Catalysis Today 78 (2003) 197–201

www.elsevier.com/locate/cattod

Polymerisation of pinenes using vanadium oxide supported on activated carbon

A.C. Encarnação, A. Flores, S.I. Mota, C. Palma, A.M. Ramos,
J. Vital, I.M. Fonseca*

REQUIMTE, CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade Nova de Lisboa, 2825-149 Monte de Caparica, Portugal

Abstract

Polymerisation of α-pinene using vanadium oxide (5 wt.% metal) supported on activated carbon was carried out at room temperature and 90 °C. Polymers of low molecular weight were obtained after 100 h of reaction and 30% conversion was attained.

The presence or absence of light has an important role in the reaction, suggesting that α-pinene polymerisation takes place via a radical mechanism.

The role of the catalyst seems to be to increase the formation of radical initiator species such as peroxides.

For the bulk catalyst (1.25 g) 50% conversion was obtained after 2 h at 90 °C, and only isomerisation products of α-pinene, such as camphene and tricyclene.

In situ XRD was carried out using the same experimental conditions of catalyst pre-treatment, and the phases identified for the supported and bulk catalyst was a mixture of V_2O_5/V_6O_{13} and V_2O_5. The nature of vanadium species seems to be related to the catalyst behaviour.

Keywords: Vanadium catalyst; Carbon support; α-Pinene; Polymerisation; Isomerisation

1. Introduction

Pinenes, α- and β-isomers, are bicyclic monoterpenes, and the main constituents of turpentine oil, obtained from the distillation of pine gum [1a]. These cheap and renewable raw materials undergo cationic and radical polymerisation by ring opening of their cyclobutane ring [1b-3]. Pinene homopolymers belong to the family of terpenic resins, that are low molecular weight valuable commercial products used by adhesive, sealant, wax coating and casting industries.

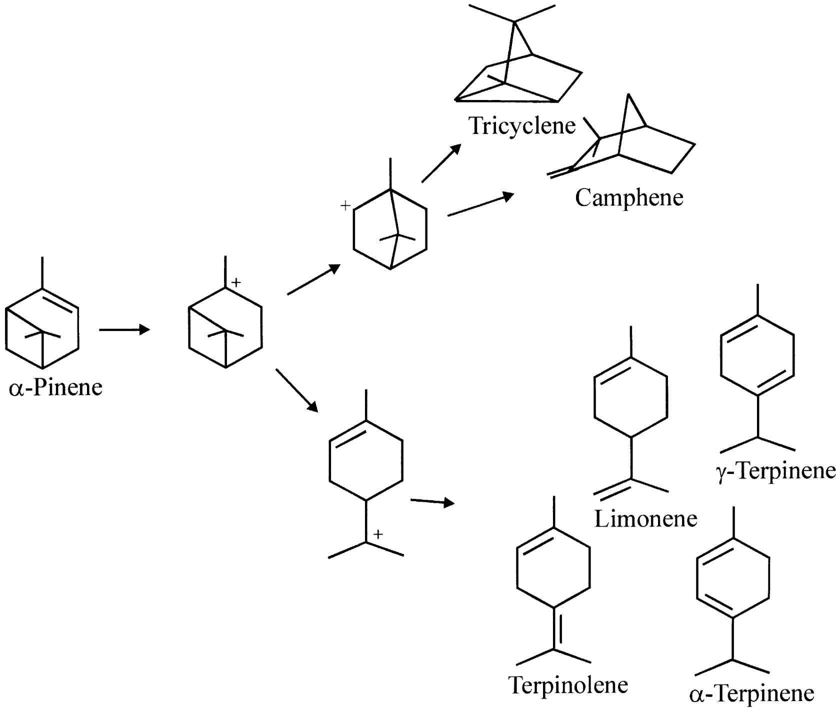
In a previous work, it was reported that cationic polymerisation of α-pinene is promoted by transition metal oxides supported on activated carbon. It was also reported that the presence of oxygen surface functional groups on the carbon surface such as phenol or carboxylic acid groups, plays an important role on the polymerisation reactions [3]. The decrease in the polymer yield observed with the most acidic samples can be explained by the increase in chain transfer reactions or by the increase of isomerisation to camphene [3].

The isomerisation of α-pinene over different heterogeneous catalysts leads to a series of valuable terpenic products. These substances are used in the pharmaceutical and perfume industries, as final products or intermediates [1c,4-10].

---

* Corresponding author. Fax: +351-21-2948385.
E-mail address: iss@dq.fct.unl.pt (I.M. Fonseca).

PII: S0920-5861(02)00333-4



Scheme 1.

