Hydrogen peroxide oxidation of D-glucose with titanium-containing zeolites as catalysts

A. Martínez Velarde, P. Bartl, T.E.W. Nießen, W.F. Hoelderich [*]

Department of Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany

Abstract

The oxidation of D-glucose with hydrogen peroxide as oxidant over several titanium-containing zeolites and titania as catalysts was studied. TS-1 and Ti-MCM-41 were synthesized directly while titanium-containing zeolites Y, L and mordenite were obtained through post-synthesis treatment using ammonium hexafluorotitanate. The oxidation of D-glucose occured mainly to gluconic acid, glucuronic acid, tartaric acid, glycolic acid and glyceric acid. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The interest in the application of carbohydrates as chemical feedstock has increased considerably during the last decade [1]. The renewable character of the carbohydrates, as well as the biodegradability of materials derived from carbohydrates, have played a role in this respect.

Glucose is used for nutritional purposes and as feedstock for the production of gluconic acid and alkyl polyglucosides (APG). In addition, glucose is used in the fermentation industry, as starting material for the production of L-ascorbic acid via D-glucitol. Selective oxidation of the hydroxyl functions of glucose has drawn considerable attention [1]. Microbial, enzymatic, catalytic and chemical routes are under investigations.

One of the major progressive steps in the past decade in the area of the heterogeneous catalysis was the report in 1983 by M. Taramasso et al. on the synthesis of TS-1, a titanium silicalite with MFI structure, which has found several applications in oxidation reaction under mild conditions with 30% aqueous hydrogen peroxide as the oxidant [2,3]. Since then the use of heterogeneous catalysts based on titanium has become more attractive in oxidation reactions.

Hölderich et al. recently reported [4,5] a method for preparing large-pore titanium-containing zeolites and their use as effective heterogeneous catalysts for oxidation reactions using

* Corresponding author. Tel.: +49-241-806560; fax: +49-241-8888291.

E-mail address: hoelderich@rwth-aachen.de (W.F. Hoelderich).

30% aqueous hydrogen peroxide as oxidant. Besides the directly-synthesized TS-1 and Ti-MCM-41, titanium-containing zeolites Y, L and mordenite were obtained through post-synthesis treatment using ammonium hexafluorotitanate as titanium source. In the case of the oxidative cleavage of *trans*-1,2-cyclohexanediol the highest selectivity to adipic acid (80%) at a conversion of the diol of 50% was obtained with the titanium-containing zeolite Y. For this reaction, the conversion is apparently determined by the pore size and the selectivity mainly by the titanium species.

The aim of the present work is to explore the potential of different titanium-containing zeolites and mesoporous molecular sieves as catalysts in the oxidation of D-glucose with hydrogen peroxide as oxidant.

2. Experimental

2.1. Catalysts

Zeolite NaY ($SiO_2/Al_2O_3 = 5,3$) and TiO_2 P25 were kindly provided by Degussa AG. Zeolites H-ZSM-5 (Zeocat PZ-2/50, $SiO_2/Al_2O_3 = 59,5$), KL ($SiO_2/Al_2O_3 = 6,7$) and H-mordenite ($SiO_2/Al_2O_3 = 15$) were kindly provided by Chemie Uetikon AG. Anatase and rutile were obtained from Aldrich. Other catalysts were prepared as described below.

2.1.1. Titanation of zeolite Y
The untreated NaY–zeolite was ion-exchanged with 2 N NH_4Cl solution according to well known procedure to obtain the ammonium form. For the titanation, following the general outlines of the procedure of G. Skeels and E. Flanigen [6] a 10 ml/g suspension of NH_4Y in a ammonium acetate solution was stirred and heated to 75°C; $(NH_4)_2TiF_6$ was added at the desidered mass ratio in relation to the zeolite and the temperature raised to 95°C. After the rection time the titanium-containing zeolite was separated through filtration, washed and dried.

2.1.1.1. Preparation of the sodium and acid forms of Ti–Y zeolites. Directly following the titanation procedure the titanated Y zeolite was essentially in the ammonium form. For the ion exchange into the sodium form the sample was suspended in 2 N sodium chloride solution at a 10 ml/g ratio. The suspension was stirred at 80°C for 2 h, then the zeolite was recovered through either filtration or centrifugation, washed with distilled water and dried; this procedure was carried out three times. In order to obtain the acid form of the titanium-containing Y zeolites, the original ammonium form was dried at 150°C for 2 h, then heated to 450°C at 2 K/min and kept at this temperature for 2 h.

