

Highly Selective Amination of *o*- and *p*-Alkyl Phenols over Pd/Al₂O₃-BaO

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A series of Pd-based catalysts were prepared and examined for the amination of 2,6-dimethylphenol in a fixed-bed reactor. The best results were obtained for Pd/Al₂O₃-BaO with a conversion of 99.89% and a selectivity of 91.16%. These catalysts were characterized using BET, XRD, XPS, TEM and NH₃-TPD. Doped BaO not only improved the dispersion of the Pd particles but also decreased the acidity of the catalyst, which remarkably enhanced the selectivity and stability of the catalyst. The generality of Pd/Al₂O₃-BaO for this kind of reaction was demonstrated by catalytic aminations of *o*- and *p*-alkyl phenols.

Key Words : Catalytic amination, Alkylanilines, Alkylphenols, Pd/Al₂O₃-BaO

Introduction

Alkylanilines are an important and large class of basic chemicals that are widely used in the manufacture of pesticides, dyestuffs, pharmaceuticals and textile additives. The traditional method for the synthesis of alkylanilines is the nitration-reduction of arenes¹⁻⁵ which is undesirable for environmental reasons so it has gradually been replaced by the catalytic amination of phenols. Pd based catalysts, such as Pd/spinel and Pd/Al₂O₃,⁶⁻¹⁴ have been studied and employed for the catalytic amination of phenols. Some positive results have been reported for this method, especially in the catalytic amination of 2,6-dimethylphenol (DMP) to 2,6-dimethylaniline (DMA).⁷⁻¹¹ However, the catalyst life, reaction selectivity and the general applicability of the method still require further improvement. In this work, Pd/Al₂O₃ was modified by adding a series of metallic oxides. The modified Pd/Al₂O₃ catalysts were then evaluated and the most satisfied catalytic performance was exhibited by Pd/Al₂O₃-BaO. The effects of BaO doped in Pd/Al₂O₃ were studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), NH₃-temperature programmed desorption (NH₃-TPD) and BET. The lifetime of the catalyst was determined and the catalyst was employed to catalyze aminations of a series of *o*- and *p*-alkyl phenols.

Experimental

Materials and Catalysts. Pseudo-boehmite was purchased from Jiangyan Chemical Auxiliary Factory (Jiangyan, China). All the commercially available reagents and solvents were used without further purification.

The Al₂O₃ carrier was prepared by kneading pseudo-boehmite with 2% nitric acid. A mixture of Al₂O₃ (80 wt %)-MO_x (20 wt %, MO_x = MgO, CaO, ZnO, Cr₂O₃, SrO, BaO

or TiO₂) was obtained by kneading pseudo-boehmite and the corresponding metallic hydroxide or metallic oxide with 2% nitric acid. Next the mixture was molded into a bar by an extruder, followed by drying at 120 °C for 6 h and then calcining at 900 °C for another 6 h. Pd/Al₂O₃-MO_x with 0.50 wt % Pd was prepared by impregnating Pd precursor (Pd(NO₃)₂ dissolved in a 10 wt % HNO₃ solution) into the Al₂O₃-MO_x support. The resulting mixture was, dried at 120 °C for 6 h and then calcined at 520 °C for 2 h. Prior to use, these catalysts were activated in a stream of hydrogen at various programmed temperatures⁹: 180 °C for 4 h, 200 °C for 2 h, 220 °C for 2 h.

General Procedure for the Catalytic Amination of Alkylphenols. All aminations were performed in a fixed-bed reactor with an inner diameter of 15 mm and length of 1100 mm. The reactor was charged with 18.0 g of catalyst in an atmosphere of hydrogen and ammonia both at atmospheric pressures. For example, the catalytic amination of DMP was carried out over Pd/Al₂O₃-BaO with a 75 wt % solution of DMP in 1,4-dioxane being dosed into the reactor at a speed of 0.05 mL/min with a syringe pump. Hydrogen and ammonia were introduced into the reactor at rates of 160 and 80 mL/min, respectively. The temperature in the reaction zone was measured by a thermocouple located in the center of the tube and the thermocouple was connected to a Proportion Integration Differentiation (PID) cascade controller. The reaction mixtures were analyzed with Gas Chromatography-Mass Spectrometer (GC-MS) using a 30 m SE-54 capillary column.