The acid catalysed isomerisation of α-pinene proceeds via two parallel pathways: one by ring expansion, giving rise to bi- and tricyclic products, such as camphene, β-pinene, tricyclene and bornylene and other yielding monocyclic products such as limonene, terpinolene, *p*-cymene, α- and γ-terpinenes (Scheme 1) [4–9].

Over solid catalysts such as clays, mineral oxides and inorganic salts the main product obtained is camphene, of particular interest as an intermediate in the synthesis of camphor.

The acid strength of the catalyst or catalyst support has a remarkable influence on reaction mechanism and selectivity [4–10].

The aim of the present work was to study the effect of catalysts consisting of vanadium oxide supported on activated carbon, on α-pinene polymerisation at different temperatures. The catalysts were prepared by impregnation of ammonium vanadate, followed by calcinations, being the transformations of the vanadium phase followed by in situ XRD.

2. Experimental

A commercial granular activated carbon (Norit, GCN, average diameter 2 mm) was used as catalyst support for vanadium oxide.

Ammonium vanadate was impregnated (5 wt.% metal) on the as-received carbon by the incipient wetness method. Metal salt was dissolved in a small amount of distilled water and the obtained solution was added dropwise to the carbon, mixing thoroughly and the obtained product was evaporated in a hot plate.

The samples impregnated were pretreated in nitrogen (100 ml min^{-1}) at 500 °C during 1 h with a heating rate of 10 °C min^{-1}, in order to decompose the precursor salt.

The bulk catalyst, was obtained by thermal decomposition of ammonium vanadate in nitrogen using the same experimental conditions referred above.

The textural characterisation was determined using a Micromeritics ASAP 2010 adsorption apparatus.

Table 1
Experimental conditions

Experiment	Catalyst		Light	Temperature (°C)	α-Pinene (ml)	Toluene (ml)
	Supported	Bulk				
E0	No	No	No	25	25	12.5
E1	No	No	Yes	25	25	12.5
E2	No	No	Yes	90	25	12.5
E3	1.25	No	Yes	25	25	12.5
E4	1.25	No	Yes	90	25	12.5
E5	No	1.25	Yes	90	25	12.5

In situ XRD was carried out in a Rigaku D/max IIIC (Cu(alfa) radiation 50 kV, 30 mA) with a high temperature cell. The experimental conditions were the same as those used for the catalysts pre-treatment.

The catalytic experiments were carried out on a batch reactor with magnetic stirring by adding 25 ml α-pinene, 1.25 g of carbon sample (5 wt.% metal) and 12.5 ml toluene. The reactor was heated at 90 °C, using a temperature controlled silicone bath.

Blank experiments were carried out in the presence or absence of light. For the experiments performed in the absence of light the reactor was covered with aluminium foil. Table 1 shows the experimental conditions used.

The experiments using the bulk catalyst were carried out in a batch reactor, in the presence of light, at 90 °C during 2 h.

Samples were taken periodically and analysed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column.

After reaction, the polymer was recovered and the average molecular weights were measured in a low temperature SEC apparatus (Waters) at 30 °C, in chloroform, using a column Styragel HR3 with 10^3 Å porosity and the calibration was performed with monodisperse polystyrene standards.

3. Results and discussion

Table 2 shows the textural characteristics of the carbon parent sample and sample after catalyst impregnation.

After impregnation, the surface area and micropore volume decreases, suggesting the presence of the catalyst dispersed in the pores.

Table 2
Textural characterisation of catalyst and support

Sample	Surface area (m^2/g)	Micropore volume (cm^3/g)
Carbon parent sample	1248	0.28
Catalyst supported	1053	0.24

After pre-treatment in nitrogen, the phases detected by in situ XRD were a mixture V_2O_5/V_6O_{13}, as also reported in literature [14]. Under inert atmosphere, carbon reduces the catalyst to lower oxidation states [14].

Fig. 1 compares the α-pinene concentration profiles for the uncatalysed and catalysed reaction (in the presence of the supported catalyst) at 90 °C and room temperature, in the presence or absence of light. In all experiments the only product observed was a

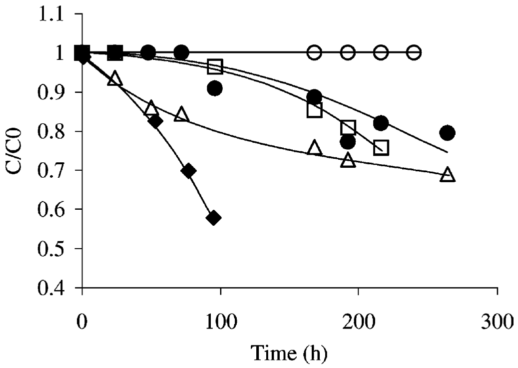


Fig. 1. α-Pinene concentration profiles for the uncatalysed and catalysed experiments in the presence and absence of light. Reaction conditions according to Table 1. ○, E0; □, E1; △, E2; ●, E3; ◆, E4; ■, E5.

monodisperse polymer, presenting an average molecular weight ranging from 700 to 900.

