



Short communication

Enhancing the selectivity of *Pare*-dihydroxybenzene in hollow titanium silicalite zeolite catalyzed phenol hydroxylation by introducing acid–base sites

Changjiu Xia^{a,b}, Lihua Long^b, Bin Zhu^b, Min Lin^b, Xingtian Shu^b^a Department of Materials and Environmental Chemistry, Stockholm University, Stockholm SE-106 91, Sweden^b State Key Laboratory of Catalytic Materials and Reaction Engineering, Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, PR China

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ABSTRACT

A facile and effective method for enhancing the selectivity of *Pare*-dihydroxybenzene in phenol hydroxylation has been developed by introducing acid–base sites (MgO–Al₂O₃ binary oxide) to the micropores of hollow titanium silicalite (HTS, Ti/Si = 25) zeolite. For MgO–Al₂O₃ modified HTS zeolites, the biggest ratio of para- to ortho-dihydroxybenzene is over 2, while that is close to 1 for conventional HTS zeolite. The high *pare*-dihydroxybenzene selectivity is ascribed to the steric hindrance and the synergistic effect between acid–base sites of mixed oxide and tetrahedral framework Ti species in HTS zeolite.

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1. Introduction

Phenol hydroxylation is of ultra-importance for the commercial production of catechol (*ortho*-dihydroxybenzene) and hydroquinone (*pare*-dihydroxybenzene), which are widely applied in many areas, e.g. agrichemical, photography chemicals, antioxidants, polymerization inhibitors, etc. [1,2]. In conventional routes, dihydroxybenzenes are commercially produced by several complex processes, including (i) the oxidation of aniline and diisopropylbenzene; (ii) sulfuration of benzene and hydrolysis of benzene sulfonate [3]. Although the selectivity of target product in conventional approaches is very high, they are still far beyond to be as ideal choices in industry, due to some serious economic and environmental issues. In order to overcome these drawbacks, heterogeneous catalysts, such as metal oxide [4,5], transition metal substituted molecular sieves [6–9], hydrotalcite-based compounds [10,11], metal incorporated mesoporous silica [12,13] and heteropoly-compounds [14], have been introduced to phenol hydroxylation reaction. Apparently, heterogeneous catalysts are stable, cheap, available, reusable, and easy to be separated/recovered from solvent. Among these solid catalysts, TS-1 zeolite presents relative excellent catalytic performance and stability in phenol hydroxylation with 30 wt.% aqueous H₂O₂ solution as oxidant under mild conditions, as proposed and scaled up by Enichem in 1980s [15,16]. Both catechol and

hydroquinone can be directly produced by TS-1 catalyzed route, without the formation of hazard pollutants and wastes. And it is worthy to note that the ratio of para- to ortho-dihydroxybenzene (*Sp/o*) is usually close to 1. Nevertheless, conventional TS-1 zeolite usually suffers the poor catalytic activity and reproducibility, owing to the mismatch of hydrolysis rate between Si and Ti species during hydrothermal synthesis. To improve its catalytic performance, hollow titanium silicate (HTS) zeolite has been synthesized by a dissolution-reassembly treatment of conventional TS-1 zeolite [17–19]. Up to now, HTS zeolite has been commercially produced, and widely applied in several oxidation processes, such as epoxidation of propylene, cyclohexanone ammoxidation and phenol hydroxylation at SINOPEC, China.

From the viewpoint of industrial application, *pare*-dihydroxybenzene is more expensive and of even larger requirement than the other one in global chemical market [20]. Thus, it is of great interest to increase the selectivity of hydroquinone based on tuning the property of TS-1 zeolite catalyst in this route. To obtain this goal, great efforts have been devoted to the modification of TS-1 zeolite, such as tuning the external surface or decreasing the pore mouth diameter by using chemical vapor deposition (CVD) and other methods [21,22]. Unfortunately, these treatments don't work well in enhancing the selectivity of *pare*-dihydroxybenzene, and there is still no efficient method developed to tune the *Sp/o* of phenol hydroxylation by modifying the property of TS-1 zeolite.

Herein, we report a novel and effective method for maximizing *pare*-dihydroxybenzene selectivity in HTS zeolite catalyzed phenol hydroxylation route, by loading the acid–base sites (MgO–Al₂O₃ binary oxide) inside the micropores at the same time. The preparation of

E-mail address: xiachangjiu@gmail.com (C. Xia).

