Available online at www.sciencedirect.com
SCIENCE DIRECT®
Applied Catalysis A: General 297 (2006) 145–150
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Silication of γ-alumina catalyst during the dehydration of linear primary alcohols

N.P. Makgoba *, T.M. Sakuneka, J.G. Koortzen, C. van Schalkwyk, J.M. Botha, C.P. Nicolaides *

Heterogeneous Catalysis Department, Sasol Technology, Research and Development, P.O. Box 1, Sasolburg, 1947, South Africa

Received 30 April 2005; received in revised form 30 August 2005; accepted 1 September 2005
Available online 13 October 2005

Abstract

The dehydration of alcohols to alkenes over heterogeneous catalysts such as γ-alumina occurs at temperatures of around 300 °C, and it could be accompanied by undesirable reactions such as double-bond shift and, in severe cases, skeletal isomerization of the alkene products. In the dehydration of 1-hexanol and of 1-octanol (separately) over γ-alumina, we found that the selectivity to 1-alkenes decreased substantially with time-on-stream (TOS), while the alcohol conversion remained virtually constant. The loss in 1-alkene selectivity is a result of an increase in the extent of double-bond isomerization with increasing TOS. Upon analysis of the catalysts (fresh and used) and of the alcohol feeds (all by ICP spectroscopy), it was found that the feeds contained on average 1 ppm silicon and that the silicon content in the used catalysts was as high as 15 times that in the fresh one (3000 ppm as compared to 200 ppm, in one of our examples). The results show, therefore, that there is accumulation of silicon on the catalyst during the reaction and that this leads to the formation of additional and stronger acid sites, such as those found in silicated aluminas, which account for the increasing isomerization activity of the γ-alumina catalyst.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Silicon; Alumina; Alcohol dehydration; 1-Hexene; 1-Octene; 1-Hexanol; 1-Octanol

1. Introduction

The dehydration reactions of alcohols to produce the ether or the alkene have been known for several centuries [1,2]. Haag and Chen [3] have compared a number of reactions on the basis of the rate constant relative to that of *n*-hexane cracking. At 450 °C and a pressure of 1.0 bar over the zeolite H-ZSM-5, they found that the double-bond shift reaction of 1-hexene was six orders of magnitude faster than that of *n*-hexane cracking. Jacobs [4] compared reactions in terms of the temperature required to attain a rate constant of over 10^{-6} moles/g s and found that alcohol dehydration required 100 °C, the double-bond shift reaction 127 °C and paraffin cracking about 400 °C. The work by these authors shows that alcohol dehydration and double-bond shift reactions occur very easily over solid acid catalysts. Any of the vast array of available solid acid catalysts can be used for alcohol dehydration [5]. However, γ-aluminas are the most commonly used, especially for the longer chain alcohols (with more than three carbon atoms). This is because catalysts with stronger acidity, such as the silica-aluminas, molecular sieves, zeolites or resin catalysts can promote double-bond shift, skeletal isomerization and other olefin inter-conversion reactions [6,7].

Detailed studies reported in the literature [5,8–11] on the dehydration of alcohols over γ-alumina have shown that the alcohol molecules bond to the alumina surface through hydrogen bonding, where the alcohol and the alumina surface have complimentary functional groups, each being both a proton donor and a proton acceptor. In this proposed mechanism, a proton is transferred from a surface hydroxyl group to the alcohol oxygen, facilitating the transfer of a proton on the neighbouring carbon to a basic oxygen atom on the surface. An olefinic product then desorbs and the water molecule remains adsorbed on the surface and acts as a reaction inhibitor [12]. From these studies, however, there is also evidence for carbenium ion intermediates in some cases and for

* Corresponding authors. Tel.: +27 16 9604013; fax: +27 11 5225034.
E-mail addresses: petrus.makgoba@sasol.com (N.P. Makgoba), chris.nicolaides@sasol.com (C.P. Nicolaides).

0926-860X/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2005.09.003

Symrise AG, EX1027
Symrise AG v. Inolex Inc.
IPR2023-01035

concerted reactions in others, depending on the catalyst used. Alumina is generally considered a typical E_2 oxide [5,11], i.e. elimination of the proton and the hydroxyl group from the alcohol is a concerted reaction without formation of ionic intermediates. With zeolites, on the other hand, the reaction has been shown to proceed via carbenium ion intermediates (E_1 mechanism) [12].