2.1.2. Dealumination and titanation of mordenite
Following the procedure developed by one of the authors as described elsewhere [4], H-mordenite was dealuminated in a tubular reactor at 650°C for 2 h under a nitrogen stream which was saturated with water at 80°C. A suspension (30 ml/g) of the recovered zeolite in hydrochloric acid (12 N) was stirred under reflux for four hours. The dealuminated mordenite thus obtained was separated through filtration, washed and dried. A suspension of this material in water (10 ml/g) was stirred and heated to 100°C; $(NH_4)_2TiF_6$ was added at a mass ratio of 0.388 in relation to the dealuminated mordenite. After stirring for 16 hours the titanium-containing mordenite was separated through filtration, washed and dried.

2.1.3. Titanation of zeolite L
Zeolite L was exchanged into the ammonium form with 2 N NH_4Cl solution. For the titanation, following the general outlines of the procedure of Skeels and Flanigen [6], a 10 ml/g suspension of NH_4L in a 10 M ammonium acetate solution was stirred and heated to 75°C; $(NH_4)_2TiF_6$ was added at a mass ratio of 0.658 in relation to the zeolite and the temperature raised to 95°C. After 90 min the titanium-con-

taining zeolite was separated through filtration, washed and dried.

2.1.4. Synthesis of TS-1

TS-1 was synthetisized with $(NH_4)_3$-$[Ti(O_2)F_5]$ as the titanium source, a method first introduced by Shilun et al. [7] and further studied by Niessen et. al. [5]. First the titanium source was dissolved in water under stirring, then sodium bicarbonate ($NaHCO_3$) as mineralizing agent, tetrapropylammonium bromide (TPABr) as template and the silicon source (Ludox AS-40) were added. The mixture was stirred for two hours at room temperature and placed into a stainless-steel autoclave fitted with a stirrer, and then held at 195°C for 168 h under stirring. The crystals thus obtained were filtered, washed , dried at 140°C and calcined for 12 h.

The molar ratios of the reaction mixture were:

$$1SiO_2 : 0.027(NH_4)_3(Ti(O_2)F_5):$$

$$0.22NaHCO_3 : 0.1TPABr : 22.2H_2O$$
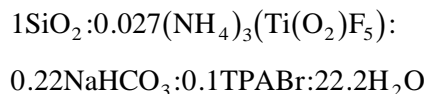
2.1.5. Synthesis of Ti-MCM-41

According to the procedure developed by Niessen [5], at first 18% of the total silicon source (Cab-O-Sil-M5) were suspended in water. To this suspension cetyl–trimethyl–ammonium chloride (CTMACl), as a 25% aqueous solution, was added under stirring, and tetraethylammonium hydroxide (TEAOH) (as a 40% aqueous solution) was then added dropwise. After the addition of $(NH_4)_3[Ti(O_2)F_5]$ and further stirring for one hour, the remaining silica was added. The mixture was then stirred for one hour and held at 90°C in a polypropylene flask for 168 hours. The product thus obtained was filtered, washed, dried at 140°C and calcined at 540°C, having been heated with 1 K/min.

The molar ratios of the reaction mixture were:

$$1SiO_2 : 0.0125(NH_4)_3(Ti(O_2)F_5):$$

$$0.15CTMACl : 0.28TEAOH : 35H_2O$$
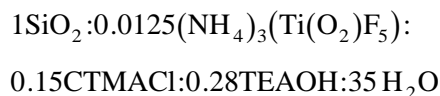
2.1.6. Synthesis of Si-MCM-41

Titanium-free Si-MCM-41 was synthesized by adapting the procedure of Corma et al. [8] for Ti-MCM-41, leaving the titanium source out. 20 g of water, 20 g of tetradecyl-trimethyl-ammonium bromide and 87.2 g of a 40% aqueous solution of tetraethylammonium hydroxide were stirred for 1 h at room temperature. Thereafter, 8.7 g of Aerosil 200 were added and the mixture stirred for 2 h, after which further 23.8 g of Aerosil 200 and 50 g of water were added. After 3 h of stirring, this final mixture was placed into an autoclave and held at 130°C for 168 h. The product thus obtained was filtered, washed, dried at 140°C and calcined at 540°C (first under nitrogen, then air), having been heated at 1 K/min.

2.2. Catalyst characterization

The catalysts were studied through FT-IR and diffuse reflectance UV–Vis (DRS) spectroscopy as well as through X-ray powder diffractometry. Their pore structure and surface were analyzed with nitrogen adsorption measurements using an Omnisorp 100, and their chemical composition with an ICP Spectroflame D, after the samples had been dissolved in a solution of hydrofluoric (0.45 wt.%) and sulphuric (1.8 wt.%) acids. The infrared measurements were carried out with a Nicolet 510P spectrometer, using KBr pellets. The DSR spectra were obtained with a Lambda 7 spectrometer from Perkin Elmer, the titanium-containing samples were diluted 1:50 with the corresponding parent materials, which also provided the background. For the X-ray diffractograms a Siemens D5000 diffractometer was used.

