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Catalysis Today 49 (1999) 131–139

CATALYSIS TODAY

An investigation into the preparation of high surface area zirconia

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Abstract

Hydrous zirconia was digested in solutions containing different cations at constant ionic strength. The influences of the cations, Na^+, K^+, and NH_4^+, on the hydrous zirconia and the resulting zirconia were studied. The anions of the digestion medium, Cl^- and OH^-, were the same in all series. At a constant pH, zirconia formed from the Na-series had the highest surface area, followed by the K-series and the NH_3-series. This was explained by a more effective neutralization of the charged gel by the Na ions so that agglomeration of the primary particles to a porous but stabilized framework resulted. The surface area of the zirconia formed increases with pH. Above pH 11, lower surface area was obtained for samples that had been digested for long times. Digestion between pH 8 and 11 resulted in a preferential crystallization of the tetragonal phase. However, at pH 12, faster Ostwald ripening leads to the stable monoclinic phase for samples subjected to more than 96 h of digestion. The adsorption of cations on the hydrous zirconia is small for pH 8–11 but increased significantly from pH 12. These adsorbed ions affect the crystal phase of zirconia. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrous zirconia; pH; Adsorbed cations; Digestion

1. Introduction

Zirconium oxide (zirconia) is increasingly used as a support in catalysis. It has several useful properties that favour its application in catalysis [1]. Among the physical properties that make it a useful support under harsh conditions are its high melting point of 2370°C, low thermal conductivity, and high corrosion resistance. Chemically, zirconia is an amphoteric support similar to alumina with oxidizing as well as reducing capabilities [2]. It can be made into a very strong acid by sulphating zirconium hydroxide followed by calcination [3]. Sulphated zirconia is active in the isomerization of linear to branched hydrocarbons. Various reactions such as hydrodesulphurization [4], methanol synthesis [5,6], and the Fischer–Tropsch reaction to give higher hydrocarbons [7,8] were reported to show higher activity and selectivity with zirconia than with conventional supports. However, compared to these supports, the surface area of zirconia is usually rather low, in the order 20–50 m^2/g. Different routes to obtain high surface area zirconia have been reported [9,10]. Afanasiev et al. [11] used a molten salt method to prepare high surface area Mo/ZrO_2 catalyst, $\sim$160 m^2/g, for hydrodesulphurization. Due to the enhanced surface area, a higher loading of Mo can be obtained than with low surface area zirconia. We have found an easy route to improve the surface area of zirconia by digesting the precursor,

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PII: S0920-5861(98)00417-9

hydrous zirconia, prior to calcination [12]. The resulting zirconia has a surface area of around 250 m^2/g depending on the conditions used. Another feature of this preparation is that the zirconia tends to crystallize in the pure tetragonal form and this structure persists even up to 1000°C. This is useful if the crystal phase affects the catalytic activity. At room temperature, zirconia can exist in the stable monoclinic or the metastable tetragonal form or as a mixture of both. The transformation from the tetragonal to the monoclinic usually occurs above 600–700°C. As such, during catalytic reactions, zirconia may undergo a phase transformation to the thermodynamically stable monoclinic form. Centi et al. [13] studied the decomposition of N_2O over copper/zirconia catalysts. The tetragonal form was found to be twice as active as the monoclinic zirconia.

The properties of zirconia are affected by the preparative conditions, and hence, studies on the zirconium hydroxide precursor are important. However, such studies are hindered by the normally amorphous state of the hydrous zirconia. Only at very high pH above 13 does crystallinity develop. The ordering in hydrous zirconia has been studied using dynamic diffraction techniques [14,15]. The pH of the liquid in contact with the final hydroxide precipitate was found to affect the crystallization temperature and the rate of crystallization. Crystallization occurred at a lower temperature when the pH was higher. The transformation of the metastable tetragonal to the monoclinic phase was also found to occur at a lower temperature if the pH of the contacting liquid was high. It was proposed that a higher pH promotes a faster ordering of two- or three-dimensional units which act as nucleation centres for crystallization of the oxide.