The dehydration of alcohols with four or more carbons over solid acid catalysts is expected to be accompanied by the double-bond shift reaction of the alkene product. This is because the two reactions occur readily and at comparable rates [4]. In a chemical process for the dehydration of primary alcohols to produce 1-alkenes, the isomerization of the 1-alkene product to the internal alkenes presents many disadvantages. Firstly, the isomers have boiling points very close to that of the 1-alkene, and are therefore difficult and expensive to separate. Secondly, the isomerization reaction results in a loss of the useful 1-alkene products and therefore affects the efficiency of the process, since the isomers may not be suitable for the same end-use as the 1-alkene. This can have considerable cost implications for the process. As can be anticipated, therefore, it is desirable to have a high selectivity to the 1-alkene.

In the area of alcohol dehydration using γ-alumina as the catalyst, there is a considerable number of reports detailing methodologies used in trying to obtain high selectivities to 1-alkenes. These include: co-feeding of ammonia or amines during the reaction [13,14], the use of metal cations to modify the catalyst (by minimizing the number of acid sites that are thought to increase the rate of isomerization) [15–17], and also the transformation of the γ-alumina into another phase [18]. It is, however, not clear from all these work as to whether the driving force behind the quest for high selectivity is an inherent insufficient selectivity offered by the γ-alumina, or is due to catalyst changes occurring during the reaction, which cause the alumina to be less selective than required.

It is our intention in this paper to provide data showing that γ-alumina on its own, without any modifications, can give high 1-alkene selectivities. It is also our aim to show that the loss of 1-alkene selectivity observed in the present study is a consequence of the accumulation of silicon on the catalyst during the dehydration reaction. The silicon is present in the alcohol feeds (even in small concentrations at the 1 ppm range and lower) and implants on the catalyst during the reaction.

The deliberate deposition of silicon on γ-alumina is beneficial to some reactions and has been carried out, for example, for the skeletal isomerization of 1-butene to increase the activity of the catalyst [19–24]. The acid sites produced after the silication were found, however, to be weaker than those of silica-alumina [19,20,25], but were of sufficient strength to catalyze the skeletal isomerization of alkenes. Other reports have indicated that silication of γ-alumina occurs on the strong and medium-strong Lewis acid sites [25]. DRIFTS [26] and alcohol adsorption [27] studies showed that the surface hydroxyls and Lewis acid sites of γ-alumina are positioned next to each other, and that the reactivity of the hydroxyl towards adsorbed species is determined by the strength of the Lewis acid site adjacent to it. It was also reported that there were inaccessible AlO_4 that could not be covered by a monolayer of SiO_2 during silication [28]. The silication of alumina was performed at various temperatures ranging from room temperature to ~800 °C [20–23,25]. Silicon alkoxides ($Si(OCH_3)_4$) are most commonly used, but silicon-containing vapors from FCC catalysts have also been employed to silicate γ-alumina [25].

2. Experimental

2.1. Catalytic reactions

The catalytic reactions were carried out in fixed-bed reactors of 15–20 mm internal diameter. Approximately 1.0–1.5 g of γ-alumina catalyst (Pural KR1 obtained from Sasol Germany, with a surface area of 232 m^2/g and pore volume of 1.26 ml/g) were loaded into the reactor and heated to the reaction temperature under flowing nitrogen. In the experiments where multiple catalyst beds were used in one reactor, each layer consisted of approximately 1.0 g of γ-alumina catalyst and the layers were separated by glass wool. The catalysts were heated under flowing nitrogen at the reaction temperature for a period of at least 2 h before the reaction was started. The nitrogen flow was turned off before the alcohol feed was introduced into the reactor using an HPLC pump. The 1-hexanol feeds (98% pure) were obtained from Aldrich and Fluka, and were used as received. In a separate set of experiments, 1-octanol (99% pure, Fluka) was also used as feed. The reactions were carried out at temperatures ranging from 280 to 325 °C for 1-hexanol and 280 to 330 °C for 1-octanol at room pressure. The exit streams (which consisted of alkenes, dialkyl ethers, water and unreacted alcohols) were condensed at 0 °C. The organic layer of the product, which separates from the aqueous by-product, was analyzed using a Hewlett-Packard gas chromatograph (FID) equipped with a Supelco Petrocol™ capillary column having the following dimensions: 100 m × 0.25 mm × 0.5 μm.