2.3. Oxidation of D-glucose

The zeolite samples were introduced along with the reactant in a round flask equipped with a condenser. The reactant/catalyst mass ratio used was 28.4 for all runs. The aqueous 30%

hydrogen peroxide solution was added all at once at an excess of 30% in relation to D-glucose (H_2O_2 /substrate ratio $= 1.3$ M) and the mixture heated to 70°C under vigorous stirring. After the reaction time ($t = 3$ h) the solution was freeze-dried and trimethylsilylated as follows. The product (15 mg) was diluted in pyridine (0.6 ml) and stirred for 30 min at room temperature. Then 0.6 ml hexamethyldisilazane (HMDS) and 0.15 ml trifluoroacetic acid (TFA) was added and the mixture was warmed up to 90°C for 30 min. The amounts of substrate and reaction products were determined using GC.

3. Result and discussion

3.1. Characterization of zeolite samples

The X-ray diffractograms provide evidence of the essentially retained crystalline structure of the zeolites Y, L and mordenite titanated by post treatment. The structure of the synthesized Ti-MCM-41 and TS-1 were confirmed also by XRD.

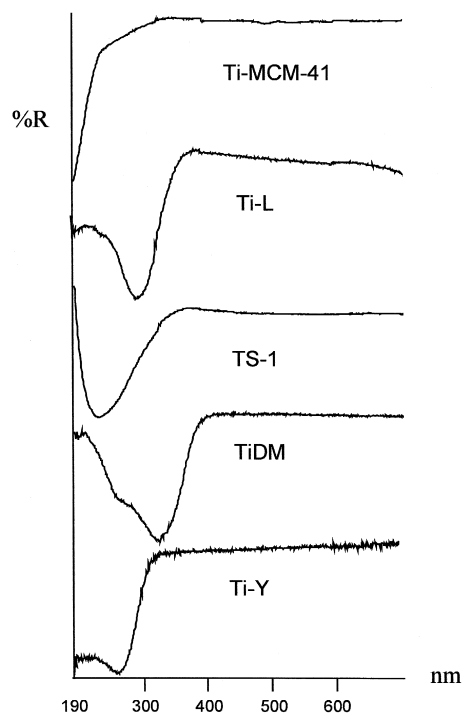The chemical composition and the nitrogen sorption data of the most relevant samples are

Fig. 1. DSR spectra of titanium-containing samples.

described in Table 1. The data shown has been expected for the samples.

The DRS spectra of the samples are displayed in Fig. 1.

Table 1
(a) Preparation and (b) characterization of the different titanium-containing Y zeolites

(a)

Ti–Y catalyst	Untreated zeolite	SiO_2/Al_2O_3	$(NH_4)_2TiF6$ (g/g zeolite)	Concentration NH_4Ac (M)	Reaction time (min)
A[a]	NH_4–USY	6.0	0.304	10	90
B	Na–Y	5.2	0.304	10	90
C	Na–Y	6.0	0.304	10	90
D[b]	Na–Y	5.3	0.304	10	90
E[b]	Na–Y	5.3	0.304	10	75

(b)

Ti–Y catalyst	SiO_2/Al_2O_3	Si/Ti	Ti (mg/g)	BJH mesoporous area (m^2/g)	BET area (m^2/g)
A	16.0	4.6	60.45	0.23	534
B	6.0	4.5	53.27	0.10	451
C	7.0	4.5	54.58	0.14	544
D	7.5	4.7	50.79	0.17	672
E	7.0	5.6	43.08	0.13	609

[a]The catalyst was dealuminated before the titanation.
[b]The catalyst was ion-exchanged into the ammonium form before the titanation.

The DRS spectra of Ti-MCM-41 and TS-1 present only a band with the adsorption centered in the range of 190–210 nm. This is usually accepted as evidence that the titanium atoms are tetrahedrally coordinated [9–12]. The titanated dealuminated mordenite (Ti-DM) presents a band centered at around 330 nm, which is usually attributed to anatase in addition to a shoulder at around 260 nm. Interestingly, the titanated zeolites Y and L present neither of those two bands at around 200 and 330 nm. Anatase is therefore absent despite the relatively large amounts of total titanium content in the material; on the other hand, the titanium seems not to be bonded in the framework in the same way as in TS-1 or Ti-MCM-41. The Ti–Y sample presents a band centered at approx. 260 nm, and Ti-L one around 290 nm. Similar bands have been attributed to partially incorporated titanium atoms, e.g., through only one or two bonds [10], to monomeric octahedral titanium or to very small titanium oxide clusters, possibly within the micropores [13,14]. The often discussed isomorphous substitution into zeolite framework does not apply to the prepared Ti-DM, Ti–L and Ti–Y samples [9].

