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η^3-Allylnickel alkoxides and their use as homogeneous and heterogeneous catalysts for the dimerization of olefins

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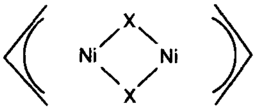
η^3-Allylnickel alkoxides $\{\eta^3\text{-}C_3H_5NiOR\}_2$ (R = Me, Et, i-Pr, Ph, $SiPh_3$) may be activated by gaseous boron trifluoride (BF_3) to give active catalysts for the dimerization of propene in homogeneous phase. In CH_2Cl_2 at −20 °C catalytic turnover numbers of 5000 mol propene(mol Ni)$^{-1}$ h^{-1} were measured. The nature of the OR group influences both the catalytic activity and the oligomerization product distribution. The ratio of methylpentenes to dimethylbutenes in the dimer fraction may be controlled by the presence of additional phosphine ligands at the nickel atom.

The nickel alkoxide precursor was heterogenized on alumina to give $\{Al_2O_3\}\text{–O–Ni–}(\eta^3\text{-}C_3H_5)$. Subsequent activation using gaseous BF_3 generates a powerful heterogeneous olefin dimerization catalyst which converts 50×10^3 mol propene (mol Ni)$^{-1}$ at −10° to −5 °C in a batchwise process and 143×10^3 mol propene (mol Ni)$^{-1}$ continuously to give 75% dimers and 25% higher oligomers. The solvent-free treatment of oxide supports, e.g. alumina or silica, with gaseous BF_3 produces strong 'solid acids'. The activated hydroxyl groups on the support surface serve as effective anchor sites for organometallic complexes to form heterogenous catalysts. By reaction of $Ni(cod)_2$ with $\{Al_2O_3\}O(BF_3)H$ or $\{SiO_2\}O(BF_3)H$, η^1,η^2-cyclo-octenylnickel–O fragments may be fixed to the surface. In the absence of halogenated solvents, the resulting catalysts, e.g. $\{SiO_2\}O\text{–}(BF_3)\text{–Ni–}(\eta^1,\eta^2\text{-}C_8H_{13})$, dimerize propene continuously at +5 °C at the rate of 800×10^3 mol liquid propene (mol Ni)$^{-1}$.

Keywords: Organonickel alkoxides, surface organometallic chemistry, catalysis, olefin dimerization

INTRODUCTION

The homogeneous oligomerization of propene, catalyzed by soluble η^3-allylnickel halides **1** and activated by Lewis acids, was discovered in 1963 by Wilke and Bogdanovic.[1] Intensive studies, over the years, of the effect of added phosphine ligands has led to an optimization of the control of the selectivity of the catalytic C–C linkage.[2–5]



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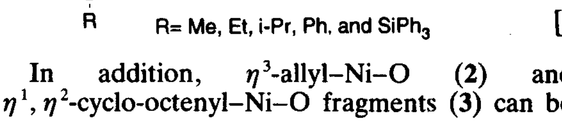
(X = Cl, Br)

The resulting linear and branched C_6- and C_9-mono-olefins are products of considerable industrial interest. The (homogeneous) Dimersol process, developed by the Institut Francais du Petrole (IFP),[6–8] is now carried out in more than 40 plant. The linear C_6–C_9 olefins are valuable intermediates for detergents and plasticizers and the branched hydrocarbons are used, after hydrogenation, as high-octane gasoline additives.

Until now, all homogeneous catalysts for the dimerization of olefins have been based on Ni^{2+} complexes such as **1** and their subsequent activation by, for example, aluminum halides or alkylaluminum halides. In the present paper we describe a new type of soluble catalyst based on η^3-allylnickel alkoxides[9] with BF_3 as the activator (Eqn [1]).



R= Me, Et, i-Pr, Ph, and $SiPh_3$ [1]

In addition, η^3-allyl-Ni-O (**2**) and η^1,η^2-cyclo-octenyl-Ni-O fragments (**3**) can be

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Dedicated to Professor F. E. Brinckman on the occasion of his retirement.

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$$[(\eta^3\text{-}C_3H_5)NiBr]_2 + 2\ MOR \xrightarrow[-30^\circ C,\ 1\text{-}2\ h]{\text{ether}} [(\eta^3\text{-}C_3H_5)NiOR]_2 + MBr$$

R = $SiPh_3$ **5**, CH_3 **6**, C_2H_5 **7**, i-C_3H_7 **8**, C_6H_5 **9**
M = K, Na

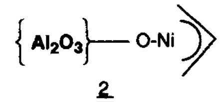
[2]

$$\left[\ M_xO_yH_z\ \right]\text{—OH} + Na[BEt_3H] \xrightarrow{\text{toluene}} \left[\ M_xO_yH_z\ \right]\text{—}OBEt_3]Na + H_2$$

M = Al; x = 2; y = 3; z = 0
M = Al; x = 1; y = 3; z = 3
M = Si; x = 1; y = 2; z = 0
M = Ti; x = 1; y = 2; z = 0

[3]

anchored on oxide supports such as alumina or silica.



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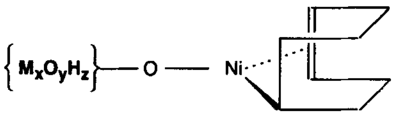

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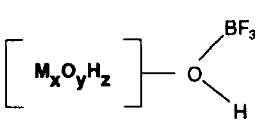
M = Al; x = 2; Y = 3; z = 0
x = 1; Y = 3; z = 3
M = Si; x = 1; Y = 2; z = 0
M = Ti; x = 1; Y = 2; z = 0

BF_3 activation of the 'quasi η^3-allylnickel alkoxides **2** and **3** on the surface leads to the formation of effective heterogeneous olefin oligomerization catalysts. Alternatively, the treatment of the dry oxide supports with BF_3 at −78 °C leads to a strong acidification of the OH groups on the surface to give the 'solid acid' **4**, which reacts smoothly with $Ni(COD)_2$ to generate the BF_3-activated heterogeneous η^1,η^2-cyclooctenyl–Ni–O catalyst **15**.



