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# Effect of Ru Nanoparticle Size on Hydrogenation of Soybean Oil

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**Abstract** Four Ru nanoparticles of different mean sizes from 1.13 to 17.22 nm were prepared and used as catalysts for the selective hydrogenation of polyunsaturated soybean oil at 353 K and initial pressure of 1.5 MPa. The catalyst with the smallest mean size (1.13 nm) had the lowest activity, the activity increased as the mean size increased to 3.10 nm, then decreased with further increase in the mean particle size. The *cis–trans* isomerization rate decreased with the increase in particle size.

**Keywords** Ru · Nanoparticles · Hydrogenation · Soybean oil · Selectivity

## Introduction

Hydrogenation of vegetable oil is an important industrial process to increase the oil's oxidative stability and to obtain products with desirable properties. Vegetable oils are complex mixtures of triglycerides of fatty acids with up to 22 carbon atoms which may have 0–3 double bonds in each of the fatty-acid chains [1]. During hydrogenation, the remaining double bonds in the fatty-acid chain can isomerize from the *cis* to the *trans* configuration. Extensive work has been done on the effect of trans isomers of mono- and polyunsaturated fatty acids on cellular metabolism. For example, Kromhout et al. [2] demonstrated that the concentration of plasma cholesterol was related to the percentage of saturated fatty acids and *trans* fatty acids in the diet. Thus, it is important to produce hydrogenated edible oils with low *trans*-isomer content.

The catalysts used in commercial hydrogenation are usually Ni supported on silica or alumina. However, traces of nickel remaining in the oil are toxic [3, 4]. Noble-metal catalysts are not often used for their high cost. This may be offset by their high activity and selectivity at low temperature and the possibility of reuse. Colloids of noble metals such as Pt and Pd group with particles in the nanometer size have been studied in the hydrogenation of soybean oil [5]. Ru as a hydrogenation catalyst for edible oil has rarely been reported, perhaps because its activity is much lower than Pt and Pd.

Colloids of noble metals can be prepared by various methods, such as electrochemical and chemical reduction as well as vapor deposition onto polymer or in ligand solution matrices, which serve as stabilizers to prevent aggregation [6–9]. Catalyst particles of different average sizes can be prepared by varying the preparation conditions, such as varying the solvent used and the reducing agent [10]. Although it is said that the activity of metal catalysts increased with decreasing size to the nanometers range [5], few reports have been published on the size effect of nanocatalysts on their activity and selectivity in hydrogenation of vegetable oils.

The present work reports the results on hydrogenation of soybean oil at 353 K and initial pressure 1.5 MPa catalyzed by Ru nanoparticles with different mean sizes.

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## Experimental

### Materials

Polyvinlpyrrolidone (PVP, Mw = 10,000), ruthenium(III) chloride ($RuCl_3$, > 99%) (ACROS ORGANICS, USA); sodium borohydride ($NaBH_4$, > 96%) (Shanghai Elab. Tech. Res. Center, Shanghai); hydrazine hydrate ($N_2H_4$, Tianjin Kermel Chem. Reagents Dev. Center, Tianjin); methanol was analytical grade were used without further treatment. Soybean oil was purchased from a local supermarket.

### Preparation of Ruthenium Catalysts

#### *Preparation of Unprotected Ruthenium Catalysts*

This catalyst was prepared by a reported method [10] with some modification. An amount of 0.0208 g $RuCl_3$ (0.1 mmol) was dissolved in a mixture of 9:1 methanol and water as solvent. The solution was refluxed under stirring for 8 h at 353 K to obtain a dark-brown homogenous dispersion. The UV-vis results showed that the $Ru^{3+}$ was completely reduced [10]. This Ru catalyst is denoted by Ru-methanol.

#### *Preparation of Polymer-stabilized Ruthenium Colloids with Methanol as the Solvent*

Ruthenium colloids were prepared according to a reported method [11] but using methanol as the solvent. The procedure was as follows: 0.22 g PVP (2 mmol as monomeric residue) and 0.0208 g $RuCl_3$ (0.1 mmol) were dissolved in 15 ml methanol and stirred for 2 h. During the process, 4 ml 0.1 M $NaBH_4$ solution was added dropwise. PVP–Ru-methanol with a molar ratio of 20:1 was prepared.

