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Selective hydrogenation of phenol to cyclohexanone catalyzed by palladium nanoparticles supported on alumina/lanthanide oxides

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Abstract

Palladium nanoparticles supported on mixture of alumina and lanthanide oxides were synthesized and employed for one stage hydrogenation of phenol to cyclohexanone. A conversion of 99.8% with a selectivity of 96.3% to cyclohexanone was obtained using Pd supported on alumina/lanthanum oxide/cerium oxide with mole ratio of 9:1:1 at mild condition of 80 °C and low H_2 pressure of 3 bar. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and volumetric isothermal nitrogen gas adsorption-desorption method (BET) were used for characterization of prepared catalysts.

Keywords Phenol hydrogenation · Supported Palladium · alumina/lanthanum oxide · Cyclohexanone · Nano particles

Introduction

Cyclohexanone is an important organic compound because of its utilization as a precursor to fabrication of caprolactam and adipic acid for nylon-6 and nylon-66, respectively [1]. Industrially, cyclohexanone is produced through cyclohexane oxidation [2] or Asahi process [3]. The first route requires harsh reaction conditions such as high temperature and pressure, producing undesirable byproducts which are complicatedly separated and suffers low cyclohexanone yield [4, 5]. In Asahi process benzene is partially hydrogenated to cyclohexene which is then hydrated to cyclohexanol, and cyclohexanol is subsequently dehydrogenated to cyclohexanone [3]. Hydrogenation of phenol is an alternative desired strategy for synthesis of cyclohexanone that can be done either in two-step or one-step process [6]. The two-step process involves hydrogenation of phenol to cyclohexanol followed

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by dehydrogenation to cyclohexanone [7]. The one-step hydrogenation of phenol to cyclohexanone avoids dehydrogenation step and favors cyclohexanone formation [8]. Therefore, direct hydrogenation process by simplifying reaction steps and improving hydrogen utilization while facilitating separation of cyclohexanone and cyclohexanol having approximately same boiling point is more preferable from the viewpoints of cost and energy saving [9, 10]. Cyclohexanone is rather active and can undergo further hydrogenation to cyclohexanol or other undesired adducts [11]. In order to overcome the drawbacks, considerable efforts have been made to develop effective catalysts for this catalytic system.

Catalytic hydrogenation of phenol has extensively been conducted over various metals such as Ni [12], Pd [13, 14], Pt [15], Rh [16], and Ru [17] in both gas [13] and liquid phase [18]. It has been established that Pd exhibits the best performance among other noble metal catalysts [13, 14]. Haruhiko et al. reported that palladium shows sufficient hydrogenation activity for phenol, so cyclohexanone is the main product.[3] The catalytic performance of Pd supported on lanthanide oxides [18], carbon nanotubes [19, 20], zeolites [21], colloidal cellulose nanocrystallites [22], hydroxyapatite [23], metal organic frameworks (MOFs) [24], SiO_2 [25], TiO_2 [26], Al_2O_3 [10] and MgO [27] have been reported. Talukdar et al. investigated the catalytic activity of palladium and platinum supported on basic zeolite LTI and none acidic alumina. it was reported that; palladium prefers the formation of cyclohexanone while platinum favors cyclohexanol formation. These results are attributed to larger charge transfer capacity of Pd to Pt [3].

Nano alumina is commonly used as a cheap support for metal catalysts due to its porous structure and high surface area [28]. Alumina supports have beneficial effects on catalytic activity of palladium. Therefore, Pd/Al_2O_3 has shown high activity for direct hydrogenation of phenol to cyclohexanone [7]. The metal-support interactions such as electronic effects improve the activity of palladium in the hydrogenation [18]. Ceria and ceria-based materials with basic character are suitable supports for hydrogenation reactions because of their reducibility character and their interactions with noble metals. These interactions provide a better charge transfer to dispersed palladium and then the electron-enriched palladium facilitates hydrogen activation [3]. As a result, Pd/CeO_2 was an efficient catalyst for selective hydrogenation of phenol [18]. Additionally, lanthanum-modified alumina was also reported as an active catalyst for phenol hydrogenation to cyclohexanone [13]. In this study a series of palladium nano particles supported on mixture of alumina and lanthanide oxides were prepared and their catalytic activities for selective hydrogenation of phenol to cyclohexanone at low hydrogen pressure were investigated.

