

Influence of water/alkoxide ratio on the properties of Ru/Al₂O₃ xerogel catalysts

Victor I. Okafor, Neil J. Coville *

Applied Chemistry and Chemical Technology Centre, Department of Chemistry, University of the Witwatersrand, Johannesburg, PO WITS 2050, South Africa

Received 4 January 1999; received in revised form 2 February 1999; accepted 4 February 1999

Abstract

A series of Ru/Al₂O₃ catalysts were prepared by the sol–gel method using water/alkoxide ratios, h , of 1, 2, 3, 6 and 9. An increase in h resulted in (i) total BET surface area (149 to 426 m² g⁻¹), (ii) particle size (SEM) distribution (1.3/1.7 mm to 0.05/0.14 mm) and (iii) pore characteristic (pore distribution, volume, size and shape) changes. Indeed the pore volume was found to increase linearly with h . Low h values ($h < 3$) produced compact gel precipitates that had comparatively lower surface areas while better hydrolysis ($h > 3$) gave rise to more porous gels with larger surface area and finer texture. Alumina crystallinity as well as ruthenium reducibility of calcined samples (773 K) were largely unaffected by h . XRD spectra revealed the presence of RuO₂ after calcination. There was a significant effect on the percent weight loss (50 to 60%) of the samples on heating for $h < 3$. The characterisation results show that the degree of hydrolysis can control the properties of Ru/Al₂O₃ catalysts in a predictable manner. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ru/Al₂O₃ catalysts; Sol–gel; Xerogel; Water/alkoxide ratio; Extent of hydrolysis

1. Introduction

The extensive application of ruthenium supported catalysts in the Fischer–Tropsch synthesis [1], selective hydrogenation [2] and oxidation reactions [3], and hydrogenolysis of paraffins and olefins [4] is well known. Performance of the catalysts in these reactions is influenced by their physical and chemical properties that are in turn influenced by their preparation methods.

The use of the highly controllable sol–gel technique [5] for the synthesis of supported

metal catalysts, including ruthenium [6–8], offers attractive advantages for catalysis preparation and continues to generate much interest. The method is based on the use of hydrolysable molecular precursors, mostly metal or semi-metal alkoxides, and leads to catalysts with unique physico-chemical properties. The catalytically active metallic element can be introduced into the liquid alkoxide *before* hydrolysis and condensation, thus enabling the catalytic metal to be incorporated into the polymer network [9]. The mechanisms by which the hydrolysis and condensation reactions form the final oxide network are not well understood [9,5], but can be represented in the simplified scheme

* Corresponding author. Tel.: +27-11-716-2219; fax: +27-11-339-7967; E-mail: ncoville@aurum.chem.wits.ac.za

(aluminum isopropoxide ($\text{Al}(\text{OPr}^i)_3$) as the precursor alkoxide) shown in Scheme 1.

According to Scheme 1, complete hydrolysis of the alkoxide should occur when the ratio of $\text{Al}(\text{OPr}^i)_3/\text{H}_2\text{O} = h = 3$.

Advantageous features of sol–gel processed catalysts include high surface area, well-defined pore sizes and high purity [10]. These properties are influenced by several preparation parameters such as solvent type [11,12], concentration, drying method [13], temperature and time of aging, calcination and water/alkoxide ratio (extent of hydrolysis) [5,14,15]. However the role of these variables on the synthesis of ruthenium/sol–gel materials has not been explored in any detail. Some pertinent studies in which the sol–gel methodology has been used in the synthesis of ruthenium catalysts are listed below.