Catalyst Characterization. The actual weight percent of Pd in each catalyst was determined by an ICP-AES instrument. 1.0 g sample of each catalyst was weighed, and then dissolved in 10 mL aqua regia (a mixture (3 + 1) of concentrated HCl and HNO₃) by microwave dissolver. The solution was diluted to 500 mL in a volumetric flask. Successively, the prepared solution was measured for three times under

Table 1. The characterized results of palladium in Pd/Al₂O₃-MO_x from ICP-AES, TEM, XPS

Catalyst	Pd ^a (wt %)	Particle size ^b (nm)	Binding energy ^c (eV)
Pd/Al ₂ O ₃	0.48	7.8 ± 2.3	335.4
Pd/Al ₂ O ₃ -ZnO	0.48	10.1 ± 3.6	335.8
Pd/Al ₂ O ₃ -TiO ₂	0.47	8.6 ± 2.9	335.6
Pd/Al ₂ O ₃ -Cr ₂ O ₃	0.49	8.3 ± 3.1	335.5
Pd/Al ₂ O ₃ -MgO	0.47	6.2 ± 1.3	335.3
Pd/Al ₂ O ₃ -CaO	0.48	6.7 ± 2.5	335.2
Pd/Al ₂ O ₃ -SrO	0.46	4.1 ± 1.1	335.1
Pd/Al ₂ O ₃ -BaO	0.47	3.4 ± 1.2	335.0

^awt % of palladium is measured by ICP-AES. ^bParticle size of palladium is derived from TEM. ^cBinding energy of palladium is characterized by XPS.

instrumental operating conditions and measuring parameters.¹⁵ Finally, the actual weight percent of palladium in each catalyst is calculated by the equation:

$$P = \frac{\bar{M} \times 500 \text{ mL}/1000}{C \times 000} \times 100$$

P is the actual weight percent of palladium in each catalyst, \bar{M} is the average analytical concentration of palladium (mg/L), C is the weight value of catalyst (g), 500 mL is the volume of the prepared solution.

The XRD patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu-K α radiation (40 kV, 100 mA) in the range of 10-90°. XPS measurements were recorded with a PHI 1600 spectrometer using a Mg-K α X-ray excitation source (1486.6 eV, 15 kV, 400 W). The binding energy was referenced to the C 1s binding energy at 284.5 eV with an error of ± 0.2 eV. TEM micrographs were obtained with a Tecnai G2 F20 high-resolution analytical electron microscope operating at an electron beam voltage of 200 kV. An energy dispersive X-ray (EDX) analyzer was used for elemental analysis using a Schottky 00 microanalysis. Powder samples were dispersed onto a carbon-coated copper grid for TEM/EDS analysis. NH₃-TPD was carried out on a TP-5000 instrument with a thermal conductivity detector (TCD). The BET specific surface area and pore size measurements were performed by adsorption/desorption of N₂ on a ZXF-06 automatic surface analyzer. Therein, the characterized results from ICP-AES, TEM, XPS were summarized in Table 1.

Results and Discussion

Catalyst Selection. Palladium has been shown to be effective for the amination of phenols.⁶⁻¹⁴ So Pd/Al₂O₃ was prepared and employed for the amination of DMP. The catalytic activity of Pd/Al₂O₃ decreased quickly with time-on-stream; the conversion of DMP decreased from 83.58 to 35.42% in 20 h (Fig. 1a).

Metallic oxides are known to improve the catalytic performance of Pd/Al₂O₃.¹¹⁻¹⁴ Thus, a series of metallic oxides, such as ZnO, TiO₂, Cr₂O₃, MgO, CaO, SrO and BaO

Table 2. Amination of DMP over Pd/Al₂O₃ and different modified catalysts

Catalyst	Conv. %	Select. %				
		<i>m</i> -xylene	DMCN ^a	DMCL ^b	DMCA ^c	DMA
Pd/Al ₂ O ₃	83.58	10.04	0.57	1.03	8.52	79.56
Pd/Al ₂ O ₃ -ZnO	71.51	12.80	0.22	1.58	6.37	78.49
Pd/Al ₂ O ₃ -TiO ₂	78.13	11.32	0.33	1.26	6.75	80.20
Pd/Al ₂ O ₃ -Cr ₂ O ₃	81.15	9.56	0.71	1.31	7.68	80.62
Pd/Al ₂ O ₃ -MgO	85.74	7.04	0.68	1.04	8.17	82.78
Pd/Al ₂ O ₃ -CaO	84.04	4.76	0.82	0.81	8.38	85.01
Pd/Al ₂ O ₃ -SrO	95.67	2.59	0.54	0.36	8.71	87.59
Pd/Al ₂ O ₃ -BaO	99.89	0.51	0.18	0.13	7.89	91.16

Reaction conditions: 230 °C, 160 mL/min (H₂), 80 mL/min (NH₃), 0.05 mL/min (75 wt % DMP in 1,4-dioxane). ^aDMCN, 2,6-dimethylcyclohexanone. ^bDMCL, 2,6-dimethylcyclohexanol. ^cDMCA, 2,6-dimethylcyclohexylamine.

were introduced into Pd/Al₂O₃. The prepared catalysts were examined for the amination of DMP, and the results are summarized in Table 2. Pd/Al₂O₃-BaO exhibits the best catalytic conversion and selectivity for the amination and effectively inhibits the formation of *m*-xylene.

