

GC–MS analysis and reaction mechanism of the gas-phase amination of 2,6-diisopropylphenol

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Abstract

The liquid product of the gas-phase amination of 2,6-diisopropylphenol (2,6-DIPP) to prepare 2,6-diisopropylaniline (2,6-DIPA) was analyzed using gas chromatography-mass spectrometry. Besides 2,6-DIPP and 2,6-DIPA, there are by-products such as water, 1,3-diisopropylbenzene, 2,6-diisopropylcyclohexamine in the liquid product, in which 2,6-diisopropylcyclohexamine is a major constitute by-product. The ratio of 2,6-diisopropylcyclohexamine to 2,6-DIPA is low when the reaction proceeds more completely at lower reaction space velocity, but this ratio increases when the reaction proceeds incompletely at higher space velocity. So that 2,6-diisopropylcyclohexamine is suggested to be the intermediate product of gas-phase amination of 2,6-DIPP. The reaction mechanism of gas-phase amination of 2,6-DIPP on the bifunctional palladium-lanthanum supported catalyst was proposed. This reaction was synergistically catalyzed by the Pd metal active sites that facilitated hydrogenation and dehydrogenation reactions and the acid sites on the catalyst support that accelerated isomerization and amination reactions. © 2003 Elsevier B.V. All rights reserved.

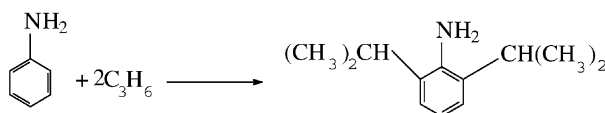
Keywords: GC–MS analysis; Reaction mechanism; Gas-phase amination; 2,6-Diisopropylaniline; 2,6-Diisopropylphenol

1. Introduction

2,6-Diisopropylaniline (2,6-DIPA) is an important fine chemical intermediate. The main preparation methods of 2,6-DIPA are alkylation of aniline (method A) and amination of 2,6-diisopropylphenol (2,6-DIPP) (method B).

The composition of product of the alkylation method was very complex and the selectivity was rather low [1]. Gas-phase amination is an ideal path to prepare 2,6-DIPA for its high conversion and high selectivity. Preparation of 2,6-DIPA by gas-phase amination over the Pd/spinel catalyst was developed by BASF [2]. Liu et al. [3] prepared Pd

Method A



Method B



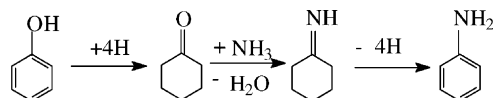
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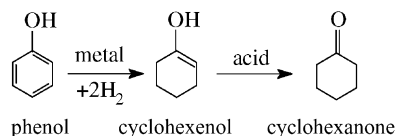
catalyst supported on MgAl₂O₄ spinel, on which the initial conversion of 2,6-DIPP was more than 90%, and initial

selectivity of 2,6-DIPA was more than 80% under the conditions of 200 °C and LHSV = 0.1 h⁻¹.

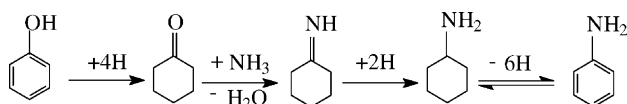
Some researchers have studied the reaction mechanism of amination of phenol and 2,6-dimethylphenol. Watanabe et al. [4] studied on the gas-amination of phenol on TiO₂-SiO₂ catalyst. The reaction proceeded through the phenol adsorption on the acid sites of catalyst. Hamada et al. [5] investigated the preparation of aniline by the amination of phenol in the presence of cyclohexanone.



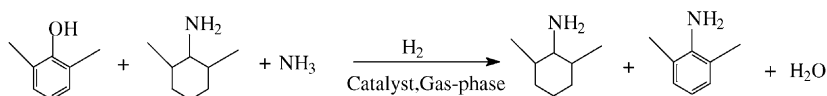
Phenol was reduced to cyclohexanone in a bifunctional system [6].



