

# The gas phase hydrogenation of 1,3-pentadiene: an FTIR study.

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## 1. Introduction:

Selective hydrogenation of mixtures of 1,3-dienes obtained from the C<sub>5</sub> cracking fraction of a petrochemical complex could be one method of obtaining high-value stereo-specific mono-olefins. This study examines whether catalysts displaying distinct stereoselective hydrogenation characteristics (isomerisation/hydrogenation) can be used to affect diene hydrogenation profiles.

## 2. Catalyst characterisation:

- Catalyst prepared by the wet impregnation technique.
- Characterised using pulsed CO chemisorption followed by CO temperature programmed desorption (TPD) using Hiden mass spectrometer (HPR-20 Q/C).
- Calculated metal dispersion = 13.4% (Pd:CO = 2:1).
- Low temperature CO peak (T<sub>max</sub> 580 K) assigned to metal bound to Pd crystallites.
- High temperature peak (T<sub>max</sub> 650 K) assigned to decay of carboxy species associated with alumina support [1].

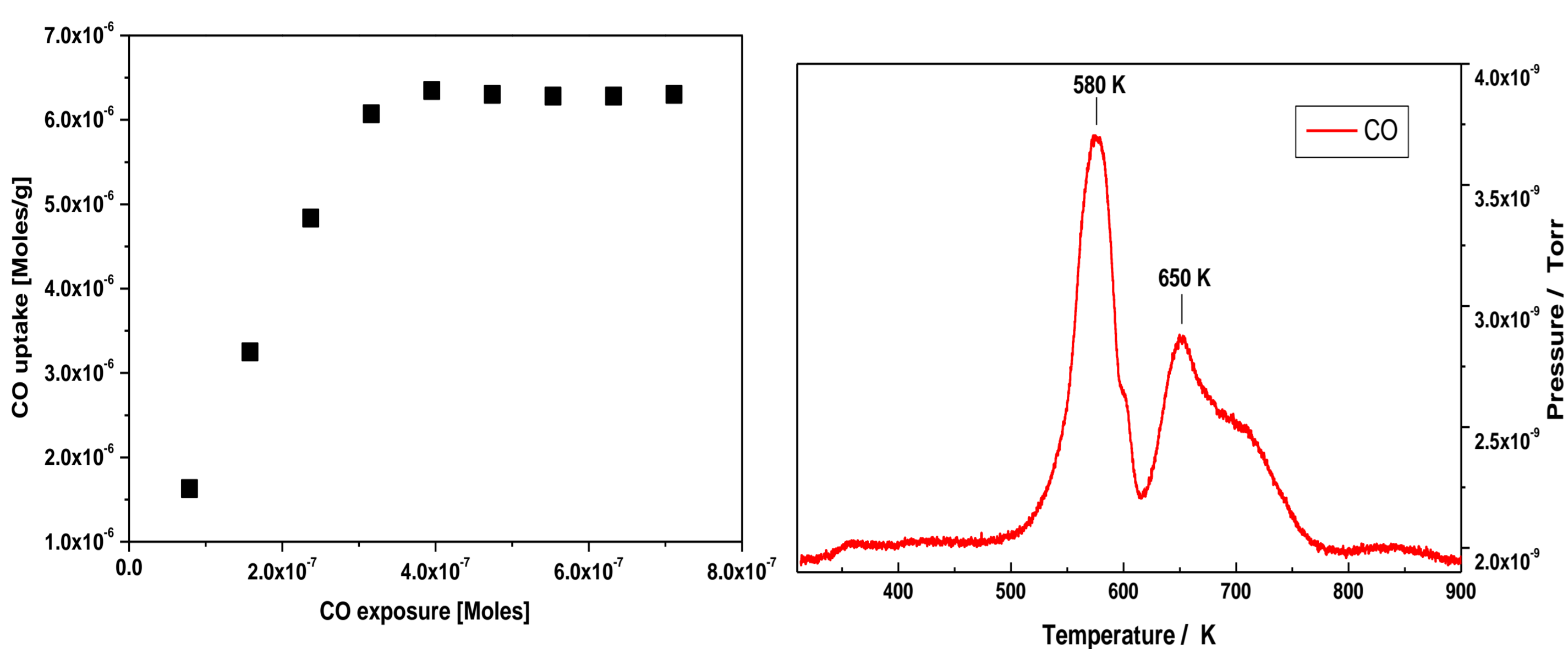


Figure 1: (a) Pulsed chemisorption profile for 1%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and (b) subsequent CO TPD profile.