The reaction parameters, including reaction temperature and the flow rates of hydrogen and ammonia, were optimized. The optimum conditions were 230 °C and flow rates of

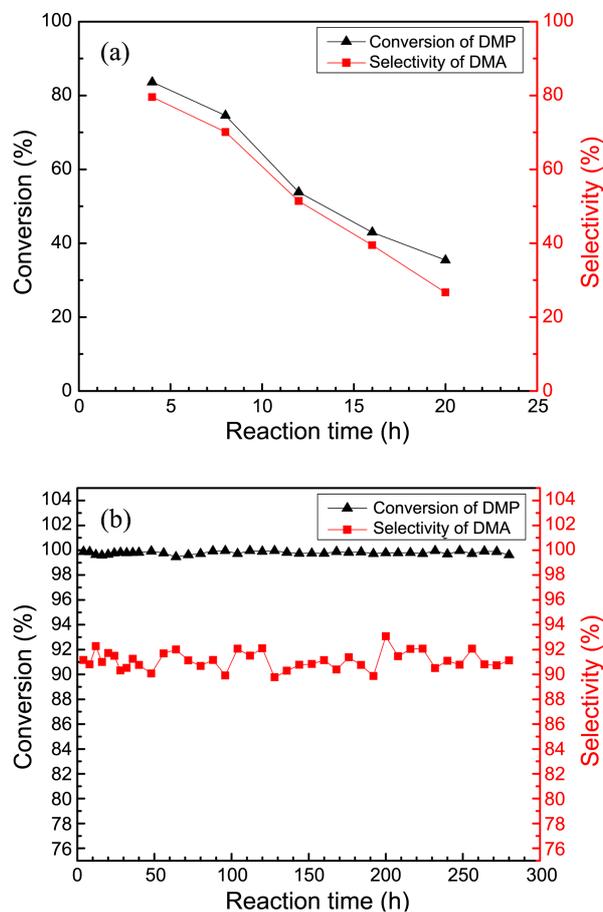
**Figure 1.** Service life of (a) Pd/Al₂O₃ and (b) Pd/Al₂O₃-BaO.

Table 3. The BET results for Pd/Al₂O₃-MO_x

Catalyst	S _{BET} ^a (m ² /g)	V _p ^b (cm ³ /g)	D _p ^c (nm)
Pd/Al ₂ O ₃	145.2	0.44	12.15
Pd/Al ₂ O ₃ -ZnO	77.4	0.37	16.07
Pd/Al ₂ O ₃ -TiO ₂	110.4	0.39	14.29
Pd/Al ₂ O ₃ -Cr ₂ O ₃	139.6	0.67	19.25
Pd/Al ₂ O ₃ -MgO	167.0	0.58	13.80
Pd/Al ₂ O ₃ -CaO	164.3	0.82	19.88
Pd/Al ₂ O ₃ -SrO	208.8	0.49	9.40
Pd/Al ₂ O ₃ -BaO	286.9	0.69	9.66

^aS_{BET}, The specific surface area. ^bV_p, Total pore volume. ^cD_p, Average pore diameter.

160 and 80 mL/min for hydrogen and ammonia respectively. Then the stability of Pd/Al₂O₃-BaO was examined under optimum reaction conditions for 280 h and the results are shown in Figure 1(b). During this period, the catalyst exhibited excellent stability. The conversion of DMP and selectivity for DMA remained around 99.9% and 91.2%, respectively. Therefore, Pd/Al₂O₃-BaO is an effective catalyst for the amination of DMP to DMA. In order to study the effects of BaO species on the Pd/Al₂O₃ catalyst, the catalysts were analyzed with BET, XRD, XPS, TEM and NH₃-TPD.