Niwa et al. [2] have studied the effects of various alcoholic solvents in the sol–gel preparation of ruthenium catalysts and found the technique useful for controlling the catalyst surface areas and porosities. Additionally, the ruthenium catalysts were purer and proved much more effective for the partial hydrogenation of benzene to cyclohexene. Yang and Shul [8] determined that the use of ethylene glycol as chelating agent in the sol–gel synthesis of $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts effectively promoted the phase transition to α -alumina with high surface area even at 1073 K. Lopez et al. prepared Ru/SiO_2 catalysts possessing different ruthenium concentrations by the sol–gel route enabling incorporation of ruthenium particles into the oxide network. The catalysts showed better selectivity and significantly greater resistance to coke formation and deactivation than those syn-

thesised by the traditional impregnation method. This effect was attributed to structural differences in the prepared catalysts [9,16].

Hydrolysis in sol–gel synthesis is often effected using excess water (i.e., high h values). Investigations into the effect of degree of hydrolysis on sol–gel derived catalysts employing low h values are few. Such a study by Balakrishnan and Gonzalez found the properties and catalytic activity of $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts to be directly influenced by h [15].

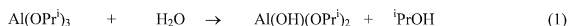
The aim of the present work is to investigate the physical property response induced by the extent of hydrolysis in $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts prepared by the sol–gel method using small h values. Performance of these catalysts in the partial oxidation reaction of methane will be reported elsewhere [17].

2. Experimental

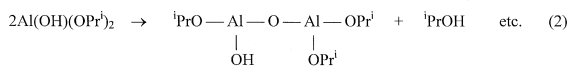
2.1. Sol–gel xerogel synthesis

The sol–gel synthesis procedure used was adapted from the work of Yang and Shul [8]. A series of 2.6 wt.% $\text{Ru}/\text{Al}_2\text{O}_3$ xerogel catalyst samples were prepared with molar water/alkoxide ratio (h) of 1, 2, 3, 6 and 9 respectively. For example, when $h = 1$, a reaction solution was made by dissolving aluminum isopropoxide (10.213 g, 0.05 mole; AIP, Aldrich) in refluxing propan-2-ol (12.182 g, 0.20 mole; BDH) for 2 h at 363 K. A separate solution of a μ_3 -oxo-triruthenium acetate complex, $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{H}_2\text{O})_3][\text{OCOCH}_3]$, (Fig. 1(a)) (0.3475 g, 4.4×10^{-4} mole), the ruthenium source [19], was made in diethylene glycol (Fig. 1(b)) (27.356 g, 0.26 mole; DEG; BDH) by vigorous stirring for 2 h. The alkoxide solution was then combined with the ruthenium solution at 363 K and the solution maintained at this temperature for 3.5 h. The mixture was cooled to room temperature and allowed to stand for 4.5 h. The solution was then reheated to 363 K whereupon distilled

Hydrolysis:



Condensation/polymerisation:



Scheme 1.

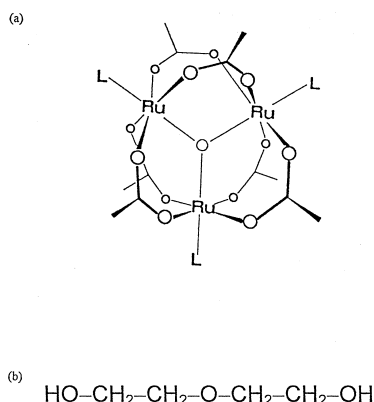


Fig. 1. Reagents used in this study: (a) the ruthenium acetate cluster unit [18], $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{H}_2\text{O})_3]^+$, and (b) diethylene glycol.

water (0.9 g, 0.05 mole) was added. The resulting mixture was thoroughly homogenised with a spatula and aged for 12 h at 363 K. The gel was dried in a convection oven for 4 days at 383 K and calcined in air for 5 h at 773 K.

The Ru/Al₂O₃ samples are denoted as DEG1, DEG2, DEG3, DEG6 and DEG9 with the digits corresponding to the molar water/al-koxide ratio employed during their synthesis.