## 3. Experimental:

A modified Graseby-Specac 5661 heated infrared gas cell housed within a Nicolet Avatar FTIR spectrometer was employed as a batch reactor. Purified helium and hydrogen flows were regulated by dedicated mass flow controllers. The catalyst was mounted on a glass boat and loaded into the reactor as described in Figure 1. The glass boat is located out with the beam path such that only gaseous components are analysed as the reaction proceeds.

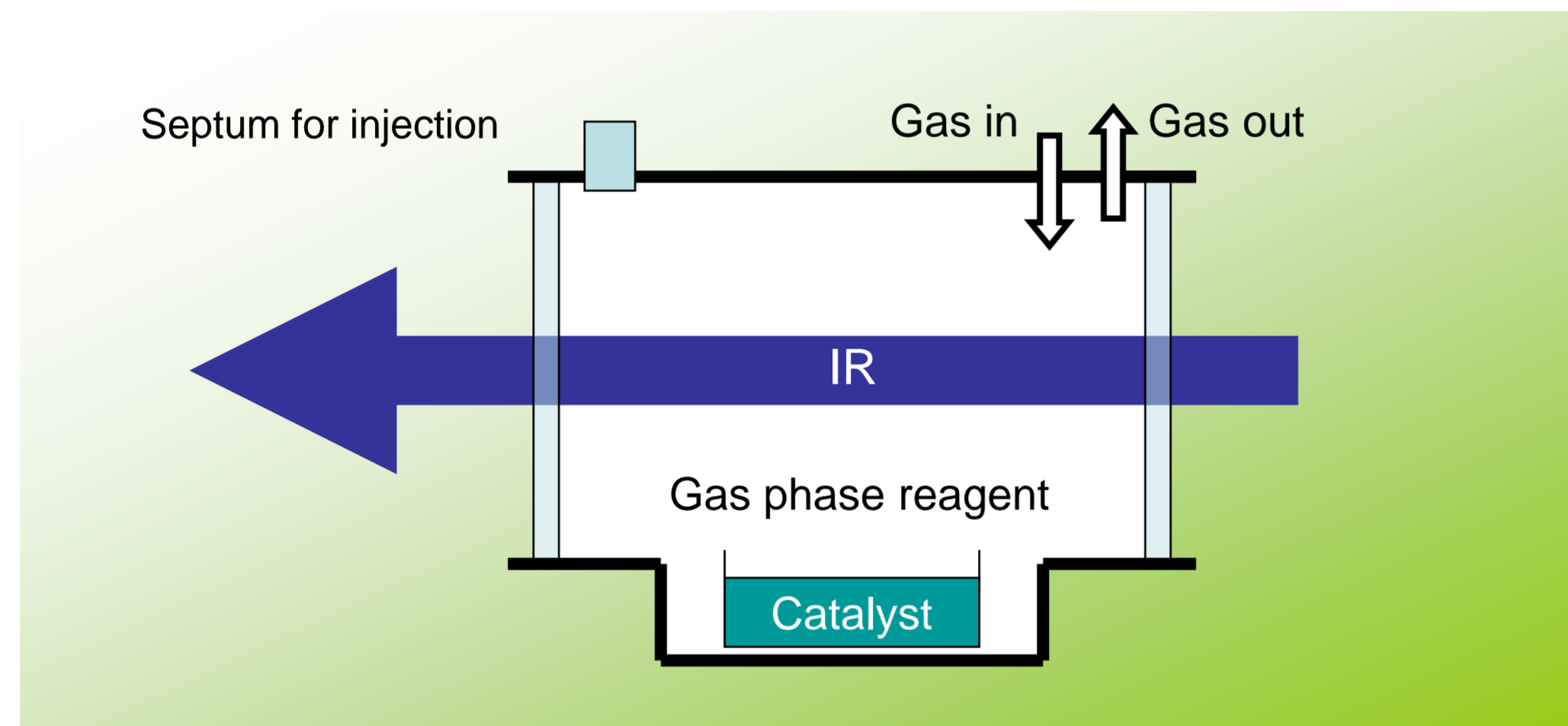


Figure 2: Schematic diagram describing reactor configuration.