#### *Preparation of Polymer-stabilized Ruthenium Colloids*

Polymer-stabilized ruthenium colloids were also prepared according to a reported method [11] with modification. An amount of 0.22 g PVP (2 mmol) and 0.0208 g $RuCl_3$ (0.1 mmol) were dissolved in 20 ml water, stirring for 2 h. During the course, 4 ml 0.1 M $NaBH_4$ solution was added dropwise. PVP–Ru–water with a molar ratio of 20:1 was prepared.

#### *Preparation of Polymer-stabilized Ruthenium Catalysts with $N_2H_4$ as the Reducer*

0.0208 g $RuCl_3$ (0.1 mmol) was dissolved in 15 ml methanol and stirred for 15 min. $N_2H_4$ (1 mmol) was added dropwise, stirring for 4 h at 313 K. The catalyst prepared was denoted by Ru–$N_2H_4$.

### Measurements

Tunneling electonc microscopy (TEM) micrographs were obtained using an FEI Tecnai $G^2$ 20 microscope operated at an accelerating voltage of 200 kV. The samples were diluted in ethanol to give a 1:3 volume ratio and sonicated for 2 min. A Cu grid covered with a thin film of amorphous carbon was dipped in the ethanol slurry and then allowed to dry. To obtain the size distribution of the ruthenium particles, the diameter of more than 250 black spots was measured.

The fatty-acid composition of the methylated reaction products was analyzed using a HP 5890A gas chromatograph equipped with Flame ionization detector (FID) with a glass-packed column (*L*: 2 m). The column temperature was programmed from 373 to 433 K at 5 K $min^{-1}$, then raised to 453 K at 2 K $min^{-1}$ and held for 20 min with nitrogen as the carrier gas. The injection and detection temperatures were set at 493 and 513 K, respectively. Palmitic acid served as the internal standard.

For the quantitative determination of the *cis–trans* isomer ratio [13–15], the methyl esters obtained were dried under an $N_2$ atmosphere and then injected into a liquid Fourier-transform infrared (FTIR) ZnSe cell using a Nicolet 470 spectrometer equipped with a computer [1]. The IR spectra at 2 $cm^{-1}$ resolutions in the range from 3,200 to 800 $cm^{-1}$ with 32 scans were collected.

### Hydrogenation of Soybean Oil

Selective hydrogenation was performed at 353 K in a continually stirred slurry reactor (CSTR, 150 ml) with a stirring rate of 500 rpm. The ruthenium catalysts and 0.045 mol soybean oil (total volume 50 ml) were added to the reactor. Hydrogen was allowed to flow for 5 min to replace the air and pressurized to 1.5 MPa (0.067 mol). Heating to 353 K with stirring, the reaction was started. An electro-manometer measured the hydrogen consumption and a computer recorded the data. The reaction was stopped after 12 h. The hydrogenated soybean oil was analyzed using gas-chromatography mass spectrometry (GC-MS) after the samples were converted into their methyl esters according to a reported method [16].

## Results and Discussion

### Particle Size Distribution

Typical TEM micrographs and size distribution histograms of the four samples prepared are shown in Fig. 1. The particles are of nanometer sizes with average diameters of 1.13 ± 0.43, 3.10 ± 0.65, 9.06 ± 0.70 and 17.22 ± 1.3 nm. The catalysts have narrow size distributions except for Ru–$N_2H_4$, which has a slightly wider distribution.