2.2. ICP analysis of the catalysts and liquid samples

A Varian Vista-AX CCD spectrometer (ICP-AES) was used for the ICP analysis of the samples. For the alcohols, approximately 20 g of sample was diluted to 50 ml with tetrahydronaphthalin (THN, obtained from Merck) prior to analysis. For the alkene-containing samples, such as the dehydration products, a solution consisting of about 5 g of the organic products diluted to 50 ml with THN, was used for the analysis. Calibration solutions of 10 and 50 mg/l Si in THN were prepared from a standard containing 1 mg/g silicon.

For the analysis of the γ-alumina materials, approximately 1.0 g of sample was placed in a standard digestion vessel, followed by a 10 ml mixture of phosphoric and sulphuric acid and 1 ml of concentrated nitric acid. The vessel was closed and digestion was carried out in a microwave. After cooling for 20 min, the clear solution was diluted with 20 ml of doubly-distilled water. The solution was then transferred into a 100 ml polyethylene measuring flask and diluted further with distilled water to 100 ml. The sample was then analyzed by ICP-AES.

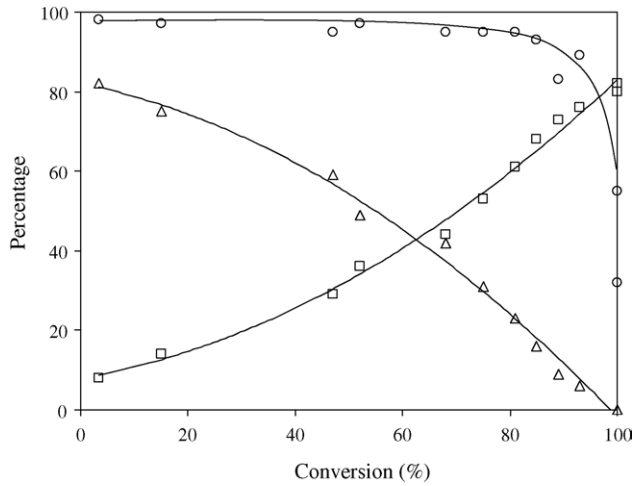

Fig. 1. Selectivity to ether (△), hexenes (□) and 1-hexene purity (○) as a function of conversion for the dehydration of 1-hexanol over γ-alumina.

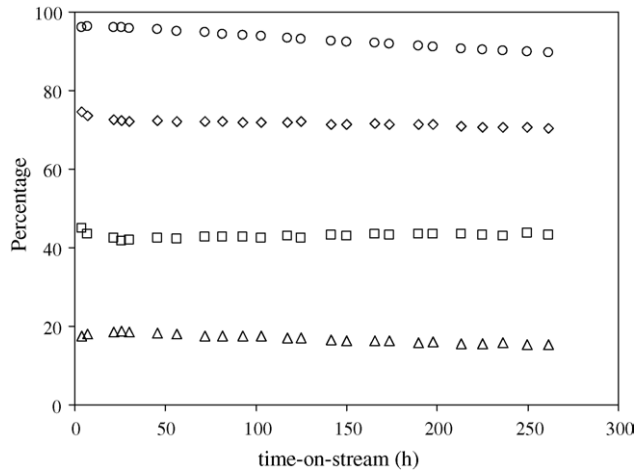

Fig. 2. 1-Hexanol dehydration over γ-alumina at 300 °C and WHSV = 8 h^{-1}: 1-hexene purity (○), conversion (◇), yield of hexenes (□) and yield of dihexyl ether (△).

2.3. Percolation of the alcohol feed

Percolation experiments were carried out at room temperature by passing the alcohol through a column of neutral activated alumina (Aldrich, 150 mesh) at room temperature. The mass ratio of alumina to alcohol was kept constant at 1:2. Approximately 1 kg of alcohol was percolated in each experiment.