## Reaction conditions:

- 5 mg catalyst diluted in 100 mg of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- Temperature maintained at 298 K.
- Reactor charged with 5% H<sub>2</sub>/He to a pressure of 0.2 bar gauge.
- 10  $\mu$ L of hydrocarbon was introduced *via* a septum. This represents A<sub>0</sub>.
- [H<sub>2</sub>] > [hydrocarbon] >> [Pd<sub>(s)</sub>]

Under these conditions the cell was operating as a batch reactor.

## 4. Density Functional Theory (DFT) calculations:

- Vibrational modes for all relevant C<sub>5</sub> molecules were calculated using the Gaussian03 software package [2].
- B3LYP/cc-AUG-pVDZ was selected as the basis set.
- Calculated spectra used to aid the assignment of bands in the recorded spectra.
- The discrepancy between band positions for stretching modes in the calculated and recorded spectra is due to the harmonic approximation.

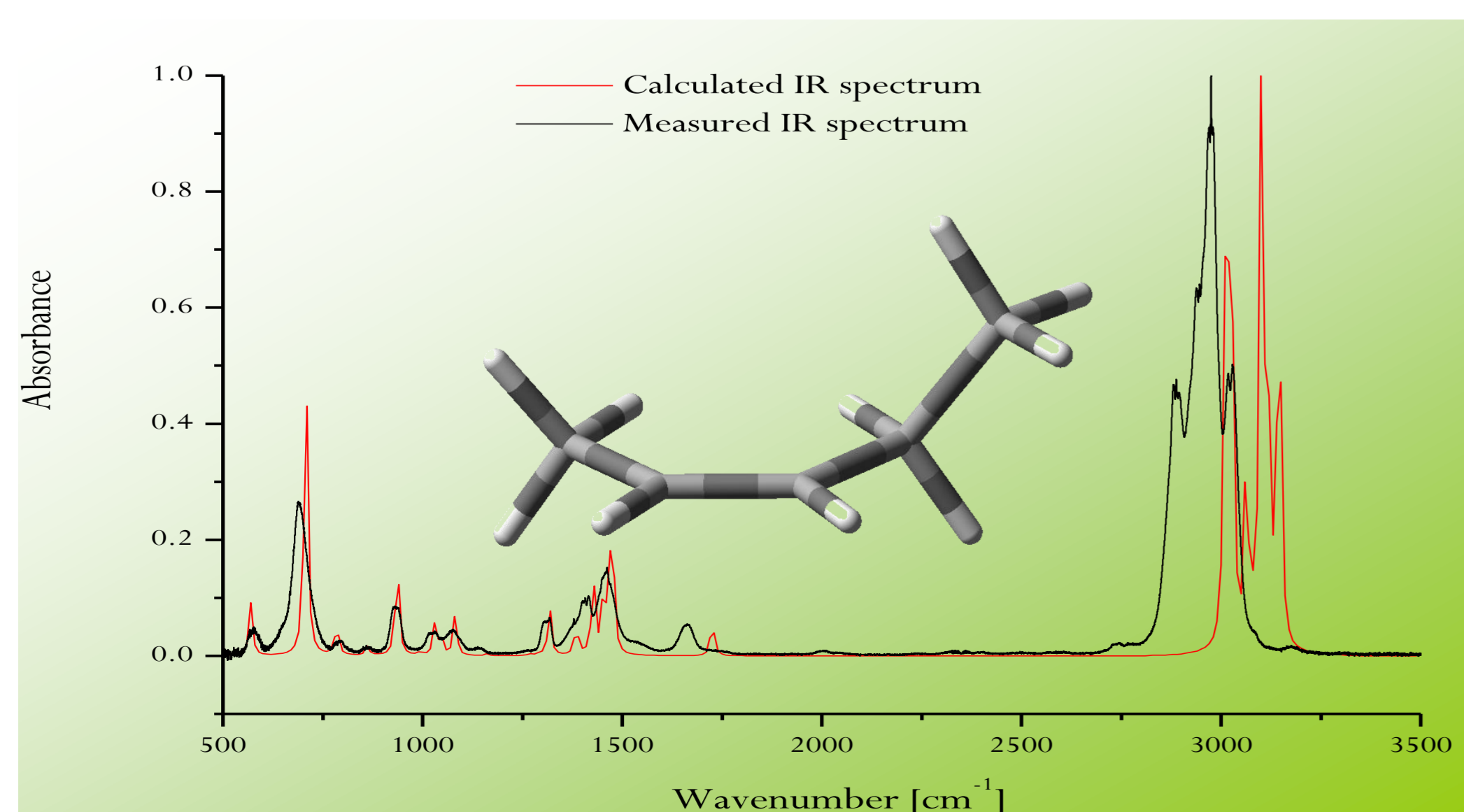


Figure 3: Comparison of calculated and measure FTIR spectra of *cis*-2-pentene.

