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The catalytic performance of gas-phase amination over Pd–La catalysts supported on Al_2O_3 and $MgAl_2O_4$ spinel

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Abstract

Both γ-Al_2O_3 and $MgAl_2O_4$ spinel used as support for the palladium–lanthanum catalyst in the preparation of 2,6-diisopripylaniline (2,6-DIPA) by the gas-phase amination of 2,6-diisopropyl phenol (2,6-DIPP) were studied. The bulk and surface properties of Pd–La/Al_2O_3 and Pd–La/$MgAl_2O_4$ catalysts were characterized by XRD, BET, NH_3-TPD, pyridine-IR, and XPS techniques. The replacement of Al_2O_3 with $MgAl_2O_4$ spinel in the palladium–lanthanum supported catalyst not only neutralized some strong acid sites, but also transformed them into relatively weaker acid sites according to the NH_3-TPD and pyridine-IR results. The XPS analysis showed that the $MgAl_2O_4$ spinel support improved the reduction of PdO. All these factors increased the catalytic performance for gas-phase amination of 2,6-DIPP. On the Pd–La/$MgAl_2O_4$ catalyst, under the LHSV 0.3 h^{-1}, the highest conversion of 2,6-DIPP was 98.5%, the highest selectivity and the highest yield of 2,6-DIPA was 88.9% and 87.5%, respectively. The whole run time of Pd–La/$MgAl_2O_4$ catalyst was up to 400 h, and the yield of 2,6-DIPA after 200 h reaction was still more than 80%.

Keywords: Supported catalyst; Alumina; Magnesia-alumina spinel; Gas-phase amination; 2,6-Diisopropylaniline

1. Introduction

2,6-Diisopropylaniline (2,6-DIPA) is an important intermediate in fine chemical industry. The methods to prepare 2,6-DIPA have been developed in two different ways: alkylation of aniline and amination of 2,6-diisopropylphenol (2,6-DIPP). The selectivity of 2,6-DIPA on aniline in the alkylation was very low. The gas-phase amination method to prepare 2,6-DIPA was reported by BASF Corp., in which the catalyst Pd, Ru, Rh was active component, and Mg–Al, Li–Al, Zn–Al, Co–Al, and Ni–Al spinel was used as catalyst support [1]. Liu et al [2] prepared Pd catalyst supported on $MgAl_2O_4$ spinel, on which the initial conversion of 2,6-DIPP was more than 90%, and initial single pass selectivity of 2,6-DIPA was more than 80% under the conditions of 200 °C and LHSV = 0.1 h^{-1}. The overall run time of this catalyst was 300 h.

Both of the two references used spinel as the catalyst support. $MgAl_2O_4$ spinel has a cubic crystal system, and its crystal cell is made up from 32 oxygen ions packed into a close-packed cubic structure, 16 octahedral Al ions and 8 tetrahedral Mg ions. The molecular structure of $MgAl_2O_4$ spinel is similar to γ-Al_2O_3, with 32 oxygen ions packed into a close-packed cubic structure. The difference lies in that there are totally 24 cations inserted into oxygen ion gaps in $MgAl_2O_4$ spinel, while only 21 and 1/3 aluminium cations are distributed among the close-packed cubic matrix in γ-Al_2O_3. This “saturated” structure makes $MgAl_2O_4$ more thermally stable than γ-Al_2O_3, with its melting point at 2135 °C [3]. Morterra and Ghiotti [4] studied the L acidity by the adsorption of pyridine, CO and CO_2 on $MgAl_2O_4$ spinel. It indicated that the adsorption of CO_2 occurs at two types of L acidic centers, the low frequency band (2360 cm^{-1}) involving octahedral Al ions and the high-frequency one (2375 cm^{-1}) involving tetrahedral Mg ions. Lercher et al. [5] reported that the strength of the acid sites decreased and that of the basic sites increased with increasing magnesia content in the alumina magnesia mixed oxides. Three different kinds of L acid sites (OH groups, Mg^{2+}, and Al^{3+}cations) were observed.

Pd/Al_2O_3 catalyst used for the gas-phase amination of phenol has been reported [6]. In our previous work, the

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Pd–La/$MgAl_2O_4$ catalyst was prepared for the preparation of 2,6-DIPA by gas-phase amination, in which the addition of promoter La can decrease the coke formation by neutralizing the strong acid sites on the catalyst [7]. 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 [8]. In this paper, the comparison of palladium–lanthanum catalysts supported on γ-Al_2O_3 and $MgAl_2O_4$ spinel for gas-phase amination of 2,6-DIPP were studied.