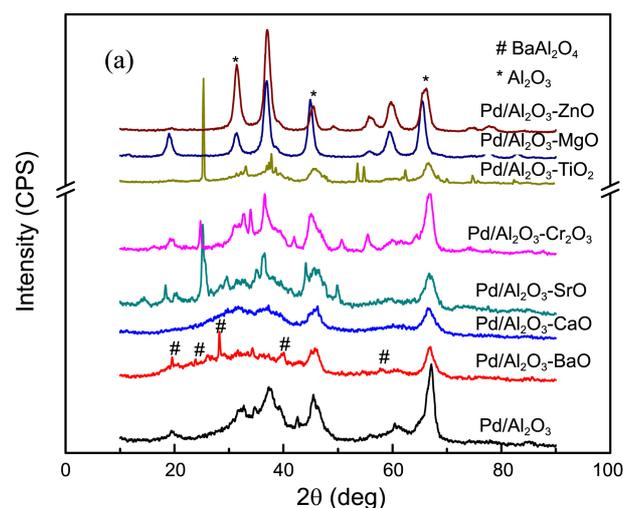
Reaction Conditions: 230 °C, 160 mL/min (H₂), 80 mL/min (NH₃), 0.05 mL/min (75 wt % DMP in 1,4-dioxane).

Characterization of Catalysts.

Textural and Structural Properties of Catalysts: The specific surface areas and pore structural parameters of Pd/Al₂O₃-MO_x are summarized in Table 3. Compared with the results in Table 1, it is found that the Pd particle size is decreased with the increase of the specific surface areas of the catalysts. It implied that a higher specific surface area of the catalyst resulted in a better dispersion of Pd particles, which could cause a preferable activity. The conclusion is proved by the results in Table 2, therein, Pd/Al₂O₃-BaO shows the best catalytic activity. The similar phenomenon was also reported in some other literatures.^{16,17}

XRD: The XRD curves for Pd/Al₂O₃-MO_x are shown in Figure 2. Al₂O₃ phase are observed in all prepared catalysts. No visible Pd phase can be observed for all catalysts, indicating that the Pd was either well dispersed or had a low content on the supports. For BaO modified samples, the typical diffraction peaks at about 19.5°, 28.9°, 34.2°, 57.7° and 79.2° in the XRD pattern of Pd/Al₂O₃-BaO can be assigned to BaAl₂O₄, which is formed by the interaction of BaO and Al₂O₃.^{18,19}

XPS: As shown in Table 1, the binding energy (BE) values of Pd 3d_{5/2} in all prepared catalysts at about 335.0-335.8 eV are assigned to the Pd⁰ species. Compared with Pd/Al₂O₃, the addition of ZnO makes the Pd 3d peaks shift to higher BE value by 0.4 eV, while the doping of BaO makes them shift to lower BE by 0.4 eV. The reason for the lower binding energy of Pd/Al₂O₃-BaO may be that there is a better dispersion of Pd⁰ or there is an interaction between Pd and Ba.²⁰⁻²² The binding energy of Ba 3d_{5/2} is at 780.5 eV (Fig. 3(e)) and reveals that Ba exists mainly as BaAl₂O₄,

**Figure 2.** XRD curves for Pd/Al₂O₃-MO_x.

which is in agreement with the XRD measurements.

Additionally, in order to investigate the deactivation reasons of Pd/Al₂O₃, XPS was also used to characterize the fresh and used Pd/Al₂O₃, Pd/Al₂O₃-BaO (shown in Figure 3(a), (b), (c) and (d)). Compared with the fresh Pd/Al₂O₃ catalyst (Fig. 3(a)), a new XPS peak at 398.2 eV is found on the used catalyst (the deactivated Pd/Al₂O₃, Fig. 3(b), (f)), which is attributed to high molecular polymer containing nitrogenous. It can be generated by the amino-compounds strongly adsorbed on the surface of Pd/Al₂O₃, leading to Pd/Al₂O₃ deactivation.¹³ Contrarily, no obvious change is observed on the surface properties of the fresh and used Pd/Al₂O₃-BaO (Fig. 3(c), (d)). It is clearly demonstrated that addition of BaO favored the adsorption-desorption equilibrium of the reactant and products, and improved the catalytic properties of Pd/Al₂O₃.

TEM: In order to study the morphology and size of the metal particles distributed over the fresh and used Pd/Al₂O₃, Pd/Al₂O₃-BaO, TEM was performed on the catalysts and the results are shown in Figure 4. The EDX spectrum shows that the Pd crystals are spherical or elliptical in shape. The mean particle diameter of Pd crystals in the fresh Pd/Al₂O₃ (Fig. 4(a)) is 7.8 nm while 3.4 nm in the fresh Pd/Al₂O₃-BaO (Fig. 4(b)). Furthermore, the standard deviation value of the Pd particles in the fresh Pd/Al₂O₃ is ± 2.3, and this value of the Pd particles is ± 1.2 in the fresh Pd/Al₂O₃-BaO. Therefore, it can be concluded that the Pd crystals in the fresh Pd/Al₂O₃-BaO are better dispersed and have a narrower particle-size distribution. This explains why the activity of Pd/Al₂O₃-BaO was much better than that of Pd/Al₂O₃. In addition, TEM micrograph of the deactivated Pd/Al₂O₃ catalyst (Fig. 4(c)) also provides clear evidence of carbon formation during the amination of DMP to DMA. It is also noted that the mean particle diameter of Pd crystals in the deactivated Pd/Al₂O₃ is enlarged to 9.1 nm. As shown in Figure 4(d), no carbon formation is observed on the surface of the used Pd/Al₂O₃-BaO. Meanwhile, the mean metal particle size of this catalyst has no changes after reaction. Apparently, the introduction of BaO into Pd/Al₂O₃ would effectively inhibit the formation

