# HYDROXYLATION OF PHENOL OVER Ti-MCM-41 AND TS-1*

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In the oxidation of phenol by hydrogen peroxide over titanium containing MCM-41 materials, prac-
tically only *para* isomers are formed. The exclusive *para* selectivity is proposed to be due to the
different strength of adsorption for the *para* and *ortho* isomers influencing the overall reaction rate
or the faster polymerization of the *ortho* product. The former mechanism is more probable.

In the hydroxylation of phenol, hydroquinone (1,4-dihydroxybenzene) is the desired
product used for the production of photographic developers, polymerization inhibitors
and dyes[1]. Therefore, an increased interest is given to the catalysts exhibiting improved
*p/o* product ratio.

Recently, titanium containing MCM-41 mesoporous molecular sieves (Ti-MCM-41)
have been synthesized[2–5] and used in the oxidation of several organic molecules ($\alpha$-ter-
pineol, norbornene[2,3], 2,6-di-*tert*-butylphenol and benzene[4]).

In the present work the catalytic properties of Ti-MCM-41 in the phenol oxidation
are studied and compared with those of titanium silicalite (TS-1). The latter may be
regarded as a standard catalyst in liquid phase heterogeneous oxidations[6–8].

## EXPERIMENTAL

Two samples of Ti-MCM-41 differing in the content and state of titanium were prepared. The standard
zeolite material TS-1 was synthesized according to the procedure given in a patent[9].

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Preparation of Ti-MCM-41

The reaction mixture was prepared as follows: 19.26 g of Ludox AS-40 (Du Pont, 40 wt.% colloidal silica in water) were put into a 400 ml polypropylene beaker and stirred by a magnetic stirrer at ca 1 200 rpm. Afterwards, 18.52 g of tetraethylammonium hydroxide solution (TEAOH, Merck, 20 wt.% solution in water) and subsequently 16 g of hexadecyltrimethylammonium chloride solution (HDTMACl, 25% water solution, Fluka, 1/3 of the total amount) were added. To the gel formed, the other 2/3 of the surfactant and either 0.84 or 1.68 g of tetrabutyl orthotitanate (TBOT, Merck) diluted with 0.9 g of 2-propanol (Merck) were added simultaneously. All vessels, except that with TBOT, were washed with 10 g of deionized water to achieve a quantitative transfer of the reagents. As the vessel with TBOT could not be washed with water because of the hydrolysis, extra 0.05 g of TBOT were always added to make up for the losses. All components were cooled down to 10 °C in an ice bath. The gel formation also occurred at this temperature.

The gel was agitated for 1 min and then allowed to react with stirring (150 rpm) in a 250 ml polypropylene autoclave at 110 °C for 24 h. The resulting solid product was recovered by filtration, extracted with ethanol for 4 h in a Soxhlet apparatus and finally calcined under air flow at 600 °C for 20 h. The reaction mixture of both samples contained the components in the following oxide molar ratio: 32.94 $SiO_2$ : 0.317 or 0.634 $(TBOT)_2$ : 3.3 $(TEA)_2O$ : 4.72 $(HDTMA)_2O$ : 1 021 $H_2O$. The differing amounts of TBOT given correspond to samples Ti-MCM-41-a and Ti-MCM-41-b.

Preparation of TS-1

The synthesis was carried out according to a patent[9], i.e. tetraethyl orthosilicate (Merck) and tetra-ethyl orthotitanate (Merck) were used as silicon and titanium sources. The template tetrapropylam-monium hydroxide was prepared from the corresponding bromide (Aldrich) by anion exchange (Amberlite IRA-400). The crystallization was carried out without stirring in a Teflon-coated auto-clave (166 °C, 10 days). The obtained crystalline product was washed, dried and calcined under oxygen flow at 400 °C for 6 h.

Characterization

The titanium content was determined by atomic absorption spectroscopy (AAS Philips PU 9200). Prior to the analysis, samples were digested by a mixture of HCl, HF and $H_2SO_4$ in an autoclave (180 °C, 2 h).

Powder X-ray diffraction data were obtained on a Seifert 3000 P diffractometer in the Bragg–Brentano geometry arrangement, using $CoK\alpha$ radiation with a graphite monochromator and a scintil-lation detector.