2. Experimental

2.1. Catalyst preparation

The γ-Al_2O_3 (152 m^2/g) prepared by kneading boehmite (Shandong Alumina Factory) with acetic acid as a peptizing agent into Ø 3 × 5 mm column, then it was calcinated at 550 °C for 4 h. The alumina-based out-layer magnesia-alumina spinel support was prepared by impregnating γ-Al_2O_3 with a mixture solution of aluminium nitrate and magnesium nitrate. Then it was dried and calcinated at 900 °C for 6 h. The content of $MgAl_2O_4$ to the alumina based out-layer magnesia-alumina spinel support is so low as 3.55 wt.%. The incipient wetness method for impregnation was used for preparing catalyst Pd (0.5 wt.%)–La (0.1 wt.%)/Al_2O_3 and Pd (0.5 wt.%)–La (0.1 wt.%)/$MgAl_2O_4$ with an aqueous HCl solution (0.12 mol/L) of $PdCl_2$ (0.06 mol/L) and $La(NO_3)_3$ (0.01 mol/L). The chlorine in these catalysts was removed by washing with distilled water.

2.2. Catalyst evaluation

The gas-phase amination of 2,6-DIPP was carried out in a fixed-bed flow system with a stainless steel tubular reactor of 20 mm inner diameter and 30 cm length. Twenty grams of palladium–lanthanum-supported catalyst was pretreated in a flow of H_2 at 220 °C for 6 h so that Pd(II) was reduced to Pd(0). 2,6-DIPP was pumped through the preheater where it was vaporized and then entered the reactor together with NH_3 and H_2. The reaction temperature is 220 °C and reaction pressure is 1.5 MPa. The reaction products passed through a cooling trap with ice water and were taken out every 2 h. The liquid products were analyzed with the HP4890 GC instrument on a HP-35 column.

The conversion of 2,6-DIPP (X (%)), selectivity of 2,6-DIPA (S (%)), and yield of 2,6-DIPA (Y (%)) were defined as follows:

Conversion,

$$X\,(\%) = \frac{2,6\text{-DIPP}_{\text{fed}}\,(\text{mol}) - 2,6\text{-DIPP}_{\text{recovered}}\,(\text{mol})}{2,6\text{-DIPP}_{\text{fed}}\,(\text{mol})} \times 100$$

Selectivity of 2, 6-DIPA,

$$S\,(\%) = \frac{2,6\text{-DIPA}_{\text{produced}}\,(\text{mol})}{2,6\text{-DIPP}_{\text{fed}}\,(\text{mol}) - 2,6\text{-DIPP}_{\text{recovered}}\,(\text{mol})} \times 100$$

Yield of 2, 6-DIPA,

$$Y\,(\%) = \frac{\text{conversion} \times \text{selectivity}}{100}$$

2.3. Catalyst characterization

XRD patterns were obtained with a Japanese D/Max-1400 X-ray diffraction system equipped with Cu Kα X-ray radiation (40 kV, 40 mA) and the 2θ scanned angle was 5–70°.

BET specific surface areas and pore distribution were measured with an automatic sorptometer on a Micromeritics Digisorb-2600 apparatus. Samples were reactivated in a vacuum ($<6.67 \times 10^{-2}$ Pa) at 300 °C for 4 h.

Acid site densities were measured by TPD of NH_3 preadsorbed at 100 °C. Samples (500 mg) were treated in He ($\sim$30 mL min^{-1}) at 500 °C for 1 h and then exposed to a 9.40% NH_3/He stream at 100 °C until saturation coverage were reached. Weakly adsorbed NH_3 was removed by flowing He at 100 °C for 0.5 h. Temperature was then increased to 500 °C at 10 °C/min, and the NH_3 concentration in the effluent was measured by HP 4890 gas chromatography.

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 of 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.