We have previously investigated the digestion of hydrous zirconia in the mother liquor at pH 10 and 13.7 [16]. Different bases were used; NH_4OH was used for pH 10, and NaOH and KOH for pH 14. Hence, the mother liquor differed in the cation – Na^+, K^+, and NH_4^+ – but had the same anions, Cl^- and OH^-. Differences in the surface area and crystal phase of zirconia were found for the various bases used. It is not known if these differences are due to the presence of foreign ions at the zirconia, in particular, sodium and potassium, or the effect of pH. At pH 14, up to ~1.4 wt% Na was found in the NaOH-digested samples while a lower concentration of about 0.25 wt% Na was detected in the KOH-digested ones. The presence of cations and anions is known to cause the crystallization of zirconia in the metastable tetragonal form and a higher surface area. Hence, in this study, a comparison of the different cations is made at constant pH values of 8, 9.5, 11 and 12. The ionic strength of the digestion medium was kept constant by addition of the corresponding chloride, i.e., NH_4Cl, KCl or NaCl.

2. Method

2.1. Preparation

The hydrous zirconia was prepared by the hydrolysis of zirconium chloride in excess 5 M NH_4OH as previously described [12]. The precipitate was thoroughly washed with dilute ammonium nitrate until free of chloride. One portion of the precipitate (0 h) was immediately removed. The rest was divided into three portions and redispersed in 1.66 M NH_4Cl, NaCl or KCl solution. The pH was adjusted to 8 with the respective alkali, NH_4OH, NaOH or KOH. One portion of each series was aged at room temperature for 192 h. The remainder was digested under open reflux at 100°C for various lengths of time – 12, 24, 48, 96 and 192 h. The preparation was repeated at constant ionic strength but at different pH values of 9.5, 11, and 12. For pH 11 and 12, only the Na- and the K-series were prepared. The salt concentration was chosen so that a comparison can be made of previously measured K- and Na-series at pH 13.7 [16]. The mother liquor at this pH contained 0.55 M OH^-, 1.11 M Cl^- and 1.66 M K^+ or Na^+.

After the respective digestion time, the solids were recovered, washed free of chloride and dried overnight at 100°C. The hydrous oxides were then calcined at 500°C for 12 h to convert them to zirconia. A heating rate of 1°C/min was used. The thermal stability of the zirconia was determined by successive heating up to 1000°C. Similar heating conditions as for 500°C were used.

The samples are coded as follows: *h-X-y-T*, where *h*=pH, *X*=NH_3, K or Na for digestion using NH_4OH/Cl, KOH/Cl and NaOH/Cl, respectively, *y* the digestion time in hours or RT for the aged sample, *T* stands for the temperature of calcination, and *P* for the hydrous oxide precursor.

2.2. Characterization

The hydrous zirconia was analysed by thermogravimetric analysis (Dupont SDT 2960) and differential scanning calorimetry (Dupont DSC 2920) for the degree of hydration in the hydrous zirconia and any heat absorption/evolution during its transformation to zirconia, respectively. A heating rate of 20°C/min was used for both TGA and DSC measurements with a gas flow of 80 ml/min of air and nitrogen, respectively. The surface area of the samples was determined by a single point BET using a Micromeritics 2300. Crystal structure was measured using a Siemens D5005 diffractometer (Cu anode) equipped with variable primary and secondary beam slits. Crystallite sizes were estimated using the Scherrer equation. The hydrous oxides were analysed for sodium and potassium by dissolving in concentrated sulphuric acid and measuring the concentration using atomic absorption spectrophotometry (Perkin-Elmer 1100 B). In order to find out if the cations are strongly adsorbed on the sample, 13.7-Na-192-P with 1.36 wt% Na was placed in a dialysis tube and dialysed in doubly distilled water for 1 and 8 days, respectively.

3. Results

3.1. Elemental analysis

Table 1 shows the results of the elemental analysis for hydrous oxides digested at pH 9.5 and 12. At pH 9.5, the amount of cations adsorbed onto the hydrous zirconia was very low. However, at pH 12, the uptake of sodium was higher and increased with longer digestion time to 0.16 wt% in 12-Na-192-P. The uptake of sodium in the corresponding K-series was lower, ~0.011–0.083 wt%, but the potassium increased from 0.010 to 0.102 wt% with digestion. Precursors digested at pH 13.7 [16] showed even higher amounts of sodium and potassium. At this pH, samples digested in KOH/Cl had about 0.25 wt% Na while the potassium increased from 0.002 wt% in the undigested sample to 0.55 wt% in 13.7-K-192-P. The corresponding samples digested in NaOH/Cl had 0.75–1.36 wt% Na but K concentration was below 0.026 wt%.

