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Rhodium catalysts build into the structure of a silicate support in the hydroformylation of alkenes

Research Article

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Abstract: Rhodium is build into a nano-structured calcium silicate during the synthesis of the silicate. Thereby, it was desired to create a robust heterogeneous catalyst, which does not suffer from catalyst leaching like rhodium impregnated on a pre-formed silicate. While this was achieved, the silicate structure was adversely affected by the incorporation of rhodium – the surface area and pore volume of the material were found to be comparatively low. Alcohol and acid washing were tested to address this issue. The alcohol treatment proved detrimental as catalytic material was leached from the silicate. The acid washed rhodium containing calcium silicate was quite active in the hydroformylation of alkenes and did not suffer loss of catalyst into the product phase. Acid treated rhodium containing silicates were more active than their untreated counterparts but less selective due to access to the rhodium centers being opened.

Keywords: *Hydroformylation • Hex-1-ene • Rhodium • Heterogeneous Catalysis • Nano-Structured Calcium Silicate*

1. Introduction

Industrial aldehydes are synthesized by the conversion of alkenes and alcohols using a catalytic process called hydroformylation or oxo-process [1-6]. Aldehyde products range from fine chemicals to substrates for food additives, perfumes, cosmetics and medicines. While the majority of aldehydes produced are short-chained, the conversion of longer chained and branched alkenes is gaining importance due to improvements in the technology relating to their synthesis and applications.

Most hydroformylation processes in use are homogeneous, as they allow more freedom for catalyst design and often have higher selectivity and activities, measured as turn-over-frequencies (TOF) and turn-over-numbers (TON) [1-6]. Concerns regarding the recovery of the metals used as catalysts and the purity of the products have driven technology towards the development of heterogeneous catalytic processes.

Aqueous biphasic hydroformylation systems are known to work well for short-chained linear alkenes [7-9]. However, longer chained and branched alkenes present a problem, as they are not soluble in water. Therefore, aqueous processes aimed at synthesizing these show only very low activities. Biphasic approaches employing phase transfer catalysts may provide solutions but encounter issues like entrainment and loss of catalyst into the product phase [7-9].

Consequently, several research groups have attempted the formation of solid-state catalysts, mainly based on rhodium. Substrates for the immobilization of catalytically active species have been chosen out of the field of zeolites [10-17], silica [18-20], carbon [21], titania [22] and siloxane [23] substrates. Organic based polymers

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[24], dendrimers [25] and liquid ionic crystals [26,27] in combination with other supports or on their own have been used as well.Some of the approaches introduced are very elegant and promising. For example, Chaudari et al have synthesized catalysts, where rhodium has been incorporated into porous zeolites, alumina and silica, which open the possibility of use in continuous processes [23]. One of the issues remaining with some of the supported catalysts is that the catalyst can still be lost into the product phase.

Previously, we have reported synthesis and modification of a nano-structured calcium silicate [28], NCaSil, and use of said material in the uptake of metal ions from solution [29]. It is proposed that rhodium can be readily absorbed by NCaSil and that the resulting material can be used as a supported, heterogeneous catalyst in a hydroformylation reaction. However, Cairns et al, and Barassi have found that metals can be released from the surface of NCaSil again [29,30]. Therefore, a different approach to the synthesis of a supported catalyst was attempted. Rather than impregnating preformed NCaSil with rhodium, the metal was built into the NCaSil structure during synthesis of the silicate. In this study we show, whether rhodium built into the structure of a silicate remains catalytically active, and if the metal is bound strongly enough into the silicate support matrix to not contaminate the product.

2. Experimental procedure

2.1. General

Reactions and measurements were carried out in air and unless otherwise stated at room temperature. Synthesis gas, (99.90%) H_2:CO, 1:1, was obtained from Gerling. Solvents used were distilled prior to use. NMR spectra were measured using a Varian Inova 300 MHz spectrometer at room temperature. Tetramethylsilane was used as an external standard for ^{1}H NMR. Key to NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Infrared spectra were recorded on a Bio-Rad FTS-7 or a Perkin Elmer System 2000 NIR FT-Raman spectrometer. Samples were prepared as KBr pellets. Key to IR data: st, strong; m, medium; w, weak; br, broad; sh, sharp; sd, shoulder.

A Philips FEG-SEM scanning electron microscope was used to investigate samples, which were coated with carbon, gold or platinum to avoid charge build-up during measurements.

The amount of rhodium not incorporated into the silicate structure was analysed gravimetrically as the trichloride [31].