Hamada [7] also prepared aniline and cyclohexylamine by amination of phenol and cyclohexanol. High yield can be obtained in this reaction, but there was relative low conversion in the amination of phenol or cyclohexanol, respectively. Based on the research, it can be concluded that hydrogen transfers between phenol and cyclohexanol. Ono [8] suggested the following reaction scheme about amination of phenol over palladium catalyst supported on alumina.



Novbert [2] proposed that the gas-phase amination of 2,6-dimethylphenol proceeds through the following process, in which 2,6-dimethylcyclohexamine is an intermediate product.



However, nearly no study on the reaction mechanism of gas-phase amination of 2,6-diisopropylphenol has been reported. In this paper, the catalyst Pd-La/spinel was prepared for the preparation of 2,6-DIPA by gas-amination [9]. On the basis of gas chromatography-mass spectrometry (GC-MS) analyses of the products and the reactive feature of amination, the reaction mechanism of gas-phase amination was proposed.

2. Experimental

2.1. Catalyst preparation and evaluation

The preparation and evaluation of Pd (0.5 wt.%)–La (0.1 wt.%) /spinel catalyst was as described in [9].

2.2. Catalyst characterization

The Pd-La/MgAl₂O₄ catalyst was characterized after pretreated in H₂ at 220 °C for 6 h.

For pyridine-IR characterization, a self-supported wafer of about 10 mg with a diameter of 15 mm was placed in an infrared quartz cell and connected to a vacuum system. The wafer was dehydrated at 400 °C and 1.33 × 10⁻³ Pa for 6 h. The background spectra of samples were recorded after the self-supported wafer was cooled to ambient temperature and pyridine vapour was admitted to the cell. The temperature of the sample was increased to 100 °C, and the pyridine was adsorbed for 5 min. Finally, excess pyridine was desorbed by evacuation the samples at the desired temperature (namely, 100, 200, and 300 °C) for 5 min. The samples were cooled to ambient temperature, and the spectra were recorded on a Nexus 470 spectrometer.

The surface composition and structure of catalyst were studied by XPS in a Microlab 310F system. An Mg Kα electron source was used with a power setting at 250 W. In order to correct possible deviation caused by electric charge of samples, the binding energy of the C_{1s} peak at 284.8 eV was taken as an internal standard.

2.3. Treatment of product sample

The liquid product taken out from the reaction system was volatilized the excessive ammonia firstly. The solvent methanol was added and then the product was shaken into homogeneous phase.

2.3.1. Analytical conditions of capillary gas chromatography

Chromatographic column: HP-PONA (100%-polydimethylsiloxane) capillary chromatographic column 50 m ×

0.20 mm × 0.50 μm) HP-35% (35%-diphenyl-65%-dimethylsiloxane multipolymer) capillary chromatographic column 30 m × 0.25 mm × 0.25 μm. The temperature of injection opening 300 °C. Helium was used as carrier gas, and its flow was 0.6 ml/min. The injection volume of analytical sample 0.6 μl and the split ratio was 100: 1. The temperature

program for both columns was held at 120 °C for 15 min and programmed to 250 °C at a rate of 5 °C/min with a hold time of 25 min.

2.4. Mass spectral analysis conditions

GC–MS analyses were performed by using HP 6890 GC with a HP 5973 mass selective detector. The ion source was EI source. The ionization voltage was 70 eV, and the source temperature was 230 °C. The emission current was 34.6 μ A, and the electron multiplication was 1576 V. The scanning scope was 10–300.

3. Results and discussion

3.1. Analysis of mass spectrometry

Both HP-PONA column and HP-35 column can separate the liquid product of the gas-phase amination, but the number and retention time of peaks are different. In order to ascertain its component, the product was analyzed by capillary column gas chromatography-mass spectrometry. The total ion current chromatograms from both separation of the liquid product with different chromatographic columns were listed in Fig. 1.