2.2. Physico-chemical characterisation

The specific surface areas (A_{BET}), average cylindrical pore diameters d_p and specific adsorption pore volumes V_p were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2010 instrument. Degassing of the samples to 0.1 Pa at 393 K preceded every measurement. V_p was calculated by the Barret–Joyner–Halenda (BJH) method [20] that is assumed to cover the cumulative adsorption pore volume of pores in the range 1.7 to 300 nm. Pore size distributions were obtained from the desorption branch of the isotherms employing the BJH method [21]. A_{BET} values were calculated in a relative pressure range 0.06 to 0.2 assuming a cross-sectional area of 0.162 nm² for the nitrogen molecule at 77 K. Assessment of micropore volume was made from t-plot constructions using the Harkins–Jura correlation

Table 1

Textural properties of Ru/Al₂O₃ xerogel catalysts calcined at 773 K for 5 h

Sample	A_{BET}^a (m ² /g)	V_p^b (cm ³ /g)(nm)	d_p^c (nm)	Weight loss (%)
DEG1	149	0.16	4	52.5
DEG2	249	0.24	4	59.0
DEG3	273	0.33	5	74.4
DEG6	314	0.53	7	79.0
DEG9	428	0.81	8	79.1

^a A_{BET} : Specific surface area. ^b V_p : BJH cumulative adsorption pore volume of pores in the maximum range 1.7 to 300 nm. ^c $d_p = 4 V_p / A_{\text{BET}}$, the pore size diameter inferred from the desorption branch of nitrogen physisorption isotherms.

[22]. A JEOL JSM 840 electron microscope was utilised to obtain scanning electron micrographs (SEM) of the samples applying a 15 keV electron beam. Xerogel samples were initially coated with a gold layer; their microstructure was not affected by the beam and remained unchanged throughout the measurements. X-ray powder diffraction data were obtained from a Philips PW1820 instrument with a graphite monochro-

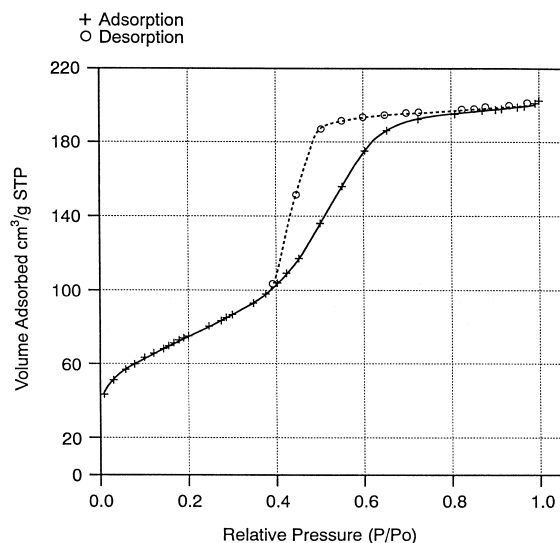


Fig. 2. Nitrogen physisorption on Ru/Al₂O₃ xerogel catalysts calcined at 773 K for 5 h: adsorption (↑)/desorption (↓) isotherm hysteresis loop of sample DEG3 ($h = 3$).

mator using CuK α radiation generated at 40 kV and 20 mA. Data were collected by a step-scan method within a 2θ region of 10 to 100°. Thermal analysis was carried out in an air convection oven at 773 K for 5 h and the weight loss determined after the sample was cooled to ambient temperature. Reducibility of the catalyst samples was determined by temperature programmed reduction measurements over hy-

drogen (5% H₂ in nitrogen) at a heating rate of 10° per minute up to 1173 K.