The FT-IR spectra of the titanium-containing samples are displayed in Fig. 2. The treatment with $(NH_4)_2TiF_6$ resulted in a slight dealumination of the zeolite framework in the case of zeolites L and Y, shown by a shifting of the external symmetric stretching vibration (750–840 cm^{-1}) towards higher wavenumbers [15]. In the case of mordenite, the dealumination had already been accomplished before the titanation step.

It can be also seen that the treatment with $(NH_4)_2TiF_6$ created a shoulder, in the range of 900–950 cm^{-1}, in the FT-IR spectra of zeolites L and Y. This shoulder seems at first to be similar to the one present in the spectrum of Ti-MCM-41 which in turn resembles the band at 960 cm^{-1} in the spectrum of TS-1. In the case of TS-1 this band has often been attributed to tetrahedrally coordinated titanium atoms incorporated in the crystalline framework and this
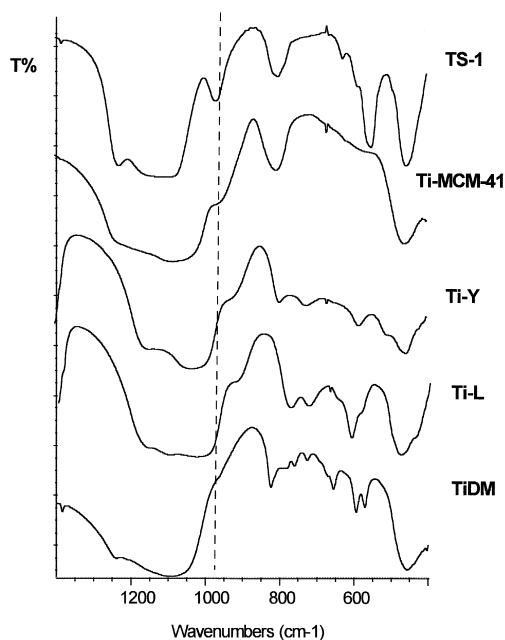

Fig. 2. FT-IR spectra of titanium-containing samples.

attribution has been extended to other microporous titanosilicates [2,9,16–20]. However, it has been proposed, and increasingly accepted, that the band at ca. 960 cm^{-1} would be better attributed to the Si–O stretching vibration of Si–O...H groups [8,12,21]. A similar band can also be observed in titanium-free dealuminated zeolites which supports this attribution [5,21,22]. Thus, in our samples silanol groups might cause the band as well.

3.2. Oxidation of D-glucose

Titania is known to be an effective catalyst for the cleavage of diols when hydrogen peroxide is used as oxidant [4,23]. In a previous study, we have demonstrated that in the case of the oxidative cleavage of *trans*-1,2-cyclohexanediol in the presence of titanium-containing zeolites and mesoporous molecular sieves as catalysts and with hydrogen peroxide as oxidant, the conversion was determined by the pore size and the selectivity to adipic acid by the titanium species [4].

In the case of heterogeneous catalysis in the presence of micro-and mesoporous materials the

Table 2
Characterization of the main titanium-containing samples

Catalyst	SiO_2/Al_2O_3	Si/Ti	t-plot microporous volumen (ml/g)	BJH mesoporous area (m^2/g)	BET area (m^2/g)
TS-1	–	46	0.194	17	389
Ti–DM	> 350	23.1	0.154	33	360
Ti–L	5.5	12.8	0.091	20	216
Ti–Y	16.0	4.6	0.296	81	534
Ti-MCM-41[a]	–	51.6	0.268	112	1155

[a]Approx. 40 Å diameter.

question always arises whether the reaction takes place inside the pore system or at the outer surface of the catalyst and whether the reaction is really heterogeneous, that means in present case if there is leaching of the titanium or not. Preliminary tests with trans-1,2-cyclohexanediol as feedstock in the presence of Ti-containing materials as used in the present investigation and at almost the same conditions demonstrated that all the catalysts used can be re-used, at least three times, without any loss in activity and selectivity as well as without regeneration steps besides drying. No leaching of titanium was detected. No Ti could be analyzed by ICP-AES in the reaction mixture after filtration of the catalyst. That is a strong indication that the catalysts are indeed heterogeneous [4]. The decom-

position of hydrogen peroxide could be observed as side reaction at the reaction temperature, also without the addition of metal containing materials. But the oxidation of D-glucose needs the presence of a catalyst.

