An example of the valorization of terpenes: The selective isomerization of 3-carene to 2-carene in the presence of silica supported nickel catalysts modified by tetrabutyl tin

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Abstract

The cyclic olefin, 3-carene, undergoes an isomerization of the carbon–carbon double bond to produce 2-carene, a precursor in the synthesis of (−)-menthol. This isomerization is observed over silica supported nickel, but the selectivity is reduced by side reactions producing trimethylheptenes by hydrogenative ring opening of the cyclopropyl ring. Selectivity for C=C bond isomerization is dramatically increased by surface modification of the nickel metal catalyst by reaction with tetra-*n*-butyl tin. The most selective of these silica supported nickel/tin catalysts produces 2-carene with 91% selectivity at 48% conversion.

Keywords: Carene isomerization; Ni/SiO_2 catalyst; Tetra-*n*-butyl tin modified catalyst; Surface organometallic chemistry

1. Introduction

The cyclic olefin, 3-carene (3,7,7-trimethyl-[4,1,0]-bicyclohept-3-ene), is a monoterpene present in the 'essences de térébenthine' in its naturally occurring form, (+)-3-carene. There is little industrial exploitation of this product which is sometimes used as a solvent in coatings.

(+)-3-carene can be isomerized by carbon–carbon double bond migration to (+)-2-carene.

(+)-2-carene has a higher reactivity than (+)-3-carene because the C=C bond is conjugated with the cyclopropyl C–C bonds. Thus 2-carene can be a precursor for numerous fine chemical syntheses. For example, above 220°C (+)-2-carene undergoes a thermal rearrangement to (+)-*trans*-isolimonene, an important starting material in perfume industry (Scheme 1).

The isomerization of 3-carene to 2-carene has been previously observed in basic solution, for example in the presence of ethylenediamino lithium [1], of *tert*-butyl potassium [2], or various other strong bases (Na, *t*-BuOK, BuLi, ...) [3,4].

These methods involve the production of

waste product, the disposal of which present an environmental hazard. Heterogeneous hydrogenation catalysts (Raney Ni, Pd/C) have also been used at low hydrogen pressure to isomerize (+)-3-carene to (+)-2-carene [5] but the selectivity of these reactions is low because of the significant hydrogenation to carane. At 100°C the thermodynamic equilibrium between (+)-3-carene and (+)-2-carene corresponds to a mixture of ca. 60% (+)-3-carene and 40% (+)-2-carene. Our objective in these studies was to approach this equilibrium mixture while avoiding side reactions, notably hydrogenation to carane, dehydrogenation to cymenes, and ring opening hydrogenolysis to trimethylcyclohep-

tenes (Scheme 1). To accomplish this, we used silica supported nickel catalyst modified by an 'inert' metal, tin. The addition of tin is accomplished by surface organometallic chemistry [6]. It has been established that the addition of tetrabutyl tin to supported iron triad metals considerably reduces the hydrogenolysis property of these catalysts [7–14].

In this work, we report the beneficial effect of tin on the selective isomerization of (+)-3-carene to (+)-2-carene. In particular, we have determined the optimal surface tin/surface nickel ratio (Sn/Ni_s) and the catalytic conditions with respect to the selectivity of olefin isomerization.
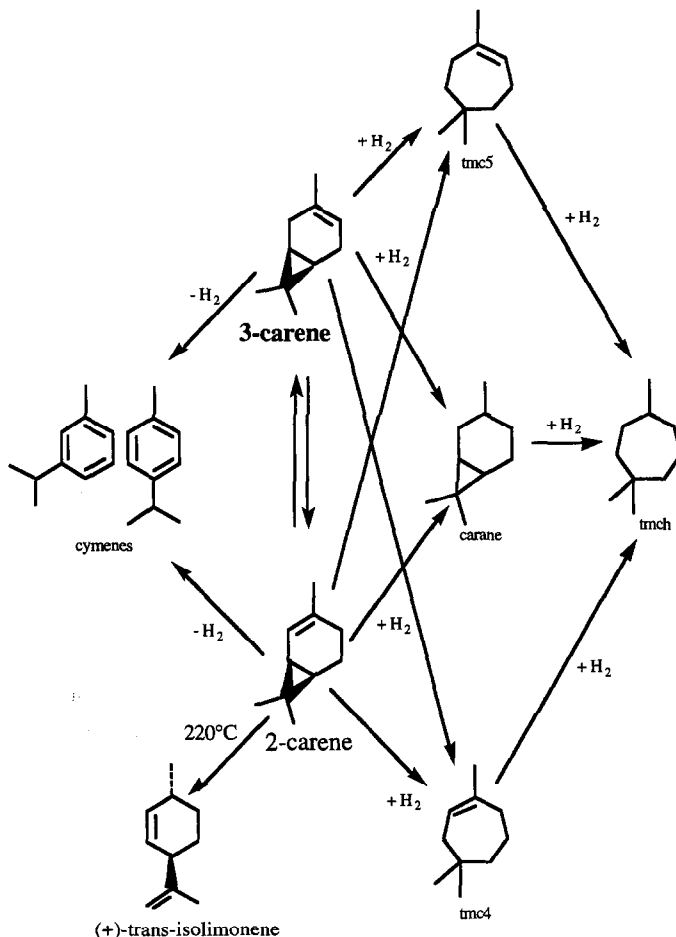
Scheme 1. Possible reactions starting from 3-carene.