$x\text{MgO}-y\text{Al}_2\text{O}_3$ -HTS zeolite is based on the incipient wetness impregnation method, which is facile to be operated in both laboratory and industry.

2. Experimental

2.1. Catalyst preparation

HTS zeolite was commercially produced by SINOPEC via following the published literatures [18,23]. Mg–Al modified HTS zeolites are prepared by using incipient wetness impregnation, as following steps: (i) amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 9\text{H}_2\text{O}$ solid salts were dissolved in water; (ii) 6 g HTS zeolite was added into the Mg–Al containing solution at 40 °C with continuous stirring for 4 h; (iii) and then the mixture was put into 110 °C oven for 12 h to remove the water; (iv) the dried powder was calcined at 550 °C for 6 h. The final product was labeled as $x\text{MgO}-y\text{Al}_2\text{O}_3$ -HTS zeolite, while the x and y stand for the weight ratio of MgO and Al_2O_3 to HTS zeolite in the starting gel material, respectively.

2.2. Characterization method

Powder X-ray diffraction (PXRD) analysis was operated by a PANalytical powder diffractometer equipped with a $\text{Cu K}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$, under the following conditions: beam voltage of 40 kV, dwell time 500 s, and 2θ range 5° – 80°. The N_2 physisorption isotherm was measured on a Micromeritics AS-6B apparatus, using conventional BET and BJH methods to quantify the surface areas and pore volume of zeolite samples. Prior to analyses, the samples were heated to a constant weight under vacuum (10^{-1} Pa) at 300 °C for 6 h. Transmission electron microscope images were taken on a JEM-2100 microscope.

2.3. Catalytic evaluation

Phenol hydroxylation reaction was carried out in the three necked flask reactor, with continuous heating and magnetic stirring. For each reactor, 0.63 g HTS zeolite, 12.5 g phenol and 10 ml acetone were mixed together homogeneously in the flask. And the reactor was fixed in the stirring apparatus, and heated to 80 °C. Then, 4.98 g 30 wt.% H_2O_2 solution was injected in this reactor. Two hours later, small amount of reaction mixture was picked up from the reactor, and analyzed by Agilent-6890 GC equipment, which is of HP-5 column and hydrogen flame detector.

3. Results and discussion

Fig. 1 (a) and (b) depict the TEM images of HTS and $0.09\text{MgO}-0.05\text{Al}_2\text{O}_3$ -HTS zeolites. Similar as HTS zeolite, $0.09\text{MgO}-0.05\text{Al}_2\text{O}_3$ -HTS is still of abundant intracrystalline cavities, which are in favor of the mass diffusion of reagents and products inside zeolite crystal. Moreover, there is no apparently large MgO– Al_2O_3 particles observed in the TEM image of Mg–Al modified HTS zeolite. It is suggested that the Mg and Al containing species are highly dispersed in the internal and external surface of HTS zeolite. Thus, we can confirm that the mixed MgO– Al_2O_3 precursors can be homogeneously introduced via incipient wetness impregnation method. Consequently, there is no new diffraction peak detected in the PXRD pattern (at the region between 5° and 50°) of Mg–Al modified HTS zeolite, as shown in Fig. 1 (c). Furthermore, the structure and texture properties of Mg–Al modified HTS zeolite have been identified by using low temperature N_2 adsorption–desorption isotherm, as shown in Fig. 1. (d). It is observed that Mg–Al modified HTS zeolite also has the hysteresis loop from $P/P_0 = 0.45-1$, which is in good agreement with the hollow cavities illustrated in TEM image. Particularly, it is worthwhile to note that the micropore size distribution of $0.09\text{MgO}-0.05\text{Al}_2\text{O}_3$ -HTS (around 5.0 Å) calculated by Horvath–Kawazoe (HK) model for slit-shaped micropores, is more narrow than that of HTS zeolite

(around 5.4 Å). Thus, it indicates that MgO– Al_2O_3 coats the internal surface of HTS zeolite by forming a thin binary oxide layer, making the pore size become narrow. Therefore, *para*-dihydroxybenzene molecule can diffuse more flexibly than *ortho*-dihydroxybenzene inside the modified HTS zeolite, due to the steric hindrance effect.