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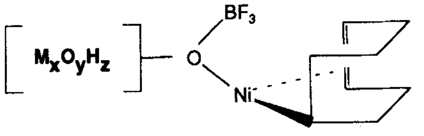

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This special approach to catalyst design has been named 'surface organometallic chemistry' by Basset.[10] In contrast to earlier attempts to fix homogeneous dimerization catalysts on supports,[11–20] the synthesis of well-defined organonickel species on the surface enables heterogeneous olefin dimerization catalysts to be generated whose activities and lifetimes are, for the first time, comparable with those of the homogeneous system.[21]

EXPERIMENTAL

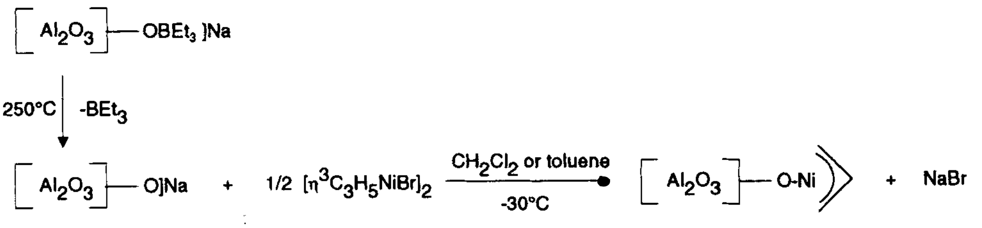
All experiments were carried out strictly under argon.

Preparation of the homogeneous catalysts

η^3-Allylnickel alkoxides were prepared according to Ref. 9 by metathesis of η^3-allylnickel bromide with the corresponding alkoxides of sodium or potassium at −30 °C in ether suspension (Eqn [2]) In the course of the reaction [2], the red colour of the dissolved η^3-allylnickel bromide turns to orange–yellow, insoluble MBr is filtered off, and the products may be obtained from the mother liquors in 75–90% yield after recrystallization. The pure η^3-allylnickel alkoxides should be kept in a refrigerator at −18 °C. The addition of either an excess of gaseous BF_3 or a stochiometric amount of $BF_3.OEt_2$ to a nickel alkoxide dissolved in CH_2Cl_2 or C_6H_5Cl yields the activated homogeneous catalysts (Eqn [1]).

Pre-treatment of the supports

Alumina (Condea), silica (Merck), Bayerit (Degussa) and rutile (Bayer) were dried in two steps and the free-surface OH-groups available as anchoring groups on the dehydrated surfaces were quantitatively determined by volumetric measurement on the evolution of hydrogen on the reaction of the dry support materials with $Na[BEt_3H]$ in toluene (see Eqn [3] and Table 1).



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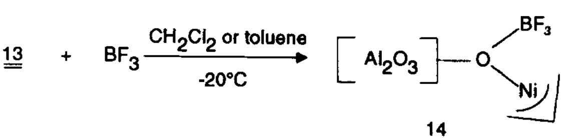
[4]



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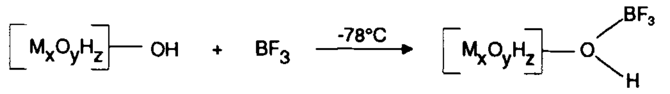
[5]



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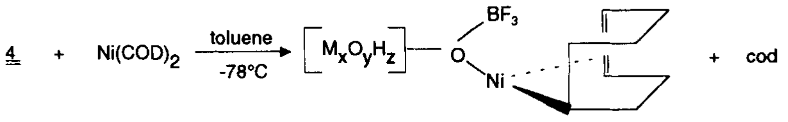
[6]

M = Al; x = 2; y = 3; z = 0
M = Al; x = 1; y = 3; z = 3
M = Si; x = 1; y = 2; z = 0
M = Ti; x = 1; y = 2; z = 0



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[7]

M = Al; x = 2; y = 3; z = 0 15
M = Si; x = 1; y = 2; z = 0 16
M = Al; x = 1; y = 3; z = 3 17
M = Ti; x = 1; y = 2; z = 0 18

Preparation of the heterogeneous catalysts

For the synthesis of η^3-allyl–Ni–O on alumina (for example), the free OH groups of the support were first transferred into the O–Na form by quantitative addition of $Na[BEt_3H]$ in toluene (Eqn [3]) and then exchanged with **1** (X = Br) in CH_2Cl_2 or toluene (Eqn [4]). The suspended heterogeneous catalyst precursor, e.g. **13**, was activated either by the addition of $BF_3.Et_2O$, or solvent-free using gaseous BF_3 (Eqn [5]).

Table 1 Dehydration conditions for the supports and free OH groups present in the dry oxides

Name (Source)	Formula	Specific BET area ($m^2 g^{-1}$)	Wet oxide Σ H_2O, OH ($mmol g^{-1}$)	Drying conditions	Dry oxide OH groups ($mmol g^{-1}$)
Pural SB (Condea)	Al_2O_3	300	11.0	1. 150 °C, 16 h 2. 150 °C, 3 h, 0.1 Pa	3.5
Bayerit (Degussa)	$Al(OH)_3$	20	6.5	1. 150 °C, 16 h 2. 150 °C, 3 h, 0.1 Pa	2.8
Lichroprep Si 100 (Merck)	SiO_2[a]	250	10.0	1. 150 °C, 16 h 2. 150 °C, 3 h, 0.1 Pa	3.0
Rutil (Bayer)	TiO_2[b]	10	3.0	1. 150 °C, 16 h 2. 150 °C, 3 h, 0.1 Pa	2.0

[a] Dissolves with excess $NaBEt_3H$ below pH 9. [b] Turns blue with excess $NaBEt_3H$.

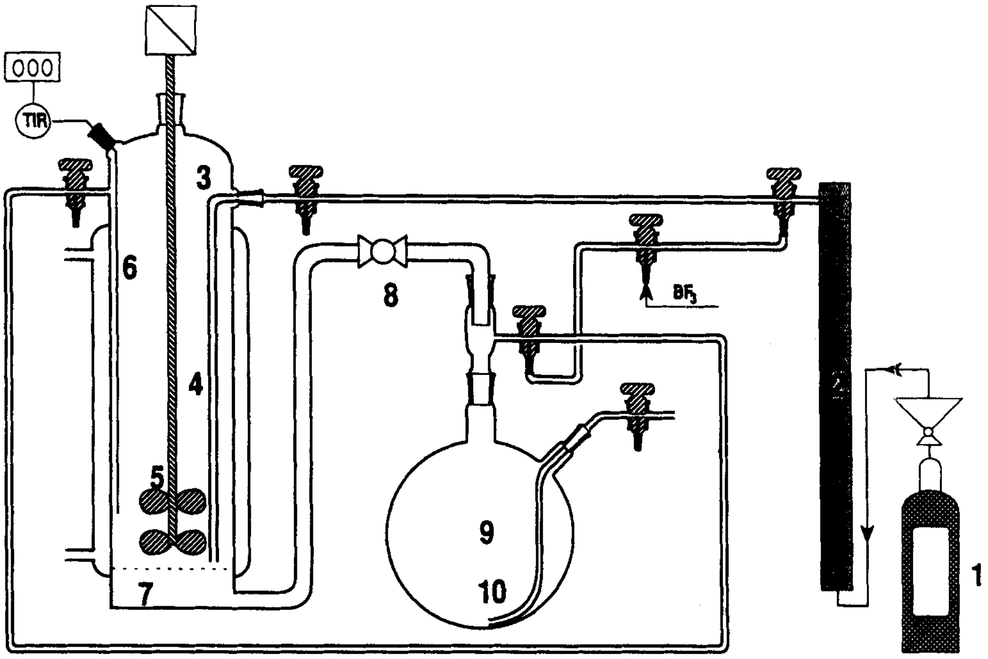


Figure 1 Apparatus for continuous propene dimerization: **1**, Propene source; **2**, dryer; **3**, reactor; **4**, gas inlet tube; **5**, stirrer; **6**, thermocouple; **7**, D-3 frit; **8**, cut-off valve; **9**, product receiver; **10**, plunge tube.