2. Experimental conditions

2.1. Preparation of the monometallic catalysts

The silica used was an Aerosil from Degussa, a non-porous silica having a specific area of 200 m^2/g. In each case, 10 g of silica were calcinated at 450°C under a stream of oxygen for four hours, then they were suspended in 100 ml of aqueous ammonia (pH = 10) for 24 h. The metal is grafted to the silica surface by ion exchange with an appropriate metal amine complex. Nickel hexamine hydroxide, $Ni(NH_3)_6(OH)_2$ was obtained by dissolving 2 g of nickel nitrate $Ni(NO_3)_2 \cdot 6 H_2O$ (Aldrich) in aqueous ammonia. Impregnation of the silica was accomplished by stirring the aqueous suspension of the silica and the nickel hexamine complex during 24 h at room temperature. The resulting material was washed with distilled water, filtered, and dried in an oven for 24 h at 80°C. The Ni precursor was directly reduced under a flow (100 ml/min) of a nitrogen/hydrogen mixture (3/1). This reduction was achieved via a gradual increase in temperature (1.5°C/min) to 500°C, a temperature which was held for four hours.

The dispersion defined as the number of surface atoms divided by the total number of atoms, M_s/M, was estimated from the hydrogen adsorption capacity (at 25°C under 200 mbar of H_2) as measured by volumetry. The stoichiometry was assumed to be one hydrogen atom per surface metal atom [15]. The total loading of metal was 2.7% wt with a dispersion of 24%.

2.2. Catalytic test procedure

The reactions were performed under hydrogen in a 200 ml three-necked round bottom flask equipped with a gas inlet, a condenser, a septum (to allow the withdrawal of samples by syringe) and a magnetic stirrer. 3-carene (15 ml, 95 mmol) and the catalyst (which had been previously reduced under hydrogen) were added at room temperature under a flow of argon. The substrate/M_s ratio was equal to 350. Argon was replaced by hydrogen which was gently bubbled through the substrate. The flask was placed in an oil bath and the temperature raised to the desired level. The reaction was followed by gas chromatography, the samples being withdrawn from the liquid phase by syringe. The two chromatographic columns used were CP-WAX 57 CB and SUPELCOWAX 10 which allowed identification and quantification of 3-carene, 2-carene, para- and meta- cymene (not resolved), 1,5,5-trimethylcycloheptene (tmc5), 1,4,4-trimethylcycloheptene (tmc4), 1,1,4-trimethylcycloheptane (tmch) and carane. The identity of the product was confirmed by GC-IR and GC-MS.

The argon was furnished by Air Liquide (U quality) and purified by passage through a DE-OXO and a 4 Å zeolite trap. The 3-carene used was 92% pure, the impurities being essentially pinene, dipentene, and myrcene.

