor of the *o*-cresol by the study of phenol methylation over ferrospinels [12]. In the present case, we suppose that the uniform crystallinity spinel phase and the special acidity of the cobalt chromite should be important factors for the remarkably high *ortho*-selectivity (C-alkylation). Further work is still required in order to understand the concrete role of the spinel structure and the surface acid–base properties on the catalytic performance of cobalt chromite catalysts.

4. Conclusion

In summary, the spinel-type cobalt chromite catalysts exhibit superior performance for the gas phase catalytic *ortho*-alkylation of phenol with methanol. The Co/Cr ratio and the calcination temperature can considerably influence the surface area and acidity of the catalysts, thus changing the catalytic activity and selectivity for the phenol alkylation reaction.

Acknowledgments

This work was supported by the Development Project of Science and Technology of Jilin Province (20040563), and the Specialized Research Fund for the Doctoral Program of Higher Education (20040183003), China.

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