Alternatively, the free OH groups in the various dehydrated supports were first acidified by passing gaseous BF_3 at −78 °C (Eqn [6]). Subsequent oxidative addition of $Nicod_2$ to the resulting 'dry acid' **4** in toluene at −78 °C generated the BF_3-activated η^1,η^2-cyclo-octenyl-Ni–O species on the support (Eqn [7]).

Catalytic dimerization of propene

The propene used was polymerization grade (99.5%; Messer–Griesheim).

The batchwise dimerization of propene was carried out in a 2-litre four-necked flask equipped with stirrer, inlet pipe and thermometer. After the reactor had been charged with the homogeneous or heterogeneous catalysts, the system was evacuated to a residual pressure of 5 Pa and then propene was supplied. The reaction temperature was maintained constant at −20 °C by cooling with dry ice. The homogeneous reactions were stopped after 60 min by interruption of the propene supply and deactivation of the catalyst by air/ammonia. In the heterogeneous version the propene supply was maintained until the consumption ceased. The products were filtered to give a clear, colorless liquid.

The continuous dimerization process using heterogeneous catalysts was performed in the reactor shown in Fig. 1 The apparatus consisted of propene supply, drying tower (molecular sieve and $NaAlEt_4$), the reactor with stirrer, inlet pipe and thermocouple and a 2-litre flask for product collection. The reactor included a D3-filter frit, a cooling jacket, and an overflow pipe at the side. A filter kept the catalyst in the reaction zone, and the liquid product was continuously separated from the catalyst suspension. Reactor and flask were connected by an internal pressure balance line. The product was easily squeezed out through the dip pipe.

The continuous dimerization of liquid propene was performed in a continuous-flow stirred autoclave (Fig. 2). After drying (molecular sieve/$NaAlEt_4$), the propene was liquefied at the operating pressure by a diaphragm compressor. The liquid propene was precooled and then passed on to the catalyst suspension. The catalyst was kept back by a polypropylene filter. The products left the reactor together with unconverted propene at the bottom. After expansion to standard pressure, unreacted gaseous propene could be recycled whereas the products accumulated in the separator. The product analysis was performed by GLC using hydrogen as the carrier gas.

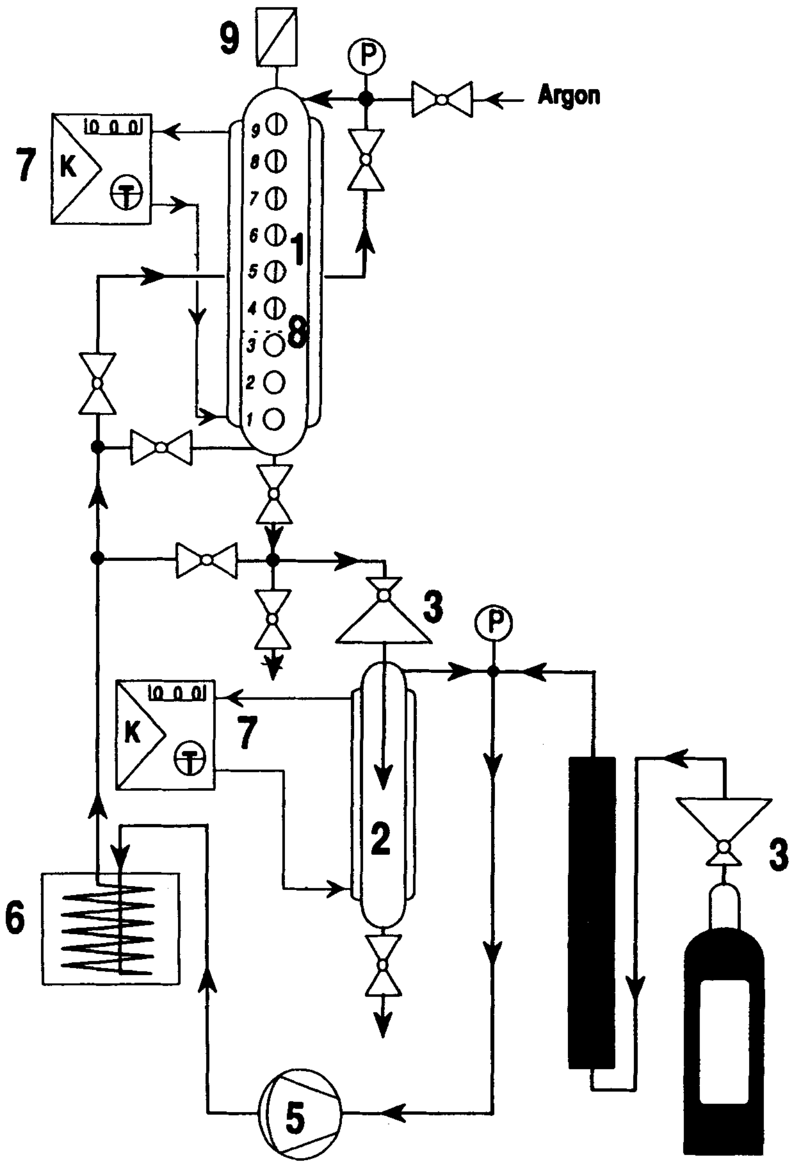


Figure 2 Apparatus for propene dimerization with liquid propene: **1**, window autoclave; **2**, separator; **3**, relief valve; **4**, dryer (mole sieve/$NaAlEt_4$); **5**, membrane compressor; **6**, cryomat; **7**, thermostat; **8**, polypropylene net; **9**, stirrer.