The conversion of 3-carene (conv.), selectivity for carenes, $S_{(\Delta 3 + \Delta 2)}$ and the selectivity for 2-carene, $S_{(\Delta 2)}$ are described by the following equations in which $[\Delta 3]_o$ represents the initial concentration of 3-carene and $[\Delta 3]_t$ and $[\Delta 2]_t$ represent the concentration at time t of 3-carene and 2-carene, respectively.

$$\text{conv.} = ([\Delta 3]_o - [\Delta 3]_t)/[\Delta 3]_o$$

$$S_{(\Delta 3 + \Delta 2)} = ([\Delta 3]_t + [\Delta 2]_t)/[\Delta 3]_o$$

$$S_{(\Delta 2)} = [\Delta 2]_t/([\Delta 3]_o - [\Delta 3]_t)$$

It was verified that under the experimental conditions described above and at temperatures below 200°C silica alone cannot promote the transformation of 3-carene. The induction period during the first 10 min may be due to impurities (7% of dipentene, myrcene and pinene) which are first adsorbed on the catalyst and poison reversibly the active surface.

2.3. In situ modification of the monometallic catalyst

The modification of the monometallic catalysts was accomplished in situ in the reactor described above, using 3-carene as solvent. A

known amount of tetra-n-butyl tin correspond-
ing to the desired ratio Sn/Ni$_s$ (0 < Sn/Ni$_s$ <
0.08) was introduced at room temperature to the
reactor containing the 3-carene and the reduced
catalyst. The system was then placed under a
flow of hydrogen and stirred at room tempera-
ture for 30 min. Under these conditions in the
range of Sn/Ni$_s$ ratios studied, the tin intro-
duced was entirely fixed by the catalyst (as
confirmed by GC). It should be noticed that
under these conditions, silica alone does not
react with tetra-n-butyl tin [16]. The reactor was
then heated to the desired temperature of reac-
tion.

3. Results

3.1. Reactions of 3-carene in the presence of a monometallic catalyst

The evolution of products formed during the
transformation of 3-carene in the presence of
silica supported Ni catalyst at 120°C is shown in
Fig. 1. It is clearly seen that the maximum
concentration on 2-carene is reached after 1 h of
reaction. At this time the conversion of 3-carene
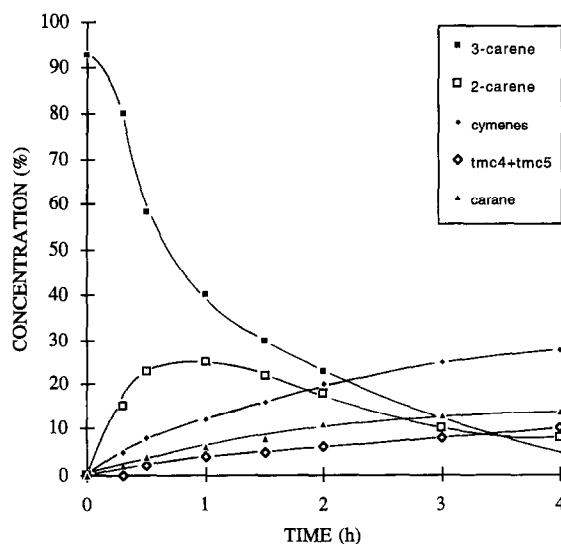is 61% and the selectivity for 2-carene is 50%

Fig. 1. The transformation of 3-carene at 120°C in the presence of Ni/SiO$_2$.

Table 1
Effect of reaction temperature on the maximum of 2-carene concentration [Δ2] and on the selectivity for carenes at t_{max} over Ni/SiO$_2$

Temp. (°C)	t_{max} (h)	[Δ2] (%)	$S_{(Δ2+Δ3)}$ (%)
80°C	1.5	23	71
120°C	1.0	28	70
180°C	0.25	25	69

(Table 2). Side reactions lead mostly to the
formation of para- and meta-cymenes.

The influence of temperature on the maxi-
mum of 2-carene formation and on the selectiv-
ity for carenes $S_{(Δ2+Δ3)}$ in the presence of
Ni/SiO$_2$ is collected in Table 1. The maximum
concentration of 2-carene is reached after 0.25 h
at 180°C. The selectivity for carenes $S_{(Δ2+Δ3)}$
does not depend to a great extent on the temper-
ature, but clearly the proportion of 2-carene is
the highest at 120°C.