Experimental

Materials

All hydrated Lanthanum nitrate salts (cerium, lanthanum, europium, terbium, holmium) were purchased from Alfa Aesar. Palladium(II) acetate, phenol, aluminum isopropoxide and Pluronic P123 were purchased from Merck. Hydrogen gas with purity of >99.999% was supplied from local manufacturer.

Instruments

X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu K_α radiation. Scanning electron microscopy (SEM) was performed using a Zeiss DSM 960A microscope with acceleration voltage of 10 k. To determine the specific surface area and pore volume of the supported catalysts, a BELSORP mini instrument nitrogen adsorption desorption equipment was used at 77 K. The palladium content of the catalysts was determined using an ICP-OES (Varian Vista-MPX) spectrometer. For monitoring of reaction products and their identity, a gas chromatograph, Agilent Technologies 7890A Instrument, equipped with a HP-1 capillary column, a FID detector, and a mass spectroscope model 5975C with a triple-axis detector was used

Synthesis

The synthesis of alumina was according to a published method with slight modification [29]. First, nonionic surfactant Pluronic P123 (1 mL, 0.16 mmol), was dissolved in ethanol (40 mL) at room temperature. To this solution aluminum isopropoxide (4.08 g, 20 mmol) and concentrated nitric acid (1.5 mL, 15.8 M) were added. The mixture was stirred at room temperature for 5 h, then the solution was cast into a crystallization dish. The dish was placed into a pre-heated 65 °C oven to undergo solvent evaporation for 12 h. The light yellow solid was calcined in air at 600 °C for 5 h.

A series of Al_2O_3/lanthanide oxides, were synthesized by a published method [30]. Different weight ratios of alumina powder were added to ethanol solution of lanthanum nitrates and stirred vigorously for 3 h. The mixture was then poured into crystallization dish and pre-heated at 65 °C for 12 h. The final product was obtained after calcination at 500 °C for 4 h. The chemical composition of the prepared samples with various Al_2O_3/lanthanide oxide mol ratios are shown in Table 1. For incorporation of palladium on the support, dry impregnation method was used [18]. Palladium loading was adjusted to 1 wt% relative to the total mass of the support. In a general synthesis, palladium acetate (0.021 g, 0.09 mmol) was dissolved in acetone (2 mL). The support was placed in a mortar and impregnated with the palladium solution dropwise. After each impregnation step, the palladium and support was mixed thoroughly to a homogeneous dry powder. The prepared materials were later calcined at 450 °C for 3 h. For activation of catalysts, the prepared samples were reduced under flowing of pure hydrogen gas (99.999%) in a quartz tubular reactor at 355 °C for 3 h. Activated catalysts were stored in a closed container for catalytic test.

Table 1 Catalytic activity and selectivity of Palladium/lanthanum oxides/alumina catalyst for conversion of phenol to cyclohexanone

Entry	Lanthanide oxide 1	Lanthanide oxide 2	Alumina/Lanthanid oxides ratios	Conversion (%)	Selectivity to cyclohexanone (%)	Selectivity to cyclohexanol (%)
1	Ce	–	12:1	12.5	32.8	67.2
2	Ce	–	9:1	99	89.3	10.7
3	La	–	9:1	99.7	49.4	50.6
4	Eu	–	9:1	80.4	25.3	74.7
5	Tb	–	9:1	100	56.3	43.7
6	Ho	–	9:1	32.3	42.7	57.3
7	La	Ce	9:1:1	99.8	96.3	3.7
8	Tb	Ce	9:1:1	99.3	63.2	36.8
9	Eu	Ce	9:1:1	86.7	36.2	63.8
10	La	Ce	3:1:1	89.7	51.7	48.3
11	Eu	La	9:1:1	84.3	31.7	68.3
12	Eu	Tb	9:1:1	100	37.6	62.4
13	Eu	Ho	9:1:1	54.8	50.9	49.1
14	Tb	La	9:1:1	97.1	65.3	34.7
15	Tb	Ho	9:1:1	100	39.2	60. 8

Catalytic Hydrogenation

All reactions were conducted in a high pressure stainless steel reactor under constant hydrogen pressure of 3 bar. In a typical procedure, the catalyst (0.5 g, 1 wt% Pd loading), phenol (0.5 g) and 10 mL cyclohexane as solvent, was charged into the reactor. Reactor was purged three times with nitrogen to displace any residual oxygen in the reactor, then reactor temperature was set to 80 °C and pressure adjusted to 3 bar for six hours under a stirring rate of 1000 rpm. Reaction products were filtered and analyzed by gas chromatography. The used solid catalyst was separated by centrifugation and washed with ethanol then it was dried in oven in order to be used in next cycles.