3. Results and discussion

3.1. Catalytic reactions

In the dehydration of 1-hexanol, the selectivity to the hexenes increases with increasing conversion while that to the dihexyl ether decreases (see Fig. 1). We have used an additional parameter for monitoring the 1-alkene content in the hydrocarbon fraction of the dehydration product, i.e. the 1-alkene purity. In the case of the dehydration of 1-hexanol, for example, the 1-hexene purity is the mass percent of 1-hexene in the C_6 hydrocarbon fraction. A typical composition of the C_6 hydrocarbon fraction from the dehydration of commercial 1-hexanol is presented in Table 1. The 2-hexenes (*cis* and *trans*) account for nearly 80% of the isomers of 1-hexene in the C_6 fraction. The 3-hexenes constitute only a small fraction of the total, but their boiling points are closer to that of the 1-hexene, which makes their separation more difficult. In Fig. 1, it can be observed that the 1-hexene purity is high (95–97%) at conversions less than 80%. At higher conversions, the extent of double-bond shift is more pronounced and the 1-hexene purity drops to below 95%. Based on process considerations, we have set a minimum 1-alkene purity of 95%. The data presented in Fig. 1 were obtained for runs of up to 8 h on-stream, and the conversion and the purity, were virtually constant for each reaction.

It was, however, found that during the reactions conducted over longer periods (>50 h on-stream), the 1-hexene purity decreased at a constant rate, even though the conversion remained approximately constant (see Figs. 2 and 3). An average conversion of 72% was obtained, and the yield of hexenes was 42% while that of the dihexyl ether was 17%. From Fig. 3 it can be seen that the 1-hexene purity had decreased from 96.2 to 89.6% after 261 h on-stream. The data

Table 1
A typical composition of the C_6 hydrocarbon fraction (normalised to 100%) obtained from the dehydration of 1-hexanol at 300 °C and WHSV = 8 h^{-1} over γ-alumina

Component	Mass (%)	Boiling point (°C)
1-Hexene	95.14	63.4
2-Ethyl-1-butene	0.18	64.7
n-Hexane	0.22	68.7
trans-3-Hexene	0.10	67.1
cis-3-Hexene	0.14	66.4
trans-2-Hexene	1.01	67.9
cis-3-Methyl-2-pentene	0.04	67.7
cis-2-Hexene	2.84	68.8
trans-3-Methyl-2-pentene	0.33	70.4

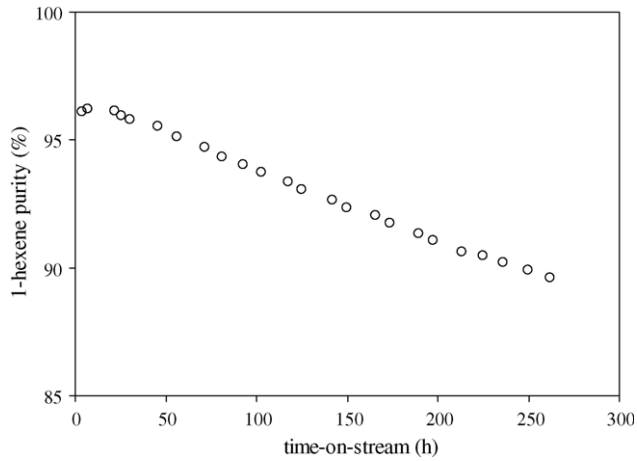

Fig. 3. Expanded plot of 1-hexene purity versus time-on-stream from the dehydration of 1-hexanol over γ-alumina.