RESULTS AND DISCUSSION

Homogeneous catalysts based on $[\eta^3\text{-}C_3H_5\text{–}Ni\text{–}OR]_2$ (5, 6, 7, 8, 9)

Because of its formal analogy to the inorganic Si–O support, the η^3-allylnickel triphenylsilanolate **5** serves as a soluble model compound for the heterogeneous η^3-allyl–Ni–O–Si catalyst precursor **2**. In contrast to **1**, the corresponding nickel alkoxides **5**, **6**, **7**, **8** and **9** (Eqn [2]) cannot be activated by aluminum halides or alkyl alumina halides. It was found, however,[21] that the activation of the η^3-allylnickel alkoxides **5**, **6**, **7**, **8** and **9** can be brought about using BF_3 as the Lewis acid (see Eqn [1]). Passing gaseous BF_3 through a CH_2Cl_2 solution of the η^3-allylnickel triphenylsilanolate **5** leads to a color change to deep red. From the red solution the BF_3-activated catalyst complex **10** may be isolated by removal of the solvent *in vacuo* at −30 °C. The very air sensitive, dark red, solid compound **10** may be stored for a long

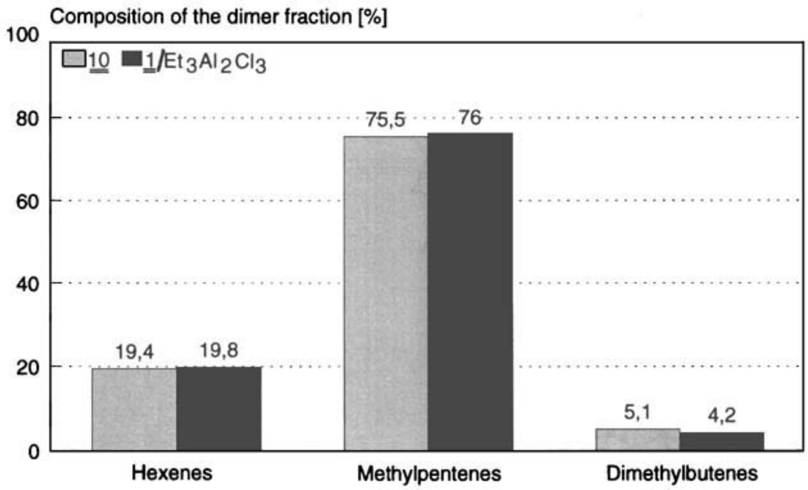
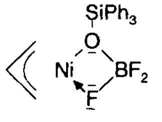


Figure 3 Distribution of the C_6 isomers using the catalysts **1**/$Et_3Al_2Cl_3$ and **10**

time at −78 °C (decomposition above −15 °C). The complex **10** exhibits its full catalytic activity when redissolved in CH_2Cl_2.



10

The structure of the BF_3 adduct **10** was confirmed by IR and NMR data.[21] The η^3-allyl and phenyl groups were identified by ^1H NMR at −30 °C. The ^{11}B NMR signal at −0.45 ppm confirms the tetracoordination of boron, and the back-coordination of the OBF_3- anion to nickel through fluorine was demonstrated by NMR through ^{31}P-coupling in a phosphine complex of analogous structure to **10**.[21]

The activity of the catalyst **10** in CH_2Cl_2 was found to be 4.1×10^3 mol propene (mol Ni)$^{-1}$ h^{-1} to give 80% C_6 isomers and 20% higher oligomers. The standard system based on **1**/$Et_3Al_2Cl_3$, for comparison, yields 90% dimers and 10% higher olefins. As shown in Fig. 3, the distribution of isomers in the C_6 fraction was found to be identical with both homogeneous catalysts **1**/$Et_3Al_2Cl_3$ and **10**.

In order to investigate the influence of excess BF_3 on the activity of **10**, increasing amounts of $BF_3.OEt_2$ were added to **5**. The results are summarized in Fig. 4.

The catalytic activity [mol propene (mol Ni)$^{-1}$ h^{-1}] increases from 4×10^3 at a Ni:B ratio of 1:1 to a maximum of 9×10^3 at Ni:B = 1:4. The proportion of C_6 olefins to higher oligomers in the product is independent of the BF_3 concentration. As shown in Fig. 5, however,

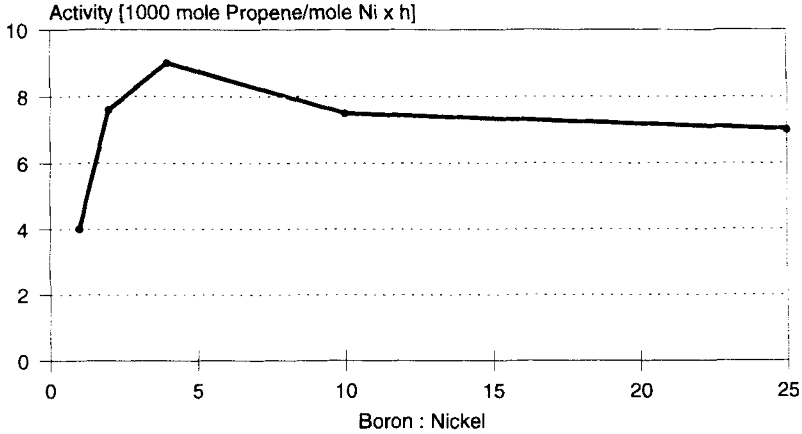


Figure 4 Activation of **5** using BF_3–OEt_2: influence of B:Ni on the activity.

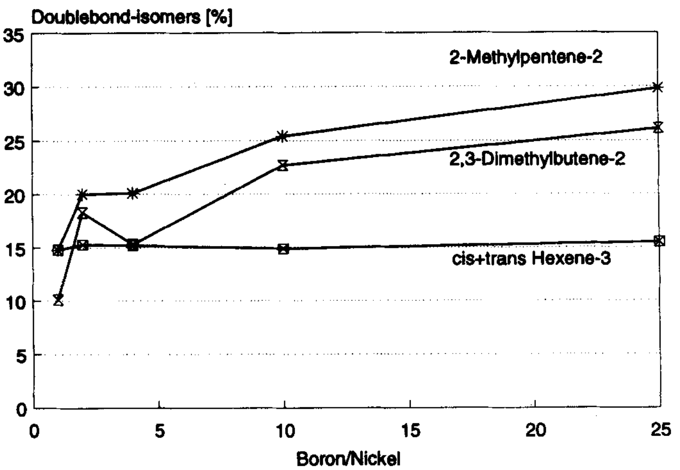


Figure 5 Influence of excess $BF_3.OEt_2$ on **5**, on the secondary isomerization.

increasing concentrations of the Lewis acid cause secondary double-bond isomerization in the C_6 fraction.