Such titanium-containing catalysts (Table 2) were used in the oxidation of D-glucose as a model reaction for the oxidation of carbohydrates. In order to investigate only the influence of the pore structure on the catalytic performance, titanium-free materials, having a structure as similar as possible to the titanium-containing ones such as zeolite Y, L and mordenite, were tested as catalysts. The results shown in Fig. 3 prove that the oxidation of D-glucose with hydrogen-peroxide takes place also in the absence of titanium over the catalyti-
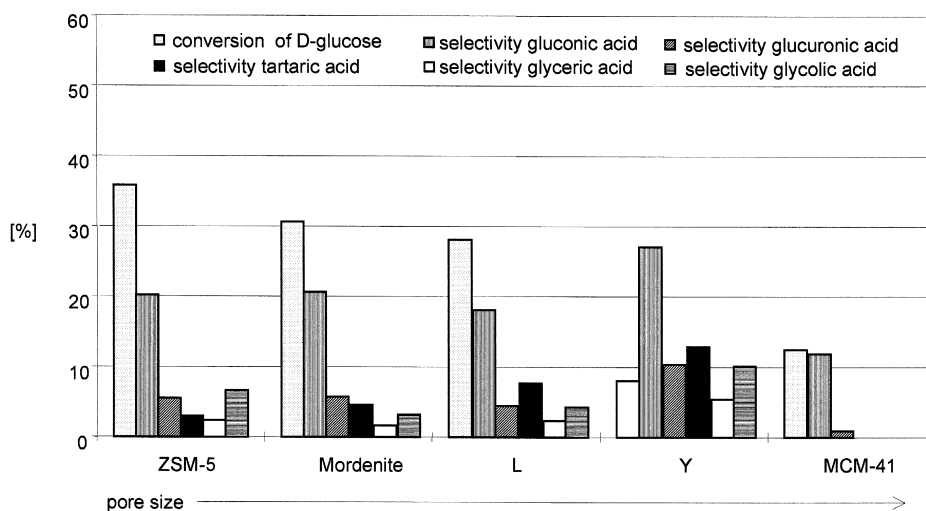

Fig. 3. Oxidation of D-glucose in the presence of titanium-free catalysts.

Table 3
Oxidation of D-glucose in the presence of homogeneous and heterogeneous titanium-containing catalysts

Catalyst	Conversion (%)	Selectivity gluconic acid (%)	Selectivity glucuronic acid (%)	Selectivity tartaric acid (%)	Selectivity glycetic acid (%)	Selectivity glycolic acid (%)
Ti–Y (A)	23.2	27.9	3.7	2.7	1.4	8.4
Y	8.0	27.0	10.4	12.9	5.4	10.2
TEOT	19.0	24.6	7.5	2.5	1.7	6.4

cally active materials. A correlation between pore size and conversion as it was found in the case of the oxidative cleavage of trans-1,2-cyclohexanediol [4] could be not observed.

In Fig. 3 the tested titanium-free zeolites are ordered with increasing pore size. As products obtained with a selectivity higher than 2% the following substances were detected: gluconic acid, glucuronic acid, tartaric acid, glyceric acid and glycolic acid. A number of unknown products with selectivities less than 2% were also present in the product mixture.

Surprisingly, the medium-pore ZSM-5 delivered almost the same results as the large pore zeolites mordenite and L as well as better results than over the mesoporous molecular sieve MCM-41 regarding the selectivity to the desired gluconic acid. The highest selectivity with 27% to the main product gluconic acid was found in the presence of the large pore zeolite Y, however, at a low conversion of 8%. These experiments show that the oxidation of D-glucose probably takes place already on the outer surface of the catalysts and not only inside the pore system. It could be seen that the conversion was lowest when large pore zeolite-Y and the mesoporous MCM-41 were used as catalysts. That also means that other catalytic features are responsible for high conversion. However, the acidity investigations also show that the acidity of the different untreated materials had no influence on the reaction.

Different reasons let titanium-containing Y zeolites appear as particularly attractive candidates in the oxidation of D-glucose; titanium-containing Y zeolites showed good selectivities of 80% at a conversion of 50% in the oxidative cleavage of trans-1,2-cyclohexanediol. Not only the titanation of the Y zeolites with $(NH_4)_3[Ti(O_2)F_5]$ was reproducible but also their catalytic activity [4,5]. Table 3 shows the results obtained by using untreated Y zeolite, homogeneously solved titanium ions (TEOT) and the titanium-containing Y zeolite (A) as catalysts. The latter Ti-Y(A) leads to an increase in the conversion from 8% to 23% in comparison with the titanium-free Y zeolite still maintaining the selectivity to gluconic acid constant at 27%. In comparison with the homogeneous catalyst (TEOT) catalyst Ti–Y(A) shows only a slight increase in the conversion of D-glucose and selectivity to gluconic acid. Nevertheless, the re-usability of the heterogeneous system provides a decisive advantage over the homogeneous one.

3.3. Reuse of catalysts

In heterogeneous catalysis by micro-and mesoporous materials another question always arises: whether the reaction is really heterogeneous catalyzed, or if there is leaching involved and homogeneous catalysis takes place by solved Ti-species.

Table 4 displays the results observed for the first three runs using Ti–Y(A) as catalyst by the oxidation of D-glucose.