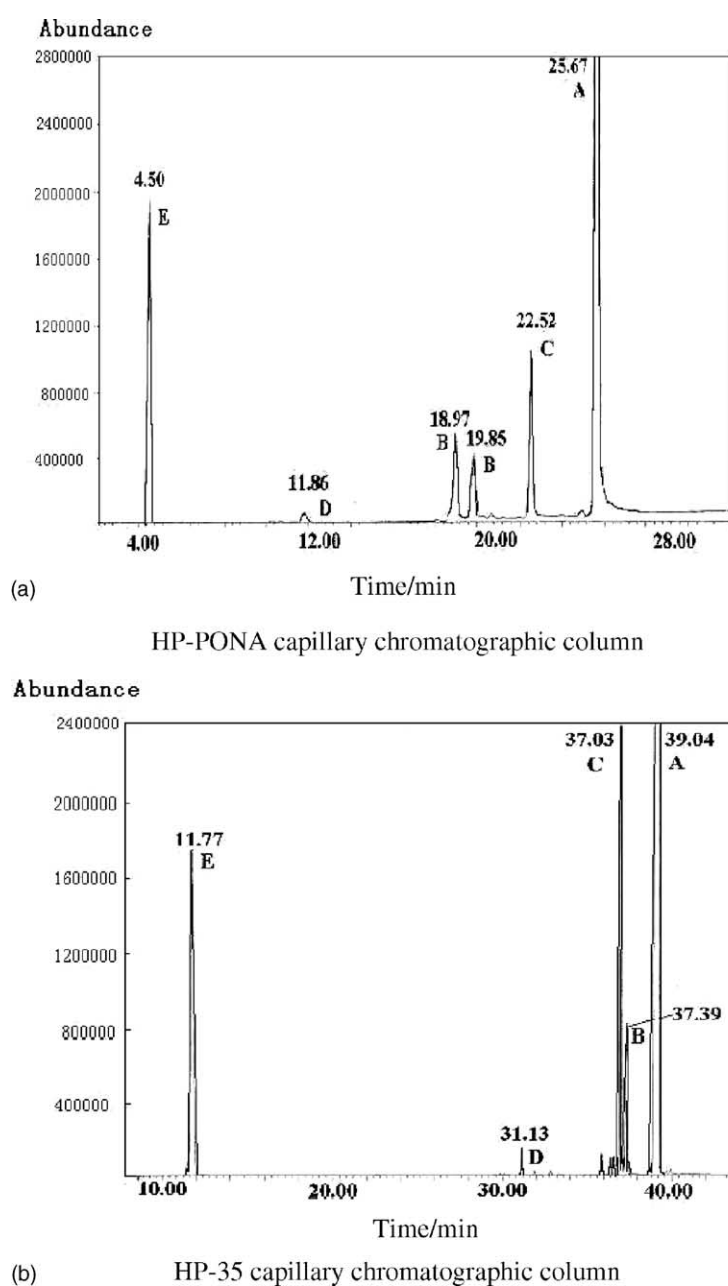


Fig. 1. The total ion current chromatogram of liquid product.

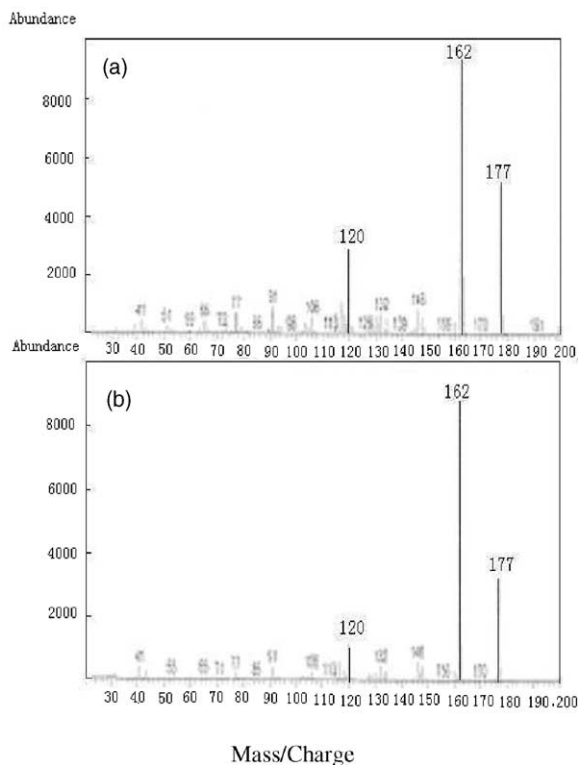


Fig. 2. The mass spectra of 2,6-diisopropylaniline: (a) in product and (b) standard.