3.2. Thermogravimetric analysis

The degree of hydroxylation of the hydrous zirconia is deduced from the water loss during thermogravimetric analysis. The undigested precursor for all series had about one mole of water per mole zirconia, $ZrO_2 \cdot H_2O$ or $ZrO(OH)_2$. After digestion at 100°C, the hydrous oxide from the K- and Na-series suffered significant water loss as compared to the undigested precursor. The amount of water in the hydrous oxide decreased with digestion time. In the K-series, the hydrous zirconia contained 0.88–0.53 mol of water/ZrO_2 while a slightly lower water content of 0.86–0.48 mol water/ZrO_2 was determined for the Na-series. The hydrous oxides from the NH_3-series ranged from 0.91 to 0.78 mol water/ZrO_2.

Hydrous zirconia is usually amorphous and its crystallinity is difficult to deduce from X-ray crystallography. However, some insight into the degree of

Table 1
Elemental analysis of hydrous zirconia digested at pH 9.5 and 12

Sample	Na (wt%)	K (wt%)	Sample	Na (wt%)	K (wt%)
9.5-Na-RT-P	0.008	0.001	9.5-K-RT-P	0.007	0.009
9.5-Na-12-P	0.007	0.004	9.5-K-12-P	0.005	0.007
9.5-Na-24-P	0.007	0.003	9.5-K-24-P	0.006	0.008
9.5-Na-48-P	0.005	0.005	9.5-K-48-P	0.004	0.010
9.5-Na-96-P	0.009	0.006	9.5-K-96-P	0.007	0.014
9.5-Na-192-P	0.007	0.009	9.5-K-192-P	0.005	0.016
12-Na-RT-P	0.018	0.010	12-K-RT-P	0.011	0.010
12-Na-12-P	0.024	0.009	12-K-12-P	0.017	0.029
12-Na-24-P	0.027	0.008	12-K-24-P	0.017	0.029
12-Na-48-P	0.060	0.009	12-K-48-P	0.041	0.062
12-Na-96-P	0.070	0.007	12-K-96-P	0.049	0.072
12-Na-192-P	0.157	0.023	12-K-192-P	0.083	0.102

Table 2
Water content ($ZrO_2 \cdot nH_2O$), enthalpy and peak temperature of glow exotherm, and activation energy of crystallization in hydrous zirconia

Sample	n (mol)	ΔH (kJ/mol)	T_g (°C)	E_a (kJ/mol)
9.5-0-P	0.995	19.63	442	178
9.5-Na-RT-P	0.962	19.46	455	181
9.5-Na-12-P	0.885	14.46	519	197
9.5-Na-24-P	0.793	13.90	565	209
9.5-Na-48-P	0.781	–	–	–
9.5-Na-96-P	0.760	–	–	–
9.5-Na-192-P	0.480	–	–	–
9.5-K-RT-P	1.09	19.85	452	180
9.5-K-12-P	0.887	15.07	492	191
9.5-K-24-P	0.798	14.37	532	201
9.5-K-48-P	0.766	7.31	577	213
9.5-K-96-P	0.678	–	–	–
9.5-K-192-P	0.528	–	–	–
9.5-NH_3-RT-P	1.01	20.18	453	180
9.5-NH_3-12-P	0.919	16.76	482	188
9.5-NH_3-24-P	0.910	15.12	510	195
9.5-NH_3-48-P	0.895	10.93	547	205
9.5-NH_3-96-P	0.893	–	–	–
9.5-NH_3-192-P	0.780	–	–	–

atomic ordering in the hydrous zirconia can be obtained from DSC measurements. A highly exothermic peak is often observed during the crystallization of zirconia from the hydrous precursor. This glow exotherm has a typical value of ~20 kJ/mol and is found to be present when the amorphous precursor transforms to a crystalline oxide. It is absent when the hydrous oxide is already crystalline or when the final oxide is amorphous [17]. Between pH 8 and 12, the glow exotherm moved to higher temperatures when the hydrous oxide was digested (Table 2). In the undigested precursor, the peak temperature for the exotherm was at 442°C but increased to 565°C after digestion for 24 h in NaOH/Cl. The amount of heat released decreases with digestion. This implies that the hydrous zirconia rearranges to a lower energy state with digestion. Comparing the series, it can be seen that the peak temperature shift and the reduction in the enthalpy of the glow exotherm are biggest in the Na-series, followed by the K- and finally the NH_3-series. Depending on the cation, hydrous oxides digested for longer than 48 or 96 h do not show the glow exotherm despite heating up to 600°C. By this temperature, zirconia is already formed. Hence, in these hydrous oxides, the transformation occurs without any glow exotherm. The activation energy for the transformation to zirconia can be estimated by applying the Redhead equation to the maximum of the glow exotherm: $E_a = RT[\ln(\nu T_p/(\beta) - 3.64]$, where ν is taken as $10^{13}\ s^{-1}$, T_p the peak temperature, and β is the heating rate. The activation energy involved in the crystallization to zirconia is ~180 kJ/mol; digested hydrous oxides encounter increasingly higher activation barriers.