Side reactions include the ring opening of
cyclopropane (leading to trimethylcycloheptenes
and cymenes) and the hydrogenation of the
double bonds (leading carane and trimethylcy-
cloheptane). Thus, the Ni/SiO$_2$ monometallic
catalyst is weakly selective for the isomerization
of 3-carene to 2-carene due to these side reac-
tions. However, the selectivity is still too low to
be of practical interest.

3.2. Influence of tin content on the isomeriza-tion of 3-carene with a Ni–Sn / SiO$_2$ at 120°C

The influence of tin loading on the maximum
of selectivity for 2-carene, $S_{(Δ2)}$, at 120°C is

Table 2
The effect of Sn/Ni$_s$ ratio on the reaction of 3-carene over NiSn/SiO$_2$ at 120°C

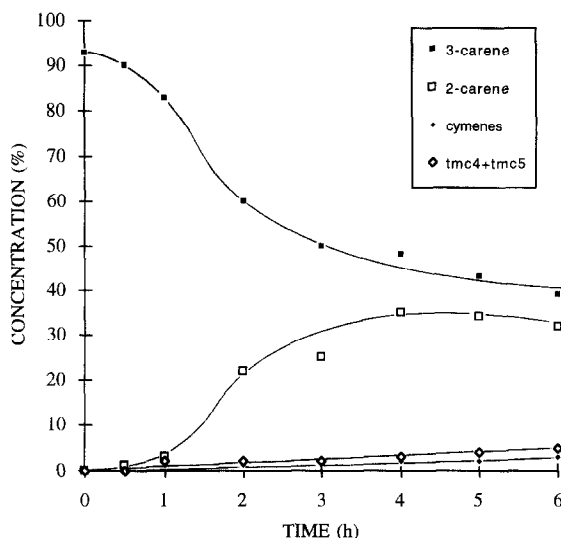| Sn/Ni$_s$	[Δ2] (%)	$S_{(Δ2)}$ (%)	t_{opt} (h)	Conv. (%)	$S_{(Δ2+Δ3)}$ (%)
0	30.5	50	1	61	70
0.02	36	58	4.5	52	80
0.03	31	78	4	40	93
0.04	37	77	4	48	91
0.05	33.5	57	4	50	81
0.06	30	60	7	49	82
0.08	32.5	65	7	50	84

Fig. 2. The transformation of 3-carene at 120°C in the presence of SnNi/SiO$_2$ (Sn/Ni$_s$ = 0.04).

shown in Table 2. Also shown is the reaction time (t_{opt}) corresponding to this maximum of selectivity, the concentration of 2-carene ([$\Delta2$]), the conversion of 3-carene (conv.), the selectivity for carenes ($S_{(\Delta3+\Delta2)}$) and at that optimum time.

The best results are obtained for the catalyst containing 0.04 tin atoms per surface nickel atom. With this catalyst the selectivity for carenes, $S_{(\Delta2+\Delta3)}$, is above 90% and the selectivity for 2-carene, $S_{(\Delta2)}$, is 77% at 48% conversion. The evolution of all the products for the isomerization of 3-carene over this particular catalyst at 120°C is shown as an example in Fig. 2.

4. Discussion–conclusion

The nickel catalyst presents interesting catalytic properties with respect to the isomerization of 3-carene to 2-carene. Nonetheless the occurrence of important side reactions due to dehydrogenation with exocyclic carbon–carbon bond cleavage (leading to cymenes), endocyclic carbon–carbon bond cleavage (leading to trimethylcycloheptenes), and hydrogenation

(leading to alkanes) make the commercial application of this catalyst impractical.