## 5. Results:

Reaction profiles were constructed by examining the intensity of infrared bands uniquely diagnostic of each species present in the gas phase. A list of the diagnostic bands used to identify gaseous species is presented in the table below:

Compound	Band position (cm <sup>-1</sup> )	IR intensity	Assignment
1,3-pentadiene	899	vs	ethylenic rock and C-C-C deformation
<i>trans</i> -2-pentene	969	s	in-phase <i>trans</i> -CH wag
<i>cis</i> -2-pentene	688	m	in-phase <i>cis</i> -CH wag
1,4-pentadiene	1642	s	out-of-phase C=C stretch
pentane	2965	vs	in-phase antisymmetric CH <sub>3</sub> stretch
1-pentene	3087	S	antisymmetric ethylenic stretch

### 5.1 Mono-olefins

#### Hydrogenation of *trans*-2-pentene:

Here, *trans*-pent-2-ene is directly converted to pentane (Figure 4). Analysis of the mass balance showed 69% of the incident moles of *trans*-pent-2-ene had been converted to pentane, with 31% of the hydrocarbon retained at the catalyst surface.

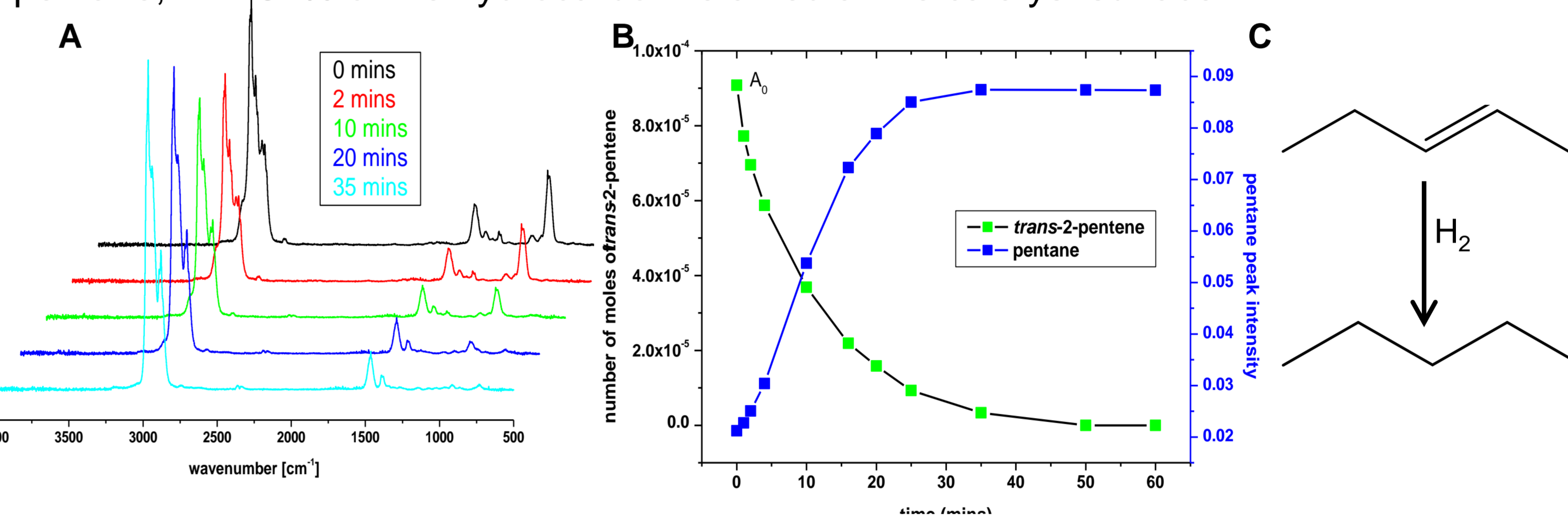


Figure 4: (a) FTIR spectra of gaseous species acquired at selected reaction times, (b) reaction profile for the hydrogenation of *trans*-pent-2-ene and (c) associated reaction scheme.