3.3. Surface area

Fig. 1 compares the surface area of zirconia formed after calcination at 500°C for the three series where the hydrous oxides had been digested at pH 8. The surface area increases with digestion time: from 34.2 m^2/g in the undigested sample to ~160 m^2/g after 192 h of digestion. Both the Na- and K-series were very similar in surface area but the NH_3-samples had ~30% lower surface area. In the latter, even after 192 h, the highest surface area attained was only 116 m^2/g. Increasing the pH to 9.5 resulted in a much higher surface area. For samples that had been digested for 192 h, the zirconia formed had 214–263 m^2/g. Although the three series showed the same dependence with digestion time, their surface areas differed in the order NH_3<K-<Na-hydrous oxides.

The surface area of zirconia increased with further increase of pH to 12 (Fig. 2(a)). A maximum in the

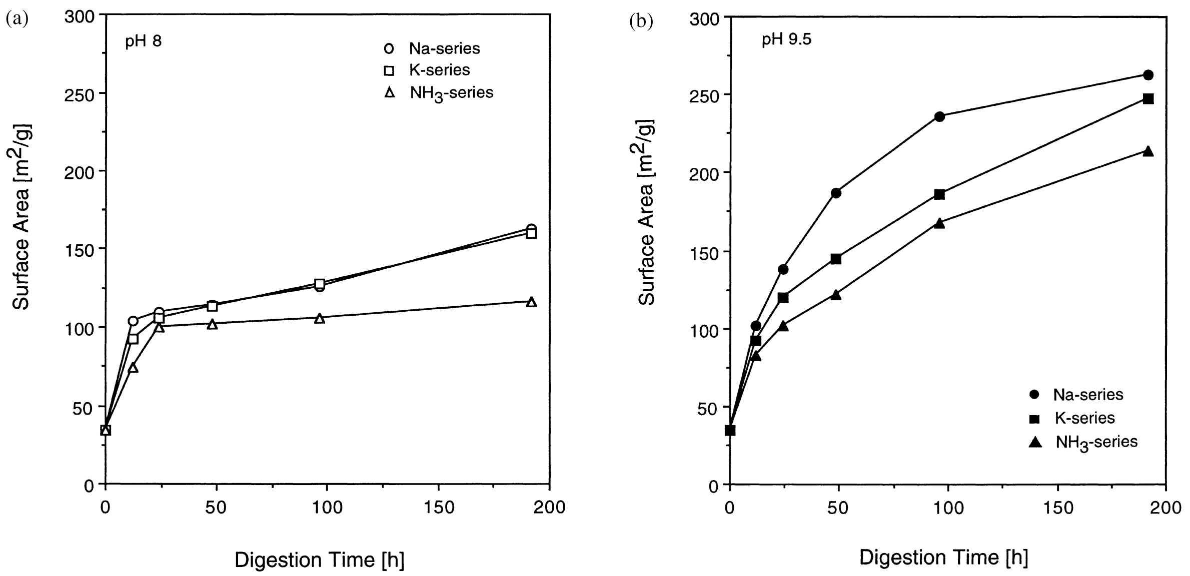

Fig. 1. Surface area of zirconia as a function of digestion time at (a) pH 8 and (b) pH 9.5.