As provided in Figs. 2–5, it can be concluded from the analysis results of mass spectrometry that both of these two chromatographic columns can separate the components in the product well. The peaks of every component are well matched in the results of these two chromatographic columns. The peak E represents solvent methanol. By comparing standard mass spectra with those of the product, the component in the product can be confirmed. The component A (Fig. 2) is the object product 2,6-DIPA, as indicated by the characteristic mass spectrum (molecular ion of 177 and a base peak at 162 amu). The component C (Fig. 3) has a mass spectrum with a molecular ion at 178 and a base peak of 163 amu, which suggests that the component C is reactant 2,6-DIPP. The component D has a mass spectrum consistent with 1,3-diisopropylbenzene (Fig. 4).

No standard mass spectrum matches the component B. There is a pair of isomeric compounds B in the liquid product because it has two different peaks with retention time of 18.97 and 19.85 min, respectively, in the total ion current chromatogram with HP-35 column (Fig. 1(a)), but both of them have the same mass spectrum in Fig. 5. The component B shows major fragments at m/z 98, 168, and 140, as well as a molecular ion at 183. Because the mass of its molecular ion is an odd number, according to the Nitrogen Rule, the number of nitrogen atom must be an odd number. Based on the analysis, by-product 2,6-diisopropylcyclohexamine can be envisioned. The breakage pattern of mass spectra peak and the ascription of the main mass spectra peak

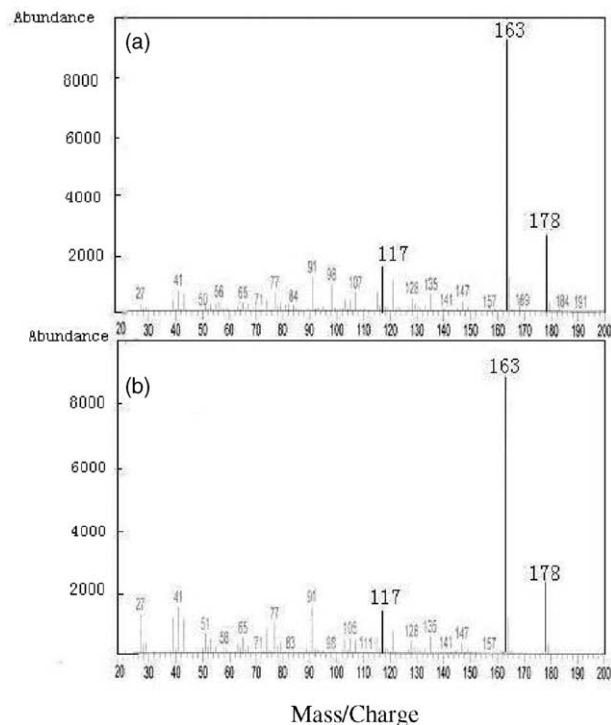
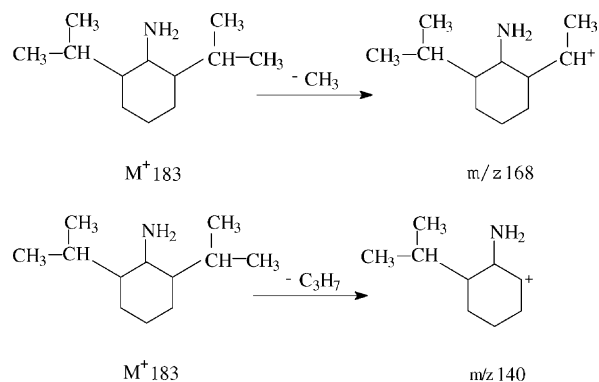


Fig. 3. The mass spectra of 2,6-diisopropylphenol: (a) in product and (b) standard.

of 2,6-diisopropylcyclohexamine are expressed as follow patterns (Scheme 1), furthermore they are entirely consistent with the mass spectrum of the component B in Fig. 5. All these confirm that the component B is by-product 2,6-diisopropylcyclohexamine.