The catalytic conversion of alkenes to aldehydes was determined by gas chromatography using n-nonane as internal standard in all samples. The relative amounts of the standard, reactants and hydroformylation products was measured on a HP 6890 Series GC gas chromatograph equipped with a HP-5 column 30 m × 0.32 mm × 0.25 μm and FID detector. The carrier gas was helium.

A Micrometrics Flowsorb II 2300 was employed to record specific surface areas by measurement of desorption of 30% nitrogen and 70% helium at 21°C and 1 atm.

X-ray powder diffraction patterns were collected on a Philips PW 3710 MPD diffractometer; anode material Cu, $\lambda = 1.54060$ Å.

Oil absorptions were measured using the standard test for the oil absorption of pigments by spatula rub-out (ASTM D281).

2.2. Synthesis and characterization of catalysts

Rhodium polyethylene glycolate was synthesized according to literature [7,8].

A modified synthesis of nano-structured calcium silicate, NCaSil, was employed to improve binding of rhodium to the silicate. Instead of absorbing rhodium onto a already prepared NCaSil, rhodium trichloride was added during the silicate synthesis.

Reagent A: A solution of sodium silicate was prepared in a plastic beaker from 5.65 g (0.0269 mol, 28.5%wt SiO_2) sodium silicate and 8.5 mL of water.

Reagent B: In a separate beaker 2.03 g (0.0270 mol) calcium hydroxide and 0.142 g (0.538 mmol) rhodium trichloride trihydrate were suspended in 2.5 mL of water. 1.71 mL (2.01 g, 33%wt, 1.18 g mL^{-1}, 0.0364 mol) HCl were added to the calcium hydroxide suspension carefully under stirring. Then further 6.2 mL of water were added. The suspension formed had a pH-value of 11.3 to 11.5.

Reagent A and **Reagent B** were mixed vigorously in a plastic beaker. The resultant slurry was aged for 30 minutes, filtered (vacuum) and the filter cake washed with 40 mL of water. The filtrate was collected and its rhodium content analysed according to the literature [31].

Water washed catalysts, **Cat-W**: The resulting slightly yellow filter cake was dried at 110°C for 2 days.

2-Ethoxyethanol washed catalysts, **Cat-EE**: After washing the filter cake with water as described above, the very pale red filter cake was washed with 20 mL of 2-ethoxyethanol and then dried at 110°C for 2 days.

Acid washed catalysts, pH adjusted to a value of 9, **Cat-A9**: The filter cake was washed with water as

Table 1. Comparison of rhodium content, oil absorption and specific surface area.

Catalyst	Cat-W	Cat-EE	Cat-A9	Cat-A7
Rhodium content (mol g^{-1})	3.29 × 10^{-5}	1.64 × 10^{-5}	3.19 × 10^{-5}	2.31 × 10^{-5}
Rhodium retention (%)	100	50	95	67
pH adjustment	None	none	to pH 9.0	to pH 7.0
Oil absorption (g oil per 100 g)	127	159	142	123
Specific surface area (m² g^{-1})	73	111	109	89

described before and then re-suspended in distilled water. The pH-value of the resulting slurry was adjusted to 9.0 using hydrochloric acid. Then the slurry was filtered (vacuum) and the filter cake washed extensively with water again. The very pale yellow filter cake was dried at 110°C for 2 days.

Acid washed catalysts, pH adjusted to a value of 7, **Cat-A7**: Synthesis followed the instructions **Cat-A9** with the difference that the pH-value of the suspension was adjusted to 7.0. The filter cake was very pale grey prior to drying.

All catalysts: IR (KBr): { = 3619 (w, sd), 3561 (w, sh), 3438 (st, br), 2931 (w, sh), 1630 (m, sh), 1447 (m, br), 1389 (w, sd), 1154 (st, sh), 1094 (st, sh), 1017 (st, sd), 882 (m, sd), 781 (w, sh) 669 (m, sh), 606 (m, sh) cm^{-1}.

All catalysts: XRD, Cu K$_\alpha$ radiation, *d*-spacing [Å] (rel. intensity [%]): 6.02819 (55.86), 4.35711 (7.46), 3.47207 (58.17), 3.00823 (100.0), 2.80728 (80.90), 2.72261 (19.47), 2.34454 (13.00), 2.14243 (13.80), 1.90977 (10.99) 1.84801 (33.35), 1.73964 (5.05), 1.69496 (11.20), 1.35544 (0.87), 1.30201 (5.89), 1.28662 (7.43).