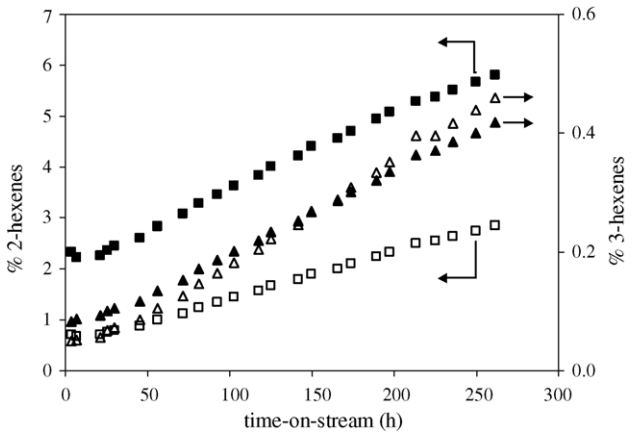

Fig. 4. Mass percentages of *cis*-2-hexene (■), *trans*-2-hexene (□), *cis*-3-hexene (▲) and *trans*-3-hexene (△) in the hexene fraction as a function of time-on-stream.

in Fig. 4 shows that the concentrations of the major isomers (the 2- and 3-*cis*- and *trans*-hexenes) increase with increasing time-on-stream (TOS), leading to a lower 1-hexene purity. This indicates that the degree of the isomerization of 1-hexene to form internal isomers is increasing with TOS, which suggested that the catalyst was undergoing changes, i.e. becoming more acidic. The temperature of the reaction was kept constant during the reaction and could, therefore, not have been responsible for the gradual increase in the isomerization of the 1-hexene to the internal isomers. After this particular catalytic run, the catalyst was removed from the reactor and part of it was regenerated by calcination at 550 °C for 3 h. The calcined catalyst was then re-loaded in the reactor and pre-treated and used under the same conditions as for the fresh catalyst; i.e. 300 °C and WHSV = 8 h^{-1}. With this catalyst, the conversion obtained was about 5% higher than with the fresh one (77% as opposed to 72%), and a 1-hexene purity of 90% was obtained at the start of the reaction, which was the same as that observed before calcination. The purity also subsequently declined at the same rate (−0.65% per day) as was found with the fresh catalyst. These results further indicated that the catalyst was indeed becoming more acidic with TOS. Similar results not shown here, i.e. decline in 1-octene purity with TOS, were obtained in the dehydration of 1-octanol over γ-alumina. Two other experiments were performed to confirm that the silicon accumulating on the catalyst originated from the feed rather than from the packing materials inside the reactor. In one, the packing material used was glass wool and glass balls (silica packing), while stainless steel balls only were packed in the reactor for the second experiment (stainless steel packing). The reactions were carried out under similar reaction conditions, using the same 1-octanol feed. The results obtained showed that the 1-octene purity declined at the same rate in both experiments.

3.2. ICP analyses of the catalysts, alcohol feeds and dehydration products

The ICP analysis of the fresh and used catalysts (Table 2) shows that, apart from that of silicon, there were no major changes in the concentrations of the other elements. The silicon content increased from nearly 200 ppm in the fresh catalyst to over 3000 ppm in the catalyst used for a total of 380 h on-stream. Thus, the regenerated and re-used catalyst contained 15 times more silicon than the fresh one. No significant change in the BET surface area of the catalyst was observed either. A similar accumulation of silicon on the γ-alumina catalyst was observed in the dehydration of 1-octanol (see Table 3). These results show that there is an accumulation of silicon on the catalyst during the dehydration reaction. A plausible explanation for the increasing isomerization activity with TOS is that the accumulated silicon leads to the formation of stronger acid sites, such as those found in silicated aluminas [19–24]. These stronger acid sites increase the rate of isomerization of the 1-alkene to the internal alkenes (under the same reaction conditions). Since the silicon source is in the feed, and the silicon deposition is continuous as the alcohol feed passes over the catalyst, the generation of the stronger sites is also a continuous process. This explains the gradual increase in the degree of isomerization or the decline in the 1-alkene purity. We wish to point out that after acid digestion of the samples, the chloride and fluoride contents were analysed by turbimetric and potentiometric techniques, respectively. These analyses showed that there was no accumulation of chloride or fluoride ions on the samples.