The activation of η^3-allylnickel methanolate (**6**), ethanolate (**7**), isopropanolate (**8**) and phenolate (**9**) using BF_3 works equally well. However, in the case of compounds **6–9**, $BF_3.OEt_2$ fails to activate the complexes even if added in excess. As shown in Fig. 6, the activity of the catalysts and the yield of dimers depends on the nature of the R group present in the nickel alkoxides **5–9**. The corresponding values for the system **1**/$EtAlCl_2$ are added for comparison. For example, in comparison with the methoxide **6**, six-fold catalytic activity was observed using the isopropoxide **8**. In general, the proportion of the dimer fraction yielded by the alkoxide/BF_3 system is lower than in case of **1**/$EtAlCl_2$. The lowest propene conversion, along with only 15% C_6-olefins in the product, was found in the system based on catalyst **6**. In this case the C_{12} oligomers were the main product (36%). Probably the small methyl residue favors the formation of long-chain olefins at the nickel centre. In contrast, the R group in the alkoxides **5–9** has no influence on the composition of the C_6 fraction, as can be deduced from Fig. 7.

Again, the methoxide **6** has a special effect, giving 38% on linear hexenes in the C_6 fraction. The nature of R in the alkoxide has no influence on the proportion of methylpentenes to dimethylbutenes in the C_6 fraction. This selectivity control

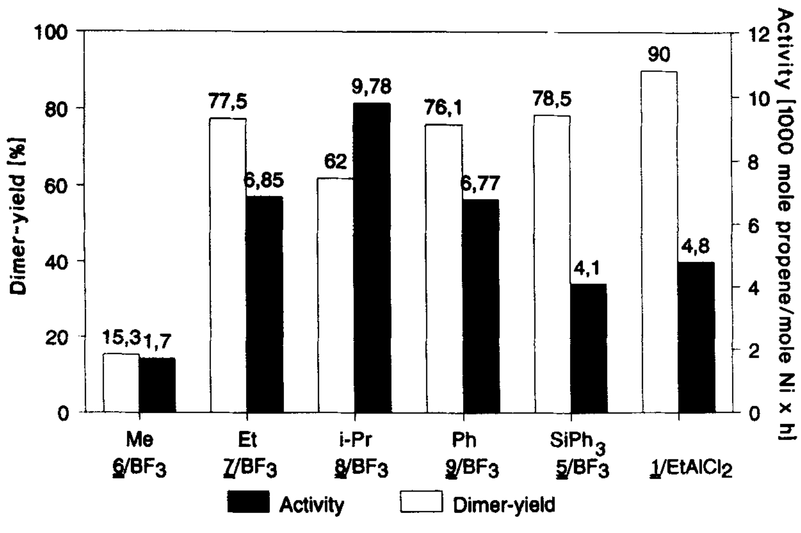


Figure 6 Activity and dimer yield: dependence on R in the homogeneous nickel alkoxide catalysts.

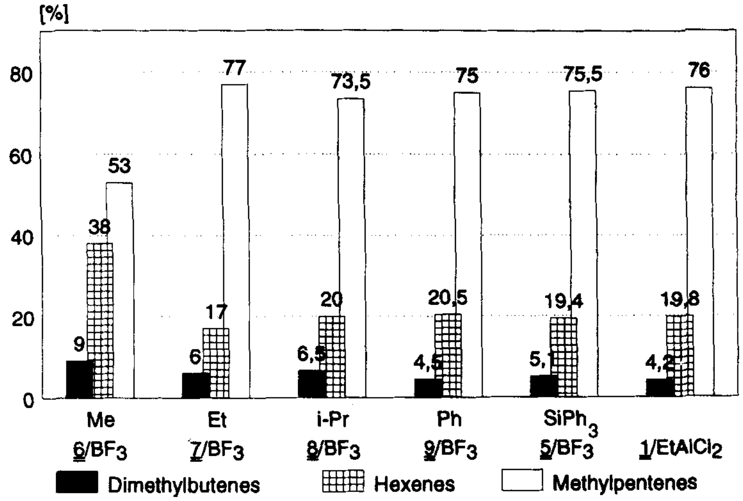


Figure 7 Effect of R in [η^3-$C_3H_5NiOR]_2/BF_3$ catalysts on the composition of the dimer fraction.

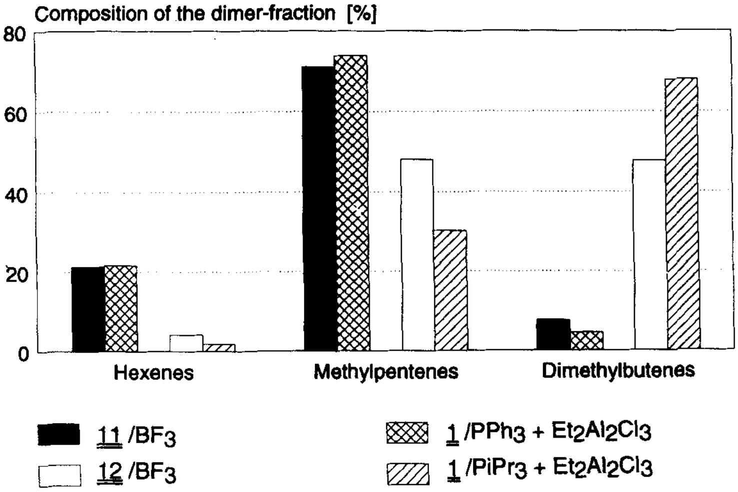
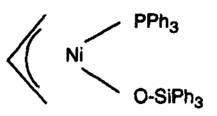


Figure 8 Influence of the phosphine ligand on propene dimerization.

can however be achieved by the addition of phosphine ligands. For example, tri-isopropylphosphine is well known for giving high yields of dimethylbutenes on the standard catalyst $1/EtAlCl_2$.[2] On the other hand, triphenylphosphine acts as a strongly isomerizing ligand.[2]

Table 2 Propene dimerization using **14** (Nos 1–3) or **13**/BF_3–OEt_2 (No. 4) in CH_2Cl_2 at −20 °C

No.	Solvent Catalyst preparation Eqn [4]	 Eqn [5]	Amount of catalyst (g)	(mmol)	Activity, TON [mol propene (mol Ni)$^{-1}$]	Time (h)
1	CH_2Cl_2	CH_2Cl_2	12.2	0.80	52 400	10.5
2	Toluene	CH_2Cl_2	13.8	0.23	6 500	1.5
3	Toluene	—	7.0	0.17	3 100	1.0
4	CH_2Cl_2	CH_2Cl_2	10.1	0.66	0	1.0



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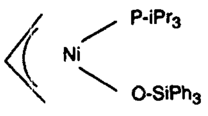

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Compounds **11** and **12**, when activated by gaseous BF_3 or $BF_3.OEt_2$ in CH_2Cl_2, convert 6.2×10^3 mol propene (mol Ni)$^{-1}$ h^{-1} to give 92% of dimers. In the case of $BF_3.OEt_2$, however, a 25-fold molar excess of the activator is necessary to obtain the full catalytic activity. The selectivity control of the phosphine ligands is shown in Fig. 8.