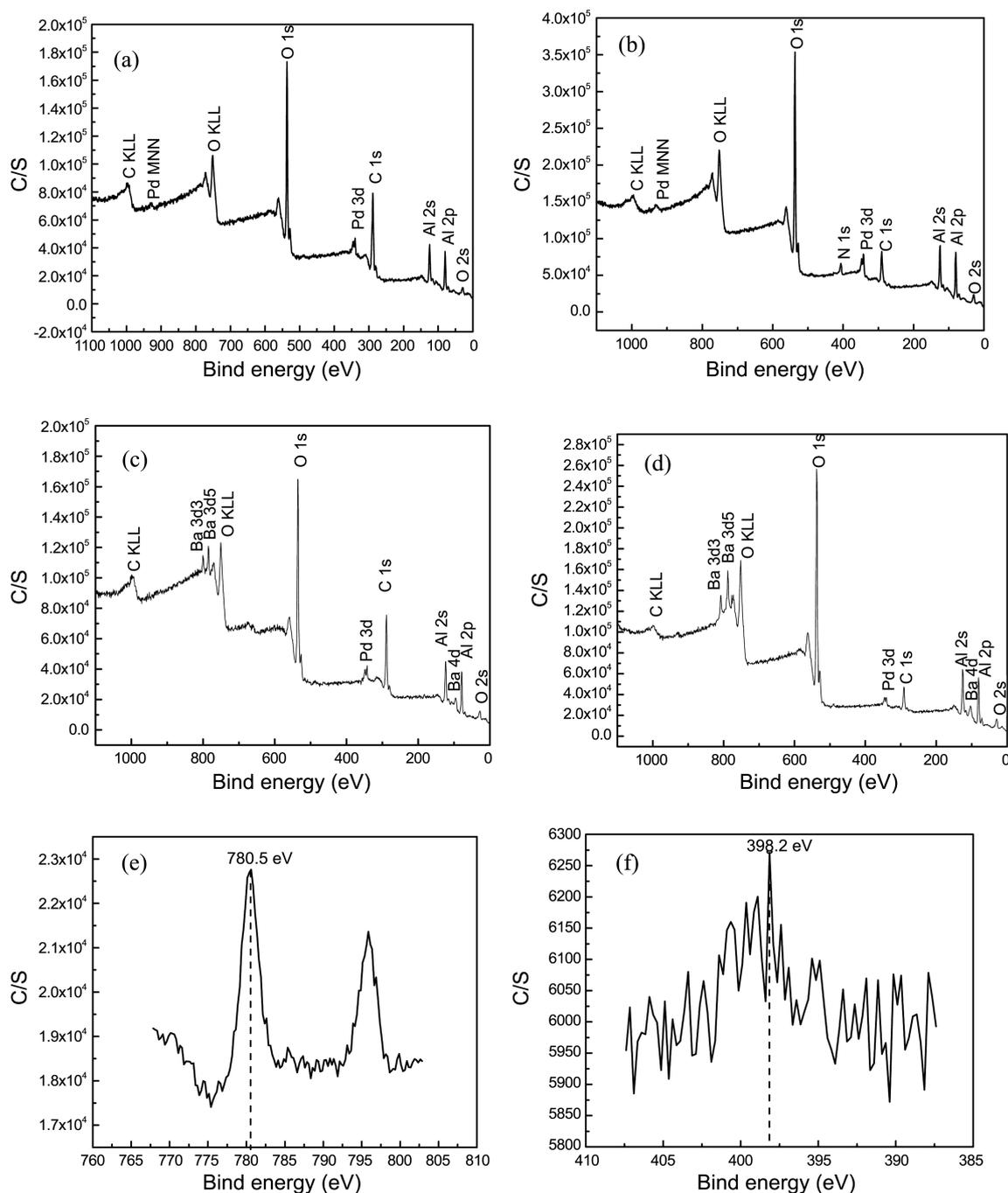


Figure 3. XPS spectra of (a) the fresh Pd/Al₂O₃, (b) the deactivated Pd/Al₂O₃, (c) the fresh Pd/Al₂O₃-BaO, (d) the used Pd/Al₂O₃-BaO, (e) Ba3d XPS spectra of Pd/Al₂O₃-BaO and (f) N1s XPS spectra of the deactivated Pd/Al₂O₃.

of coke and sintering of Pd crystals, which can result in the long lifetime of Pd/Al₂O₃-BaO.