The results obtained show that even in the absence of the catalyst and at room temperature the polymerisation of α-pinene takes place (experiments E1 and E2). However, the presence of catalyst strongly increases the rate of consumption of α-pinene, as can be clearly seen by comparing the α-pinene concentration profiles for the uncatalysed (E2) and catalysed (E4) experiments, carried out at 90 °C. The increase of temperature also leads to an increase of reaction rate. In the absence of both light and catalyst, no consumption of α-pinene is detected even after 250 h (E0).

A common feature to almost all the concentration profiles shown in Fig. 1 is a well-pronounced initial inductive period. This feature is common to the uncatalysed and catalysed experiments, therefore suggesting a common mechanism. As it is well known, the light catalysed polymerisations take place via a radical mechanism, corresponding the initial inductive period to the formation of trace amounts of initiator species, usually peroxides or hydroperoxides, through a slow autoxidation.

Vanadium pentoxide is a non-stoichiometric oxide used in selective oxidations of hydrocarbons, selective catalytic reduction of nitrogen oxides and oxidation of sulphur dioxide [11–13]. It is known that the catalytic activity of vanadium oxides involves a redox mechanism in which the catalyst supplies oxygen to the hydrocarbon molecule [12]. Therefore, the polymerisation of α-pinene in the presence of carbon supported vanadium oxide, seems to take place via a radical mechanism, in contrast with the cationic mechanism observed in a previous work, also in the presence of vanadium oxide supported on the same parent carbon [3]. Although in this case the catalyst was also impregnated by incipient wetness, it was pretreated in air at 300 °C for 30 min. Treatment with oxygen increased the amount of oxygen surface groups, mainly phenolic groups, which play an important role on α-pinene polymerisation [3].

In the presence of a heterogeneous catalyst, the polymerisation of α-pinene is likely to take place in the homogeneous phase rather than on the catalyst surface because, otherwise, the growing polymer would block the catalyst pore system and, therefore, the catalyst would be readily deactivated. Instead, the role of the vanadium catalyst is likely to be the catalysis of α-pinene oxidation leading to the formation of peroxides or hydroperoxides, which on their turn would behave as polymerisation initiators.

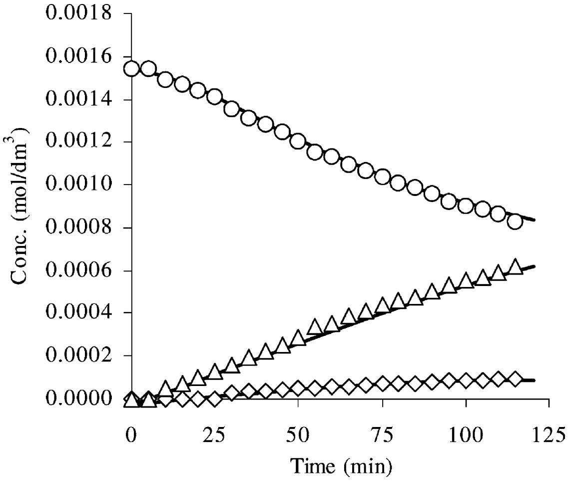


Fig. 2. Concentration profiles for the isomerisation of α-pinene in the presence of the bulk catalyst (experiment E5). ○, α-pinene; △, camphene; ◇, tricyclene.

Fig. 2 shows the concentration profiles of reagent and products for the α-pinene reaction in the presence of the vanadium oxide bulk catalyst at 90 °C. In this case the main product is camphene, being also formed a small amount of tricyclene. There is no evidence of polymer formation.

It is notorious that the reaction rate is much higher with the bulk catalyst (2.60×10^{-7} mol/min g_{cat}) than with the supported catalyst (2.49×10^{-9} mol/min g_{cat}, both reported to the amount of vanadium oxide). This observation suggests that the isomerisation reaction of α-pinene to camphene and tricyclene takes place via a very different mechanism than the polymerisation reaction. The observation of a constant selectivity for both camphene and tricyclene, as α-pinene conversion increases (Fig. 3) is a strong indication of a parallel reaction network for the reaction carried out with the bulk catalyst.