The catalytic tests were carried out like described above. Afterwards the catalyst was recovered by centrifugation, dried at 100°C for 24 h and used in the next test. It is realized that Ti-Y(A) catalyst can be re-used, without additional regeneration steps to the drying procedure. At least three times and possibly more

Table 4
Re-use of titanium-containing zeolite Y(A) as catalysts in the oxidation of D-glucose

Run	Conversion (%)	Selectivity gluconic acid (%)	Selectivity glycolic acid (%)
1	26.2	20.8	9.2
2	22.3	16.2	6.4
3	25.4	15.9	7.0

often, without significant loss of activity and selectivity to the main products gluconic and glycolic acids, the other acids which were formed show a selectivity less than 2%. After the first run, no leaching was observed because titanium could not be detected by ICP-AES in the solution and the materials retained their catalytic properties for the further two runs. That is a strong indication for a heterogeneously catalysed reaction. Analogous results were obtained with the other titanated zeolites.

Different titanium-containing Y zeolites (A–E) were synthesized (see experimental part). A characterization of the titanium-containing Y zeolites used in this work are given in Table 1. As shown in Table 5 each of the Y zeolites achieves different catalytical results though neither in the XRD-spectra nor in the DRS spectra any perceptible differences could be realized.

In order to study these differences, the influence of the catalyst parameters like SiO_2/Al_2O_3 ratio, titanium content and ion exchange were investigated.

3.3.1. Influence of aluminium content

The sole influence of the aluminium content of titanium-containing Y zeolites on their cat-

alytic activity is very difficult to investigate. One of the reasons is the potential formation of mesopores during the synthesis of the titanium-containing Y zeolites which are formed in the course of the steaming or during the process of the titanation with ammonium hexafluorotitanate.

In order to avoid the influence of the mesopores a dealumination with $SiCl_4$ instead of steaming would be interesting. On the other hand, early results obtained in our group [4] have demonstrated that the structure of Y zeolites previously dealuminated with $SiCl_4$ is destroyed during the titanation with ammonium hexafluorotitanate. Besides, it was not possible to treat a non-mesoporous Y zeolite of SiO_2/Al_2O_3 ratio greater than 10 without structural collapse.

In Table 6 only essentially microporous titanium-containing Y zeolites (B, C, D), with a SiO_2/Al_2O_3 ratio between 6.0 and 7.5 were compared. Neither for the conversions nor for the selectivities to the main products a general trend can be observed. Probably the SiO_2/Al_2O_3 ratio of the used titanium-containing Y zeolite was not significantly different. Therefore a determination of the sole influence of the aluminium content on the catalytic performance was not possible.

Furthermore, the comparison of the more hydrophobic material A $(SiO_2/Al_2O_3 = 16)$ with the hydrophobic catalyst B $(SiO_2/Al_2O_3 = 6)$ demonstrates that there is an effect on the conversion. In contrary to the expectation that higher hydrophobicity would repel the water stronger yielding in higher conversion, the more hydrophilic Ti–Y zeolite B converted D-glucose to

Table 5
Oxidation of D-glucose over different Y zeolites

Catalyst	SiO_2/Al_2O_3	Si/Ti	Conversion (%)	Selectivity gluconic acid (%)	Selectivity. glycolic acid (%)
A	16.0	4.6	23.2	27.9	1.4
B	6.0	4.5	33.7	15.1	2.9
C	7.0	4.5	32.9	18.0	0
D	7.5	4.7	37.3	16.4	4.1
E	7.0	5.6	29.4	13.8	2.4

Table 6
Use of titanium-containing materials as catalysts in the oxidation of D-glucose

Catalyst	SiO_2/Al_2O_3	Si/Ti	Conversion (%)	Selectivity gluconic acid (%)	Selectivity glycolic acid (%)
TS-1	–	46.0	27.3	11.9	0.0
Ti–DM	> 350	23.1	23.1	11.8	5.9
Ti–L	5.5	12.8	19.9	12.7	4.3
Ti–Y	16	4.6	23.2	27.9	8.4
Ti-MCM-41	–	51.6	25.4	21.5	10.5

a higher extent. An explanation for that finding could not be given yet. Maybe the mesoporosity of A has a stronger influence of the H_2O_2 adsorption in the inner part of the zeolite than the microporous material B.

3.3.2. Influence of the titanium content

In order to study an possible effect of the titanium content on the catalytic performance, the titanium-containing Y zeolites (C, E) having the same SiO_2/Al_2O_3 ratio but obviously different titanium content were compared.

Their catalytic properties regarding the oxidation of D-glucose are shown in Table 6. It can be seen that with lower titanium content the

conversion decreases even though the effect is not very significant.

3.3.3. Influence of ion exchange

Since Na cations are larger than protons, the free space in the channels of zeolites in the sodium form is narrower than in the acid form of the zeolites and the acidity is neutralized as well.