### Factors Influencing the Particle Size

The catalysts with different particle size stabilized with PVP were prepared by varying the reducing agent and solvent. Using a 9:1 methanol-to-water mix as the solvent the prepared ruthenium particles were smaller than when using a 1:1 mix. Similar results were obtained between PVP-Ru-methanol and PVP-Ru–water. This is because the solubility of ruthenium chloride in methanol is small, so that in the methanol-rich solution the ruthenium particles formed are sparse and hence not easily aggregated. In this sense, methanol also functioned as a stabilizer. Under the same conditions, different reducing agents produced ruthenium particles with different sizes. It is expected that smaller particles will be produced at higher reduction rates for $Ru^{3+}$ [10] as more $Ru^0$ seeds are produced simultaneously with stronger reducing agents. Thus, the size of particles formed using $NaBH_4$ was smaller than that prepared using $N_2H_4$ as the reducing agent.

### Hydrogenation of Soybean Oil

The rate of hydrogenation of excess soybean oil was measured from the hydrogen consumption at 353 K and initial pressure of 1.5 MPa. As shown in Fig. 2 curve (b), the hydrogen consumption of the catalyst with mean size of 3.1 nm initially increased nearly linearly, after which the rate decreased as fatty acids with multiple double bonds were depleted. Finally, the rate of reaction decreased further as fatty acids with one double bond were hydrogenated. From curve (a), hydrogen consumption catalyzed by Ru–methanol having a mean size of 1.13 nm increased linearly throughout the course of the reaction. From the fatty-acid composition of the product, it could be deduced that the rate of hydrogenation of the fatty-acid moeties with different numbers of double bond proceeded simultaneously as the activity of this catalyst was low and apparently had low selectivity. Curves (c) and (d) were similar in that the rates decreased after reacting for three hours because of the depletion of substrate with multiple double bonds. The catalyst with a 3.1 nm mean size had a maximum activity that decreased for either smaller or larger particle sizes. The decrease of activity with increasing mean size is attributable to the decrease in the metal surface area. This effect is similar with Pd and Pt catalysts [6]. The low activity of the Ru-methanol with the largest metal surface area was apparently because their surface energy was so high that the catalyst particles aggregated easily, as can be observed from the TEM images after the reaction (Fig. 3). Other catalysts also showed obvious aggregation.

Commercial hydrogenation of vegetable oils usually uses supported Ni catalysts at elevated temperature and pressure. For a typical hydrogenation of soybean oil, using a 0.05% $Ni/SiO_2$ at 493 K and near-atmospheric pressure in a slurry reactor, the rate was 0.8 mol of $H_2\ h^{-1}\ g^{-1}$ Ni [17]. The rates of hydrogen consumption using the colloidal Ru catalysts calculated from data presented in Fig. 2 are 0.115, 0.406, 0.191 and 0.121 mol $H_2\ h^{-1}\ g^{-1}$ at 353 K and an initial pressure of 1.5 MPa; these activities are lower than that with the Ni catalyst. This may be because of the lower reaction temperature and catalyst doses. The rates are much lower than Pd and Pt, which have been reported as 45 and 70 mol $H_2\ h^{-1}\ g^{-1}$ at 308 K and atmospheric pressure [5]. However, these comparisons may not be directly relevant as the reaction conditions including catalysts dose, feedstock type, and feedstock impurities are different.