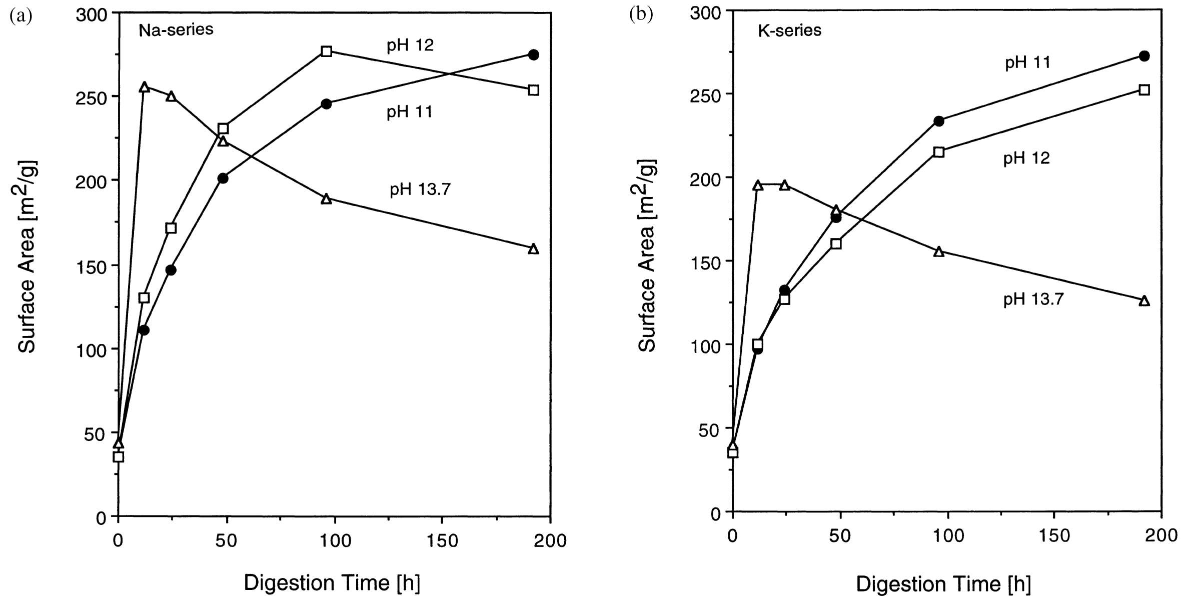

Fig. 2. Surface area of zirconia from (a) Na- and (b) K-series as a function of digestion time and pH.

surface area at 277 m^2/g was observed for 12-Na-96-500. Longer digestion time led to a decrease in the surface area of the resulting zirconia. At pH 13.7, the maximum surface area was obtained only after 12 h of digestion. However, the surface area was slightly lower than for pH 12, 256 m^2/g. Further digestion resulted in zirconia with lower surface areas.

The K-series shows a similar dependence of surface area on digestion time and pH although the surface area was lower than the corresponding Na-samples

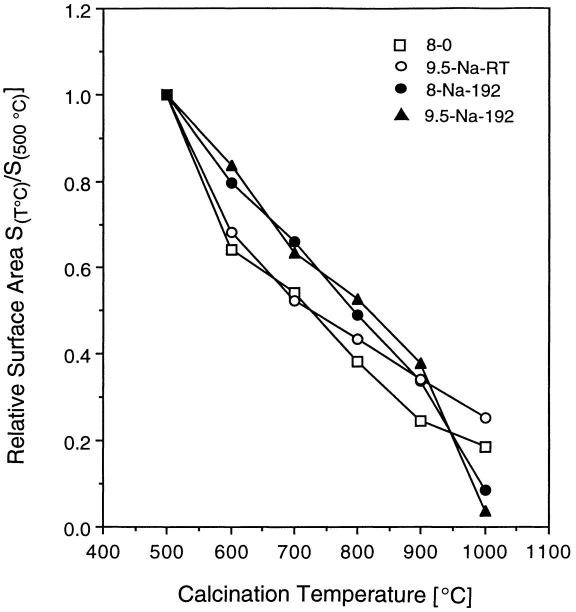

Fig. 3. Relative surface area as a function of calcination temperature for undigested, aged and digested zirconia from the Na-series.

(Fig. 2(b)). Digestion at pH 11 gave the highest surface area zirconia in this series, 247 m^2/g. In contrast to the Na-series, digestion at pH 12 resulted in a lower surface area than at pH 11. At pH 13.7, the highest surface area was observed in the samples that had been digested for 12–24 h, 195 m^2/g.

The surface area of the zirconia is monitored as a function of increasing calcination temperatures. With a slow heating ramp of only 1°C/min to reach the final temperature, the material is subjected to heat treatment for more than 12 h. The surface area is rather stable and does not decrease significantly even when calcined for up to 7 days. The relative surface area (surface area after calcination at temperature *T*/surface area at 500°C) versus calcination temperature shows that the zirconia formed from the undigested precursor lost the most surface area when calcined to 600°C (Fig. 3). Beyond this temperature, the loss in surface area was smaller. The sample that had been aged at room temperature showed the same temperature dependence as the undigested sample. In contrast, zirconia from the digested precursors were better stabilized against surface area loss with a more gradual decrease with calcination. Hence, they retained a higher surface area even after calcination to 900°C. For example, 8-Na-192-900 had 55.2 m^2/g while 8-0-900 and 8-Na-RT-900 were only 8.30 and 15.0 m^2/g, respectively. Digestion at pH 9.5 enhanced the surface area more than pH 8; however, zirconia formed under the former conditions showed similar thermal stability. As the former had a higher surface area to start with, the surface area was between 75 and 100 m^2/g even after calcination to 900°C.