The adsorption isotherms of nitrogen at −196 °C were measured with an Accusorb 2100E instru-ment (Micromeritics). Each sample was degassed at 330 °C for at least 20 h until a pressure of $10^{-4}$ Pa was attained.

The dispersion of titanium species in titanosilicates was determined by the diffuse reflectance UV/VIS spectroscopy (DRS), which was performed on a Varian Cary-4 double beam spectrometer with $BaSO_4$ as the standard.

Catalytic Hydroxylation

The hydroxylation of phenol by hydrogen peroxide to give dihydroxybenzenes was performed in a batch reactor under reflux at 65 °C for 6 h. A suspension of 9.4 g of phenol, 0.5 g of a catalyst, and 28 ml of methanol was uniformly stirred by a nitrogen flow. A total of 4.4 ml of $H_2O_2$ (34 wt.%, Jansen) were added by a Hamilton syringe over 10 min. Prior to the sample withdrawal (0.15 ml) for

analysis, the nitrogen flow was interrupted, to allow the catalyst to deposit. The products were analyzed by high-performance liquid chromatography (Merck), using a LiChrosorb RP 18 column and a UV detector L-4000 at 280 nm. The conversion of hydrogen peroxide was determined by a standard iodometric titration.

## RESULTS AND DISCUSSION

The characteristic feature of powder X-ray diffractograms of both Ti-MCM-41 samples containing 2.2 and 4.3 mole % of $TiO_2$ (Table I) is that they exhibit reflections only at small angles $2\theta$ (Fig. 1). From the comparison with published data it follows that they can be indexed[10] on a hexagonal lattice typical of MCM-41. The lattice constant $a_0$ and the structure parameters derived from adsorption data are given in Table I. The mesopore volume $V_{me}$ of Ti-MCM-41 was obtained as the adsorption at the relative pressure of 0.75 corresponding to the horizontal plateau of the adsorption isotherm, converted to the liquid volume. The size (diameter) of mesopores was calculated using a tubular

TABLE I
Chemical composition and structure parameters

| Sample[a] | $x$ | $S_{BET}$, $m^2$ $g^{-1}$ | $V$, $cm^3$ $g^{-1}$ | $D_{me}$, nm | $a_0$, nm | $t$, nm |
|---|---|---|---|---|---|---|
| Ti-MCM-41-a | 0.022 | 770 | 0.621 | 3.22 | 4.46 | 1.24 |
| Ti-MCM-41-b | 0.043 | 827 | 0.712 | 3.44 | 4.38 | 0.94 |
| TS-1 | 0.021 | – | 0.205 | – | – | – |

[a] $x = TiO_2/(TiO_2 + SiO_2)$ molar fraction of $TiO_2$, $S_{BET}$ surface area, $V$ pore volume, $D_{me}$ mesopore size (see text), $t = a_0 - D_{me}$ pore wall thickness.
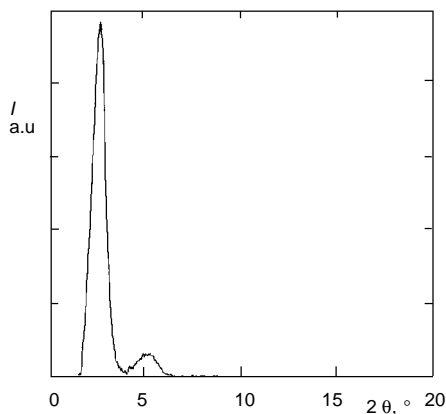


FIG. 1
X-Ray diffractogram of Ti-MCM-41-a

model as $4V/S$, where $S$ stands for the BET surface area minus the external surface area. The pore wall thickness of Ti-MCM-41 was estimated as a difference between the lattice constant $a_0$ and the diameter. With the TS-1 sample, the volume of micropores was obtained similarly as with Ti-MCM-41.

From the above mentioned data and a detailed analysis of nitrogen isotherms[5], it clearly follows that both titanium-containing MCM-41 sieves are characterized by a porous structure identical with that of aluminosilicate MCM-41 materials. They contain a regular, hexagonal array of uniform channels with the pore size of 3.2 – 3.4 nm, the pore wall thickness being about 1 nm.