3.2. Elementary study on the reaction process

The liquid product in the preparation of 2,6-DIPA by gas-phase amination of 2,6-DIPP was analyzed by gas chromatography-mass spectrometry, and the composition of the product was determined. Besides 2,6-DIPP and 2,6-DIPA, there are by-products such as water, 1,3-diisopropylbenzene, 2,6-diisopropylcyclohexamine in the liquid product, in which 1,3-diisopropylbenzene is the minor constitute by-product, and 2,6-diisopropylcyclohexamine is the major constitute by-product.

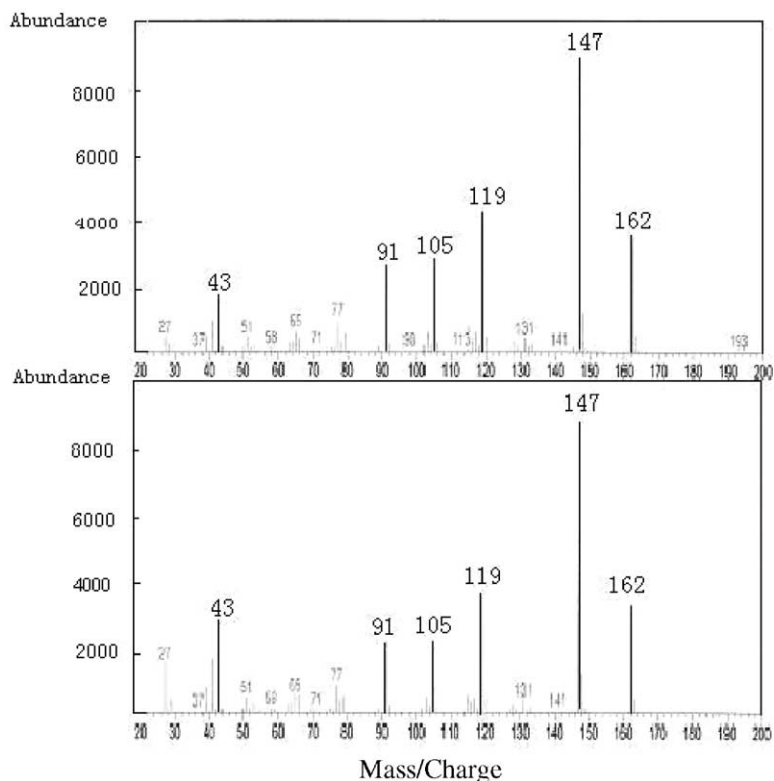


Fig. 4. The mass spectra of 1,3-diisopropylbenzene: (a) in product and (b) standard.

The distribution of liquid products at different SV on the Pd-La/ MgAl₂O₄ catalyst is listed in Table 1. Along with the increase of space velocity, the contact time becomes shorter, and then the reaction proceeds incompletely. If 2,6-diisopropylcyclohexamine is a by-product resulted from secondary side reaction, the increase of space velocity should

decrease the content of 2,6-diisopropylcyclohexamine because secondary side reaction is inhibited due to the decrease of contact time. If 2,6-diisopropylcyclohexamine is a by-product resulted from parallel side reaction, the increase of space velocity should not influence the content of 2,6-diisopropylcyclohexamine. If 2,6-diisopropylcyclohexamine is a by-product resulted from intermediate side reaction, the increase of space velocity should increase the content of 2,6-diisopropylcyclohexamine. As listed