The commercial alcohol feeds (i.e. both the 1-hexanol and the 1-octanol) were analyzed by ICP and found to contain silicon in the range 0.5–1.5 ppm. The dehydration products (organic fraction) also contained silicon corresponding to about 30–50% of that in the feed. This indicates that as much as 50–70% of the silicon in the alcohol feed was retained by the catalyst bed during the dehydration reaction. In separate experiments conducted using multiple layers of catalyst bed, it was shown that the greatest silicon accumulation takes place on the first layer that comes into contact with the alcohol feed (see

Table 2
ICP analysis of the fresh and used γ-alumina catalysts from the dehydration of 1-hexanol at 300 °C and WHSV = 8 h^{-1}

Catalyst	Total TOS (h)	BET (m^2/g)	Trace elements (ppm)				
			Si	Fe	Na	Ca	K
Fresh	0	235	186	199	142	154	<10
Used	261	221	2723	196	146	173	<10
Regenerated and re-used (120 h)	381	223	3112	243	190	165	<10

Table 3
ICP analysis of the fresh and used γ-alumina catalyst from the dehydration of 1-octanol at 280 °C and WHSV = 10 h^{-1}

Catalyst	TOS (h)	Trace elements (ppm)				
		Si	Fe	Na	Ca	K
Fresh	0	194	175	135	139	<10
Used	370	2677	177	156	139	<10

Table 4
The distribution of silicon along multiple layers of catalyst beds used during the dehydration of 1-hexanol at 290 °C and WHSV = 8 h^{-1} over γ-alumina

Catalyst bed layer	Silicon content (ppm)	
	γ-alumina catalyst (1.8 mm extrudates), 310 h on-stream	Crushed γ-alumina (75–150 μm), 330 h on-stream
1	1060	n.a.
2	640	2552
3	870	614
4	–	316
5	–	370
Fresh catalyst	~200	~200

n.a. = not available.

Table 4). The subsequent layers accumulated progressively less silicon, except for the very last layer, as indicated by the analysis.

We were also able to demonstrate that the accumulation of silicon on γ-alumina occurs even at room temperature (although the mechanism might be different from that at high temperatures). Percolation of 1-hexanol through a column of neutral activated alumina has shown that the top layer of the column accumulates most of the silicon (see Table 5). This may be a chromatographic effect as opposed to that taking place at high temperatures in the reactor, which is most probably due to a chemical reaction of silicon species with the alumina surface [20]. Since it is difficult to isolate or concentrate the silicon species, their speciation is presently not known. However, it is speculated that the silicon species present might range from triethyl silane to SiR_4, where R can vary from H, ethyl to butyl, but also OH, and alkoxides [29]. Our results suggest that the silicon species need to be reactive with the γ-alumina in order to form a chemical bond with the surface.

ICP analysis of various 1-hexanol batches showed that the silicon content of the alcohol varied from batch to batch, even when obtained from the same supplier (see Fig. 5). A number of dehydration runs were therefore carried out with these various batches. From the plots of the 1-hexene purities versus time-on-stream obtained from these experiments, the loss in 1-hexene purity per day was calculated, and the results were plotted against the silicon content in the feed. The results are shown in Fig. 5.

It can be observed that there is a direct relationship between the concentration of silicon in the feed and the rate at which the 1-hexene purity decreases with TOS. Thus, as the silicon content in the alcohol feed increases, the rate in the loss of 1-alkene purity is faster.

Table 5
Silicon distribution along a column of neutral activated alumina after percolation of commercial 1-hexanol at room temperature (500 g of alumina in a column of 2.5 cm i.d.)

Neutral alumina layer	Silicon content (ppm)
Top	128
Middle	38
Bottom	36
Fresh (unused) neutral alumina	27

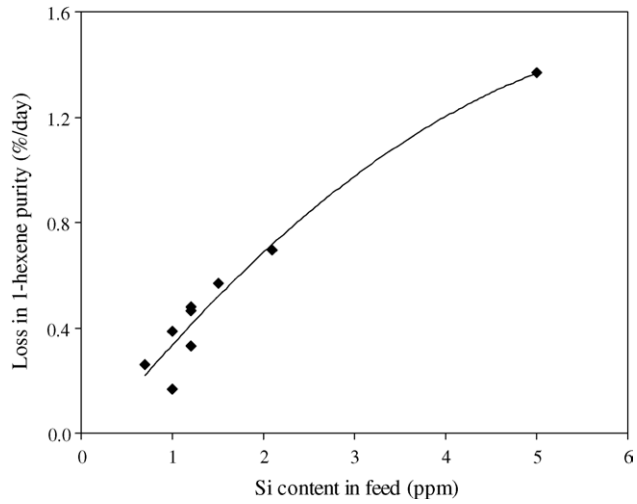

Fig. 5. Plot of the loss in 1-hexene purity per day versus the silicon content of the 1-hexanol feeds.