Cat-W, **Cat-A9**, **Cat-A7**: ^{1}H NMR: 1.603 (s, **H**$_2$O), 1.303 (SiO…**H**$_2$O), 0.892 (SiO**H**, m) ppm.

Cat-EE: ^{1}H NMR: 3.750 (-C**H**$_2$OH, m), 3.530 (OC**H**$_2$CH$_2$O H, t), 3.408 (CH2OC**H**$_2$C**H**$_2$OCH$_2$-, m), 1.890 (-CH$_2$O**H**, t), 1.543 (s, **H**$_2$O), 1.255 (SiO…**H**$_2$O), 0.879 (SiO**H**, m) ppm.

2.3. Catalysis testing

Hydroformylation reactions were carried out in a Parr Mini-reactor 4560 (300 mL) equipped with temperature, stirring and pressure control device. The consumption of carbon monoxide and hydrogen gas was monitored at constant pressure by the pressure drop from a gas reservoir. The pressure in the reservoir was recorded using a pressure transducer and recorder system.

For a typical experiment, 270 mg of a rhodium-containing calcium silicate was dispersed in 20 mL toluene was placed in the reaction vessel, which then was charged with the reaction gas (H_2/CO, 7 MPa). Under stirring the autoclave was heated to 80°C for 1 hour. Then the alkene (20.0 ml) and *n*-nonane (1.00 mL, 0.718 g cm^{-3}, 5.60 mmol) as internal standard were added. The reaction mixture was stirred (1000 rpm) for 5 h at 80ºC and the consumption of reaction gas was recorded. Catalytic reactions were terminated by depressurization after cooling in a water bath. The catalyst was recovered by filtration and the product phase analysed.

Using catalyst, an experiment was carried out with 250 mg of catalyst **Cat-W** in the absence of toluene.

In a further experiment, 210 mg of recovered catalyst **Cat-A7** were employed.

3. Results and discussion

Nano-structured calcium silicates, NCaSil, have been reported with surface areas up to 500 m^2 g^{-1} and pore volumes able to accommodate 7 times the weight of the silicate in linseed oil (determined by spatula rub-out method) [28]. The silicate can be used to absorb metal ions from solution, but doing so has a detrimental impact on the silicate structure [29,30]. Calcium and silica are known to be dissolved out of the structure [30]. Additionally, it is possible that the metal ions absorbed are released again into solution [30]. Therefore, it was decided to include rhodium into the synthesis of the silicate and create a rhodium-containing calcium silicate. It was thought that doing so would improve the binding of rhodium to the silicate backbone and prevent loss of rhodium during catalytic tests. To test this assumption a sample of rhodium-containing calcium silicate, **Cat-W**, was compared to a sample where rhodium was absorbed onto premade NCaSil. In a simple leaching test 0.1 g of each catalyst were suspended in 100 mL of ethanol for 2 days. Comparative experiments were carried out using 100 mL of water and 100 mL of toluene. In toluene no leaching within the margin of error was observed (Table 1). In ethanol and water **Cat-W** experienced no loss of rhodium within the margin of error but some loss of calcium in water (Table 1). The rhodium absorbed onto NCaSil was leached out to a significant degree both in ethanol and water (Table 1). Consequently, only rhodium-containing calcium silicates were investigated in catalysis tests and toluene was used to aid dispersal

Table 2. Leaching test: Exposing rhodium containing calcium silicate **Cat-W** and rhodium absorbed on NCaSil to different solvents. Numbers express the percentage of rhodium lost.

Material	Water	Ethanol	Toluene
Rhodium absorbed on NCaSil	58.9	77.3	0.1
Rhodium Containing Silicate Cat-W	0.1	0.2	0.0

of the catalyst during reaction and recovery of the silicate by filtration.

While the rhodium-containing calcium silicates had been proven to be more robust, incorporating rhodium into the silicate structure appeared to have a detrimental effect on the surface properties of the silicate (Table 2).