3.4. Crystal phase

The hydrous oxides, digested and non-digested, for preparations at pH 8–12 were X-ray amorphous. After calcination at 500°C, the resulting zirconia in most samples were crystalline (Table 3). The zirconia formed from the undigested precursor at pH 9.5 was predominantly monoclinic with only about 17% tetragonal phase. However, after digestion, the resulting zirconia was mainly in the tetragonal phase. The percentage tetragonal phase increased with digestion time. At pH 8, the Na-series had the highest fraction of tetragonal phase, followed by the K-series and finally the NH_3-series. At pH 9.5, the fraction of tetragonal phase was higher than for pH 8 and the pure tetragonal phase was observed in samples that had been digested for more than 24 h. Longer digested ones such as 9.5-Na-96-500, 9.5-Na-192-500, and 9.5-K-192-500 were X-ray amorphous. The same trend was observed at pH 11 and 12 although for 12-K-96-500 and 12-K-192-500, some tetragonal and monoclinic phases can be distinguished from the broad amorphous background. After calcination to 600°C, 12-K-96-600 became crystalline with about 7.7% monoclinic phase. 12-K-192-600 remained mainly amorphous but with a higher fraction, 24.5%, of the monoclinic phase. The corresponding samples from the Na-series also contained some monoclinic and tetragonal phases although they were even more amorphous than the K-samples. In comparison, hydrous oxides that had been digested at pH 13.7 were already crystalline [17]. All digested hydrous oxides and resulting zirconia from the K-series crystallized with ~20% monoclinic phase while the Na-series were purely tetragonal. Fig. 4 shows the average crystallite size of monoclinic and tetragonal phases for the Na-series at different pH and digestion times. The tetragonal crystallites are smaller than the monoclinic ones, in accordance with

Table 3
Crystal phase in zirconia (calcined at 500°C, 12 h) prepared at different pH

Sample	Tetragonal (%)				
	pH 8	pH 9.5	pH 11	pH 12	pH 13.7
h-0-500	16.5	17.1	17.5	17.5	41.6
Na-RT-500	16.2	22.1	25.3	25.8	75.6
Na-12-500	83.4	89.5	97.4	96.3	100
Na-24-500	89.8	100	100	95.0	100
Na-48-500	90.4	100	100	74.0	100
Na-96-500	93.1	Amorphous	Amorphous	Amorphous	100
Na-192-500	97.2	Amorphous	Amorphous	Amorphous	100
K-RT-500	14.6	20.9	25.6	21.8	–
K-12-500	80.0	83.2	94.6	94.8	91.0
K-24-500	82.1	98.7	100	96.5	86.9
K-48-500	84.4	100	100	94.8	86.2
K-96-500	92.8	100	Amorphous	Amorphous	81.2
K-192-500	96.0	Amorphous	Amorphous	Amorphous	76.7
NH_3-RT-500	11.7	15.0	–	–	–
NH_3-12-500	58.3	73.4	–	–	–
NH_3-24-500	85.9	88.7	–	–	–
NH_3-48-500	88.8	96.1	–	–	–
NH_3-96-500	89.9	100	–	–	–
NH_3-192-500	94.0	100	–	–	–

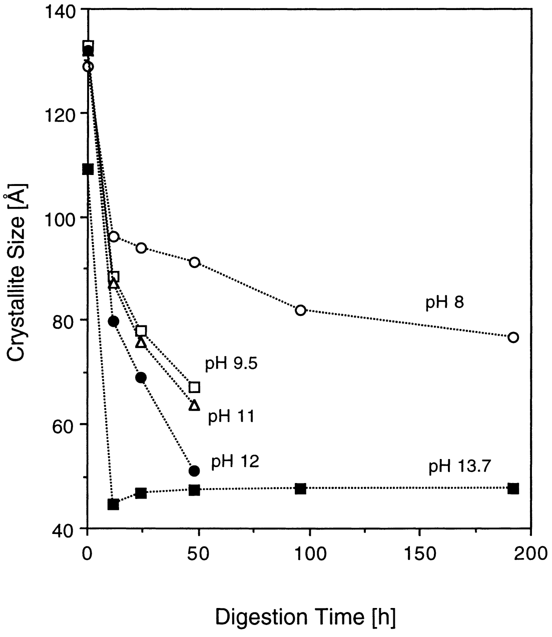

Fig. 4. Average crystallite size of zirconia from Na-series as a function of digestion time and pH.

the postulation of Garvie [18,19] that the metastable tetragonal phase is stabilized for small sizes due to their surface energy. At a constant pH, the crystallites decreased with digestion time. However, as the pH was increased, the crystallites also became smaller.