3. Results

Table 1 contains values depicting the textural properties of the catalysts calcined in air at 773 K for 5 h. For all molar water/alkoxide ratios

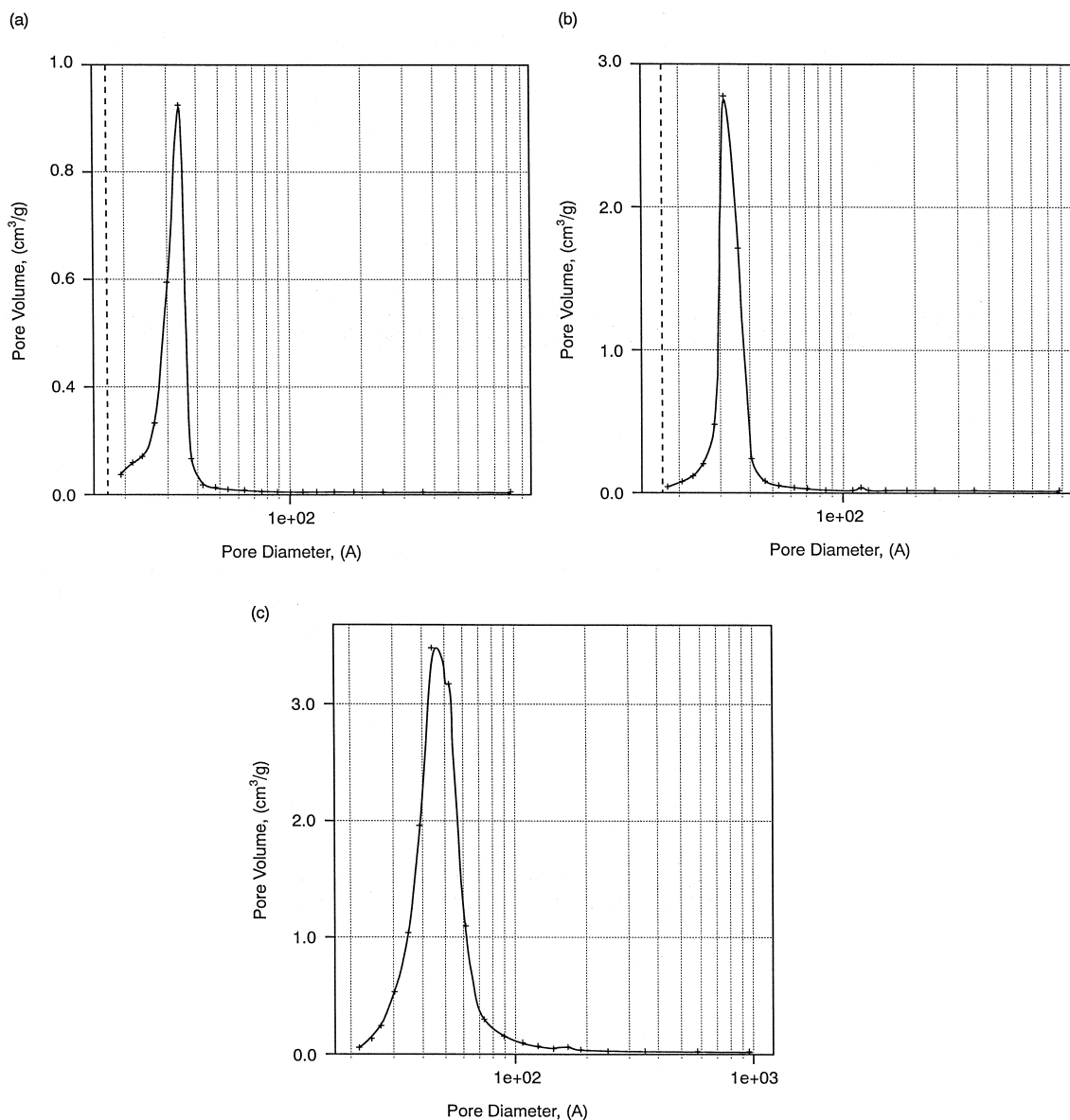


Fig. 3. Pore size distributions of calcined catalysts: (a) $h = 1$, (b) $h = 3$ and (c) $h = 9$.

(h) employed, the resulting catalysts exhibited similar Type-IV isotherms with Type-H2 desorption hysteresis indicative of mesoporosity and an insignificant presence of microporosity [23].