The 3-carene can adsorbed on nickel atom by a coordination of π bond which could be followed by insertion into a surface nickel–hydride bond, leads to an intermediate of either the desired isomerization (if followed by β-hydride elimination), Scheme 2, or the hydrogenation side reaction (by reductive elimination with a second surface hydride).
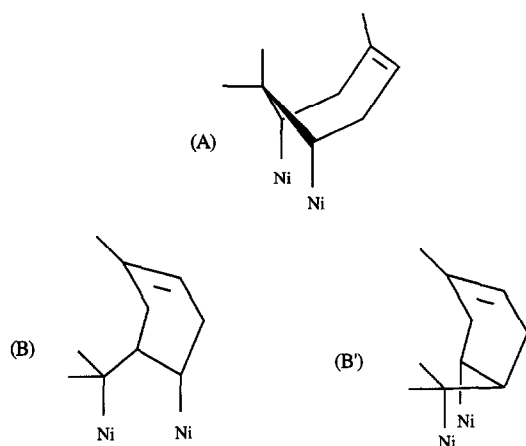
The other side reactions from both 2-carene and 3-carene are derived from a process of oxidative addition of a strained cyclopropane C–C σ bond, previously observed for the adsorption of cyclopropane on nickel [17,18]. Two types of C–C bonds can be cleaved (Scheme 3): The one which belongs to both cycles, which will lead to the dimetallocycle (A) or the one which belongs to one of the two exocyclic C–C bonds, which will lead to the metallocycles (B) and (B').
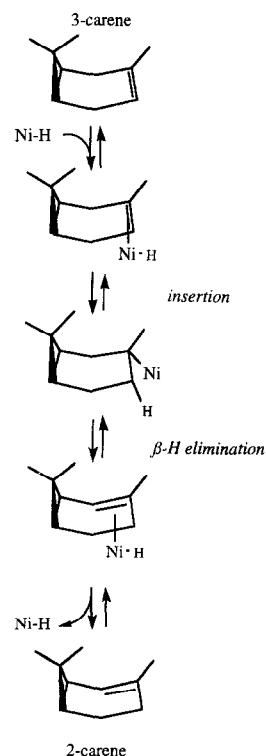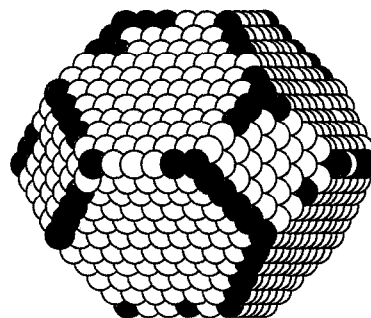

Scheme 2. Possible mechanisms for 3-carene isomerization into 2-carene.

The resulting cleavage of the metal–carbon bonds of these two types of metallocycle by reductive elimination will lead to trimethylcycloheptene from (A) or to para or meta cymene by reductive elimination and two successive β-H elimination from metallocycles (B) and (B').

Concerning the role of tin, it has been previously demonstrated that the addition of small quantities of tin can considerably attenuate the hydrogenolysis activity of a supported iron group metal [7–14]. This effect is especially pronounced when the tin is added using the method of surface organometallic chemistry [6,12,19]. Our previous works have shown that at high coverage of Ni_s by tin, the reaction of tetra n-butyl tin with silica supported nickel is accompanied by the release of butane and the modified surface has a lower capacity for the adsorption of hydrogen and carbon monoxide at room temperature [19]. Furthermore, in the infrared spectra of carbon monoxide adsorbed on the modified metal surface, absorbances associated with linear carbon monoxide ligands are observed, bands associated with bridging carbon monoxide ligands totally disappear. These results were interpreted as evidence for 'site isolation' [14,20] in which inert tin atoms surround the isolated reactive metal sites. In the present case, it is difficult to invoke this particular

Scheme 4. A cubo-octahedral nickel particle partially covered on corners and edges with tin.

effect due to the very small ratio Sn/Ni_s required. It is suggested, but without real proof, that at very low coverage, the hydrogenolysis of the tetra n-butyl tin occurs selectively on low coordination nickel atoms located on edge and corners of the particles (2–4 nm). It would result that the tin atoms would remain located on these edge and corners (Scheme 4). Their presence would avoid the ring opening of the cyclopropyl ring of 2-carene which would require these low coordination sites. The isomerization of 3-carene to 2-carene would occur more easily on faces of the particles.

5. Conclusion

In conclusion, the modification of the surface of a Ni/SiO_2 catalyst by the reaction of tetra-n-butyl tin allows considerable improvement of the selectivity for the isomerization of 3-carene to 2-carene under mild conditions. This simple modification reduces side reactions in these process below 10% and eliminates the need for strong bases to achieve this improvement.

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Scheme 3. Dimetallacycles obtained by cleavage of two types of cyclopropane C–C bonds of 3-carene.

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