Table 4
Properties of untreated zirconia and zirconia purified by dialysis after calcination at 500°C

Sample	Na (wt%)[a]	Surface area (m^2/g)	Crystallite size (Å)
Undialysed	1.36	160	43.8
Dialysed 1 day	1.04	155	42.6
Dialysed 8 days	0.74	157	42.8

[a] Determined in hydrous zirconia.

3.5. *Dialysis of hydrous zirconia*

The hydrous zirconia, 13.7-Na-192-P, had a very high Na content of 1.36 wt% (Table 4). Following dialysis for one and eight days, the Na content decreased slightly. Calcination of the hydrous oxide resulted in zirconia with similar surface area of ~160 m^2/g. The crystallite size as deduced from XRD measurements shows no significant change.

4. Discussion

We have previously discussed the effects of digestion on hydrous zirconia [17]. The initially precipitated hydrous zirconia undergoes dissolution and reprecipitation during digestion so that the network of particles is strengthened. This allows a porous network to be formed which can withstand collapse during drying and calcination. Greater crystalline perfection also occurs in the samples so that mass transport leading to nucleation and grain growth is hindered during the transformation to zirconia. Hence, the high surface area of the hydrous oxide is to much extent retained in the resulting zirconia.

The hydrous oxide is of the formula $ZrO_2 \cdot H_2O$. The isoelectric point of hydrous zirconia is around 6–7 [20] so that at high pH, the gels are negatively charged. Counterions are attracted to the sphere closest to the primary particles. The high temperature during digestion increases the rate of collisions between the particles so that a stabilized network is formed via condensation of hydroxyl groups. This is supported by the decreasing exotherm in the DSC measurements, which indicates that a more stable hydrous oxide is formed during digestion. Despite the same ionic strength and pH of the digestion medium, the hydrous oxides from the Na- and K-series lost more water during digestion than the NH_3-series. This may imply that the former ions are more effective in charge neutralization than the NH_4^+ ion. Hence, the particles can easily agglomerate to a network structure by neck formation. Such network-strengthening mechanisms are absent in the undigested and aged precursors. The low temperature of the mother liquor reduces the encounters between particles. Hence, the loose agglomerate of primary particles collapses and loses its porous structure during calcination, resulting in low surface area zirconia.

Hydrous zirconia is known to be a cation exchanger at alkaline pH [21]. Hence, besides acting as counterions, Na^+, K^+ and NH_4^+ are also adsorbed on the hydrous zirconia. Even when KOH is used as the precipitant, more Na^+ is detected than K^+. Na^+ is most probably present as an impurity in the salt and base used. Both Na^+ and K^+, unlike the NH_4^+ ion, remained even after calcination. The adsorption of cations (and anions) helps to stabilize the surface area. The presence of these ions also favours the tetragonal phase. Indeed, at any pH, zirconia formed from the Na-series has the highest surface area and highest per cent tetragonal phase, followed by the K-series and finally the NH_3-series. The uptake of the cations increases with pH. Hence, the difference in the surface area between the series increases with pH, with the smallest deviation between the series at pH 8. It is not possible to completely remove the adsorbed cations by washing. Even prolonged dialysis did not reduce their concentration to a negligible level.

Besides the role of the cations, the pH of the mother liquor also strongly influences the textural properties of the hydrous zirconia and the resulting product. The surface area of zirconia increases with pH of the digestion medium up to pH 11. This may be related to the increased solubility of the hydrous zirconia, as found by Adair et al. [22]. The crystallite size of the hydrous zirconia was found to decrease with pH. Due to digestion, defect sites are minimized, which in turn hinder grain growth during calcination. Hence, the crystallites remained small even after conversion to the oxide, resulting in high surface area. However, at pH 12, the high solubility led to the formation of the thermodynamically stable monoclinic phase at long digestion times. This is in accordance with the Ostwald ripening mechanism. Hence, the surface area decreases as the monoclinic crystallites are bigger than the tetragonal ones. The effect is even more obvious at pH 13.7, where digestion longer than 24 h led to a considerable decrease in the surface area.