The α-pinene isomerisation has been reported as an acid catalysed reaction, yielding camphene, tricyclene and menthadienes as primary reaction products. The formation of monocyclic products is favoured on strong acid sites [1c,4-10]. Severino et al. [4] reported that isomerisation of α-pinene takes place also on the Lewis acid sites. A terpene molecule adsorpted on a

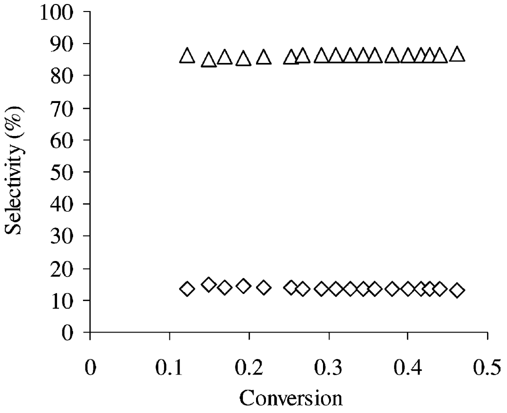


Fig. 3. Isomerisation of α-pinene in the presence of the bulk catalyst (experiment E5). Plot of selectivity vs fractional conversion. △, camphene; ◇, tricyclene.

Lewis site would be a proton donor acting like a Brönsted site. As Lewis sites are weaker than Brönsted sites, camphene and byciclic products are preferentially formed on the Lewis sites [4,7–10].

Studies on the surface properties of V_2O_5 by FT-IR spectroscopy, suggested the presence of acidic sites of Lewis type [11]. After decomposition of the precursor in nitrogen at 500 °C, the bulk catalyst was identified by XRD and the only phase detected was V_2O_5. Therefore, with the bulk catalyst, the α-pinene reaction is likely to take place via a cationic mechanism, on the Lewis acid sites of vanadium oxide.

4. Conclusions

Vanadium catalysts supported on activated carbon is an active catalyst for α-pinene polymerisation. When the supported catalyst is used, only polymer is formed. The role of the catalyst seems to be to increase the formation of radical species such as peroxides, which, on their turn, act as polymerisation initiators. Polymerisation itself takes place in the homogeneous phase.

With the bulk V_2O_5 a change in the mechanism occurs and only isomerisation of α-pinene takes place. The vanadium species seems to have an important role on the reactivity of α-pinene, acting as Lewis acid sites. As the isomerisation reaction is much faster than the polymerisation reaction, in a situation in which a very high number of Lewis acid sites is present, such as what is verified with the bulk catalyst, only isomerisation takes place.

References

[1] (a) A.R.V. Lawrence, in: D.F. Zinkel, J. Russels (Eds.), Naval Stores, Pulp Chemicals Association, New York, 1989, Chapter 4, p. 123;
(b) E.R. Ruckel, H.G. Arlt, in: D.F. Zinkel, J. Russels (Eds.), Naval Stores, Pulp Chemicals Association, New York, 1989, Chapter 13, p. 510;
(c) R.M. Traynor, R.M. Albert, R.L. Webb, in: D.F. Zinkel, J. Russels (Eds.), Naval Stores, Pulp Chemicals Association, New York, 1989, Chapter 12, p. 479.
[2] A.M. Ramos, L.S. Lobo, J.M. Bordado, Macromol. Symp. 127 (1998) 43.
[3] A.M. Ramos, I.F. Silva, J. Vital, D.W. Mckee, Carbon 32 (1997) 1187.
[4] A. Severino, A. Esculcas, J. Rocha, J. Vital, L.S. Lobo, Appl. Catal. A 142 (1996) 255.
[5] J.C. van der Waal, H. van Bekkum, J. Vital, J. Mol. Catal. A 105 (1996) 185.
[6] A. Allahverdiev, S. Irandoust, B. Andersson, D.Y. Murzin, Appl. Catal. A 198 (2000) 197.
[7] T. Yamamoto, T. Matsuyama, T. Tanaka, T. Funabiki, S. Yoshida, Appl. Catal. A 155 (2000) 43.
[8] C.M. López, F.J. Machado, K. Rodríguez, B. Mendez, M. Hasegawa, S. Pekerar, Appl. Catal. A 173 (1998) 75.
[9] C.M. López, K. Rodríguez, B. Mendez, A. Montes, F. Machado, Appl. Catal. A 197 (2000) 131.
[10] L. Grzona, N. Comelli, O. Masini, E. Ponzi, M. Ponzi, React. Kinet. Catal. Lett. 69 (2000) 271.
[11] J. Sambeth, L. Gambaro, H. Thomas, J. Mol. Catal. 139 (1999) 25.
[12] R.S.G. Ferreira, P.G.P. de Oliveira, F.B. Noronha, Appl. Catal. B 29 (2001) 275.
[13] M.M. Koranne, J.G. Goodwin Jr., G. Marcelin, J. Catal. 148 (1994) 369.
[14] S.A. Carabineiro, F.B. Fernandes, A.M. Ramos, J. Vital, I.F. Silva, Catal. Today 57 (2000) 305.