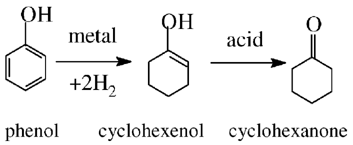
The surface composition and structure of catalyst were studied by XPS in a Microlab 310 F system. An Mg Kα electron source was used with a power setting at 250 W. In order to correct possible deviation caused by electric charge of samples, the binding energy of the C_{1s} peak at 284.8 eV was taken as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

3. Results and discussions

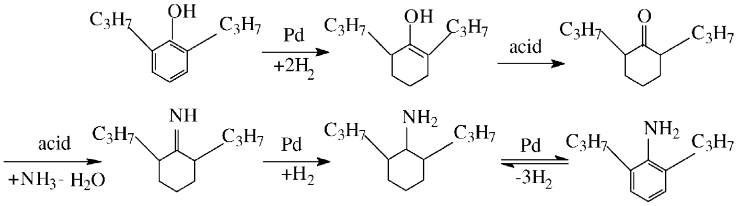
3.1. Proposed reaction mechanism of amination

Phenol was reduced to cyclohexanone in a bifunctional system [9].

Cullo [10] noted that gas-phase amination of phenol was catalyzed by weak acid site. In our previous work [8], 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. Based on the analysis of liquid product, the reaction mechanism of the preparation of 2,6-DIPA by the gas-phase amination of 2,6-DIPP was suggested, simultaneously the by-product 2,6-diisopropylcyclohexamine and water was produced.



The Pd–La/$MgAl_2O_4$ catalyst provided Pd metallic active sites and acid sites, in which Pd metallic active sites catalyzed hydrogenation and dehydrogenation reactions, and acid sites catalyzed isomerization and amination reactions. The strong acid sites on the catalyst can result in coke formation that is the main reason for catalyst deactivation [7]. It can be concluded that the gas-phase amination was synergistically catalyzed by the Pd metallic active sites and relatively weaker acid sites.

3.2. Support and catalyst characterization

Fig. 1 showed the XRD patterns of Al_2O_3 and $MgAl_2O_4$ spinel supports. Some characteristic peaks of $MgAl_2O_4$ are included in the $MgAl_2O_4$ spinel support, which was confirmed by XRD patterns with the data from JCPDS (card number: 21-1152) [11].

The Pd–La/Al_2O_3 and Pd–La/$MgAl_2O_4$ catalysts were characterized after pretreated in a flow of H_2 at 220 °C for 6 h.

Table 1
Physical properties of palladium–lanthanum catalysts supported on different supports

Catalysts	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average diameter (nm)
Pd–La/Al_2O_3	144	0.454	12.6
Pd–La/$MgAl_2O_4$	172	0.398	9.2

The physical properties of palladium–lanthanum catalysts supported on Al_2O_3 and alumina-based out-layer magnesia-alumina spinel $MgAl_2O_4$ were shown in Table 1. The $MgAl_2O_4$ content is so low as 3.55 wt.% that its influence on pore structure mostly reflected in the micropore. Then the BET surface area beame larger, and the pore volume and average diameter became smaller slightly.

As listed in Table 2, the amount of relatively weak acid sites (acid[1] and acid[2]) was 0.098 mmol g^{-1}, and that of the

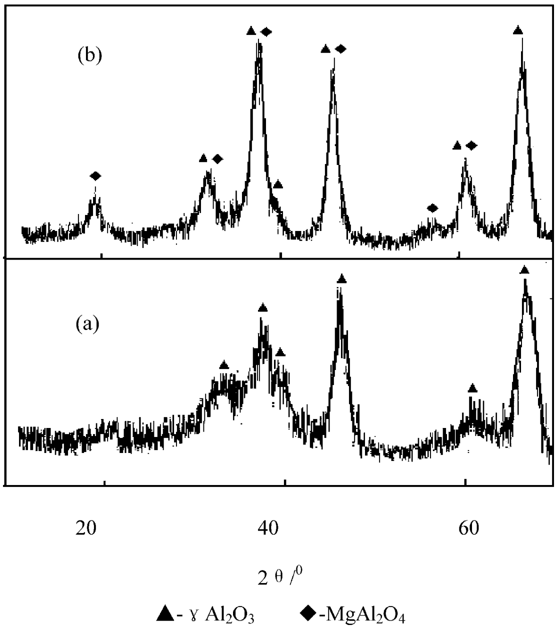


Fig. 1. XRD patterns of Al_2O_3 and $MgAl_2O_4$ spinel supports.