Result and discussion

According to Fig. 1, the XRD pattern of Pd/alumina/lanthanum oxide/cerium oxide catalyst indicated diffraction peaks corresponding to alumina, ceria, and lanthanum oxide at [18, 31, 32]. No diffraction peak was observed for palladium particles due to very low palladium loading and highly dispersed over the support [18].

The average size of cerium and lanthanum crystallites was estimated 1.11 nm using the well-known Scherer equation: ($L= K \lambda/\beta.\cos\theta$) with $\lambda = 10$, $\beta = 0.835$, $K = 0.9$, and $2\theta = 28°$, where K is a constant related to crystallite shape, λ is the X-ray wavelength in nanometer, β is the full width of the diffraction peak profile at

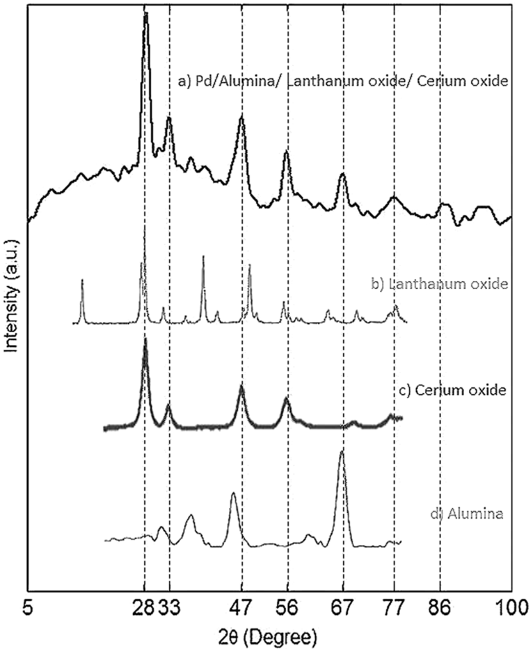


Fig. 1 XRD pattern of (**a**) Pd/ alumina/ lanthanum oxide/ cerium oxide, (**b**) lanthanum oxide [31], (**c**) cerium oxide [18], and (**d**) alumina [32]

half maximum height in radians, and K is a constant related to crystallite shape, and θ is the Bragg Angle in radians. Broad peaks confirmed the small crystallite size of catalyst.

The result of scanning electron microscopy, shown in Fig. 2, confirmed that Pd/alumina/lanthanum oxide/cerium oxide catalyst was comprised of collective particles of tiny 13 nm voids.

The weight ratios of containing particles in Pd/alumina/lanthanum oxide/cerium oxide catalyst was obtained via energy dispersive X-ray analysis and confirmed by ICP. EDXA data confirmed presence of 27.44 wt% Al, 15.56 wt% La and 16.17 wt% Ce and 1.03 wt% palladium in Pd/alumina/lanthanuum oxide/cerium oxide catalyst.

According to the nitrogen adsorption-desorption isotherm plots of the Pd/alumina/ lanthanum oxide/ cerium oxide catalyst, Specific surface area, pore volume and mean pore diameter values were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Specific surface area, pore volume and mean pore diameter values of all Pd/alumina/lanthanide oxide catalysts were between 172–195 m^2 g^{-1}, 6.83–6.92 nm and 0.21–0.23 cm^3 g^{-1}, respectively. Type IV BET isotherm and calculated values confirmed mesoporous structure of catalysts. The quite similar results obtained by BET, proved the main surface area of catalysts were mostly due to porous structure of alumina.

The catalytic performance of palladium supported on variable lanthanide oxide/alumina were examined. First two mixtures of cerium oxide/alumina based support with different molar ratios were tested (Entries 1,2). Assuming 9:1 as the best ratio which resulted in both better conversion and selectivity, other lanthanide oxide/alumina support mixtures were also synthesized in this proportion. The catalytic activity

