Catalysis Letters 2 (1989) 43–48

A TEST REACTION FOR TITANIUM SILICALITE CATALYSTS

B. KRAUSHAAR-CZARNETZKI and J.H.C. VAN HOOFF

Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 27 September; revised 11 November 1988

The catalytic hydroxylation of phenol to hydroquinone and catechol can be used for checking the quality of titanium silicate catalysts since the selectivity of these catalysts is strongly affected by the presence of small amounts of non-framework titania. Titanium silicates prepared by modification of [Al]ZSM-5 exhibits the same catalytic properties as hydrothermally synthesized TS-1 of high purity.

1. Introduction

In 1983, Taramasso et al. discovered a new material with the structural features of zeolite ZSM-5 containing framework titanium atoms instead of aluminum atoms [1]. This material, denoted as titanium silicate-1 or TS-1 was reported to have promising catalytic properties in the oxidations of organic compounds involving hydrogen peroxide [2–6]. TS-1 can be synthesized hydrothermally by crystallization of gels containing silicon and titanium compounds, TPAOH and water under autogenous pressure at about 450 K. The tetraethylorthoesters of silicon and titanium are preferred as reagents for the preparation of the gel [7]. Recently, we reported that titanium silicalite can also be obtained from [Al]ZSM-5 by dealumination and subsequent treatment with titanium tetrachloride. Conventional spectroscopic techniques have been used for the characterization of the products [8]. By means of XRD, the increase in unit cell constants and the change from monoclinic to orthorhombic crystal symmetry with increasing amount of framework titanium atoms can be observed. But the differences between TS-1 and highly siliceous ZSM-5 are very small. The IR spectra of TS-1 exhibit a typical adsorption band at about 960 cm^{-1} and the ^{29}Si MAS NMR spectra show an additional shoulder at about -115 ppm relative to TMS [10]. But these spectral features could not yet be interpreted since the coordination of the titanium atoms is unknown and their concentration in the framework (maximum 2.3 per unit cell) is very low.

In this study we applied XRD, IR and ^{29}Si MAS NMR in order to check the crystallinity and the amount of framework titanium atoms. Moreover, we choose the catalytic oxidation of phenol as a test reaction since the quality of the TS-1 catalysts strongly affects the product distribution. It can be shown that TS-1 catalysts with similar spectral features can exhibit very different activities and selectivities in the oxidation of phenol depending on the presence of small amounts of non-framework titania.

2. Experimental

The materials tested in the oxidation of phenol are listed in table 1. Sample 1 has been prepared from [Al]ZSM-5 according to the recently reported modification procedure [8]. The samples 2 and 3 have been synthesized by reproducing essentially the patent procedure, example 1 [1]. Both samples have been prepared from the same amounts of tetraethylorthosilicate (Selectipur, Merck), tetraethylorthotitanate (p.s., Merck) tetrapropylammoniumhydroxide (Aldrich, 1.0 m aqueous solution) and bidest water. For sample 2, the TPAOH solution was added to the ethylates at 273 K. The mixture was kept stirring at this temperature for 1 hour, and was then carefully heated at 353 K in order to evolve the formed ethanol. The obtained mixture was a clear, opalescent liquid. In contrast, the components for sample 3 were mixed at room temperature, and a white precipitate was formed upon addition of the TPAOH. Calcination of the crystallization products was performed in a vertical quartz tube reactor at 773 K in a flow of dried air. At calcination temperatures above 773 K framework titanium can be removed from the lattice positions [9]. Samples 4 and 5 are physical mixtures of 1 part titania with 99 parts of sample 2 or highly siliceous ZSM-5 ($Si/Al = 4000$), respectively. The titania, obtained from tetraethylorthotitanate by precipitation in water, washing and drying, was found to be XRD-amorphous. The characterization by means of XRD, IR and ^{29}Si MAS NMR has already been described elsewhere [8,10]. The samples 1, 2, 3 and 4 exhibit very similar spectral features with respect to XRD, IR and ^{29}Si MAS NMR. Table 1 shows the the amount of framework titanium is about the same in these samples. Non-framework titanium, as e.g. added to the samples 4 and 5, was not detectable.

Table 1

Sample	Preparation	Framework Ti/u.c. [1]	Reaction mixture [2]
1	from [Al]ZSM-5	1.1–1.3	yellow-orange
2	hydrothermal	1.1–1.3	yellow-orange
3	hydrothermal	0.9–1.2	brown
4	sample 2 + TiO_2	1.1–1.3	deep brown
5	silicalite + TiO_2	0	deep brown

[1] calculated from XRD and IR data.

[2] methanol + phenol + H_2O_2 + catalyst at 353 K after 15 min reaction time.

The catalytic oxydation of phenol with hydrogen peroxide was performed according to the patent literature, example 1 [2]. Instead of acetone, the "UV-silent" methanol was used as solvent. The reaction products were analyzed by means of high pressure liquid chromatography (HPLC) using a 100 mm polygosil 60-5C8 column and an UV detection system operating at a wavelength of 280 nm. The consumption of hydrogen peroxide was measured by means of iodometric titration.