A representative adsorption/desorption isotherm hysteresis loop of a sample (DEG3) is shown in Fig. 2. Pore size distributions varied with h : the pore size distribution maxima broadened with larger h values. Pore size distributions for $h = 1$, $h = 3$ and $h = 9$ are shown in Fig. 3.

The level of hydrolysis clearly affected the specific surface areas (A_{BET}) of the xerogel catalysts. After calcination the samples had A_{BET} values of 149 to 429 $\text{m}^2 \text{g}^{-1}$, with values increasing with h . The adsorption pore volume as well as the average pore diameter also increased with h ranging from 0.16 to 0.81 $\text{cm}^3 \text{g}^{-1}$ and 4 to 8 nm respectively (Table 1).

XRD patterns recorded after calcination of the samples revealed that they were largely amorphous. The low crystallinity exhibited was independent of h (Fig. 4). The measured diffraction lines and intensities of the samples were compared with a PDF database file which

showed that the only contribution to crystallinity was from RuO_2 crystallites.

Scanning electron micrographs of xerogel catalysts synthesised with varying h are shown in Fig. 5. The samples consist of plate-like, stacked particles with sharp edges and terraces. Particle size was dependent on h and decreased when h increased. The ranges are $h = 1$, 1.3 to 1.7 μm ; $h = 2$, 0.9 to 1.7 μm ; $h = 3$, 0.5 to 0.8 μm ; $h = 6$, 0.2 to 0.8 μm ; $h = 9$, 0.05 to 0.14 μm .

All the samples showed similar TPR behaviour with the ruthenium reduction occurring in a broad temperature band between 418 and 603 K.

The weight loss recorded after calcination for all the samples investigated are given in Table 1. The weight loss mirrors the trend in h and increased as h increased. The weight loss arises mainly from the condensation and subsequent evolution of alcohol and water as well as the evolution of diethylene glycol and its oxidation residues in the catalyst matrix. There is a large increase in weight loss at $h = 3$, the theoretical stoichiometric water/alkoxide ratio. From this

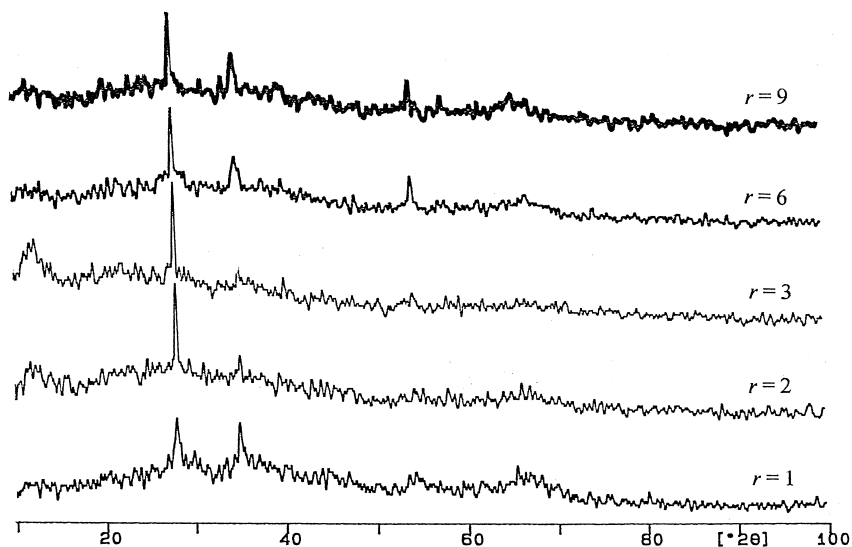


Fig. 4. X-ray diffraction patterns of $\text{Ru}/\text{Al}_2\text{O}_3$ xerogel catalysts prepared with various water/alkoxide ratios, h , and calcined at 773 K for 5 h.