With triphenylphosphine as the ligand, the isomer distribution in the C_6 fraction was found to be equal in both the modified alkoxide catalyst based on **11** and the halide system **1**/$Et_3Al_2Cl_3$. The tri-isopropylphosphine adduct to **1**/$Et_3Al_2Cl_3$, however, produces 20% more dimethylbutenes than the corresponding alkoxide complex **12**. Compared with phosphine-free systems, the addition of tri-propylphosphine to the nickel complex increases the yield of dimethylbutenes from 5 to 50%. In summary, the selectivity control of the different phosphine ligands known for **1**/$Et_3Al_2Cl_3$[2] was confirmed for the BF_3-activated organonickel alkoxide catalyst based on **5–9**.

Heterogeneous η^3-allyl–Ni–O and η^1,η^2-enyl–Ni–O catalysts (15, 18)

Since oxide supports such as Al_2O_3, SiO_2 or TiO_2 contain surface hydroxyl groups and may formally be regarded as 'solid alcohols' bearing extremely bulky substituents, η^3-allylnickel halides were made to react with $\{Al_2O_3\}ONa$, for example, via the metathesis reaction shown in Eqn [4] to obtain the η^3-allyl–Ni–O fragment σ-bonded to the alumina surface (**13**). The 'sodium salts' of alumina and other oxide supports are easily accessible by reaction of the dried powders with $Na[BEt_3H]$ in toluene and subsequent heating to 250 °C in order to eliminate the BEt_3 completely (see Eqn [4]).

The metathesis reaction in Eqn [4], which is performed alternatively in CH_2Cl_2 or toluene, yields an orange–yellow, extremely air-sensitive, solid. Samples of the catalyst precursor **13** have been stored at −30 °C for months without decomposition. Above 0 °C slow reduction of the organo–Ni^{2+} on the surface is observed, giving ill-defined black products. Although the color of **13** is typical for η^3-allylnickel alkoxides, and the chemical behavior of **13** is totally consistent with the presence of η^3-allyl–Ni–O species on the surface, further work is necessary for an unambiguous assignment of the structure. For activation, the precursor **13** is suspended in CH_2Cl_2 or toluene and gaseous BF_3 added under vigorous stirring for 1 h to give **14** in a Lewis acid–base reaction (5).

The activity of the heterogeneous $\{Al_2O_3\}$–$O(BF_3)$–Ni–η^3-allyl catalyst **14** was tested in the batchwise dimerization of gaseous propene (see the Experimental section). The results are listed in Table 2.

The total turnover number [TON] of propene in the heterogeneous system $\{Al_2O_3\}$–$O(BF_3)$–Ni–η^3-allyl (**14**) strongly depends on the solvent used for the metathesis (Eqn [4]) and the activation step (Eqn [5]). The most active catalyst (Table 2, No. 1) was generated using CH_2Cl_2 as the solvent both for metathesis (Eqn [4]) and activation (Eqn [5]). Using toluene as the solvent results in a marked decrease of activity (Table 2,

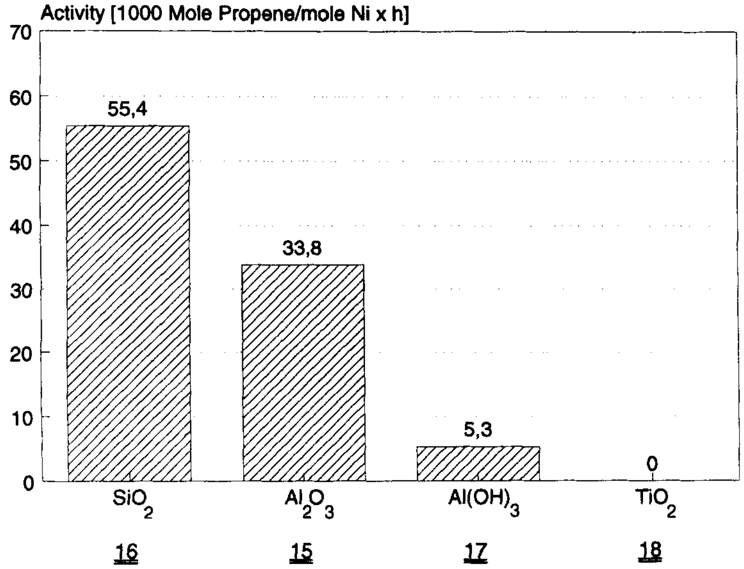

Figure 9 Catalytic activity of **15–18**.

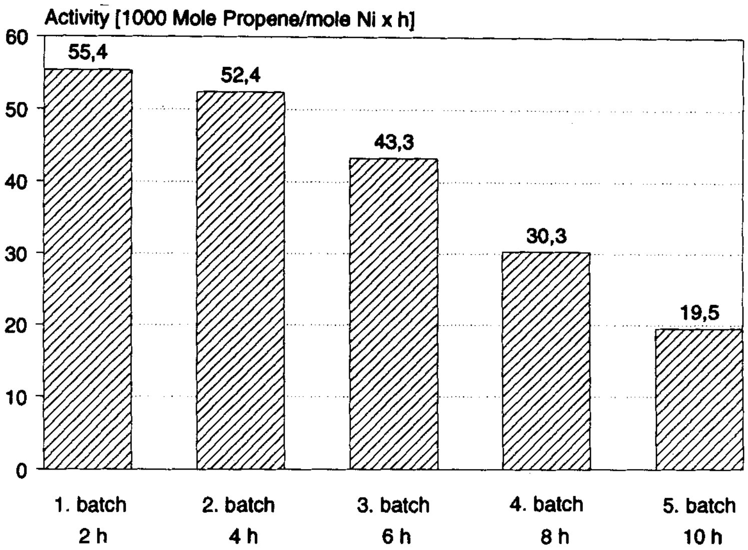

Figure 10 Activity of reused catalyst charges **16**.

No. 2). The solvent-free activation of a catalyst precursor **13** prepared in toluene leads to a further loss in activity (Table 2, No. 3). The activation of **13** using $BF_3.OEt_2$ fails (Table 2, No. 4). The products consist of 55% dimers and 45% higher oligomers. The distribution in the C_6 fraction produced by **14** (20% hexenes, 75% methylpentenes and 3% dimethylbutenes) was found to be nearly identical to the results of the homogeneous standard system **1**/$Et_3Al_2Cl_3$.[2] In a continuous run over seven days at −20 °C using the apparatus shown in Fig. 1, 4.2 kg of gaseous propene was converted using 0.7 mmol of **14** in CH_2Cl_2, which corresponds to a TON of 143 × 10^3 mol propene $(\text{mol Ni})^{-1}$ at the heterogeneous organonickel catalyst.