In order to investigate the influence of the cations associated to the zeolite framework acid sites, some samples of titanium-containing Y zeolites were ion exchanged with a sodium chloride solution (catalysts A(Na) and D(Na)). Their acid forms were obtained through calcina-
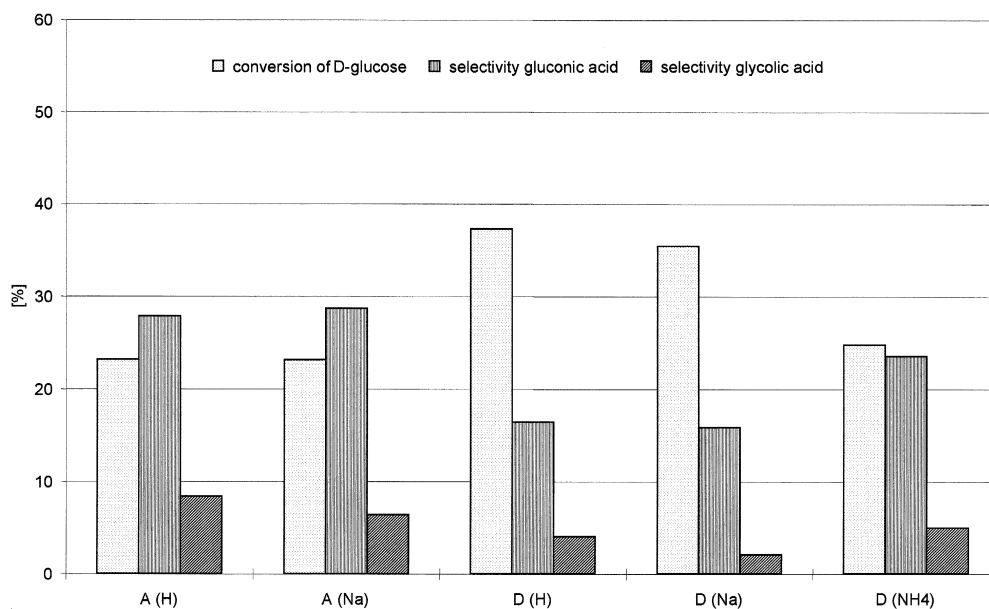

Fig. 4. Effect of cation by mesoporous (A) and microporous (D) titanium-containing Y zeolites in the oxidation of D-glucose.

tion of the ammonium form (catalysts A(H) and D(H)). FT-IR spectra showed that both the calcination and the sodium ion exchange completely removed a band at 1401 cm^{-1} associated with N-H vibrations, confirming that the ammonium cations present had been totally eliminated [24]. Consequently, the calcined samples must be predominantly in the acid form, and the ion exchanged samples in the sodium form.

The catalysts A and D were tested in the sodium form as well as in the acid form under standard conditions. The results obtained for the mesoporous material (A) and for the almost microporous one (D) are displayed in Fig. 4.

Catalyst A shows in the H-form as well was in the Na-form the same conversion of D-glucose by very similar selectivities to the main products gluconic and glycolic acid. The presence of mesopores in these catalysts does not reveal the influence of the ion exchange. On the other hand, in the case of the almost purely microporous catalyst (D), the conversion decreases with increasing atomic radius of the ions. This effect would not be found in the case of the mesoporous material A. If the differences in the acidity would play a role than a decline of the conversion should be observed also over the mesoporous material A (Na) in comparison with A (H).

3.4. Active titanium species

It is self-evident that the titanium-containing materials tested differ from each other in a number of ways: not only in their pore structure and titanium content, but also in aluminium content and acidity. Moreover, TS-1 and Ti-MCM-41 were directly synthesized while Ti–Y, Ti–L and TiDM were obtained by treatment with $(NH_4)_2TiF_6$. Table 6 shows the result of different titanium-containing catalysts.

The presence of titanium in the catalysts does not have the expected influence on the selectivity and conversion of the reaction. TS-1, Ti–DM and Ti–L show less selectivity to glyconic acid and less conversion compared to the Ti-free

analoges. In the case of the Y-type zeolite catalysts Ti–Y gave better conversion maintaining the same selectivity to gluconic acid compared to the corresponding Ti-free material. Only in the case of Ti-MCM-41 the selectivity obtained to gluconic acid as well as the conversion was significant higher.

In spite of the huge differences in the catalytic performance and characteristic features between all the materials tested, general observations can be made. The main reaction observed in all cases was the oxidation of the aldehyde carbon. Beside the formation of gluconic acid, the oxidation of the primary hydroxyl group and also a further oxidation to lower acids was detected, i.e. oxidative destruction of d-glucose occurs stepwise.

3.5. Titanium oxide species as catalysts

As a further investigation, three different forms of titanium oxide were tested: anatase, rutile and TiO_2–P25, as kindly provided by Degussa. These materials are often used as catalysts or supports for catalytically active components (e.g., Ref. [25]). The results are presented in Fig. 5.