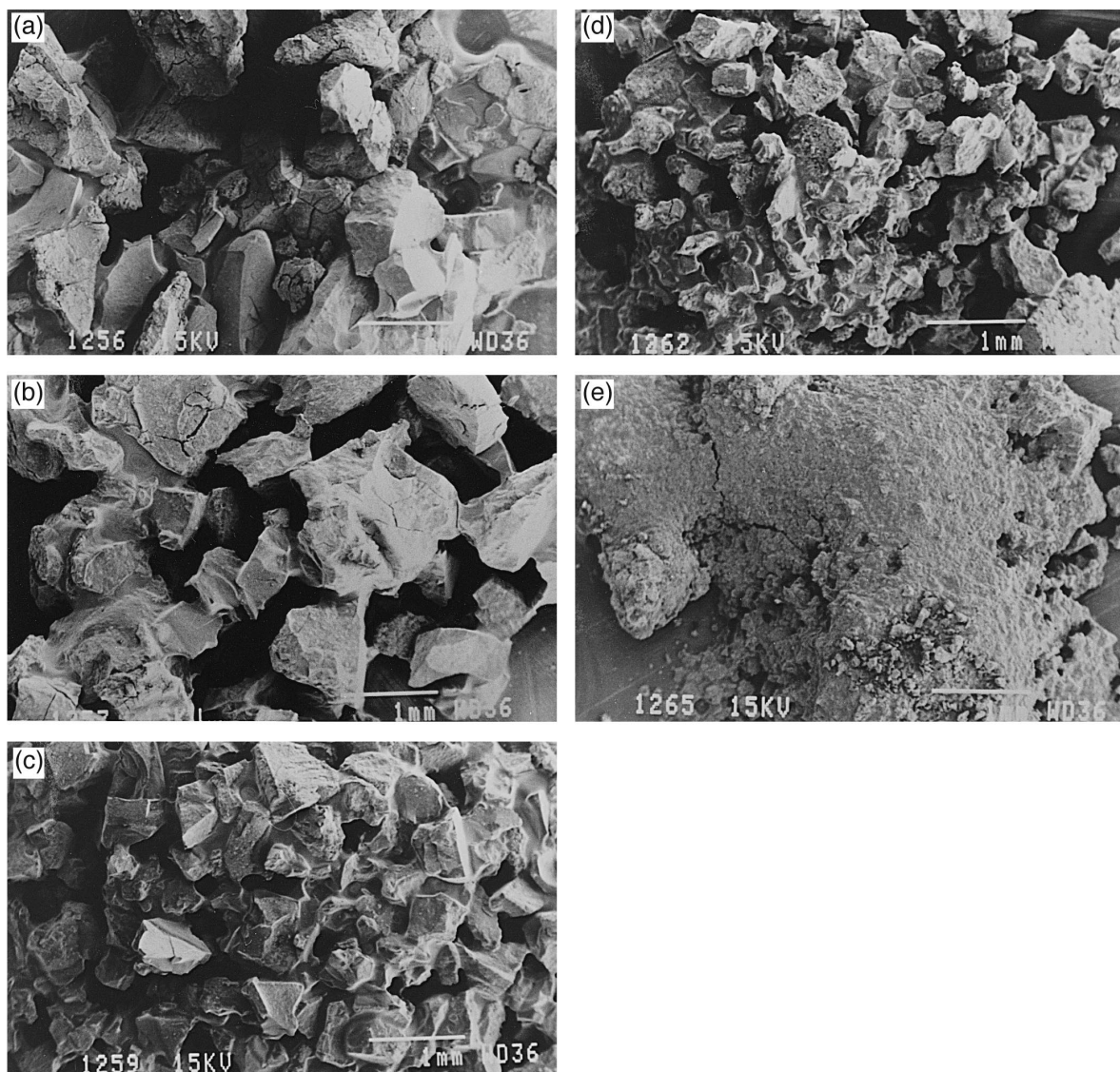


Fig. 5. Scanning electron micrographs of the calcined catalysts: (a) $h = 1$, (b) $h = 2$, (c) $h = 3$, (d) $h = 6$ and (e) $h = 9$.

point onwards weight loss does not change significantly.