NH₃-TPD: Next NH₃-TPD was used to measure the amount and strength of acid in the catalysts. The TPD curves of Pd/Al₂O₃ and Pd/Al₂O₃-BaO are shown in Figure 5. Both curves can be divided into two peaks using the Gauss curve fitting method. The two desorption peaks at the lower temperature (231-250 °C) and the higher temperature (333-370 °C) correspond to the weak and strong acid sites on the catalyst surfaces, respectively.²³ Normally, the area of a specific peak can be used to estimate the amount of ammonia

desorbed from a sample, and it can be used as a standard to quantify the acidity of the sample.²⁴ Obviously, the peak temperatures for Pd/Al₂O₃-BaO are lower than the corresponding ones for Pd/Al₂O₃, which implies that the acid strength of Pd/Al₂O₃-BaO is weaker.²⁵ Further, the addition of BaO to Pd/Al₂O₃ led to a decrease in the peak area at high temperature, which indicates that the doped BaO efficiently neutralized the strong acid sites.

It has been reported that with a Pd/Al₂O₃ catalyst, phenols are preferentially hydrogenated to cyclohexanols which is attributed to the strong acidity of Pd/Al₂O₃.^{26,27} In this work,

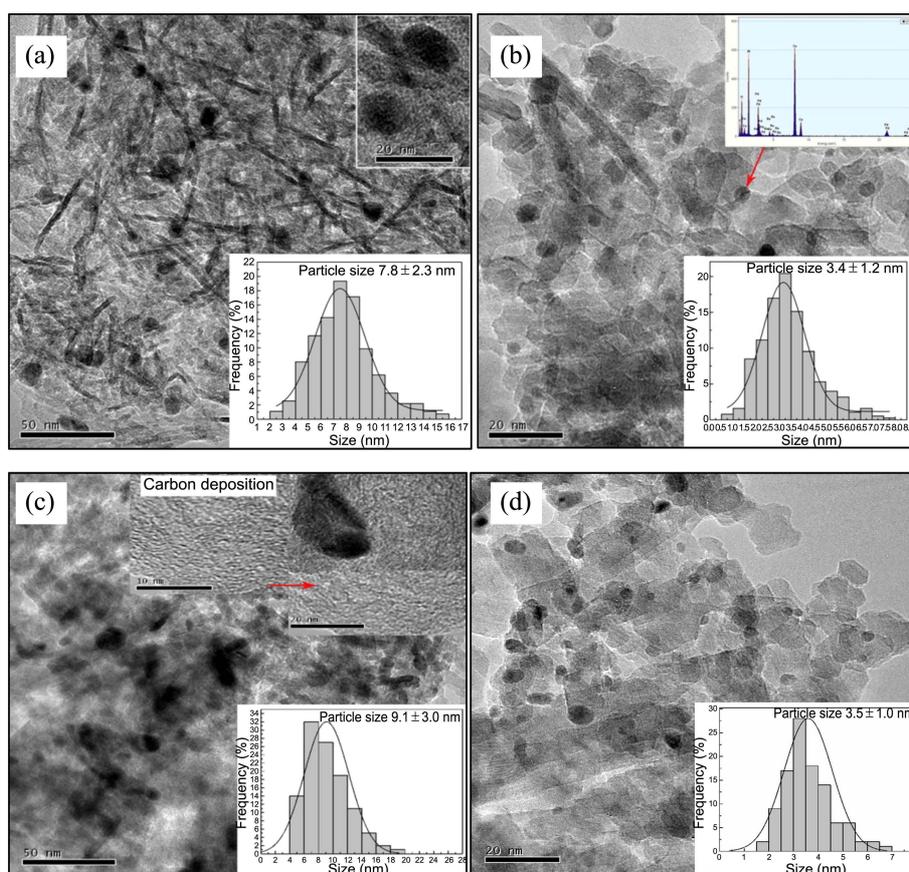


Figure 4. The TEM images, EDX spectra and size distribution histograms of (a) the fresh Pd/Al₂O₃, (c) the deactivated Pd/Al₂O₃, (b) the fresh Pd/Al₂O₃-BaO and (d) the used Pd/Al₂O₃-BaO.