Surface areas did only reach about 110 m^2 g^{-1} for rhodium-containing silicates. The pore volume appeared to be significantly reduced compared to NCaSil as well. It is known that during drying of NcaSil, surface tension can collapse the silicate structure and reduce its surface area [32]. Several methods have been developed to prevent the collapse, like washing the silicate with a solvent with a lower surface tension than water, like ethanol or 2-ethoxyethanol, or washing the silicate with acids [32]. It was attempted to use these methods to improve the pore volume and surface area of rhodium-containing calcium silicate as well. The rhodium-containing calcium silicate washed only with water will be referred to as **Cat-W** in the following. The three variations were termed **Cat-EE** for the silicate washed with 2-ethoxyethanol, **Cat-A9** for the material washed with HCl to pH 9.0, and **Cat-A7** for the one adjusted to pH 7.0. Table 2 shows a comparison of the rhodium content and surface properties of these catalysts. It was noted that acid washing resulted in the loss of rhodium from the structure, with 5% of the rhodium being leached out at pH 9.0 and 33% at pH 7.0. The XRD patterns of all catalysts were identical and comparable to NCaSil, the proton NMR spectra revealed the residues of 2-ethoxyethanol remaining in **Cat-EE**. Washing with 2-ethoxyethanol also led to a significant amount of rhodium loss from the silicate. Only about half the silicate remained bound in **Cat-EE** compared to **Cat-W**.

The infrared spectra of the rhodium-containing calcium silicates are similar to those of NCaSil [28,32]. This was expected due to the small amount of rhodium incorporated into the structure. However, two additional weak signals at 3619 and 3561 cm^{-1} are present. These signals shift to 2588 and 2543 cm^{-1} if the sample is treated with D_2O and can therefore be attributed to hydroxyl groups. These signals are found in all rhodium-containing calcium silicates studied and indicating the presence of either additional silanol groups or of rhodium hydroxide formed due to the basic environment, pH > 11.5, present during the silicate formation. The measurements carried out did not allow any distinction between these two possibilities. The presence of these groups though is concurrent with the catalysts having a lower surface area compared to NCaSil and might be an indicator of structural differences in the silicate backbone between the rhodium modified and unmodified materials.

The reduced surface area and porosity of rhodium-containing calcium silicates compared to NCaSil [28,32] was also noticeable in electron microscope images of the material (Fig. 1). The micro-plate morphology of NCaSil was recognizable in **Cat-EE**, but the plates appeared thicker and the structure resembled more a collapsed NCaSil than one washed with an alcohol. All catalyst samples looked quite comparable independent of treatment. Energy dispersive X-ray Analysis showed rhodium to be present close to the limit of detection (Fig. 1). The peak associated with rhodium was of similar intensity to the one from the platinum coating deposited during sample preparation. As the samples were prepared on carbon tape, the carbon signal was neglected. However traces of a hydrocarbon impurity can be detected by infrared spectroscopy.

The **Cat-EE** sample was further investigated by X-ray mapping. The data from the energy dispersive X-ray spectroscopy is related to spatial information in regards to the location of elements on a sample. Clear red, blue or green dots represent presence of these elements. Mixed colours originate, where two or more elements are present at the same location. Large areas in only one colour indicate pure crystals or compounds. The rhodium content is very low only just above the background level. This means that conclusions in regards to the presence and distribution of rhodium have to be taken as indications only. However, the even spread of signals (green dots) in the overlay chart on the left and the good correlation between the elements in the ternary chart (Fig. 1) imply an even distribution of all elements investigated. In the ternary correlation chart no dots near the rhodium tip of the triangle are observed. Such dots would indicate the presence of discrete rhodium species. An even distribution of rhodium on the silicate support was considered to be beneficial for catalytic conversions as it influences the number of available catalytic sites.