#### Hydrogenation of *cis*-2-pentene:

The reaction profile here differs significantly from Figure 4. Instead of a direct hydrogenation, a consecutive process is observed. Firstly, *cis*-pent-2-ene is isomerised to *trans*-pent-2-ene, which is then hydrogenated to pentane.

On completion of reaction, the mass balance shows the catalyst to have retained 20% of the hydrocarbon.

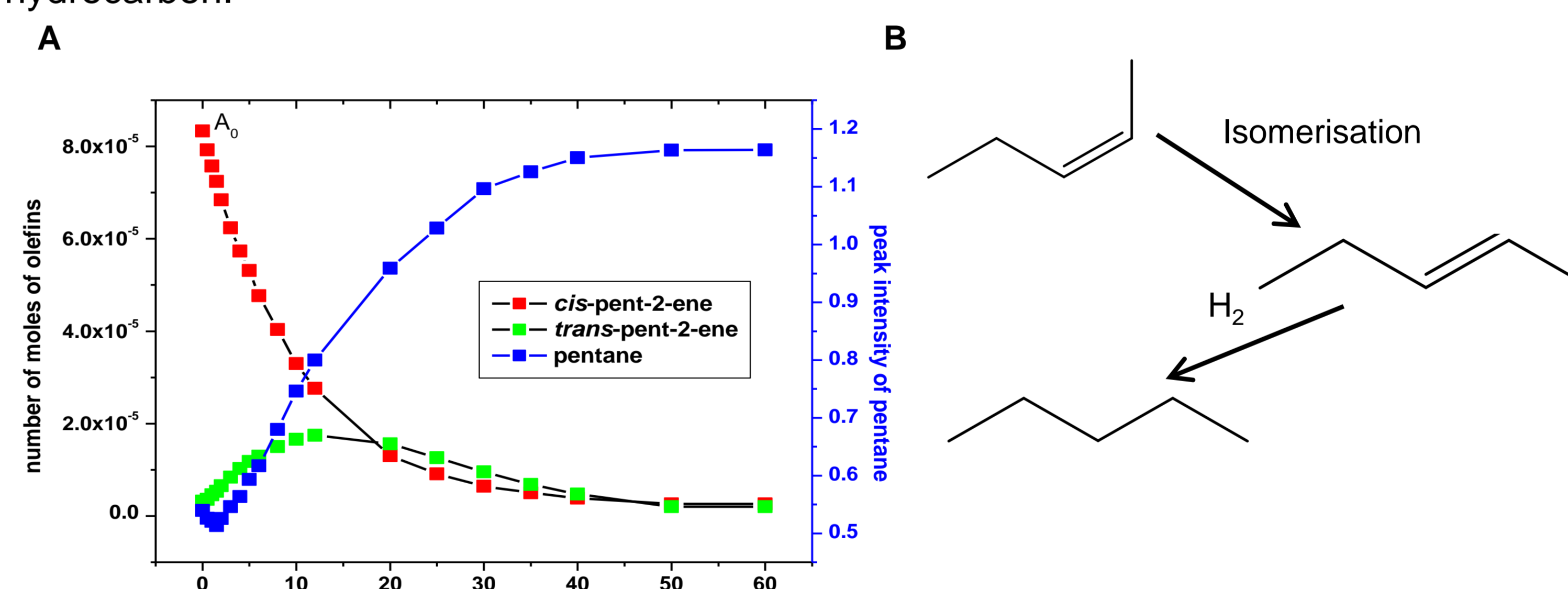


Figure 5: (a) Reaction profile for the hydrogenation of *cis*-pent-2-ene and (b) associated reaction scheme.