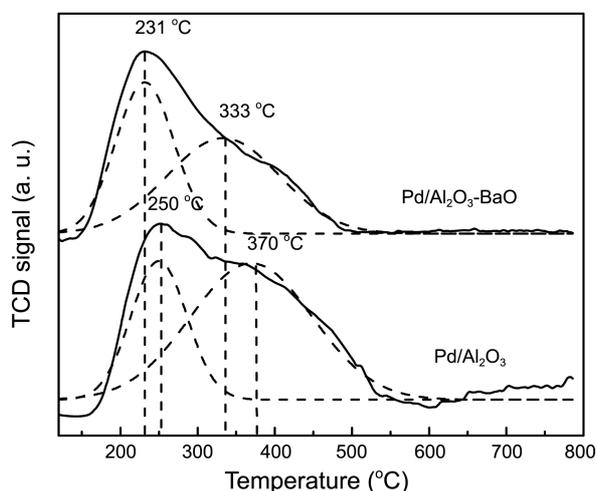


Figure 5. NH₃-TPD profiles of Pd/Al₂O₃ and Pd/Al₂O₃-BaO.

DMCL was formed with a selectivity of only 1.03% in the amination of DMP over Pd/Al₂O₃, whereas the selectivity for *m*-xylene was 10.04%. It can be deduced that the strong acidic sites in Pd/Al₂O₃ are helpful for the dehydration of DMCL, leading to a considerable amount of *m*-xylene. As expected, with the introduction of BaO to Pd/Al₂O₃, the selectivities for DMCL and *m*-xylene were significantly reduced to 0.13% and 0.51%, respectively. This implies that the addition of BaO dramatically decreased the acidity of

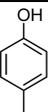
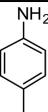
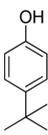
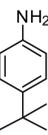
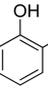
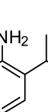
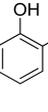
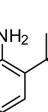
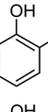
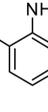
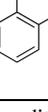
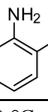
Pd/Al₂O₃, and effectively inhibited the formation of *m*-xylene, which is the reason why the selectivity for DMA increased sharply. Furthermore, the presence of BaO facilitated the desorption of the amino-compounds and inhibited carbon deposits on Pd/Al₂O₃-BaO,¹³ which could be responsible for the long lifetime of the catalyst.

Amination of *o*- or *p*-Alkyl Phenols. The above work proves that Pd/Al₂O₃-BaO is effective for the amination of DMP with ammonia. So, Pd/Al₂O₃-BaO was employed for the catalytic amination of various *o*- and *p*-alkyl phenols, and the results are summarized in Table 4.

The size, location and number of substituent groups on the phenol aromatic ring significantly influence the catalytic amination results. The aminations of single *p*-substituted phenols, such as *p*-methylphenol and *p*-*t*-butylphenol, proceeded effectively with excellent conversion and selectivity (Entries 1 and 2). A similar conversion but lower selectivity was obtained in the aminations of single *o*-substituted phenols, such as *o*-iso-propylphenol and *o*-*t*-butylphenol (Entries 3 and 4). For the double *o*-substituted phenol, 2-methyl-6-tertbutylaniline was obtained with a moderate yield from the corresponding phenol (Entry 6).

The above results indicate that the selectivity of alkylanilines is significantly affected by the size of the substituent groups. It appears that the Pd/Al₂O₃-BaO catalyst can be widely used in the catalytic amination of single *p*- or *o*-substituted phenols, and double *o*-substituted phenols with

Table 4. Catalytic amination of alkylphenols over Pd/Al₂O₃-BaO

Entry	Substrate	Product	Conv. %	Select. %	Yield. %	I.Y. ^a %
1			100	96.63	96.63	91.36
2			99.56	98.01	97.58	93.68
3			99.39	86.01	85.49	79.41
4			99.20	85.61	84.92	81.92
5			99.89	91.16	91.06	86.56
6			90.14	60.64	54.66	39.68

Reaction conditions: 230 °C, 160 mL/min (H₂), 80 mL/min (NH₃), 0.05 mL/min (75 wt % DMP in 1,4-dioxane). ^aIsolated yield (I.Y) is obtained by rectification.

small (sterically unhindered) substituent groups, such as DMA. Thus, a general catalyst for the catalytic amination of *p*- and *o*-alkyl phenols is confirmed.

Conclusions

The catalytic amination of 2,6-dimethylphenol with ammonia over a Pd/Al₂O₃-BaO catalyst in a fixed-bed reactor gave 2,6-dimethylaniline with a 91.06% yield. The active species for the reaction is believed to be Pd⁰. The doped BaO not only improved the dispersion of the Pd particles but also decreased the acidity of the catalyst, which remarkably enhanced its catalytic performance. The reaction parameters were optimized and the catalyst exhibited a long lifetime. Catalytic aminations of some *p*- and *o*-alkyl phenols were performed and the catalyst exhibited a general

applicability for this kind of reaction.