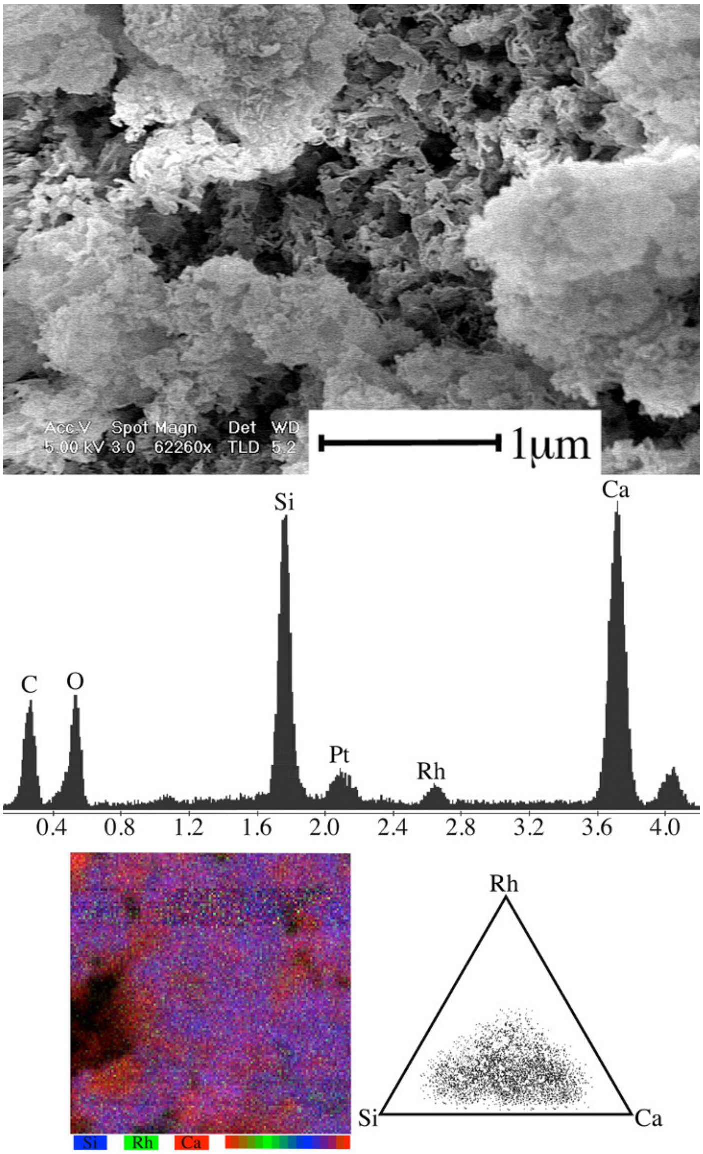

Figure 1. Scanning electron microscope image, energy dispersive X-ray spectrum (excitation energy 15 keV, spot size 3.0) and derived pseudo-colour X-ray mapping and elemental correlation chart for **Cat-EE**.

The number of available sites should be in direct relation to the activity of a catalyst. Considering the amount of rhodium per gram of catalyst and the porosity of the materials, expressed in their surface area and oil absorption, it was assumed that the catalysts active in the following order: Most active **Cat-A9** > **Cat-A7** > **Cat-EE** > **Cat-W** least active. To investigate catalytic activity the conversion of alkenes into the corresponding aldehydes in hydroformylation reactions was attempted. Mainly hex-1-ene was used as alkene as significant data on this hydrocarbon had been collected in prior studies [7,8]. The conversion of hex-1-ene into heptanals (linear and branched) was recorded after 5 hours along with the ratio of linear to branched aldehydes. A 5 hour reaction time was chosen to make the tests comparable to prior studies [7,8]. In one attempt it was established that close to 100% conversion was reached after about 9 hours. Occurrence of non-volatile products from side reactions and loss of catalyst was noted as well. The activity of catalytic conversions was recorded as turn over frequency (TOF) in mol product per mol catalyst, in this case rhodium, per hour.

All rhodium-containing calcium silicates showed a high activity in the hydroformylation of hex-1-ene (Table 3) quite comparable in magnitude to the catalyst, **PEG**, investigated in a previous study [8]. In comparison to the phase transfer catalyst used previously [8], which needed to be recovered by phase separation, catalysts

Table 3. Hydroformylation of hex-1-ene using rhodium-containing calcium silicates.

Catalyst	Cat-W	Cat-W	Cat-W	Cat-EE	Cat-A9	Cat-A7	Cat-A7	PEG
[Rh] (mol × 10^{-6} (ppm))	8.88 (27.9)	8.20 (26.0)	8.88 (27.9)	4.43 (13.9)	8.61 (27.1)	6.24 (19.6)	4.85 (32.6)	6.9 (18.7)
Conversion (mmol (%))	133 (73.8)	129 (69.8)	104 (76.1)	135 (75.1)	148 (82.6)	150 (83.1)	112 (65.5)	102 (60.2)
iso/n-products	0.58	0.55	0.63	0.59	0.54	0.67	0.68	1.08
TOF [mol mol^{-1} h^{-1}]	2978	3050	2529	6096	3447	4810	4618	4818
Special conditions		(1)	(2)				(3)	(4)

(1) no toluene
(2) oct-1-ene not hex-1-ene converted
(3) recycled catalyst
(4) catalyst from [8]

investigated here were solids. As such they could be recovered after reaction from the product phase by simple filtration. However, due to the small amounts of catalyst used, recovery of the pure catalyst was difficult. Therefore toluene was added to the process to improve catalyst dispersion and product separation. Toluene has been shown to not leach rhodium from the catalyst earlier. Furthermore, it was proven to not influence the activity and selectivity of the process significantly. Two catalytic tests were carried out – one in the presence, one in the absence of toluene. The selectivity and turn over frequency recorded for these tests was comparable within the margin of error (Table 3). In all cases some catalyst was lost, trapped in a sticky, potentially polymeric, non-volatile residue. The total amount of non-volatile solids produced was about 3% for the conversion of hex-1-ene. If oct-1-ene was converted, this amount increased to 8.9%.