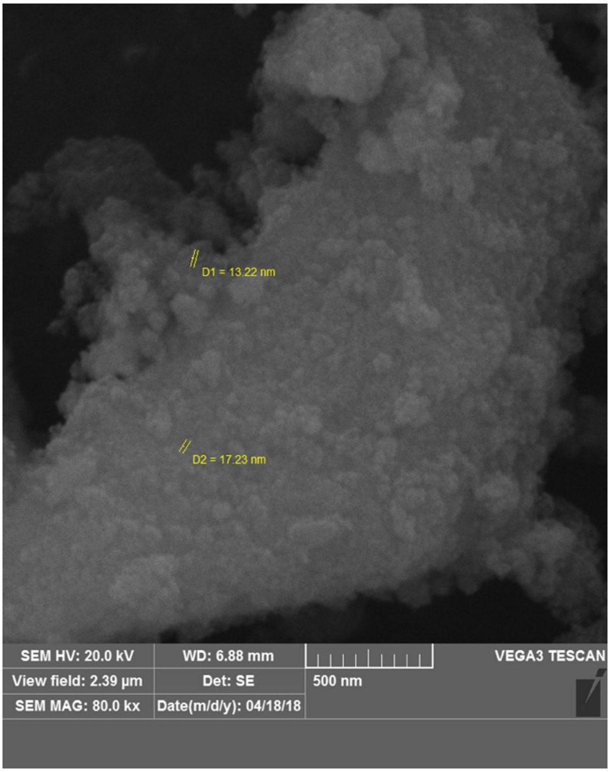
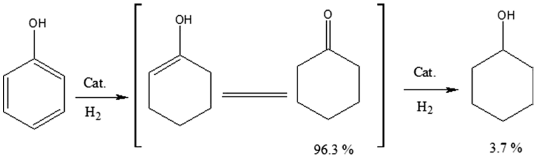


Fig. 2 SEM imaging of Pd/alumina/ lanthanum oxide/ cerium oxide catalyst

of prepared individual lanthanide oxide/alumina supports were tested under hydrogenation conditions separately (Entries 3–6). From the corresponding conversions and selectivity listed in Table 1, phenol conversion over alumina mixed with lanthanum oxide (Entry 3) and terbium oxide (Entry 5) was almost 100 % complete and high selectivity of about 89.3% to cyclohexanone was achieved by hydrogenation of phenol over cerium oxide/alumina support (Entry 2). It was expected that the combination of lanthanum oxide/cerium oxides and terbium oxide/cerium oxide with alumina could result in both higher conversion and selectivity. Under the experimental conditions using lanthanum oxide/cerium oxide/alumina with 9:1:1 molar ratios (Fig. 3), high conversion of 99% and significant selectivity of 96% to cyclohexanone was achieved (Entry 7). However, terbium oxide/cerium oxide/alumina with phenol conversion of 86% was less selective to cyclohexanone (Entry 8). As it was expected, Europium oxide/cerium

Fig. 3 Phenol hydrogenation over Pd supported on Al_2O_3/ La_2O_3/CeO_2



oxide/alumina showed both less conversion and selectivity to cyclohexanone (Entry 9). Later, by decreasing the amount of alumina respected to lanthanum oxide with phenol conversion of almost 90%, the selectivity to cyclohexanone decreased significantly to 51% (Entry 10), which showed the important impact of total surface area of catalyst dependent on alumina, for hydrogenation performance. Tracing the effect of other mixtures of lanthanide oxides, e.g. (Entries 11–15) supports containing terbium oxide were not selective to cyclohexanone despite having 100% conversion (Entries 14, 15).

Selectivity to cyclohexanol was more favorable by using combination of europium oxide with other lanthanide oxides (Entries 9, 11–13) and mixture of terbium oxide/holmium oxide/alumina (Entry 15). In case of using europium oxide/cerium oxide, 74.7% selectivity to cyclohexanol was obtained (Entry 9). Presence of europium was crucial for the formation of cyclohexanol.

Reaction conditions: phenol 0.5 g, and 10 mL cyclohexane as solvent, catalyst 0.5 g, (1 wt% Pd), H_2 pressure 3 bar at 80 °C for 6 h, stirring rate 1000 rmp.

At the end, the recyclability/reusability of catalyst was tested by using the recycled Pd/alumina/lanthanum oxide/cerium oxide in three other runs. As illustrated (Fig. 4), the activity of catalyst dropped about 5% and selectivity to cyclohexanone remained quite unchanged in further consecutive reactions, so, the reaction procedure can be repeated several times with minimum loss of activity.