Table 2
NH_3-TPD data of palladium–lanthanum catalysts supported on different supports

Catalysts	T_{peak} (°C)			Acid amount, $n(NH_3)$ (mmol g^{-1})			
	Peak[1]	Peak[2]	Peak[3]	Acid[1]	Acid[2]	Acid[3]	Total acid
Pd–La/Al_2O_3	227	295	358	0.056	0.042	0.126	0.224
Pd–La/$MgAl_2O_4$	212	257	350	0.064	0.067	0.088	0.220

1, 2, 3 represent three desorption peak of NH_3 from low temperature to high temperature respectively.

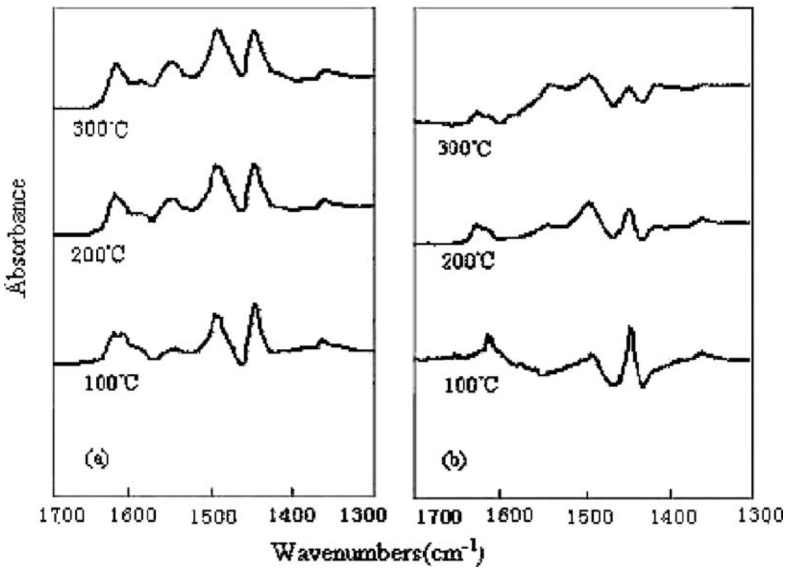


Fig. 2. Pyridine-IR spectra of palladium–lanthanum catalyst supported on different supports: (a) Pd–La/Al_2O_3; (b) Pd–La/$MgAl_2O_4$.

strong acid sites was 0.126 mmol g^{-1} on the Pd–La/Al_2O_3 catalyst. After the Al_2O_3 support replaced by $MgAl_2O_4$ support, the amount of relatively weak acid sites (acid^1 and acid^2) increased to 0.131 mmol g^{-1}, and that of the strong acid sites decreased to 0.088 mmol g^{-1}. All these indicate that the use of $MgAl_2O_4$ spinel can neutralize some strong acid sites and transform them into relatively weaker ones.

The spectra of pyridine adsorbed on Pd–La/Al_2O_3 and Pd–La/$MgAl_2O_4$ catalyst in the 1700–1300 cm^{-1} are shown in Fig. 2. The band at 1446 cm^{-1} is due to adsorption on L acid sites. There is no band at 1540 cm^{-1} due to adsorption on B acid sites. The area of absorption band at 1446 cm^{-1} of 1 mg Pd–La/Al_2O_3 or Pd–La/$MgAl_2O_4$ catalyst at different desorption temperature is presented in Table 3. From Fig. 2 and Table 3, it was obvious that the intensity of the L acid band gradually decreased with increasing desorption temperature of the catalysts samples. The acid sites, which adsorb pyridine at low temperature, contain strong acid sites and weak ones, but the acid sites that adsorb pyridine at high temperature are only strong acid sites. It is concluded that the number of strong acid sites decreases and the number of weak acid sites increases with replacing γ-Al_2O_3 support with $MgAl_2O_4$ in the palladium–lanthanum supported catalysts.

The standard binding energy of Pd in Pd^0 is 335.1 eV, and that in PdO is 336.3 eV. In the Pd–La/Al_2O_3 catalyst, the binding energy Pd_{3d} was 335.4 eV, which proved that Pd species in this catalyst was the mixture of Pd^0 and PdO. However, the binding energy Pd_{3d} was 335.1 eV in the Pd–La/$MgAl_2O_4$ catalyst, which showed that Pd species in this catalyst was reduced to Pd^0 more completely. All these indicated strong interaction between support and metal. The use of $MgAl_2O_4$ support increases the basicity and ability to provide electron, then Pd supported on $MgAl_2O_4$ is more easily reduced into metallic state (Fig. 3).

