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Short communication

Solvent-free selective hydrogenation of 1,5-cyclooctadiene catalyzed by palladium incorporated TUD-1

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Palladium (Pd) was incorporated into TUD-1 mesoporous siliceous material by using one-pot synthesis procedure. The catalytic activity of the prepared samples was evaluated in the selective hydrogenation of 1,5-cyclooctadiene (COD) at 80 °C in a solvent-free condition. Pd-TUD-1 showed > 95% conversion of COD with a selectivity > 90% towards cyclooctene (COE).

1. Introduction

Hydrogenation reactions attract significant attention in industrial catalytic processes which produce chemicals with high purity and at low costs [1,2]. The selective hydrogenation of consecutive hydrogenation reaction is very complex, particularly if one reaction intermediate is the desired product. This requires the conversion to be kept very low [2–4] in order to maintain a high selectivity of the desirable intermediate (product). This requirement reduces the economic value of the overall process. The selective hydrogenation of cyclooctadiene (COD) to cyclooctene (COE) is a good example of this kind of reactions from an academic and industrial point of view [5]. Cyclooctene is produced by partial hydrogenation of 1,5-cyclooctadiene as an intermediate in the consecutive reaction which is normally over-hydrogenated to form the undesired product; cyclooctane (COA). The challenge here is to design a catalyst which is able to catalyze the hydrogenation of COD to selectively produce COE as a major product and COA as a minor product, i.e. minimize the consecutive hydrogenation reaction.

Supported palladium nanoparticles were reported earlier as active species for COD hydrogenation, such as Pd nanoparticles supported on carbon nitride functionalized silica [5], nitrogen-doped carbon nanotubes [6], salen/FAU [7] and γAl_2O_3[8]. These catalysts exhibited high activity in the conversion of COD with a good selectivity towards COE, however, the synthesis of these catalysts was carried out in two-step synthesis procedure. Hence, the ease one-step procedure to prepare Pd nanoparticles incorporated in a high surface area support is -indeed- an advantageous.

TUD-1 is a siliceous mesoporous material which patented in 2001 by Shan and coworkers [9]. The importance of TUD-1 came from its easy synthetic procedure where no surfactant is needed (cost effective). Moreover, TUD-1 is a unique siliceous material and different from the conventional mesoporous materials such as MCM-41 and SBA-15 due to its open and 3D pore system. TUD-1 was used as a support for different metal ions or oxide particles, such as Au [10] Mo [11] Cr [12], etc., and the resultant materials exhibited high activity in different catalytic reactions such as selective oxidation reactions [10,11] and photocatalytic elimination of short chain hydrocarbons [12].

In the current study, TUD-1 mesoporous material was functionalized by Pd in one-step synthesis procedure and the prepared material was characterized by physical and chemical techniques. The catalytic activity of the prepared materials was investigated in the selective hydrogenation of COD under different reaction conditions. Optimization of reaction conditions, such as temperature, H_2 pressure, and time is reported. Moreover, recycling of used catalyst is also discussed.

2. Experimental

2.1. Pd-TUD-1 synthesis

Pd-TUD-1 was prepared by using one-pot synthesis procedure based on hydrothermal sol-gel technique. A sample with a Si/Pd ratio of 50, was prepared by using the molar oxide ratio of $1SiO_2:0.02PdO:0.5TEAOH:1TEA:15H_2O$. In a typical synthesis, 12.9 g of triethanolamine (TEA, 97%, ACROS) diluted by 7 ml of deionized water was added to palladium (II) nitrate dihydrate ($Pd(NO_3)_2{\cdot}2H_2O$,

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98% Sigma-Aldrich) solution (0.46 g of Pd salt dissolved in 5 ml of deionized water) under stirring. The obtained solution was added dropwise to 17.8 g of tetraethyl orthosilicate (TEOS, + 98%, ACROS) under vigorous stirring. After 30 min, 17.6 g of tetraethyl ammonium hydroxide (TEAOH, 35%, Aldrich) was added dropwise and the overall mixture was stirred for at least two hours at room temperature. The resulting homogeneous solution/gel was aged at room temperature for 24 h, and then dried at 98 °C for another 24 h. The obtained brownish solid was grounded and hydrothermally treated in a 50 ml Teflon-lined stainless steel autoclave at 178 °C under autogenous pressure for 4 h. The obtained solid was grounded again, and then calcined in static air at 600 °C for 10 h by applying a heating ramp rate of 1 degree/min.

2.2. Characterization

XRD was performed by using Schimadzu 6000 DX instrument diffractometer equipped with a graphite monochromator using CuK$_\alpha$ radiation (λ = 0.1541 nm). Nitrogen adsorption/desorption isotherms were recorded on a QuantaChrome NOVA 2000e instrument. ICP technique was used to quantify the amount of Pd present in the prepared material by using Thermo Scientific, ICAP 7000 series, part No: 1340910, Qtegra Soft wear, Germany. Raman spectrum was collected at ambient conditions by using a Renishaw Raman Imaging Microscope, system 2000. The green (λ = 514 nm) polarized radiation of an argon ion laser beam of 20 mW was used for excitation. DR UV–Vis spectra were collected at ambient conditions on a CaryWin 300 spectrometer in the wavelength range of 200–800 nm by using $BaSO_4$ as a reference material. Scanning electron microscopy (SEM) Jeol Model 6360 LVSEM, USA, was used to observe the pore structure of the synthesized sorbent materials.

