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A new application of clay-supported vanadium oxide catalyst to selective hydroxylation of benzene to phenol

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Abstract

The highly selective direct hydroxylation of benzene with hydrogen peroxide to phenol was observed on a clay-supported vanadium oxide catalyst. Under mild reaction conditions at 313 K, high selectivity to phenol of 94% was realized on the clay-supported vanadium oxide catalyst at 14% conversion of benzene, comparable with the well-known TS-1 catalyst. On the other hand, vanadium on other supports and other metals on the clay support gave inferior catalytic performances. V–O–Al and V–O–Si bridges in the catalyst may be responsible for the reaction.

Keywords: Clay; Benzene; Phenol; Vanadium

1. Introduction

Developing new applications of the natural resources is an interesting field. Clay that is a very versatile material has attracted more attention owing to its wide applications in various field for more than a century (Shimizu et al., 2002; Murray, 2000). The application of clay for catalysts in the organic chemical commenced at the 1970s last century, Pinnavaia et al. reported the hydrogenation of 1-hexene catalyzed by rhodium complexes immobilized in smectites (Pinnavaia and Welty, 1975). Many papers and monographs were published in recent years about the use of clay in the organic syntheses (Campanati and Vaccai, 2001). Clays have a great potential as host compounds for fancy catalysts such as shape selective and asymmetric reactions due to the characteristic layer structure and the facile intercalation properties. Some important results in this aspect are indicated (Kun et al., 2001; Bartok et al., 1999; Shimazu et al., 1996). Additional advantage of using clay as support of catalysts is the composition of clay. Clay is mainly made up of tetrahedral silicon dioxide and octahedral alumina and the ratio of the Si / Al is relatively steady (Campanati and Vaccai, 2001), which is similar to molecular sieves.

The hydroxylation of alkanes and aromatic compounds is an attractive and challenging subject, especially for the direct hydroxylation of benzene to phenol from economical and environmental point of view, which is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics (Miyahara et al., 2001). The investigations of direct oxidation of benzene to phenol with various oxidants, such as nitrous oxide (Sobolev et al., 1993; Panov et al., 1992), hydrogen peroxide (Bianchi et al., 2000; Bengoa et al., 1998; Zhang et al., 1996;

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Kuznetsova et al., 1996), molecular oxygen (Miyahara et al., 2001; Ohtani et al., 1995), or a mixture of oxygen and hydrogen (Niwa et al., 2002) have been reported. The direct hydroxylation of benzene with hydrogen peroxide to produce phenol was widely attempted as a green process (Clerici, 2001; Walling, 1975), which proceeds at the mild conditions. Vanadium is a most widely used element in catalysts, especially for the hydroxylation of alkanes and aromatic compounds with hydrogen peroxide (Gao and Hua, 2004). There were several reports for the benzene to phenol reaction on vanadium-containing catalysts (Zhang et al., 2005). However, the selectivity to phenol was less than 70% (Lemke et al., 2003; Chen and Lu, 1999) since phenol is more reactive than benzene in the reaction.

Therefore we used clay-supported metal oxide catalysts for the hydroxylation of benzene and optimized the reaction conditions, as will be shown in this paper. Further, we report the clay-supported vanadium oxide catalyst exhibits the high selectivity in hydroxylation of benzene to phenol, which is higher or comparable to the known best catalyst, TS-1.

2. Experimental

2.1. Catalyst preparation

Clay used in these experiments is composed of chlorite, illite, attapulgite, etc., and were produced in Inner Mongolia, northwest of China. The clay consists of Si and Al (ca. Si/Al=4 in atomic ratio) as major components, together with Na, K, Fe, Mn, and Ti as minor components.

The catalysts were prepared by the following procedures, 100 g of clay was added to a 300 mL of 0.25 M aqueous sulfuric acid solution, stirred for 24 h at room temperature, and filtered. The wet clay was carefully washed until no sulfate ion can be detected. Thus, all soluble basic ions were removed. The washed clay was dried at 393 K. Vanadium oxides were introduced to the dried clay by impregnation method from an aqueous ammonium metavanadate solution. The clay-supported vanadium oxide was dried at 393 K and calcined at 973 K for 5 h. The other metal oxides such as copper, iron, manganese, chromium, molybdenum, and tungsten, were supported on clay, as similarly as vanadium case, except that copper, iron, and tungsten/clay were calcined at 773 K for 5 h because the precursor of copper, iron, and tungsten could decompose under low temperature.

The TS-1 was prepared using the similar procedure as has been reported (Taramaso et al., 1983). In brief, tetraethylorthosilicate (TEOS) was added slowly to a solution of titanium *n*-butoxide (TBOT) and 25% w/w aqueous solution of tetra-*n*-propylamminumn hydroxide (TPAOH). The final compositions of TEOS:TBOT:TPAOH:H_2O were 1:0.25:0.25:68 in mole ratio. The above mixture was heated at 348 K to remove alcohols. TS-1 was statically crystallized in a Teflon-lined stainless-steel autoclave at 443 K for 5 days. The crystalline solid was centrifuged, washed, dried, and calcined at 773 K for 5 h.

2.2. Hydroxylation reaction and products analysis

The hydroxylation of benzene to phenol with hydrogen peroxide was performed in a 100 mL four-neck flask. Catalyst, benzene and acetic acid were added into the flask. The acetic acid addition was meant to enhance the activity of hydrogen peroxide, to improve the solubility of the reactants and to minimize the phase transfer problems. After heating the mixture to 313 K under stirring, hydrogen peroxide (30%) was added dropwise through a dropping funnel. The addition rate was controlled in 0.1 mL per min. After the complete addition of hydrogen peroxide, the solution was further stirred at 313 K for 4 h and then cooled down to room temperature. The GC analyses (Agilent 4890D) of products were performed with an OV-1 capillary column (35 m×0.32 mm×0.8 μm). Peaks of GC chromatogram of the reaction products were assigned to phenol, 1,4-benzoquinone, catechol, biphenyl and hydroquinone from their retention times of reference samples. The conversion and the selectivity to phenol were obtained from following equations, taking into account of sensitivity factor of each compound.

$$\text{Conversion}(\%) = \frac{\text{phenol} + \text{benzoquinone} + \text{others}}{\text{benzene} + \text{phenol} + \text{benzoquinone} + \text{others}} \times 100$$

$$\text{Selectivity}(\%) = \frac{\text{phenol}}{\text{phenol} + \text{benzoquinone} + \text{others}} \times 100$$

2.3. Characterization

The XRD measurement was performed using miniflex (Rigaku) with a CuKα radiation at 0.02 steps per second in angle range $2\theta = 5-90°$. The interaction between metal oxide and clay was estimated from the FT-IR spectra recorded by Tensor 27 (Bruker) at the resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Hydroxylation of benzene with hydrogen peroxide on various catalysts

Table 1 shows the catalytic performances in the hydroxylation of benzene on clay-supported several metal oxide catalysts, together with clay without metal oxide. Clearly, the clay-supported vanadium oxide gave the best conversion and the best yield in these catalysts under the same reaction conditions. While some metal