The results show that the hydroxide concentration up to pH 12 directly affects the crystal phase formed. The tetragonal phase is preferentially formed after digestion at pH 8–11. This may be explained by the decreasing crystallite size with digestion, which favours the tetragonal form, as well as the structural similarities between the amorphous state and the tetragonal structure. The transformation of the amorphous hydrous oxide into a crystalline state encounters an increasing activation barrier as a result of digestion. Hence, any transformation to the crystalline state would tend towards the tetragonal structure in a topotactic rearrangement of the atoms. In the pH range up to 12, the role of cations in determining the crystal structure is small as very little ions are taken up by the sample. Indeed, the observation of the thermodynamically stable monoclinic phase in long-digested samples at pH 12 is possibly due to the limited

Na^+ adsorption. At pH 13.7, considerable adsorption of Na^+ takes place for the Na-series so that only the pure tetragonal phase can be observed. A lower Na^+ content for the K-series resulted in some 20% monoclinic phase in all the digested samples. It is expected that a higher fraction of the monoclinic phase should be present in the absence of the ions.

5. Conclusion

The pH of the digestion medium affects the solubility of the hydrous zirconia and the uptake of cations. Both factors in turn influence the surface area and crystal phase of the resulting zirconia. Between pH 8 and 11, the surface area increased with pH. At pH 12, longer-digested samples suffered a decrease in surface area. This is due to the formation of the thermodynamically stable monoclinic phase with bigger crystallite size. The decrease in the surface area with digestion time is even more pronounced at pH 13.7. However, only the tetragonal phase was detected in these samples. The adsorption of Na ions is believed to result in the stabilization of the tetragonal phase. These ions are not easily removed even with dialysis. At constant ionic strength, the surface area of the resulting zirconia increases in the order of NH_3-<K-<Na-series. The hydrous oxides from the Na-series show the highest degree of atomic ordering, suggesting the effectiveness of the Na^+ ion to act as a counterion to the negatively charged gel.

References

[1] P.D.L. Mercera, J.G. van Ommen, E.B.M. Doesburg, A.J. Burggraaf, J.R.H. Ross, Appl. Catal. 71 (1991) 363.
[2] T. Yamaguchi, Catal. Today 20 (1994) 199.
[3] F. Babou, G. Coudurier, J.C. Vedrine, J. Catal. 152 (1995) 341.
[4] D. Hamon, M. Vrinat, M. Breysse, B. Durand, M. Jebrouni, M. Roubin, P. Magnoux, T. des Courières, Catal. Today 10 (1991) 613.
[5] Y. Amenomiya, Appl. Catal. 30 (1987) 57.
[6] B. Denise, R.P.A. Sneeden, Appl. Catal. 28 (1986) 235.
[7] L. Bruce, J.F. Mathews, Appl. Catal. 4 (1982) 353.
[8] L.A. Bruce, G.J. Hope, J.F. Mathews, Appl. Catal. 8 (1983) 349.
[9] M. Ozawa, M. Kimura, J. Mater. Sci. Lett. 9 (1990) 446.
[10] U. Ciesla, S. Schacht, G.D. Stucky, K.K. Unger, F. Schüth, Angew. Chem. Int. Ed. Engl. 35 (1996) 541.
[11] P. Afanasiev, C. Geantet, M. Breyysse, J. Catal. 153 (1995) 17.
[12] G.K. Chuah, S. Jaenicke, S.A. Cheong, K.S. Chan, Appl. Catal. A 145 (1996) 267.
[13] G. Centi, G. Cerrato, S. D' Angelo, U. Finardi, E. Giamello, C. Morterra, S. Perathoner, Catal. Today 27 (1996) 265.
[14] G.T. Mamott, P. Barnes, S.E. Tarling, S.L. Jones, C.J. Norman, J. Mater. Sci. 26 (1991) 4054.
[15] X. Turrillas, P. Barnes, S.E. Tarling, S.L. Jones, C.J. Norman, C. Ritter, J. Mater. Sci. Lett. 12 (1993) 223.
[16] G.K. Chuah, S. Jaenicke, Appl. Catal. A. 163 (1997) 261.
[17] G.K. Chuah, S. Jaenicke, B.K. Pong, J. Catal. 175 (1998) 80.
[18] R.C.J. Garvie, J. Phys. Chem. 69 (1965) 1238.
[19] R.C.J. Garvie, J. Phys. Chem. 82 (1978) 218.
[20] C.R. Vera, J.M. Parera, J. Catal. 165 (1997) 254.
[21] A. Clearfield, G.P.D. Serrette, A.H. Khazi-Syed, Catal. Today 20 (1994) 295.
[22] J.H. Adair, R.H. Denkewicz, Ceram. Powder Sci. 3 (1990) 25.