A straightforward synthesis of the heterogeneous η^2-enyl–Ni–O catalyst **16**, avoiding any halogenated solvents, was achieved in two steps Eqns [6] and [7]: First the strong 'solid acids' (**4**) are generated by the addition of gaseous BF_3 to the dry supports (Eqn [6]) followed by the addition of $Ni(COD)_2$ at −78 °C in toluene suspension, this results in an oxidative addition of the η^1,η^2-cyclo-octenylnickel fragment to the surface (Eqn [7]). No activation step is necessary. The catalysts **15–18** are orange–yellow (organo–Ni–O). Surprisingly, the catalyst **18**, which is fixed on

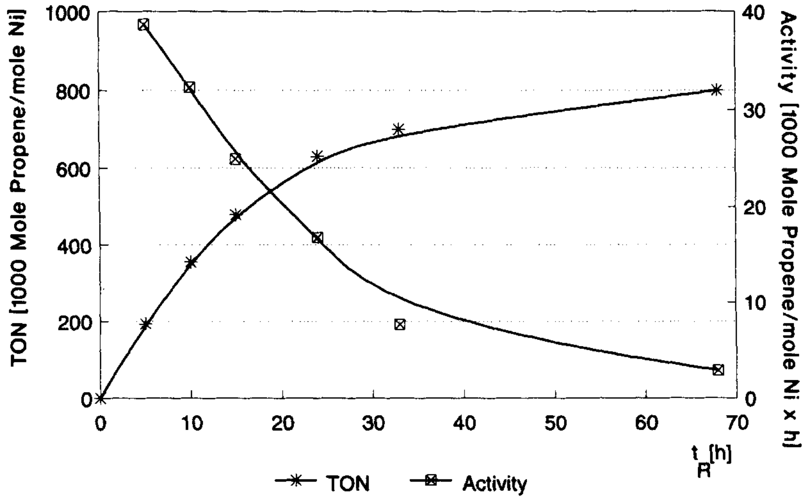

Figure 11 Lifetime of **16** in continuous propene dimerization.

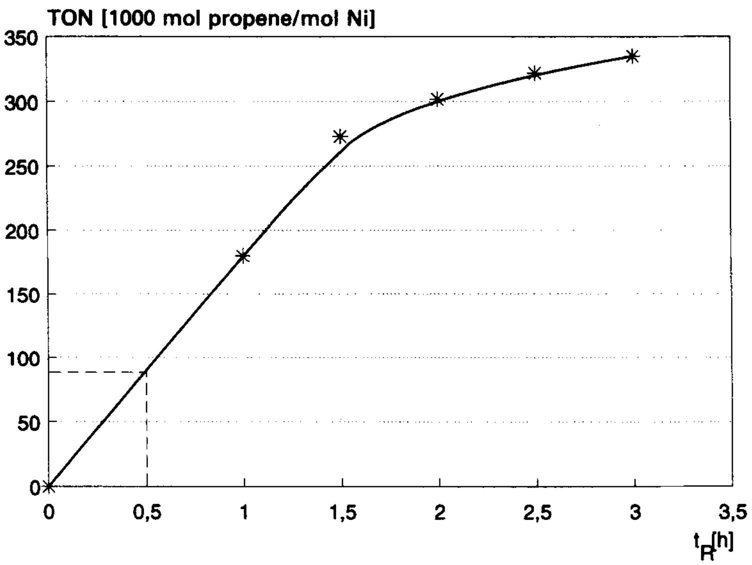

Figure 12 Conversion of liquid propene at +30 °C and 10 bar. Catalyst: **16**, 5.5×10^{-5} mol Ni (see Fig. 2).

TiO_2, is blue. Probably the TiO_2 support is partially reduced to Ti^{3+} by the zerovalent nickel. For the catalytic propene dimerization, η^1,η^2-cyclo-octenyl–Ni–O catalysts **15–18** were suspended in hydrocarbons such as pentane. Halogenated solvents are no longer necessary. Compared with the homogeneous nickel alkoxide system **10** and the heterogeneous η^3-allyl–Ni–O catalyst **14** (Eqn [5]), the supported η^1,η^2-cyclo-octenyl–Ni–O catalysts **15–18** are much more temperature-resistant. The catalytic reaction can now be carried out at 30 °C. Figure 9 shows that the catalytic activity of the η^1,η^2-cyclo-octenyl–Ni–O species depends on the various supports present in **15–18**.

The maximum propene conversion was achieved using the SiO_2-supported catalyst **16**. The conversion on η^1,η^2-cyclo-octenylnickel on Al_2O_3 (**15**) still reaches 34×10^3 mol propene mol Ni^{-1} h^{-1}. The activity of **17** expires after 30 min and the TiO_2-based catalyst **18** exhibits no catalytic activity towards propene at all. The conversion of propene observed on the catalyst **16**, based on SiO_2, is ten-fold that observed using the corresponding η^3-allyl–Ni–O system **12**/BF_3 and six-fold higher in comparison with the homogeneous catalyst **10**. These results clearly show that both the support and the η^1,η^3-cyclo-octenyl–Ni–O fragment are essential for the efficiency of the resulting heterogeneous catalysts **15–18**. Figure 10 shows that the most active catalyst, **16**, may be isolated from the batch and reused several times—one of the general advantages of heterogeneous catalysts. Even in the fifth run the TON reached 19.5×10^3 mol propene (mol $Ni)^{-1}$ h^{-1}. The overall propene conversion was as high as 400×10^3 mol propene (mol $Ni)^{-1}$.

Table 3 Influence of the organonickel fragment, the support and the process mode on the lifetime of the heterogeneous catalysts **14**, **15** and **17**

		Batch		Continuous	
No.	Catalyst	TON [mol propene (mol $Ni)^{-1}$]	Time (h)	TON [mol propene (mol $Ni)^{-1}$]	Time (h)
1	**14**	52 400	10.5	143 000	168
2	**15**	—	—	525 000	109
3	**16**	400 000	10.0	800 000	68

The lifetime of the catalyst system **16** was tested in a continuous-flow experiment. Propene conversion vs reaction time and catalytic activity vs reaction time are plotted in Fig. 11. After 68 h running time and a total conversion of 800×10^3 mol propene (mol $Ni)^{-1}$, the activity of **16** was found to expire.