3.3. Dehydration of 1-octanol with a lower level of silicon concentration

An alcohol feed with a lower level of silicon concentration (~0.1 ppm) was prepared in-house. The feed contained 98% 1-octanol, and was produced in a multi-step process involving hydroformylation of 1-heptene, a hydrogenation step and distillation to produce the high purity 1-octanol. The results of the dehydration of this feed are presented in Fig. 6. It can be observed that the 1-octene purity declined at the slower rate of only −0.022% per day, and even after 900 h on-stream, the 1-octene purity remained higher than 95%. The conversion

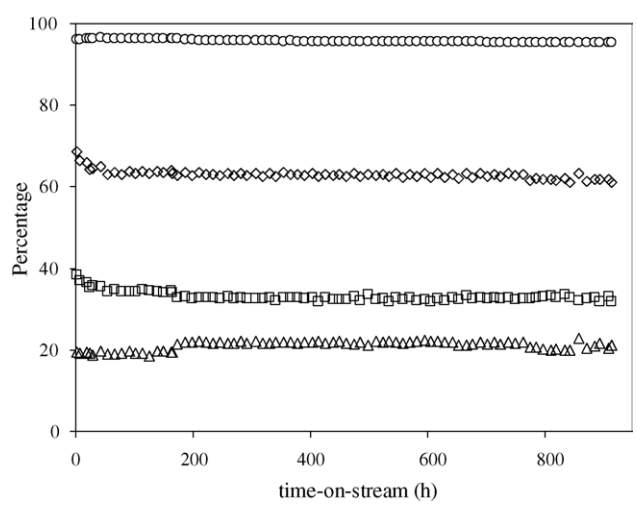

Fig. 6. Dehydration of the in-house prepared 1-octanol feed containing ~0.1 ppm silicon: 1-octene purity (○), conversion (◇), yield of octenes (□) and yield of dioctyl ether (△). Reaction conditions: temperature = 310 °C, WHSV = 25 h^{-1}, using 1.0 g of γ-alumina (500–1000 μm).

remained essentially constant for the duration of the experiment. The used catalyst at the end of the reaction contained 2196 ppm silicon compared to the fresh one, which contains approximately 200 ppm silicon. This indicates that although we were able to reduce the silicon level in the feed from the usual average of 1 ppm to the low level of ~0.1 ppm (which is the detection limits of our instrument for silicon in alcohols), there was still accumulation of silicon on the catalyst. It can therefore be concluded that even at very low concentrations of silicon in the alcohol feed (<0.1 ppm), deposition of the silicon on the γ-alumina catalyst can still take place and change its catalytic properties over a period of time.

4. Conclusions

Silicon species present in alcohol feeds (even at low concentrations such as 1 ppm and lower) lead to the accumulation of silicon on the γ-alumina catalyst used during the dehydration reaction. The accumulation of silicon on the γ-alumina causes an increase in the isomerization activity with time-on-stream, resulting in an increase in the concentration of internal isomers and a decrease of the 1-alkenes. The change in the catalytic properties of the γ-alumina catalyst, caused by the silicon accumulation, is an irreversible process. Upon regeneration of the catalyst, the original selectivity (1-alkene purity) of the fresh catalyst was not achieved, but only a slightly higher conversion was obtained under the same reaction conditions. Even at silicon levels of ~0.1 ppm and lower in the feed, the accumulation of Si on the catalyst still had an effect, albeit to a smaller extent, on the double-bond isomerization rate.