All three materials show different conversion and selectivity behaviour. The catalytic activity observed is somewhat surprising. Anatase and rutile give conversions of about 10%, by contrast the use of TiO_2–P25 results in a conversion of almost to 30%, comparable to the results obtained by the titanium-containing Y zeolites (Table 6). Rutile shows not only low conversion, also the selectivities to the main products were less than by the other catalysts tested. The selectivity to gluconic acid was the highest observed when anatase was used. A mixture of anatase and rutile does not lead to a higher conversion.

TiO_2–P25 has a BET surface area of 49 m^2/g and a BJH mesoporous surface of 31 m^2/g; no micropores were observed. Yet, to attribute the results obtained with TiO_2–P25 only to the pore structure- which according to
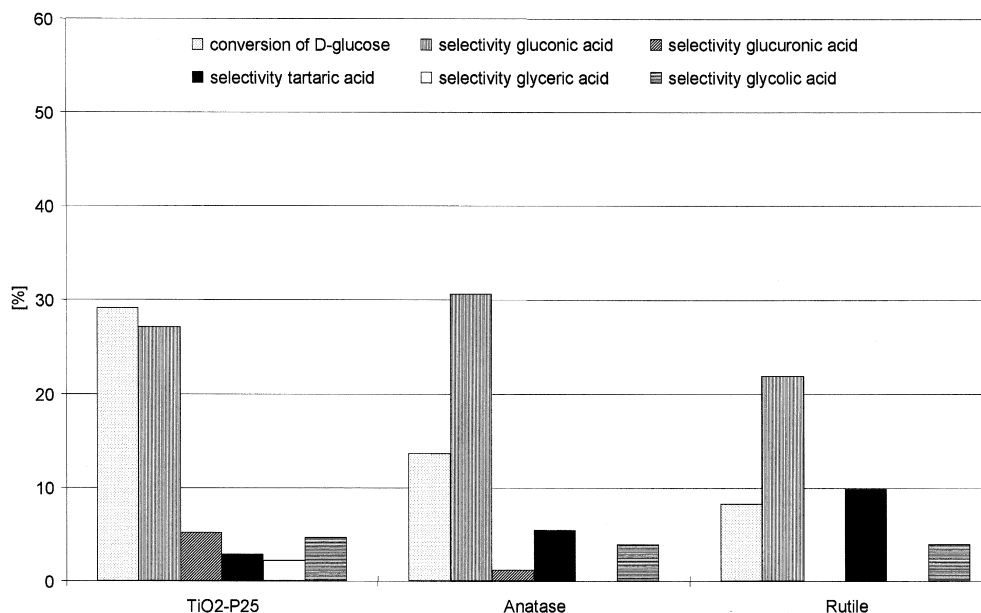
Fig. 5. Use of titanium oxide species as catalysts in the oxidation of D-glucose.

the X-ray diffractometry consists of a mixture of anatase and rutile-would seem to contradict some tendencies discussed above.

The catalytic performance of TiO_2–P25 yielding 30% conversion, could be explained with the titanium species present in it. DRS analyses have shown a titanium species causing a band at 260 nm, which also could be detected in the case of the titanium-containing Y zeolites. We believe that TiO_2–P25 and the titanium-containing Y zeolites contain approximately the same titanium species, consisting of very small titanium clusters, and that these species have an influence on the catalytic performance.

4. Conclusions

Post-synthesis titanation with $(NH_4)_2TiF_6$ is a suitable method for preparing large-pore titanium-contaning zeolites such as Y, L or mordenite which have been thought to be attractive heterogeneous catalysts in the oxidation of carbohydrates using hydrogen peroxide as oxidant.

In the case of all different titanium-containing zeolites and mesoporous molecular sieves tested in this work the oxidation at the aldehyde group was the main reaction. Besides the formation of gluconic acid, the oxidation of the primary hydroxyl group and also further oxidation to lower acids, such as tartaric, glyceric and glycolic acids was detected.

In contrast to the results previously obtained by the oxidative cleavage of *trans*-1,2-cyclohexanediol neither the conversion nor the selectivity of the oxidation of D-glucose seems to be determined by the pore size or the titanium species of the catalysts used. Several other parameters such as SiO_2/Al_2O_3 ratio, hydrophobicity of the materials, the Si/Ti ratio, acidity, size of the counterions, micro-and mesoporosity, ratio of the outer and inner surface of the materials seem to have an influence on the investigated oxidation of d-glucose. However, with respect to the achieved conversions and selectivities no tremendous change could be observed depending on one or the other of such parameters so far. Further investigations have to be done to clarify the picture in more detail. Surprisingly, TiO_2–P25 and Ti–Y zeolite

showed similar catalytic performance indicating that approximately the same titanium species are existing in these two materials. This observation is supported by UV–Vis investigations.

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