The lifetime of the catalyst **16** is very dependent on traces of air present in the reactor and leading to slow oxidative destruction. An indication of this is the typical white color of the oxidized catalyst at the end of the reaction. Further, the catalyst is deactivated by impurities in the feedstock, namely by alkynes. At a conversion of

Table 4 Selectivity of different homogeneous (Nos 1, 2) and heterogeneous catalysts (Nos 3–9)

No.	Catalyst	Process mode	Dimers (%)	Composition of the dimer fraction (%) Hexenes	Methylpentenes	Dimethylbutenes
1	**1**/$Et_3Al_2Cl_3$	Batch	90.0	19.8	76.0	4.2
2	**5**/BF_3	Batch	78.5	19.4	75.5	5.1
3	**14**	Batch	58.0	25.2	72.9	1.9
4	**14**	Continuous	80.3	20.9	75.0	3.0
5	**15**	Batch	69.4	18.8	76.2	5.0
6	**15**	Continuous	75.5	20.3	74.4	5.3
7	**17**	Batch	77.6	21.5	73.7	4.8
8	**16**	Batch	65.0	20.5	73.4	6.1
9	**16**	Continuous	80.0	21.7	73.7	4.5

nearly 10^6 mol propene (mol Ni)$^{-1}$, even impurities in the parts-per-million range are stoichiometric relative to the catalytic centre.

Propene dimerization in the liquid phase using catalyst 16

In the case of the highly active homogeneous catalysts based on **1**/$EtAlCl_2$, the velocity of the propene dimerization was found to be governed by the concentration of the substrate in solution. Consequently, the use of liquid propene under pressure accelerates the catalytic turnover dramatically.[5] Using the apparatus shown in Fig. 2 (see the Experimental section), we have tested the activity and selectivity of the heterogeneous catalyst **16** in liquid propene. This catalyst was selected from the heterogeneous systems for a comparison with the homogeneous standard catalyst **1**/$EtAlCl_2$ because it showed the highest conversion of gaseous propene, combined with the maximum lifetime. A major experimental problem resides in the removal of the considerable heat generated by the strongly exothermic dimerization process in liquid propene. However, after the catalyst had been diluted in the liquid phase to 5.5×10^{-5} mol Ni, the experiments could safely be conducted at +30 °C and 10 bar pressure.

As can be seen in Fig. 12, the use of liquid propene as the substrate substantially enhances the reaction speed. During the first 30 min, 100×10^3 mol propene (mol Ni)$^{-1}$ are converted by **16**. For comparison, in liquid propene the standard homogeneous catalyst **1**/$EtAlCl_2$ was reported to give a conversion of 5.4×10^3 mol propene (mol Ni)$^{-1}$ in 30 min.[2] After 3 h of reaction time, the total propene conversion (TON) reaches 340×10^3 mol propene (mol Ni^{1-}). With gaseous propene as the substrate, using the identical catalyst **16**, a reaction time three times longer (9 h) had to be applied to achieve this high degree of conversion. Because the high excess of propene in the substrate limits the formation of higher alkenes, the selectivity of the catalysts for the production of C_6 olefins is generally found to be optimal in the liquid phase. In the case of the heterogeneous system **16**, the dimer yield even exceeded 90%.

Influence of the organonickel fragment, the support and the process mode on the lifetime and selectivity of the heterogeneous catalysts 14, 15 and 16

The superiority of the continuous process mode to the batchwise reaction for the lifetime of the catalysts makes itself apparent on comparing the results of the heterogeneous η^3-allyl–Ni–O and η^1,η^2-cyclo-octenyl–Ni–O systems quoted in Table 3, Nos. 1 and 3. Further, the lifetime of the catalysts obviously depends on the organo-group present at the nickel atom (see Table 3). The η^3-allyl–Ni–O catalyst **14** (No. 1), which is more air- and temperature-sensitive, proves to be less efficient than the η^1,η^2-cyclo-octenyl–Ni–O systems **15** and **16** (Nos 2 and 3). Finally, the nature of the support influences the lifetime of the catalysts in the propene dimerization. The TON for the SiO_2-based η^1,η^2-cyclo-octenyl–Ni–O system **16** (No. 3) was found to be *ca* 1.5 times higher than for the same catalyst fragment fixed on Al_2O_3, **15** (No. 2).

Table 4 compares the product selectivity of the homogeneous catalysts **1**/$Et_3Al_2Cl_3$ and **5**/BF_3 (Nos 1 and 2) with the results found using the heterogeneous systems **14**, **15**, **16** and **17** (Nos 3–9). The optimum chemoselectivity with respect to a maximum yield of C_6 olefins is performed by the homogeneous standard catalyst (No. 1).[2] The different nickel alkoxide catalysts (Nos 2–9) yield slightly higher proportions of C_9 oligomers. Obviously, the degree of oligomerization is controlled mainly by the process mode. All continuous runs (Nos 4, 6 and 9), although using different nickel alkoxide catalysts, generally yield *ca* 80% propene dimers, whereas in the batchwise mode the C_6 proportion is always lower. An inspection of Table 4 shows that the composition of the dimer fraction is practically independent of the chemical nature of the different homogeneous or heterogeneous catalysts used. Obviously neither the organonickel fragments nor the support has any influence on the catalytic regioselectivity.

CONCLUSIONS

The activation of η^3-allylnickel alkoxides $[\eta^3\text{-}C_3H_5\text{–Ni–OR}]_2$ by gaseous BF_3 gives homogeneous catalysts of activity comparable with those known for the 'classical' systems based on η^3-allylnickel halides. The activation of nickel–oxygen bonds using BF_3 may be transferred to η^3-allyl–Ni–O and η^1,η^2-cyclo-octenyl–Ni–O species of alumina, silica and TiO_2, giving effective heterogeneous catalysts of the type $\{M_xO_y\}$–O–Ni–η-organoligand. η^3-allylnickel halides react with $\{Al_2O_3\}$–ONa via metathesis. The organonickel fragment is fixed to the surface via an oxygen σ-bond. This surface organometallic chemistry approach can certainly be applied for the analogous preparation of other well-defined organometallic catalysts on various supports. The reaction of dry alumina, silica and titania with gaseous BF_3 leads to the formation of 'solid acids' of the type $\{M_xO_y\}$–O–BF_3–H. These modified supports serve as valuable starting materials for selective chemical reactions of organometallic reagents such as $Ni(cod)_2$ on the surface to give compounds of the type $\{M_xO_y\}$–O–BF_3–organometal. This principle, which has been exemplified with η^1,η^2-cyclo-octenyl–Ni–O in this paper, may successfully be applied to the fixation of other organometallic fragments on oxide surfaces. Finally, it is evident from the catalytic results that the activity and selectivity of supported η^1,η^2-cyclo-octenyl–Ni–O fragments activated by BF_3 compare with the best results known from homogeneous catalysts.

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