### Selectivity of Hydrogenation Reaction

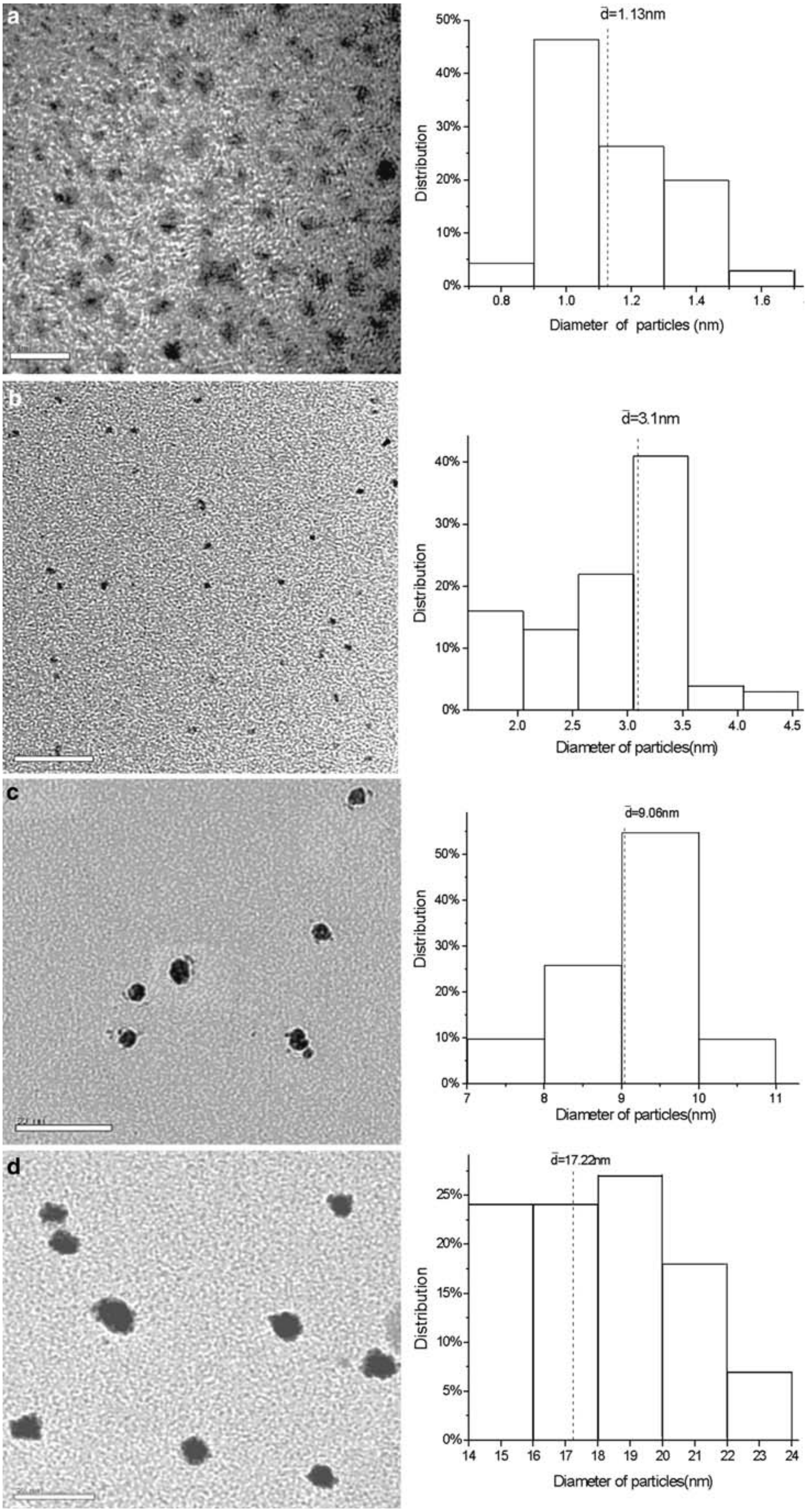
The hydrogenation is generally depicted as follows:

$$\text{Linolenic (LL)} + H_2 \xrightarrow{k_1} \text{linoleic (L)} + H_2 \xrightarrow{k_2} \text{oleic (O)} + H_2 \xrightarrow{k_3} \text{stearic (S)} \qquad (1)$$

As the fatty-acid concentrations were changing during the reaction, the rate constants were not calculated.

The fatty-acid compositions of soybean oil and the products (Table 1) showed that the concentrations of C16:1 acid remained unchanged and the C20:1 decreased only slightly. The hydrogen was consumed mainly by the C18:3, C18:2 and C18:1 acid meoties; thus only the C18 products are discussed. On hydrogenation, the concentrations of C18:3 and C18:2 decreased while the C18:1 and C18:0 increased. In general, the percentage decrease in the concentration of C18:3 is much higher than the C18:2, even after

**Fig. 1** The TEM images and particle sizes distribution. **a** Ru-methanol with a *scale bar* of 5 nm, **b** PVP–Ru-methanol with a *scale bar* of 50 nm, **c** PVP–Ru–water with a *scale bar* of 20 nm, **d** Ru–$N_2H_4$ with a scale bar of 50 nm