4. Discussion

In this study a bidentate ligand was chosen for use in the sol–gel reaction. Diethylene glycol, like ethylene glycol, could be expected to coordinate to a ruthenium complex as a chelating or bridging ligand [8] and this binding mode

will affect the hydrolysis/condensation process [2]. The influence of the degree of hydrolysis, h , is not limited to the synthesis of the aluminum alkoxide but will also influence the behaviour of the Ru complex. In addition, structural differences between ruthenium–alumina alkoxide catalysts and plain alumina supports prepared with the *same* property-modifying solvents have also been observed [12]. Diethylene glycol is a strong chelating agent [24] and, as with ethylene glycol [8], may act as a bidentate

ligand and surfactant preventing agglomeration of Ru/Al₂O₃ particles in the sol-state. Its effect is to render the alkoxide less susceptible to hydrolysis and in doing so delays or prevents complete condensation of the sol.

Low values of the molar water/alkoxide ratio, h , have been investigated in this study so that h can be related to the extent or level of hydrolysis during the sol–gel processing of the catalysts. Utilisation of a sufficiently large h achieves complete hydrolysis of the reagent, and gives fine and porous Ru/Al₂O₃ with high surface areas. The extent of hydrolysis hence determines the size of the oligomer formed before heat treatment and thus influences the morphology (particle size, pore size and surface area) of the final product.

The influence of h on the surface area and particle size of the prepared catalysts is clearly significant (see Table 1 and Fig. 5). Under the conditions employed, A_{BET} increased with increasing h while particle size decreased while the particle assumed a finer structure. Pore data and surface area values indicate that insufficient hydrolysis ($h < 3$) leads to precipitation of the gel particles yielding condensed products with diminished surface area whereas fuller hydrolysis ($h > 3$) enhanced surface area and yielded a more open, finer texture suggestive of homogeneous gels composed of polymeric building blocks. As a general rule dilution results in lower molecular association [16]. Hydrolysis (and ultimately condensation) is, therefore, better facilitated in the presence of more water.

The trend shown by the desorption pore size distribution (Fig. 2) is that the samples change from a narrow pore size distribution maxima to a broader one as h increases leading to larger pores. However, the Type-H4 adsorption/desorption hysteresis loop displayed by all the samples, as well as the diffraction patterns (see Figs. 2 and 5) show that pore shape and crystallinity are independent of h . This is not unexpected since these properties of the xerogel catalysts are known [5,8,24] to be influenced more considerably by the solvent and calcina-

tion temperature (in the case of crystallinity) than by the degree of hydrolysis. For these samples crystalline structure is enhanced at the higher calcination temperatures.

The temperature programmed reduction (TPR) measurements indicate that the reducibility of the ruthenium is not significantly affected by h , occurring in the same wide temperature band of ~ 418 to 603 K for all samples. The TPR observation is consistent with X-ray diffraction patterns of the samples that show the presence of RuO₂ as the only crystallites in the structures.

Thermal analysis results (Table 1) support the explanation that incomplete hydrolysis limits condensation leading to less porous, low surface area precipitates. As h increases, the amount of hydrolysed moieties increases. This, in turn, translates into greater condensation in the form of more expulsion of water, alcohol and some diethylene glycol molecules during calcination. The increase in weight loss with h may be also partly attributed to a concomitant increase in the amount of adsorbed water in the products. Beyond the theoretical stoichiometric water/alkoxide amount, $h = 3$, weight loss stabilises. It is conceivable that water in $h > 3$ samples resides as adsorbed water most of which is removed during drying (4 days at 383 K) before calcination. For this reason excess water has a limited impact on weight loss during calcination.