The quantified pore and structure properties of $x\text{MgO}-y\text{Al}_2\text{O}_3$ -HTS zeolites determined by BET method is shown in Table 1. We can see that the specific surface area and pore volume, especially for the micropore volume, of Mg–Al modified HTS zeolite are dramatically decreasing as a function of the increase of metal oxide content loaded. It suggests that metal oxide narrows the pore mouth of HTS zeolite, which is in good agreement with the characterization of TEM and pore size distribution. Thus, we propose that the metal oxide is majorly located in the micropores and blocked them, causing the micropore size becomes smaller. Furthermore, the acid and base properties of Mg–Al modified HTS zeolite are determined by probe molecule temperature programmed desorption (TPD) method. As shown in Fig. 2, NH_3 -TPD and CO_2 -TPD spectra are provided to illustrate the features of acid and base sites in $0.09\text{MgO}-0.05\text{Al}_2\text{O}_3$ -HTS zeolite, respectively. It is well known that, TS-1 zeolite has only very weak Lewis acid property and no basic sites, without adsorption peak in the NH_3 -TPD spectrum. Therefore, we can infer that both acid and base sites, with different strength distribution, are derived from the MgO– Al_2O_3 binary oxide. They are attributed to the isomorphous substitution of Mg^{2+} ions by Al^{3+} ions, with the formation of Mg–O–Al bonds, as illustrated in Fig. 3. Interestingly, K. Kaneda et al. pointed out that the cooperation of acid- and basic-sites at neighbor location can effectively promote the cycloaddition reaction between CO_2 and epoxides [24]. Therefore, three kinds of active sites are existed in Mg–Al modified HTS zeolite, i.e. redox sites (tetrahedral framework Ti species), acid sites and base sites.

As shown in Table 2, the phenol conversion (XPH) of $x\text{MgO}-y\text{Al}_2\text{O}_3$ -HTS zeolite is not as high as that of original HTS zeolite, which is decreasing continuously along with the increase of MgO– Al_2O_3 oxide loaded inside the micropores of HTS zeolite, owing to the steric limitation. However, the $S_{p/o}$ of Mg–Al modified zeolite is higher than that of HTS zeolite. For example, $0.09\text{MgO}-0.10\text{Al}_2\text{O}_3$ -HTS zeolite in entry 4, the $S_{p/o}$ is over 2 (the $\Delta S_{p/o}$ is about 102%), while the X_{PH} is about 13.80% (R_{XPH} is 53.3%). It is demonstrated that the X_{PH} and $S_{p/o}$ can be tuned by changing the content of MgO– Al_2O_3 mixed oxide. Under optimized catalyst composition ($0.03\text{MgO}-0.02\text{Al}_2\text{O}_3$ -HTS), the XPH is 20.8% and the $S_{p/o}$ ratio 1.67.

Seen from entry 2 and 3 of Table 2, the $\Delta S_{p/o}$ of 0.09MgO -HTS zeolite is larger than that of $0.09\text{Al}_2\text{O}_3$ -HTS zeolite under the same reaction conditions. The reducing of XPH is caused by the steric hindrance effect inside the micropores, which is attributed to the narrowing of micropore mouth. The narrow pore diameter benefits the shape selectivity in phenol hydroxylation, due to hydroquinone of smaller molecular diameter than catechol. Moreover, it is well known that MgO and Al_2O_3 are of basicity and acidity, respectively. Therefore, we can infer the basicity is of greater impact than acidity on tuning the selectivity of phenol hydroxylation. However, MgO– Al_2O_3 mixed oxide modified HTS zeolites present much higher $\Delta S_{p/o}$ than Mg- and Al-oxide solely modified HTS zeolites, even the metal oxide amount is very small (entry 9–10). It is inferred that there is a synergistic effect between acid and base sites on maximizing the $\Delta S_{p/o}$ of hydroxylation reaction [24,25]. When comparing entry 6 and 8, it suggests that Mg^{2+} (basic) sites are in favor of higher $S_{p/o}$ value than Al^{3+} ions under the similar phenol conversion level (about 16%). Thus, we infer that steric limitation and synergistic effect between redox and acid–base sites take a more major role than conversion effect in enhancing *para*-product selectivity. Consequently, to explain the effect of MgO– Al_2O_3 oxide, a possible mechanism has been proposed, according to the catalytic and spectroscopic results, as illustrated in Fig. 3. Firstly, in principle, phenol molecules are absorbed by MgO– Al_2O_3 oxide via the interactions between Al^{3+} (acidic) sites and O atoms in phenol molecules through

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