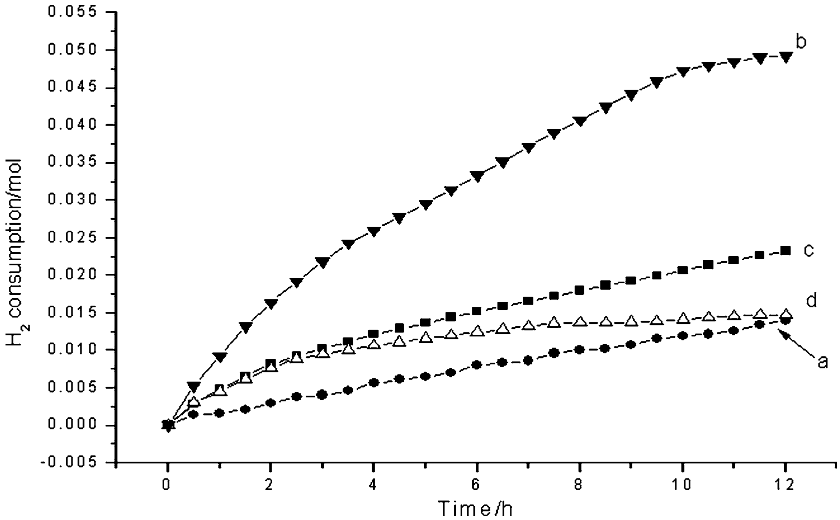


**Fig. 2** Hydrogen consumption of soybean oil with Ru as a catalyst as a function of time. Reaction conditions: soybean oil 0.045 mol; Ru 0.1 mmol; initial pressure 1.5 MPa; temperature 353 K

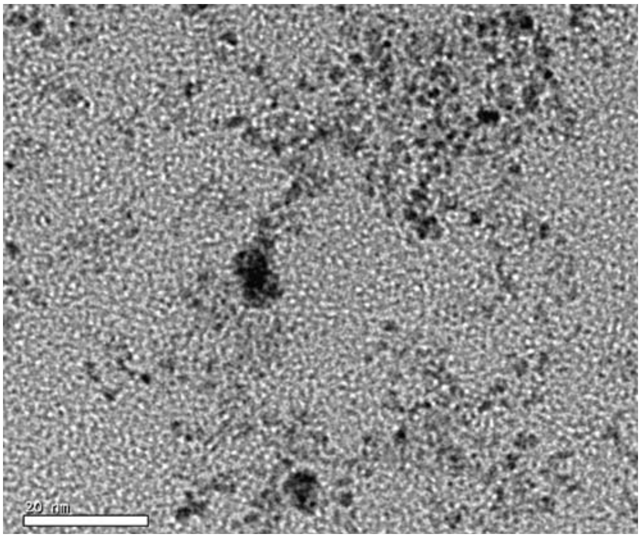


**Fig. 3** TEM image of Ru-methanol after reaction, with a *scale bar* of 20 nm

taking into consideration the conversion of the former into the latter, indicating that the rate of hydrogenation of C18:3 was much higher than that of C18:2. Comparing the increase in concentration of the saturated fatty acid C18:0 to the decrease in concentration of the mono-unsaturated acid C18:1 it can be concluded that the rate of hydrogenation of C18:2 is in turn faster than that of C18:1. Thus, the rates of hydrogenation fall in the order: C18:3 > C18:2 > C18:1, which is in agreement with what has been observed for the same reaction catalyzed by Pd and Pt nanoparticles, which are much more active catalysts [5].

Comparing the composition of the fatty acids obtained with Ru catalysts of different sizes, the activities fall in the order: Ru (3.1 nm) > Ru (9.06 nm) > Ru (17.2 nm) > Ru (1.13 nm). A possible rationale for this phenomenon has been given earlier. This result is however different from the Pd and Pt catalysts, for which the activity decreased monotonously with increasing size of the nanoparticles [5].