5. Conclusions

An increase in the degree of hydrolysis, h , in the sol–gel reaction yields Ru/Al₂O₃ catalysts possessing increasing surface areas. The porosity and particle size of catalysts are also influenced by h . Under the conditions employed, X-ray diffraction studies on the samples show that the crystallinity (alumina, RuO₂) of the calcined samples is only slightly affected by h . Weight loss of calcined samples increased up to $h = 3$, the theoretical stoichiometric water/al-

oxide amount. Variation of h did not significantly affect the reducibility of the xerogel catalysts as revealed by temperature programmed reduction studies.

It is evident from the results of this study that the extent of hydrolysis is an important parameter for controlling the properties of Ru/Al₂O₃ xerogel catalysts and permits the synthesis of Ru/Al₂O₃ complexes with *controllable* physical properties.

Acknowledgements

We wish to thank the University, Foundation for Research Development and Andrew W. Mellon Foundation for financial assistance.

References

- [1] M.A. Vannice, *J. Catal.* 37 (1975) 449.
- [2] S. Niwa, F. Mizukami, S. Isoyama, T. Tsuchiya, K. Shimizu, S. Imai, J. Imamura, *J. Chem. Technol. Biotechnol.* 36 (1986) 236.
- [3] P.D.F. Vernon, M.L.H. Green, A.K. Cheetham, A.T. Ashcroft, *Catal. Lett.* 6 (1990) 181.
- [4] J.H. Sinfelt, in: *Bimetallic Catalysts: Discoveries, Concepts and Applications*, Wiley, New York, 1983.
- [5] C.J. Brinker, G.W. Scherer, in: *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990.
- [6] P. Kluson, J. Had, Z. Belohav, L. Cerveny, *Appl. Catal.* 149 (1997) 331.
- [7] L. Gucci, G. Stefler, Zs. Koppány, L. Borko, S. Niwa, F. Mizukami, *Appl. Catal.* 161 (1997) L29.
- [8] J.C. Yang, Y.G. Shul, *Catal. Lett.* 36 (1996) 41.
- [9] T. Lopez, A. Lopez-Gaona, R. Gomez, *J. Non-Cryst. Solids* 110 (1989) 170.
- [10] U. Schubert, *J. Chem. Soc., Dalton Trans.*, 1996, 3343.
- [11] C. Stocker, M. Schneider, A. Baiker, *J. Porous Mater.* 2 (1995) 171.
- [12] V.I. Okafor, PhD. Thesis, University of the Witwatersrand, 1998.
- [13] D.C.M. Dutoit, M. Schneider, A. Baiker, *J. Porous Mater.* 1 (1995) 165.
- [14] M.A. Vicarini, G.A. Nicolaon, S.J. Teichner, *Bull. Soc. Chim. Fr.* 107 (1993) 297.
- [15] K. Balakrishnan, R.D. Gonzalez, *J. Catal.* 144 (1993) 395.
- [16] T. Lopez, R. Gomez, O. Novaro, A. Ramirez-Solis, E. Sanchez-Mora, S. Castillo, E. Poulain, J.M. Martinez-Magadan, *J. Catal.* 141 (1993) 114.
- [17] V. Okafor, M. Makoa, N. Coville, manuscript in preparation.
- [18] F.A. Cotton, J.G. Norman Jr., *Inorg. Chim. Acta* 6 (1972) 411.
- [19] A. Spencer, G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, 1972, 1570.
- [20] E.P. Barrett, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.* 73 (1951) 373.
- [21] J.C.P. Broekoff, in: B. Delmon, P. Grange, P. Jacobson, G. Poncelet (Eds.), *Preparation of Heterogeneous Catalysts II*, *Stud. Surf. Sci. Catal.* 3, Elsevier, Amsterdam, 1973, p. 3.
- [22] W.D. Harkins, G. Jura, *J. Chem. Phys.* 11 (1943) 431.
- [23] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603.
- [24] K. Maeda, F. Mizukami, S. Niwa, M. Toba, *J. Chem. Soc. Faraday Trans.* 88 (1) (1992) 97.