In Fig. 2, the diffuse reflectance UV/VIS spectra of all samples are presented and compared with that of anatase. All individual absorption bands in the diffuse reflectance spectra of titanium containing molecular sieves have not yet been assigned un-equivocally. There is a general agreement that titanium(IV) atoms in a lower coordina-

TABLE II
Oxidation of phenol

| Sample | Conversion, mole %[a] | | $Y$, mole %[b] | $p/o$ Selectivity |
|--------|---------|---------|------|------|
|        | phenol  | $H_2O_2$ |      |      |
| Ti-MCM-41-a | 1.0  | 47 | 30 | only $p$ |
| Ti-MCM-41-b | 1.4  | 54 | 14 | only $p$ |
| TS-1        | 31.8 | 83 | 81 | 2.7 |

[a] Conversion of phenol and hydrogen peroxide determined after 6 h. [b] $Y$ yield of dihydroxybenzenes per mole of the reacted phenol.
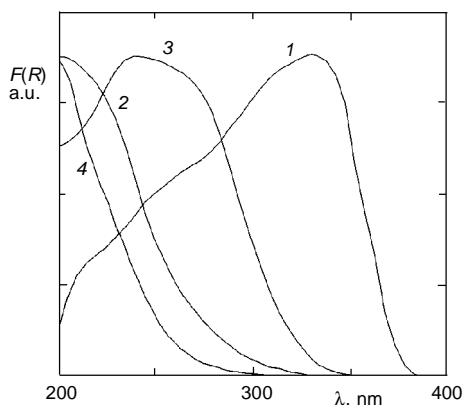


FIG. 2
Diffuse reflectance spectra of: bulk anatase *1*, Ti-MCM-41-a *2*, Ti-MCM-41-b *3*, TS-1 *4*. $F(R)$ is the Kubelka–Munk function

tion state, probably tetrahedrally coordinated, should be responsible for the peak at ca 205 nm, and the band at ca 330 nm corresponds to anatase[11–15]. The bands between these two limits could be assigned to different molecular $TiO_x$-species[15].

From Fig. 2 it follows that the diffuse reflectance spectra of Ti-MCM-41 containing 2.2% of $TiO_2$ and TS-1 are similar, both containing titanium mostly in the tetrahedral coordination. The spectrum of Ti-MCM-41 with 4.3% of $TiO_2$ is also blue shifted in comparison with that of anatase. It contains a broad band between 230 and 280 nm which can be assigned to the above mentioned $TiO_x$-species.

In Table II the results of catalytic experiments are summarized. While the conversion of phenol and hydrogen peroxide over both samples of Ti-MCM-41 is almost the same, it is much lower than that achieved with TS-1. In the case of Ti-MCM-41, the main products were hydroquinone and *p*-quinone (which was not determined quantitatively), no *ortho* products being found. The catalytic activity and selectivity of the TS-1 sample are comparable to the values obtained in other laboratories[16–19].

The practically exclusive formation of *para* isomers in the oxidation of phenol over Ti-MCM-41 is surprising. This, and also the *p/o* ratio over TS-1 higher than 2, require the assumption of additional effects favouring formation of *para* isomer molecules.

On the basis of a study of phenol oxidation[20] over TS-1, the product and transition-state shape-selectivity as well as the different diffusivities of the *para* and *ortho* molecule can be excluded as a reason of the increase in the *p/o* ratio. It has been suggested[20] that the increased *p/o* ratio over TS-1 might be explained by the different adsorption ability of the *para* and *ortho* products on the catalyst or by different rates of polymerization of both products. The stronger adsorption of the *ortho* molecule can be expected from the *ortho* hydroxyl groups enabling a twofold attachment to an active centre (structure *A*).
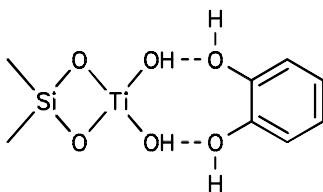


**A**

Therefore, one can suggest that the kinetics is influenced by the rate law comprising a term which considers the different strength of adsorption of both products. Alternatively, the faster polymerization of the *ortho* product can also be the cause of the observed selectivity.

As follows from DRS, both Ti-MCM-41 samples contain the titanium component in different coordination, but always in a highly dispersed state. This is in agreement with their similar catalytic properties. The explanation suggested for the *p/o* selectivity of

the phenol oxidation over TS-1 is also confirmed by the results obtained over Ti-MCM-41, because a very high *para* selectivity has been found on the purely mesoporous catalyst.

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