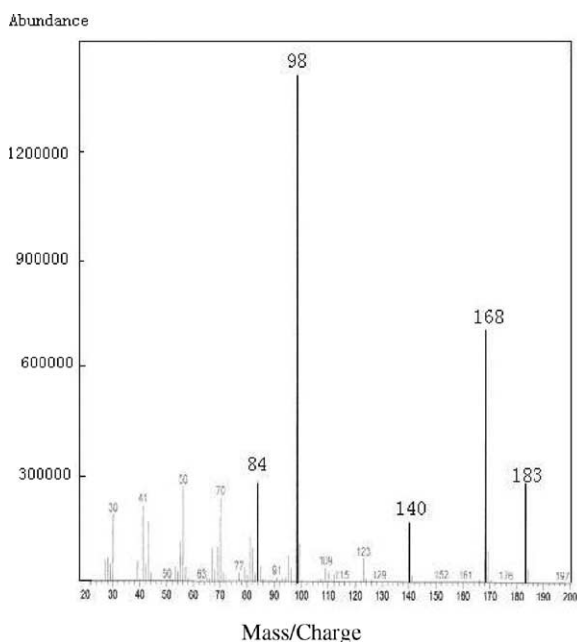
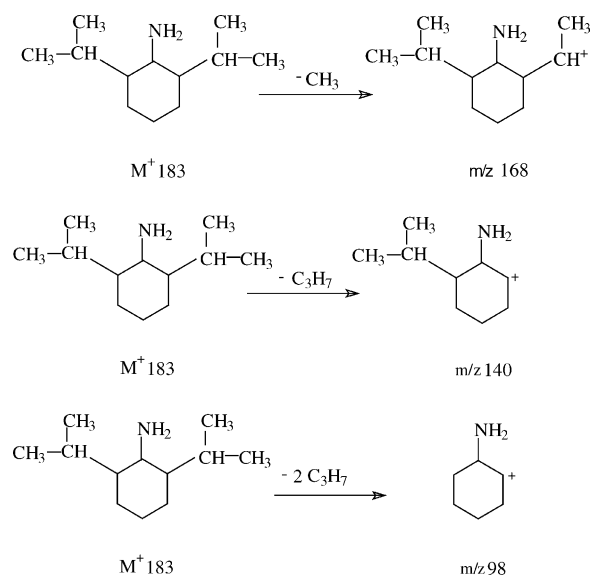


Fig. 5. The mass spectra of 2,6-diisopropylcyclohexamine sample.



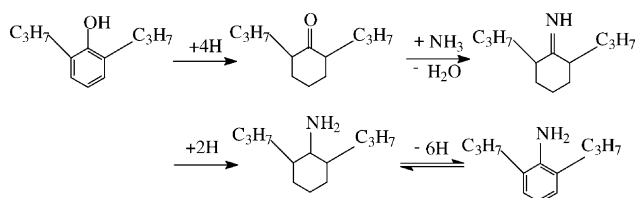
Scheme 1. Fragmentation patterns of 2,6-diisopropylaniline.

Table 1
Distribution of liquid products at different SV, wt.%

LHSV (h^{-1})	GHSV (h^{-1})	$x_{2,6\text{-DIPP}}$ (%)	$x_{2,6\text{-DIPA}}$	$x_{2,6\text{-diisopropylcyclohexamine}}$ (%)	$x_{2,6\text{-diisopropylcyclohexamine}}$ $x_{2,6\text{-DIPA}}$
0.3	150	1.5	87.5	10.0	0.11
0.6	300	3.3	79.9	14.5	0.18

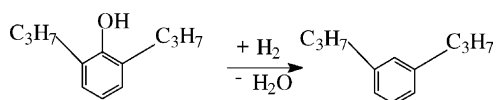
Reaction conditions: $T = 220^\circ\text{C}$; $P = 1.5\text{ Mpa}$; $\text{NH}_3/2,6\text{-DIPP}$ (mol) = 10; H_2/DIPP (mol) = 20.

in Table 1, the ratio of 2,6-diisopropylcyclohexamine to 2,6-DIPA is low when the reaction proceeds more completely at lower reaction space velocity. This ratio increases when the reaction proceeds incompletely at higher space velocity. So that 2,6-diisopropylcyclohexamine is suggested to be an intermediate product of gas-phase amination of 2,6-DIPP, then the increase of space velocity inhibits the dehydrogenation of 2,6-diisopropylcyclohexamine to 2,6-DIPA. The gas-phase amination of 2,6-DIPP is proposed to proceed according to the following process, the formation of 2,6-DIPA is accompanied by the formation of intermediate product 2,6-diisopropylcyclohexamine and by-product H_2O .



In the course of this reaction, water is an unavoidable by-product. One molecular product 2,6-DIPA is generated accompanied by one molecule of by-product water.

The other by-product 1,3-diisopropylbenzene is produced by hydrogen addition and dehydration.