Acknowledgements

We would like to acknowledge the following: (a) Dr. Uwe Böhmer, Mr. U Noack, Mr. Ernst-Otto Tönsen and Dr. Holger Ziehe, for the analyses of the catalysts and the liquid samples, performed in Sasol Germany, Brunsbüttel, (b) Ms. Heloise Winnan of the SSF Laboratories, Secunda for the GC–FID and MS analyses work and (c) Mr. Wimpie Booysen, Dr. Anton Kleingeld and Dr. Braam van Dyk for the preparation of the 1-octanol feed.

References

[1] J.H. De Boer, R.B. Fahim, B.G. Linsen, W.J. Visseren, W.F. De Vleesschauwer, J. Catal. 7 (1967) 163.
[2] H. Pines, W.O. Haag, J. Am. Chem. Soc. 83 (1961) 2847.
[3] W.O. Haag, N.Y. Chen, in: L.L. Hegedus, R. Aris, A.T. Bell, M. Boudart, N.Y. Chen, B.C. Gates, W.O. Haag, G.A. Somorjai, J. Wei (Eds.), Catalyst Design—Progress and Perspectives, John Wiley and Sons, New York, 1987, p. 163.
[4] P.A. Jacobs, Carboniogenic Activity of Zeolites, Elsevier Scientific Publishing Company, Amsterdam, 1977, p. 169.
[5] K. Tanabe, M. Misono, Y. Ono, H. Hattori, Stud. Surf. Sci. Catal. 51 (1989) 260.
[6] P.B. Venuto, Micropor. Mater. 2 (1994) 297.
[7] H. Knözinger, in: S. Patai (Ed.), The Chemistry of the Functional Groups—The Chemistry of the Hydroxyl Group, Interscience, New York, 1971, p. 642.
[8] H. Knözinger, H. Buhl, K. Kochloefl, J. Catal. 24 (1972) 57.
[9] J.M. Winterbottom, in: Catalysis (A Specialist Periodical Report), The Royal Society of Chemistry, London, 1981, p. 141.
[10] B. Shi, H.A. Dabbagh, B.H. Davies, J. Mol. Catal. A: Gen. 141 (1999) 257.
[11] B.C. Gates, Catalytic Chemistry, John Wiley and Sons Inc., New York, 1992, pp. 371–373.
[12] P.A. Jacobs, M. Tielen, J.B. Uytterhoeven, J. Catal. 50 (1977) 98.
[13] J. Fuji, O. Nakayama, T. Onishi, US Patent 2003/0065233 A1 (2003) to Kuraray Co., Ltd.
[14] T. Voeste, H. Buchold, DE 39 15493 A1 (1990) to Metallgesellschaft AG.
[15] M.R. Musaev, I.K. Magamedov, S.N. Klychkova, Z.T. Imanov, Sb. Tr. - Inst. Neftekhim. Protsessov, Akad. Nauk Az. SSR 9 (1977) 65.
[16] K. Jirátová, L. Beránek, Appl. Catal. 2 (1982) 125.
[17] R. Miranda, D.J. Collins, J. Catal. 88 (1984) 542.
[18] Research Disclosure, Union Carbide, November 1987.
[19] E. Finocchio, G. Busca, S. Rossini, U. Cornaro, V. Piccoli, R. Miglio, Catal. Today 33 (1997) 335.
[20] P. Iengo, M. Di Serio, V. Solinas, D. Gazzoli, G. Salvio, E. Santacesaria, Appl. Catal. A: Gen. 170 (1998) 225.
[21] T.C. Sheng, I.P. Gay, J. Catal. 145 (1994) 10.
[22] M. Niwa, N. Katada, Y. Murakami, J. Phys. Chem. 94 (1990) 6441.
[23] L. Basini, A. Aragno, A. Raffaeli, J. Phys. Chem. 95 (1991) 211.
[24] A.C. Butler, C.P. Nicolaides, Catal. Today 18 (1993) 443.
[25] X. Liu, J. Phys. Chem. B 103 (1999) 2647.
[26] X. Liu, R.E. Truitt, J. Am. Chem. Soc. 119 (1997) 9856.
[27] S. Cai, K. Sohlberg, J. Mol. Catal. A: Che. 193 (2003) 157.
[28] T.-C. Sheng, S. Lang, B.A. Morrow, I.D. Gay, J. Catal. 148 (1994) 341.
[29] Thoralf Groß, Unpublished results.