3. Results and discussion

The differences in catalytic behaviour of the samples can already be observed without extensive product analyses: The reaction mixture containing methanol, phenol and hydrogen peroxide remains yellow-orange in the presence of the samples 1 or 2 whereas a deep brown colour is observed in the presence of the samples 3, 4 or 5 (table 1). Moreover, the product analyses show that the samples 1 and 2 catalyze the formation of hydroquinone and catechol in a molar ratio of 1 with high selectivity (fig. 1) while in the presence of the samples 3, 4 or 5 only traces of these products are formed, and a part of the phenol is converted into unidentified brown tar species. The hydrogen peroxide consumption could not be related quantitatively to the formation of products. Especially, in the presence of the samples 4 or 5, the peroxide was consumed rapidly, and the evolution of a gas

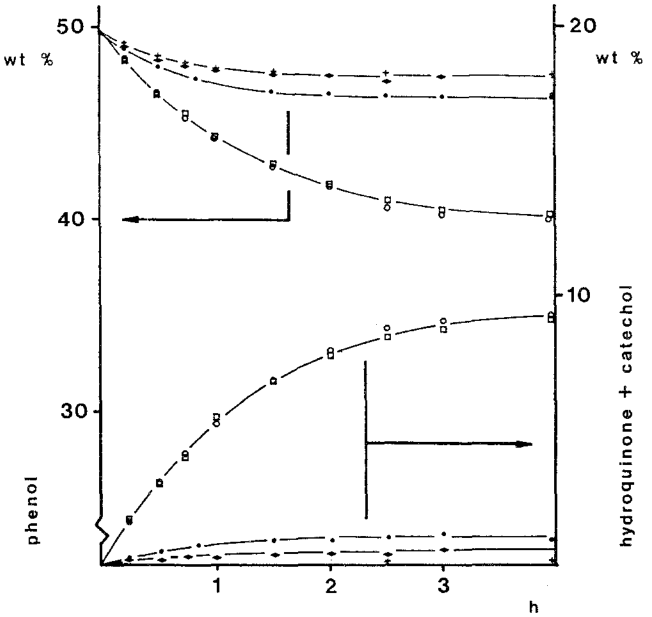

Fig. 1. Conversion of phenol and selectivity for hydroquinone and catechol versus reaction time. ○ = sample 1; □ = sample 2; ● = sample 3; ◆ = sample 4; + = sample 5.

(probably oxygen) could be observed. Since the non-selective catalyst 4 has been prepared by simply mixing the highly selective catalyst 2 with a small amount of amorphous titania it is obvious that impurities of titania are responsible for the different catalytic properties of the samples. In sample 3, the titania was probably formed during preparation of the gel precursor. The formation of a white precipitate upon mixing of the ethylates of silicon and titanium with the aqueous solution of TPAOH indicates hydrolysis and irreversible dehydration of the titanium component. Cooling of the mixture retards the hydrolysis reactions, thereby most probably favouring the built up of silica polymers with incorporated titanium. However, it is obvious that hydrolysis of the ethylates is a critical step in the preparation of TS-1 since the formation of Ti-O-Ti linkages must be prevented here [9]. Figure 1 also shows that sample 1 which was obtained from modified [Al]ZSM-5 exhibits the same catalytic properties as the hydrothermally synthesized TS-1 of high purity (sample 2). This result is of great importance since the introduction of titanium atoms by means of treatment with titanium tetrachloride may also be applied to highly siliceous large-pore zeolites while hydrothermal synthesis is still restricted to the medium-pore MFI structure.

It can be seen from fig. 1 that even the samples 1 and 2 exhibit 40–50% lower activities than those reported in the patent literature [2]. This can possibly be explained by differences in the chemical composition: The reactions reported in the patents have been performed with TS-1 containing 2 Ti atoms per unit cell [11] whereas our parent samples exhibit about 1 Ti atom per unit cell.

4. Conclusions

The catalytic oxidation of phenol with hydrogen peroxide is an appropriate test reaction for titanium silicalites. It is a sensitive tool for small impurities of titania which considerably affect the activity and selectivity of the catalysts. In hydrothermally synthesized TS-1, non-framework titania can typically be formed during preparation of the gel. The titanium silicalites prepared by modification of [Al]ZSM-5 behave as TS-1 catalysts of high purity.

References

[1] M. Taramasso, G. Perego and B. Notari, U.S. Patent 4.410.501 (1983).
[2] A. Esposito, C. Neri and F. Buonomo, Deutsche Offenlegungsschrift 3309669 (1983).
[3] A. Esposito, C. Neri and F. Buonomo, Eur. Pat. 0102655 (1984).
[4] P. Roffia, M. Padovan, E. Moretti and G. De Alberti, Eur. Pat. 0208311 (1987).
[5] C. Neri, B. Anfossi, A. Esposito and F. Buonomo, Eur. Pat. 0100119 (1984).
[6] C. Neri and F. Buonomo, Eur. Pat. 0100117 (1984).
[7] B. Notari, in: *Stud. Surf. Sci. Catal.*, Vol. 37 (Elsevier Amsterdam 1988) p. 413.

[8] B. Kraushaar and J.H.C. van Hooff, Cat. Lett. 1 (1988) 81.
[9] B. Kraushaar-Czarnetzki and J.H.C. van Hooff, in preparation.
[10] G. Perego, G. Bellussi, C. Corno, M. Taramasso, F. Buonomo and A. Esposito, in: *Proc. 7th Int. Zeolite Conf. in Tokyo* (Elsvier Tokyo, 1986) p. 129.
[11] G. Bellussi, personal communication.