3.3. Performance of palladium–lanthanum catalyst supported on different supports

As shown in Fig. 4, the catalytic performance on Pd–La/$MgAl_2O_4$ catalyst was much higher than that on the Pd–La/Al_2O_3 catalyst. Under the reaction conditions: $T = 220\,^{\circ}C$, $P = 1.5$ MPa, LHSV $= 0.3\,h^{-1}$, GHSV $= 150\,h^{-1}$, NH_3/2,6-DIPP (mol) $= 10$, H_2/DIPP (mol) $= 20$, on the Pd–La/Al_2O_3 catalyst, the highest conversion of 2,6-DIPP was 98.4%, the highest selectivity and the highest yield of 2,6-DIPA was 87.7% and 86.3% respectively at 35 h. The catalytic properties decreased after that, then the yield of 2,6-DIPA was only 54.8% at 221 h. The conversion of 2,6-DIPP, the selectivity of 2,6-DIPA, the yield of 2,6-DIPA, and the stability of catalyst are all improved greatly with the use of $MgAl_2O_4$ support in the palladium–lanthanum-supported catalyst. On

Fig. 3. XPS spectra of Pd_{3d} in palladium–lanthanum catalyst supported on different supports: (a) Pd–La/Al_2O_3; (b) Pd–La/$MgAl_2O_4$.

Table 3
Band area of palladium–lanthanum catalyst supported on different supports

Catalysts	The area of absorption band at 1446 cm^{-1} of 1 mg catalyst		
	100 °C	200 °C	300 °C
Pd–La/Al_2O_3	0.0597	0.0455	0.0434
Pd–La/$MgAl_2O_4$	0.0487	0.0278	0.0165

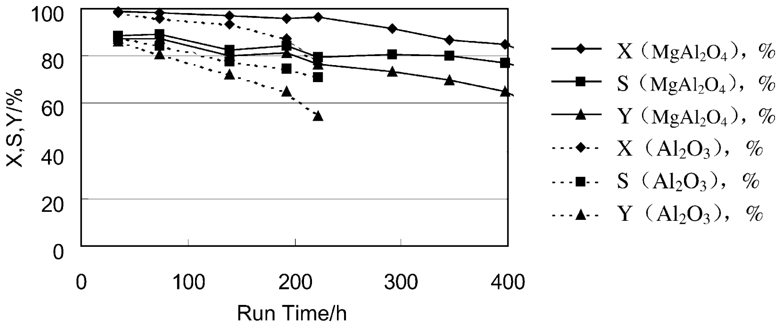


Fig. 4. Performance of palladium–lanthanum catalyst supported on different supports. Reaction conditions: $T = 220\,°C$, $P = 1.5\,MPa$, $LHSV = 0.3\,h^{-1}$, $GHSV = 150\,h^{-1}$, NH_3/2,6-DIPP (mol) = 10, H_2/DIPP (mol) = 20.

the Pd–La/$MgAl_2O_4$ catalyst, the highest conversion of 2,6-DIPP was 98.5%, the highest selectivity and the highest yield of 2,6-DIPA was 88.9%and 87.5% respectively at 73 h. The whole run time of Pd–La/$MgAl_2O_4$ catalyst was up to 400 h, and the yield of 2,6-DIPA after 200 h reaction was still more than 80%.

Compared to the reported results in Ref. [2], our catalyst has similar yield of 2,6-DIPA under the LHSV 0.3 h^{-1} to that of the Ref. [2] under the LHSV 0.1 h^{-1}. Therefore, our catalyst has a relatively higher load carrying capacity. Furthermore, our catalyst has a relatively higher stability than Ref. [2].

4. Conclusions

The replacement of Al_2O_3 support with $MgAl_2O_4$ spinel in the palladium–lanthanum-supported catalyst not only neutralized some strong acid sites, but also transformed them into relatively weaker acid sites according the NH_3-TPD and pyridine-IR results. The XPS analysis showed that the $MgAl_2O_4$ spinel support improved the reduction of PdO. All these factors increased the catalytic performance for gas-phase amination of 2,6-DIPP. On the Pd–La/$MgAl_2O_4$ catalyst, under the LHSV 0.3 h^{-1}, the highest conversion of 2,6-DIPP was 98.5%, the highest selectivity and the highest yield of 2,6-DIPA was 88.9% and 87.5% respectively. The whole run time of Pd–La/$MgAl_2O_4$ catalyst was up to 400 h, and the yield of 2,6-DIPA after 200 h reaction was still more than 80%.

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