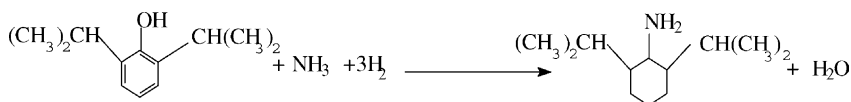


This reaction system contains three reactions chiefly.

Main reaction (I):



Side reaction (II):



Side reaction (III):

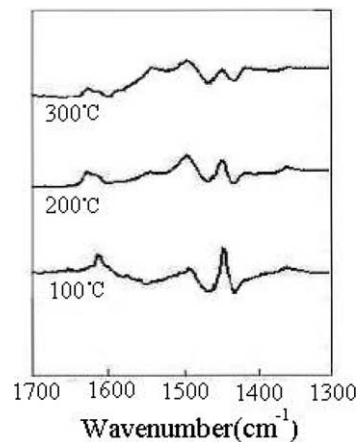
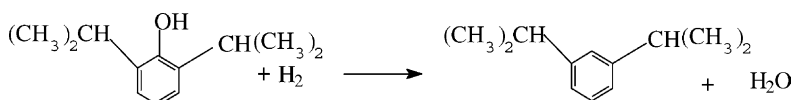


Fig. 6. Pyridine-IR spectra of Pd-La/MgAl₂O₄ catalyst.

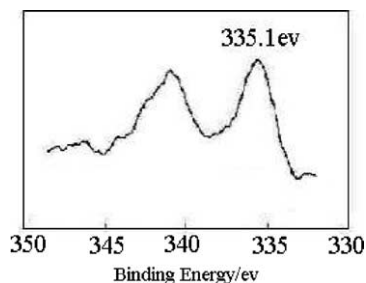
3.3. Catalyst characterization

The spectra of pyridine adsorbed on Pd-La/MgAl₂O₄ catalyst in the 1700–1300 cm^{-1} are shown in Fig. 6. The band at 1446 cm^{-1} is due to adsorption on L acid sites. There is not band at 1540 cm^{-1} due to adsorption on B acid sites.

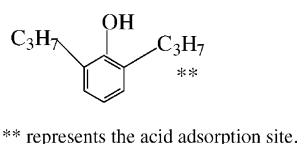
The standard binding energy of Pd in Pd⁰ is 335.1 eV, and that in PdO is 336.3 eV. As listed in Fig. 7, the binding energy Pd_{3d} was 335.1 eV in the Pd-La/MgAl₂O₄ catalyst after reduction pretreatment, which showed that Pd species in this catalyst was reduced to Pd⁰ completely.

3.4. Proposed reaction mechanism

It is known that the phenol chemisorbed on the acid sites of the catalyst support. It is therefore suggested that

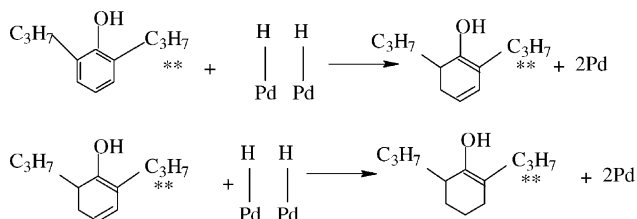
Fig. 7. XPS spectra of Pd_{3d} in Pd-La/MgAl₂O₄ catalyst.

2,6-DIPP is adsorbed on the L acid sites to form adsorption species.

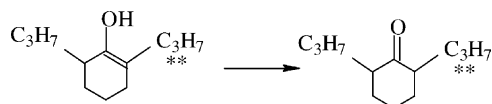


H₂ adsorbs on the Pd metal sites and is activated to H-Pd.

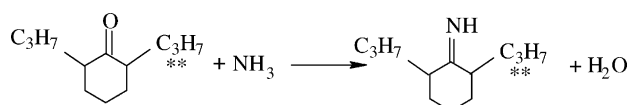
The formation of 2,6-diisopropylcyclohexenol results from the reaction between 2,6-DIPP chemisorbed on the L acid sites and hydrogen activated on the Pd metal sites.