### 5.2 Di-olefins

#### Hydrogenation of *trans*-1,3-pentadiene:

Here, firstly, the terminal double bond is hydrogenated to produce *trans*-pent-2-ene. The internal bond is subsequently hydrogenated to produce pentane. No *cis*-pent-2-ene is detected. However, on completion of reaction, inspection of the mass balance shows 56% retention of the hydrocarbon at the catalyst surface. It is possible that any *cis*-pent-2-ene that might form in the initial step is selectively retained by the catalyst.

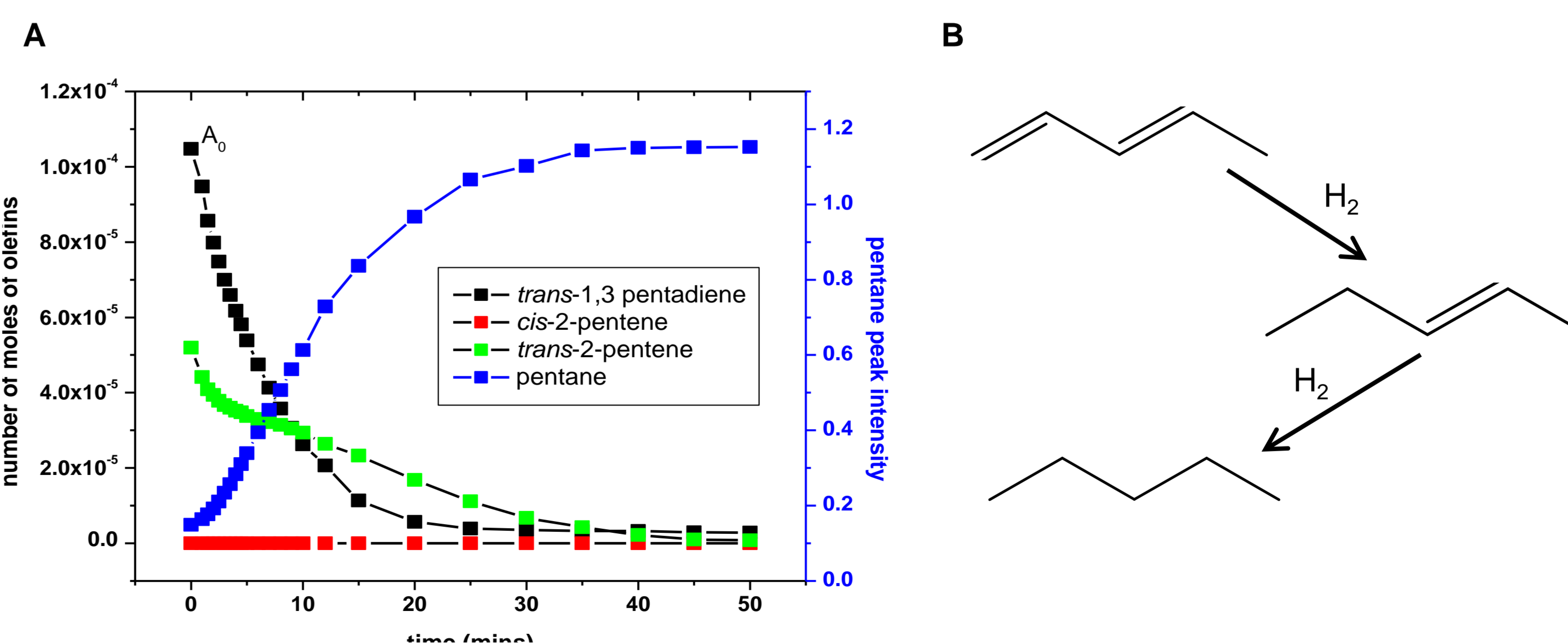


Figure 6: (a) The reaction profile for the hydrogenation of *trans*-1,3-pentadiene and (b) the associated reaction scheme.

## 6. Conclusions:

Previous studies have shown first and second stage hydrogenation of 1,3-pentadiene on Pd/Al<sub>2</sub>O<sub>3</sub> occurs at two distinct sites [3]. Work is currently underway to examine whether selective poisoning strategies can be used to block stage 2 hydrogenation, which would enable *trans*-1,3-pentadiene to be selectively hydrogenated to *trans*-pent-2-ene.