References

- Tafesh, A. M.; Weiguny, J. *Chem. Rev.* **1996**, *96*, 2035.
- Downing, R. S.; Kunkeler, P. J.; Bekkum, H. van. *Catal. Today.* **2004**, *37*, 121.
- Yu, C.; Liu, B.; Hu, L. *J. Org. Chem.* **2001**, *66*, 919.
- Borodkin, G. I.; Elanov, I. R.; Shubin, V. G. *Russ. J. Org. Chem.* **2009**, *45*, 934.
- Sreedhar, B.; Keerthi, D. D.; Yada, D. *Catal. Commun.* **2011**, *12*, 1009.
- Ono, Y.; Ishida, H. *J. Catal.* **1981**, *72*, 121.
- Norbert, G.; Peter, J.; Leopold, H.; Herbert, T.; Wolfgang, R. EP 53819, 1982.
- Norbert, G.; Leopold, H.; Wolfgang, F.; Wolfgang, R.; Wolfgang, K. EP 167996, 1986.
- Mannheim, U. K.; Kleinniedesheim, P. F.-F.; Heidelberg, M. I.; Frankenthal, J. W.-D.; Schifferstadt, M. H.; Weinheim, P. P. US 5663438, 1997.
- Liu, Z. L.; Liao, W. W.; Wang, Y.; Tan, W. N.; Chen, P. *Chin. Pestic. Intermediat.* **2006**, *200*.
- Mannheim, U. K.; Kleinniedesheim, P. F.-F.; Heidelberg, M. I.; Frankenthal, J. W.-D.; Schifferstadt, M. H.; Weinheim, P. P. US 5663438, 2008.
- Jiang, R. X.; Xie, Z. K.; Zhang, C. F.; Yang, Y. Q.; Chen, Q. L. *React. Kinet. Catal. Lett.* **2005**, *84*, 215.
- Jiang, R. X.; Xie, Z. K.; Zhang, C. F.; Chen, Q. L. *Appl. Catal. A Gen.* **2003**, *250*, 209.
- Jiang, R. X.; Xie, Z. K.; Zhang, C. F.; Chen, Q. L. *Catal. Today* **2004**, *93-95*, 359.
- Wang, S. P.; Zhang, G. L.; Ma, X. B. *Chin. Analysis. Lab.* **2008**, *27*, 282.
- Zhang, X. Y.; Long, E. Y.; Li, Y. L.; Zhang, L. J.; Guo, J. X.; Gong, M. C.; Chen, Y. Q. *J. Mol. Catal. A: Chem.* **2009**, *238*, 73.
- Pérez, Yolanda; Fajardo, Mariano; Corma Avelino. *Catal. Commun.* **2011**, *12*, 1074.
- Lin, Y.; Zhang, Z. T.; Tang, Z. L.; Zhang, J.; Zheng, Z. S.; Lu, X. *Mater. Chem. Phys.* **2001**, *70*, 156.
- Ravichandran, D.; Johnson, S. T.; Erdei, S.; Roy, R.; White, W. B. *Displays* **1999**, *19*, 197.
- Klingstedt, F.; Kalantar, K. H.; Neyestanaki, A.; Lindfors, L.-E.; Salmi, T.; Vayrynen, J. *J. Catal.* **2002**, *206*, 248.
- Zhang, X. Y.; Long, E. Y.; Li, Y. L.; Zhang, L. J.; Guo, J. X.; Gong, M. C.; Chen, Y. Q. *J. Mol. Catal. A Chem.* **2009**, *308*, 73.
- Kobayashi, T.; Yamada, T.; Kayano, K. *Appl. Catal. B Environ.* **2001**, *30*, 287.
- Yu, Ch. L.; Ge, Q.; Xu, H.; Li, W. *Appl. Catal. A Gen.* **2006**, *315*, 58.
- Ma, D.; Zhang, W. P.; Shu, Y. Y.; Liu, X. M.; Xu, Y. D.; Bao, X. H. *Catal. Lett.* **2000**, *66*, 155.
- Wang, H. L.; Xin, W. Y. *Catal. Lett.* **2001**, *76*, 3.
- Chary, K. V. R.; Seela, K. K.; Naresh, D.; Ramakanth, P. *Catal. Commun.* **2008**, *9*, 75.
- Scirè, S.; Minicò, S.; Crisafulli, C. *Appl. Catal. A Gen.* **2002**, *235*, 21.