# Kinetic studies of nopol production over Sn-MCM-41 synthesized by impregnation

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## Introduction

Nopol has been obtained under moderate reaction conditions over Sn-MCM-41 materials. Several methods have been used for Sn incorporation on MCM-41: impregnation SnMI [1], hydrothermal, SnMH, and chemical vapor deposition, SnMC [2]. We have found that SnMI is most stable than SnMH and SnMC catalysts since less activity loss is observed after four consecutive catalytic tests. In this contribution, an empirical reaction rate is reported and a possible mechanism is proposed for the Prins condensation of β-pinene over SnMI.

## Materials and Methods

MCM-41 was prepared following the procedure reported by Grün and coworkers [3]. SnMI samples were synthesized by slow addition of 3.0 mL of a solution of $SnCl_2.2H_2O$ in ethyl acetate (28.7 μmol Sn/mL) to 2 g of MCM-41. The impregnated solids were left at room temperature for 24 h and then calcined at 550 °C for 5 h (1 °C/min). Catalyst samples were characterized by XRD, TPR, FTIR, UV-vis. Catalytic tests were carried out in 2 mL vials heated in an oil bath at 90-100 ºC. The internal and external difussional problems were avoided by using catalyst particles with $\overline{dp}$ < 42 μm and by performing the reactions with a stirring speed of 2000 rpm, respectively. The stirring speed of the reaction mixture was calibrated with a digital stroboscope (Extech Instruments). The reaction products were identified by GC in a Varian Star 3400 gas chromatograph equipped with a FID detector and a DB-1 (0.32 mm x 50 m x 1.20 μm) column. The quantification of β-pinene and nopol was carried out using dodecane as internal standard.

## Results and Discussion

The synthesized material showed the typical mesoporous hexagonal array of MCM-41; according to $NH_3$-TPD analysis, the ratio between weak and medium acidity was 38 : 41 μmol $NH_3$/g catalyst. Neither Bronsted nor strong Lewis acid sites were observed; bulk SnOx species were detected by UV-vis. The initial reaction rate was determined as the slope of the concentration versus time plot at t = 0. Equation (1) is the empirical reaction rate for the disappearance of β-pinene.

$$-r_A = kC_A^{\alpha}C_B^{\beta} \tag{1}$$

Where A is β-pinene, B is paraformaldehyde, k is the reaction rate constant; α and β are the empirical reaction orders with respect to β-pinene and paraformaldehyde, respectively. As the $C_A$ versus time plot (figure 1a) is characteristic of zero order reactions, then the reaction is zero order with respect to β-pinene, α = 0. The values of k and β were determined by the excess method [4] as shown in equation (2).

$$\ln\left(-\frac{dC_B}{dt}\right) = \ln k' + \beta \ln C_B \tag{2}$$

Where $k' = kC_{A0}^{\alpha}$. It was found the reaction is second order with respect to paraformaldehyde (see figure 1b.). The apparent activation energy and the frequency factor determined from the Arrhenius plot, are 47±7 kJ/mol and $3.4x10^4$ $L^2$/(mol.g.s), respectively.
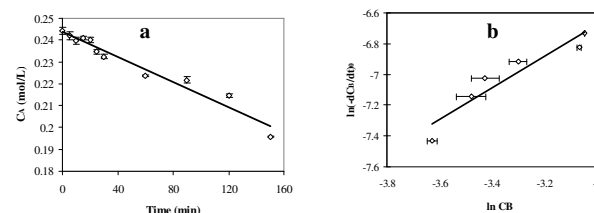


**Figure 1.** Reaction order with respect to β-pinene (a) and paraformaldehyde (b). Reaction conditions: 1.0 mL of β-pinene solution in toluene (0.25 M), β-pinene/HCHOx molar ratios of 1:2, 80- 100 ºC, 10 mg of catalyst, $\overline{dp}$ < 42, 2000 rpm.

A mechanism consisting of four reversible reactions, equations (3) - (6), was proposed. It was found that if the adsorption of two molecules of paraformaldehyde, equation (3), is the rate determining step and the value of the equilibrium adsorption constant of reaction (4) is low, the reaction rate derived from the mechanism under initial reaction conditions is coherent with the empirical reaction rate obtained. S is a vacant site, and C is nopol.

$$2B + S \Leftrightarrow B_2 * S \tag{3}$$

$$A + S \Leftrightarrow A * S \tag{4}$$

$$B_2 * S + 2A * S \Leftrightarrow 2C * S + S \tag{5}$$

$$C * S \Leftrightarrow C + S \tag{6}$$

## Significance

The empirical reaction rate for nopol production over Sn-MCM-41 synthesized by $SnCl_2.H_2O$ impregnation, shows that the reaction is not elemental. It is of second order overall. A mechanism consistent with the empirical reaction rate is proposed.

**References**
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