According to previously established proposed mechanisms the aromatic ring of phenol can be chemisorbed on the catalyst surface and hydrogenated by activated hydrogens on Pd surface [10] (Fig. 5a). Phenol absorption on acidic sites facilitates production of cyclohexanol [3], on the contrary formation of cyclohexanone is favored by chemisorption of phenol on basic sites [7]. The benzene ring of phenol interacts with Pd by formation of π-complex between the aromatic ring and Pd [10]. Hydrogenation of phenol occurs in a consecutive pathway; at first the aromatic ring of phenol is partially hydrogenated to thermodynamically unstable 1-hydroxycyclohexene which is then rapidly isomerized to cyclohexanone (Fig. 5b). Cyclohexanone tends to leave the catalyst surface quickly because of having weak interaction

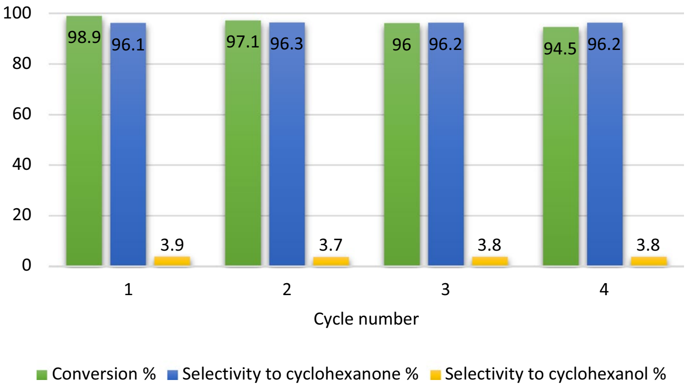


Fig. 4 Catalyst reusability in hydrogenation of phenol to cyclohexanone. Reaction conditions: phenol 0.5 g, and 10 mL cyclohexane as solvent, recycled $Al_2O_3/La_2O_3/CeO_2$ 0.5 g, (1 wt% Pd), H_2 pressure 3 bar at 80 °C for 6 h, stirring rate 1000 rmp

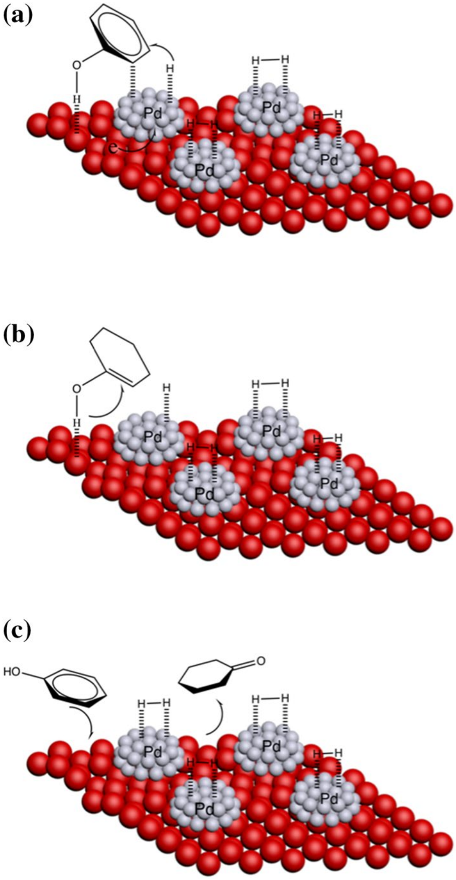


Fig. 5 Possible Reaction Mechanism of Phenol Hydrogenation

with basic sites of support and is being replaced by strongly bound new phenol molecule and further hydrogenation to cyclohexanol is prevented [10] (Fig. 5c). In case of hydrogenation of phenols, a high adsorption capacity of support has an important impact on catalytic activity and selectivity.

Conclusion

In this study, a series of palladium on alumina/lanthanide oxide supports were prepared for selective hydrogenation of phenol to cyclohexanone. All catalysts were synthesized at the same conditions with different molar ratios. Under experimental conditions in this report, 99.8% conversion of phenol with 96.3% selectivity to cyclohexanone was obtained with Pd supported on alumina/lanthanum oxide/cerium oxide with mole ratio of 9:1:1 at 80 °C and 3 bar H_2 pressure in cyclohexane as solvent. The catalyst was checked for recyclability and it was reusable with a minimum loss of activity for several runs. Terbium oxide or mixture of terbium oxide with holmium oxide or europium oxide showed 100% conversion, but without selectivity and a mixture of cyclohexanone and cyclohexanol was obtained.

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