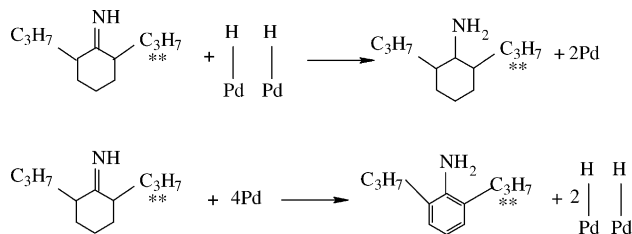
2,6-Diisopropylcyclohexenol transforms into 2,6-diisopropylcyclohexanone quickly because of the fast isomerization catalyzed by L acid sites.



Catalyzed by L acid sites, the reaction occurs between 2,6-diisopropylcyclohexanone and NH₃ would give 2,6-diisopropylcycloheximine.

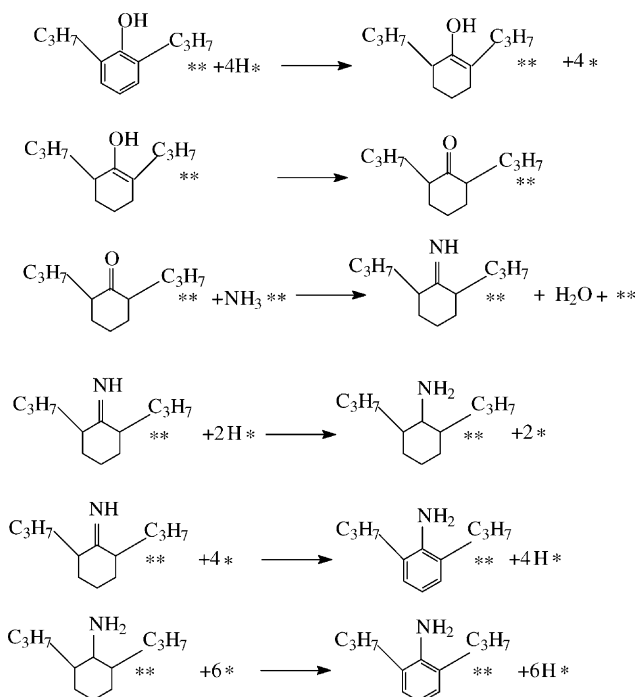


Imine is unstable and transform into other materials quickly. 2,6-diisopropylcycloheximine transforms into 2,6-diisopropylcyclohexamine by hydrogenation or into 2,6-DIPA by dehydrogenation.



Above all, the gas-phase amination of 2,6-DIPP is synergistically catalyzed by the L acid sites on the support and Pd metal sites of the bifunctional palladium-lanthanum supported catalyst.

The gas-phase amination of 2,6-DIPP with the Pd-La/MgAl₂O₄ catalyst is considered to proceed through the following reaction steps.



In these equations, * and ** represent an empty Pd catalytic site and L acid site on the catalyst support respectively. Pd-La/MgAl₂O₄ catalyst is a bifunctional catalyst. The gas-phase amination of 2,6-DIPP was synergistically catalyzed by the Pd metal active sites that facilitated hydrogenation and dehydrogenation reactions and the L acid sites on the catalyst support that accelerated isomerization and amination reactions.

4. Conclusions

1. The liquid product in the preparation of 2,6-DIPA by gas-phase amination of 2,6-DIPP was analyzed by gas chromatography-mass spectrometry, and the composition of the product was determined. Besides 2,6-DIPP and 2,6-DIPA, there are by-products such as water, 1,3-diisopropylbenzene, 2,6-diisopropylcyclohexamine

in the liquid product, in which 2,6-diisopropylcyclohexamine is a major constitute by-product.

2. The ratio of 2,6-diisopropylcyclohexamine to 2,6-DIPA is low when the reaction proceeds more completely at lower reaction space velocity, but this ratio increases when the reaction proceeds incompletely at higher space velocity. So that 2,6-diisopropylcyclohexamine is suggested to be the intermediate product of gas-phase amination of 2,6-DIPP.
3. The palladium-lanthanum supported catalyst is a bi-functional catalyst. This reaction was synergistically catalyzed by the Pd metal active sites that facilitated hydrogenation and dehydrogenation reactions and the L acid sites on the catalyst support that accelerated isomerization and amination reactions.

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