## *cis–trans* Isomerization

The formation of *trans* isomers of the remaining unsaturated fatty acids is to be avoided as far as possible for edible oils and fats as they are unhealthy for consumption. Nearly all of the double bonds in the refined soybean oil are in the *cis* configuration, which

**Table 1** Composition of soybean oil and hydrogenated soybean oil with different catalysts

| | Fatty-acid composition (percentage of fatty acid) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C16:0 | C16:1 | C18:0 | C18:1 | C18:2 | C18:3 | C20:0 | C20:1 | C22:0 |
| Soybean oil | 10.8 | 0.2 | 4.0 | 23.2 | 52.8 | 7.0 | 0.4 | 1.2 | 0.4 |
| $P^{a}_{1.13\ \mathrm{nm}}$ | 10.8 | 0.2 | 11.4 | 33.2 | 38.5 | 3.9 | 0.7 | 0.9 | 0.4 |
| $P_{3.10\ \mathrm{nm}}$ | 10.8 | 0.2 | 46.8 | 36.8 | 3.4 | 0 | 1.2 | 0.4 | 0.4 |
| $P_{9.06\ \mathrm{nm}}$ | 10.8 | 0.2 | 11.7 | 47.2 | 26.9 | 1.1 | 0.9 | 0.8 | 0.4 |
| $P_{17.22\ \mathrm{nm}}$ | 10.8 | 0.2 | 10.8 | 42.2 | 31.6 | 2.4 | 0.7 | 0.9 | 0.4 |

[a] Products of hydrogenated soybean oil with different catalysts. The subscripts denote the mean size

**Table 2** The relative amounts of *cis–trans* isomer in soybean and hydrogenated oil

| | Isomers compositions | |
|---|---|---|
| | *cis*-isomers (%) | *trans*-isomers (%) |
| Soybean oil | 92.0 | 8.0 |
| $P^{a}_{1.13\ nm}$ | 34.2 | 65.8 |
| $P_{3.10\ nm}$ | 30.6 | 59.4 |
| $P_{9.06\ nm}$ | 51.0 | 49.0 |
| $P_{17.22\ nm}$ | 54.0 | 46.0 |

[a] Products of hydrogenated soybean oil with different catalysts. The subscripts denote the mean size

exhibits a distinctive infrared (IR) band at ~3,006 cm$^{-1}$. After hydrogenation, the peak intensity of *trans* isomer, present as elaidate acid, increased at 966 cm$^{-1}$. As shown in Table 2, the *cis*/*trans* ratio of the products decreased after hydrogenation. PVP-Ru-methanol, which had the highest activity, had the lowest *cis* isomer content, only 30.6% *cis* isomers remained, with most double bonds converted to the *trans* configuration, approaching the equilibrium of a *cis*/*trans* ratio of ~2:1 [17]. The catalysts with larger mean sizes of 9.06 and 17.22 nm, which have lower activity, produced less *trans* isomer: 49 and 46%, respectively. This result indicates that the selectivity for *cis*/*trans* isomerization decreased with increasing particle size. However, the catalyst with the smallest size but the lowest hydrogenation activity, Ru-methanol with mean size of 1.13 nm, was more active for the isomerization. This anomaly may perhaps be due to agglomeration during the course of the reaction, which may have affected the hydrogenation but not the isomerization activity. This seems to be reasonable, as hydrogenation requires the simultaneous adsorption of both the hydrogen and the double bond on adjacent sites, while isomerization requires only the adsorption of the double bond. The aggregation of the particles may have reduced the number of suitable hydrogenation active sites but not the isomerization sites. As the mean particle size increases, selectivity for oleate increased while the selectivity for linolenate and linoleate decreased. When the activities of the catalysts are similar, the catalyst with larger mean particle size had a lower isomerization activity.

In general, the formation of the *trans* isomer is much higher than when catalyzed by the more active nanoparticles Pd and Pt, which were conducted at lower temperature. It is known that the *cis–trans* isomerization reaction is temperature controlled and to reduce the formation of the *trans* isomer during the hydrogenation reaction, a very active catalyst will have to be used at low temperature.

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