2.3. Catalytic performance study

The solvent-free hydrogenation experiments were carried out in a stirred batch Parr (300 ml capacity) reactor. In a typical run, 0.25 g of catalyst was placed inside the reactor with particle diameter < 40 μm and covered with 25 ml of COD. Then, the autoclave was closed and degassed twice with nitrogen and heated to the working temperature. After stabilization of the temperature to a desired value, the reactor was pressurized to the necessary pressure with hydrogen gas. The reaction was stirred by a high agitation speed (1000 rpm) to avoid external mass transfer limitations. After the reaction time was elapsed, the reactor was allowed to cool-down to the room temperature and then a liquid sample was withdrawn and filtrated. The concentration of the product and the reactants were analyzed by using a SHIMADZU GC-17 instrument equipped with RTX-5 capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID).

Conversion of cyclooctadiene, and selectivity towards cyclooctene were calculated according to the following equations:

$$\text{Conversion} = \frac{[COD]_0 - [COD]_t}{[COD]_0} \times 100$$

where $[COD]_0$ is the initial cyclooctadiene concentration, $[COD]_t$ is the concentration of cyclooctadiene at time (t).

$$\text{Selectivity} = \frac{[COE]}{[COD]_0 - [COD]_t} \times 100$$

where $[COE]$ is the cyclooctene concentration.

On the other hand, the turnover frequency (TOF) was calculated according to the equation

$$\text{TOF} = \frac{[COD]_0 - [COD]_t}{[Pd] \times 3600}$$

where numerator represents the number of converted moles of COD divided by the total mole number of Pd active phase and the reaction time in seconds.

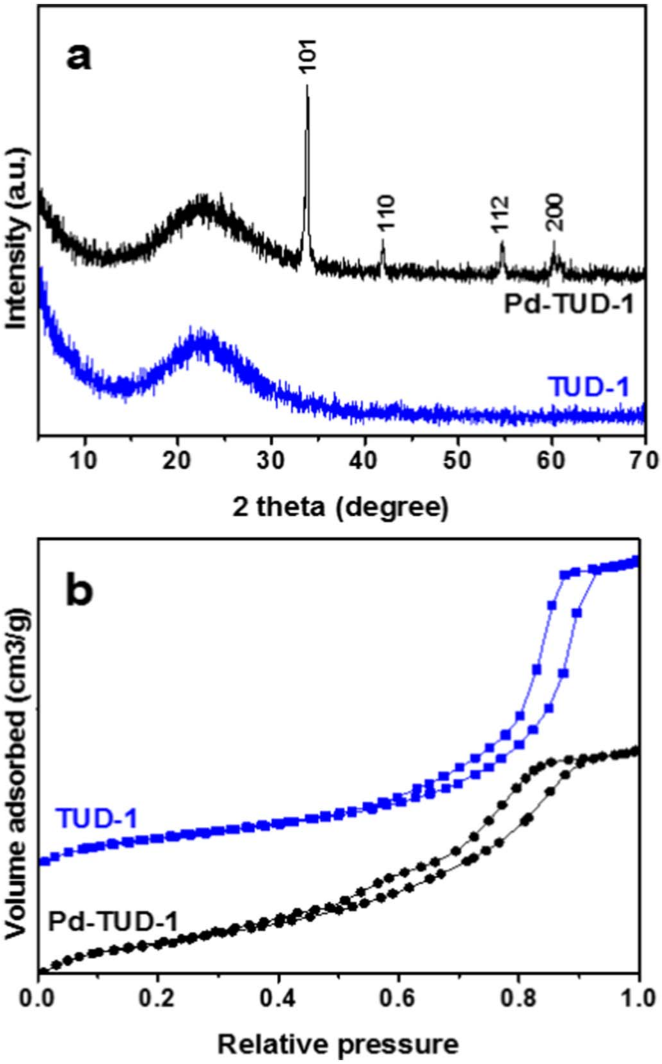

Fig. 1. a) The XRD patterns of Pd-TUD-1 and the neat TUD-1 materials, b) N_2 physisorption isotherms of Pd-TUD-1 and TUD-1.

3. Results and discussion

3.1. Characterization results

The Si/Pd ratio in the synthesized gel and in the calcined product (determined by ICP elemental analysis) are very close, i.e. in the synthesized gel Si/Pd ratio = 50 and in the obtained final solid powder Si/Pd ratio = 48.3. This indicates that all the palladium amount which added during the synthesis were found in the final solid product. Fig. 1a shows the XRD patterns of Pd-TUD-1 compared with that of neat TUD-1 sample. The amorphous TUD-1 pattern shows one broad peak at 25° 2θ which indicates the amorphous phase of SiO_2[13]. This broad peak was also observed in Pd-TUD-1 patterns, in addition to other peaks at 33.7, 41.8, 54.5, 60.7 and 71.2 2 theta. These peaks can be corresponding to the crystal planes of (101), (110), (112), (200) and (202), which according to JCPDS card no. 43–1024 is an indication to the presence of palladium oxide species [14]. Fig. 1b shows the N_2 sorption isotherm of the Pd-TUD-1 sample compare with that of neat siliceous TUD-1 sample. The two isotherms are of type IV and showed a hysteresis loop of H1 type indicating the meso-structured character of the two samples [15]. Moreover, the similarity of the two isotherms is an indication that the mesoporous property of TUD-1 did not change as a result of Pd incorporation. The measured BET surface area of Pd-TUD-1 was 868 m^2/g which is higher than neat TUD-1 which was 655 m^2/g. The