The Influences of Reductant on the Strcuture and Catalytic Activity of Co-MCM41 with High Cobalt Content

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Introduction

The incorporation of heteroatoms into mesoporous silicates has attracted much attention due to their lack of sufficient acidity and redox properties.[1] Co-MCM-41 shows high catalytic activity in the hydroxylation of hydrocarbon [2], but the cobalt content in the framework is usually very low, and the selectivity needs to be improved. In the present work, a series of Co-MCM-41s with different cobalt content were synthesized with the addition of ascorbic acid as reductant. Their catalytic performances in the direct hydroxylation of benzene by H_2O_2 were also investigated. Results indicated that most of the atoms of cobalt were in the framework of MCM41 and the addition of VC can improve the structure and catalytic activity of the materials greatly. The selectivity of phenol was 100% and acetic acid was the preferred solvent for the catalytic reaction.

Materials and Methods

The catalysts were synthesized by traditional sol-gel method, except adding VC as reductant. The products with molar ratio of xCo: 100Si (x = 5-20) in the gel were designated as xCo. Also, products synthesized without the addition of VC were designated as xCo-1. The cobalt contents were analyzed by ICP. The mseoporous structures were identified by XRD (Philips PW 170 diffract meter) and HRTEM techniques. Surface areas and pore properties were obtained on Micromeritics ASAP-2020 analyzer. FT-IR was recorded on a Bruker VECTOR22 instrument, using KBr as support. Benzene hydroxylation was carried out in a three-necked flask (50 ml) equipped with a magnetic stirrer and a reflux condenser.
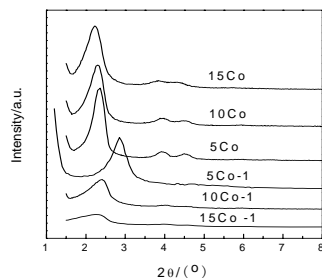
Results and Discussion
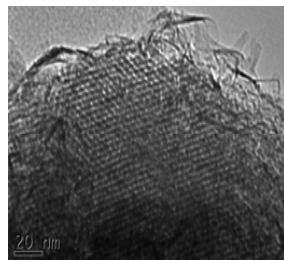

Figure 1. XRD patterns of some samples   **Figure.2** HRTEM image of 20Co sample

The small angel XRD patterns (Fig.1) and the type IV isotherms suggested the MCM-41 type hexagonal mesoporous structure and narrow pore size distribution of the samples [3], which were confirmed by the HRTEM image (Fig.2). xCo samples showed better mesoporous structure compared with xCo-1, probably because the redundant can change the statuses and the coordination environment of cobalt.

No diffraction peaks were found in the high angle XRD patterns, suggesting the atoms of cobalt might be in the framework or highly dispersed on the wall of MCM-41. The slightly red shift of the variation bands in the FT-IR spectra (Figures not given) indicated the formation of M-O-Si bonds [4], which showed that the atoms of cobalt might be incorporated into the framework of MCM-41. After the Co/Si molar ratio exceed 0.20, crystalline cobalt oxides emerged.

Table 1. Catalytic activity of some samples

samples	solvent	catalytic performance	
		Conversion	Selectivity
5Co	acetic acid	11.6	100
10Co	acetic acid	35.4	100
15Co	acetic acid	31.4	100
20Co	acetic acid	29.4	100
15Co-1	acetic acid	16.2	100
10Co	acetonitrile	-	-
10Co	isobutyric acid	3.2	100

The results of catalytic performances showed that 10Co sample had the best conversion of 35.4% using 15 ml acetic acid as solvent. 15Co-1 sample showed approximately half the reactivity of 15Co sample, indicating the addition of reductant can greatly improve the catalytic performance of Co-MCM-41.

In addition, the acetic acid used as solvent gaved the best catalytic activity. It is different from literatures in which acetonitrile was the preferred solvent. The hydroperoxide decomposed more quickly and remained nothing after half an hour in acetonitrile than in acetic acid, which demonstrated that acetic acid can prevent the decomposition of hydroperoxide due to its acidity. The quantity of the solvent had remarkable impact on the reactivity, which suggested that the reaction should be operated under proper acid surroundings.

References

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