The **PEG** catalyst investigated in the literature showed little selectivity towards branched or linear aldehydes [8]. The catalysts tested in this study produced nearly twice the amount of linear than of branched aldehydes. The selectivity was less for the conversion of oct-1-ene but still comparable.

Comparing the different catalysts produced in this study proved the earlier estimation in regards to their relative activities wrong. The 2-ethoxyethanol washed material, **Cat-EE**, was the most active by a factor of two compared to the water washed catalyst, **Cat-W**. The reason for this became apparent as it was noticed that rhodium was lost into the product phase. It is possible that the presence of the 2-ethoxyethanol residue in **Cat-EE** facilitated this leaching or that the material was the least structurally sound of the ones investigated. The loss of rhodium means that **Cat-EE** has to be considered unsuitable as catalyst. **Cat-W** as well as the acid washed materials displayed no noticeable leaching of rhodium into the product phase. Both acid washed materials, **Cat-A9** and **Cat-A7**, performed better than **Cat-W**. In the case of **Cat-A7** this was unexpected as the surface area of this catalyst was comparable to **Cat-W**. In contrast the activity of **Cat-A9** in relation to **Cat-W** could be explained quite well over an increase in pore volume and, hence, accessible catalytic sites; the amount of improvement in the oil absorption (12%) matches the better activity (15%) of **Cat-A9** quite well. The turn over frequency of the conversion using **Cat-A7** was about 60% higher than that of **Cat-W**, while their surface areas and oil absorptions were very similar. A possible explanation can be found in a closer look at the acid washing. During treatment of nano-structured calcium silicate with acid to pH 7.0 about 95% of calcium ions and silanol groups are removed [32]. While also one third of the rhodium was lost, it is likely that the residual rhodium became far more accessible. Consequently, **Cat-A7** had a considerably higher number of available sites than **Cat-W** and **Cat-A9**. This assumption is supported by the fact that the conversion of hex-1-ene using **Cat-A7** was less selective than the ones carried out with the other catalysts. It is likely that the calcium and silanol limiting access to the rhodium also influence the selectivity.

Finally, the reuse of the spent catalysts was attempted. Due to having been shown to be robust – no loss of rhodium into the product phase was noticed – and having the largest activity **Cat-A7** was chosen for this experiment. First a catalytic conversion of hex-1-ene using **Cat-A7** in the presence of toluene was carried out. Then the catalyst was recovered from the autoclave by filtration and dried for several days at 110°C in an oven. Some catalyst was lost due to the presence of a non-volatile residue as mentioned earlier. The autoclave was cleaned. The product phase was placed in the autoclave again with fresh hex-1-ene to test for catalytic material being lost into this phase or being left in the autoclave. No catalytic activity was noticed indicating that no catalytic material was leached into the product or stuck in the autoclave. The autoclave was cleaned again. The recovered catalyst was placed into the autoclave with toluene and fresh hex-1-ene. A catalytic conversion was carried out, and the products of this conversion analysed. It was found that the recycled catalyst performed very comparable to the fresh catalyst (Table 3).

4. Conclusions

Nano-structured calcium silicate can be used as catalytic support for rhodium. If rhodium is impregnated onto the silicate, the metal is not well bound to the silicate support and can be leached into the product phase or a solvent present. By adding rhodium trichloride to the synthesis of the silicate a more robust catalyst has been created, which does not loose rhodium into solvents in contact with the catalyst. However, if alcohols are used in the making of the rhodium containing silicate, the material suffers from catalyst leaching. The silicate can be acid washed, which results in the loss of some rhodium but appeared to remove blockage around the remaining catalytic centres to increase catalytic activity. The freeing of access to the rhodium had the effect of reducing selectivity. It would be interesting to attempt optimization of the catalyst by controlled acid treatment and to find a regime by which activity is increased while the selectivity is not changed. Furthermore, it would be interesting to test the rhodium containing silicates in other catalytic applications, such as hydrogenation, and also employ different metals.

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