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The Hydrogenation of Aromatic Compounds under Mild Conditions by Using a Solid Lewis Acid and Supported Palladium Catalyst

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Al₂O₃ or SiO₂ particles with abundant surface hydroxyl groups can prevent side reactions of aromatic compounds with AlCl₃ completely; this Lewis acid can potentially destroy the stable structure of aromatic compounds to a large extent. This discovery was successfully utilized in the highly efficient hydrogenation of benzene, toluene, and naphthalene under mild conditions co-catalyzed by AlCl₃ and Pd/Al₂O₃ or Pd/SiO₂. Pd, AlCl₃, and the surface hydroxyl groups on the support show excellent cooperative effects for the hydrogenation reactions. Theoretical studies indicate that formation of a complex, by an interaction between benzene, AlCl₃, and the solid oxides, plays a key role in the highly efficient hydrogenation reactions.

The transformation of aromatic compounds into value-added chemicals or high-quality fuels is a very important class of reactions.^[1] Usually, these reactions are carried out under harsh conditions because of the high stabilization energy caused by aromaticity.^[2] Lewis acid catalysts or co-catalysts have been widely used to improve the efficiency of many reactions.^[3] For example, in Friedel-Crafts reactions, substitution on aromatic rings proceeds effectively in the presence of Lewis acids.^[4] Benzene reacts with carbon monoxide to form benzoic acid or benzaldehyde in the presence of Lewis and Brønsted acids.^[5] Our previous work showed that, as a co-catalyst, Lewis acids such as AICl₃ could enhance both the reaction rate and selectivity of the hydrogenation of phenol to cyclohexanone significantly in dichloromethane or compressed CO₂ by using a Pd/C catalyst.^[6] Theoretical studies indicated that the Lewis acid interacts with one of the benzene carbon atoms, making the carbon atom highly nucleophilic, resulting in activation of the stable aromatic ring.^[7]

For aromatic compounds without a polar substituent on the aromatic ring, the activation effect of a weak Lewis acid is limited because of the very high stabilization energy that originates from the conjunction π effect. AlCl₃ is a strong Lewis

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acid, and is widely used as catalyst or co-catalyst in many reactions.^[5,8] However, simply using solid AlCl₃ can result in many undesired side reactions, in particular dehydrogenation condensation (called condensation hereafter) of aromatic compounds, known as the Scholl reaction.^[9] This side reaction limits the application of AlCl₃ for this class of compounds greatly. A viable strategy to solve this problem is the transformation of AlCl₃ into another form or the use of polar reaction media.^[10] A typical example is the hydrogenation of arenes under mild conditions cooperatively catalyzed by Pd/C and a Lewis acidic ionic liquid, [bmim][AlCl₄] (bmim=1-butyl-3methylimidazolium), in dichloroethane.^[11]

In many cases, direct use of solid AlCl₃ is highly desirable, and a method that inhibits the condensation reactions of the aromatic compounds is the key to reaching this goal. Herein, we report that Al₂O₃ and SiO₂ particles with surface hydroxyl groups can completely prevent the reactions of aromatic compounds (e.g., benzene, toluene, and naphthalene) that are initiated by AlCl₃, even though the stable structures of the aromatics are activated effectively. This discovery creates new opportunities for highly efficient transformations of nonpolar or weakly polar aromatic compounds under mild and solvent-free conditions. For example, this finding was used to realize the highly efficient hydrogenation of aromatic compounds under mild and solvent-free conditions by using commercial AICI_3 in combination with Pd/Al₂O₃ or Pd/SiO₂. Further experimental and theoretical studies indicated that the hydroxyl groups on the solid metal oxides play a critical role in the complete prevention of the side reactions.

We studied the effects of different solid particles on the reactions of benzene, toluene, and, naphthalene initiated by AlCl₃, and the results are given in Table 1. The results indicated that the substrates converted quickly in the absence of Al₂O₃ or SiO₂ solid particles. The transformations were completely prevented in the presence of Al₂O₃ or SiO₂, whereas the carbon additive (Vulcan XC-72R, Cabot Co.) did not inhibit the reaction effectively. A photograph of benzene after the reaction is shown in Figure S1. Without the addition of Al₂O₃ or SiO₂, the reaction mixture quickly turned to a dark color. On the contrary, the appearance of the reaction mixture did not change in the presence of Al₂O₃ or SiO₂. This observation is consistent with the results from gas-chromatography (GC) analysis in Table 1. The product of the experiment detailed in Table 1 entry 4 was analyzed by GC-MS, and some biphenyl compounds were identified (see the Supporting Information), confirming the occurrence of the Scholl reaction.^[9] It should be

Table 1. Effect of solid particles on the reaction of arenes initiated by $AICI_{3}^{[a]}$						
Entry	Substrates	Additives	Converted aromatics [%] ^[b]			
1	benzene	-	10.6			
2	benzene	AI_2O_3	0			
3	benzene	SiO ₂	0			
4	benzene	Vulcan XC-72R	10.1			
5	toluene	-	15.7			
6	toluene	AI_2O_3	0			
7	toluene	Vulcan XC-72R	15.0			
8	naphthalene ^[c]	-	35.5			
9	naphthalene ^[c]	AI_2O_3	0			
10	naphthalene ^[c]	Vulcan XC-72R	33.8			

[a] Reaction conditions: substrate (2 mL), AlCl₃ (2 mol% of the substrate), additive (0.4 g), 30 °C, 300 min. [b] The products of the reactions initiated by AlCl₃ were complex mixtures. [c] The reactions were conducted in dichloromethane because the neat substrate is solid. Reaction conditions: naphthalene (0.3 g), dichloromethane (2 mL), AlCl₃ (10 mol% of substrate), additive (0.2 g), 30 °C, 60 min.

emphasized that some compounds could not be identified because their molecular weight or boiling point was too high for GC-MS analysis.

Pd catalysts possesses some obvious advantages, such as simple preparation methods, high stability in air (up to $700 \,^{\circ}\text{C}$,^[12] and excellent activity. These catalysts are widely used in many different reactions, including hydrogenation.^[13] However, Pd catalysts are almost inactive for the hydrogenation of aromatic compounds at low temperature.^[6, 14] To demonstrate the application of the above finding, we carried out the hydrogenation of arenes by using Pd nanocatalysts in the presence of a Lewis acid. Pd/Al_2O_3 , Pd/SiO_2 , and Pd/C were adopted as the catalysts and the reactions were conducted with and without the addition of AICl₃. The IR spectra of the three catalysts are given in Figure S2, and illustrate that Al₂O₃ and SiO₂ in Pd/Al₂O₃ and Pd/SiO₂ have an abundance of hydroxyl groups on the surface, whereas Pd/C lacked hydroxyl groups. The density of the hydroxyl groups on the surface of Pd/Al₂O₃ and Pd/SiO₂, as determined by thermogravimetric analysis (TGA, see the Supporting Information),^[15] were 10.4 $OH\ nm^{-2}$ and 4.8 $OH\ nm^{-2},$ respectively. The size of the Pd nanoparticles in the Pd/Al₂O₃, Pd/SiO₂, and Pd/C catalysts were 3.2 nm, 3.0 nm, and 3.4 nm, respectively, as shown in Figure S3.

The results from the hydrogenation of benzene are presented in Table 2. The Pd/Al₂O₃, Pd/SiO₂, and Pd/C catalysts showed very low activity in the absence of AlCl₃ (Table 2, entries 1, 3, and 5). However, after the addition of the Lewis acid, these catalysts showed remarkably different behaviors in the reaction. AlCl₃ accelerated the hydrogenation of benzene to cyclohexane efficiently with Pd/Al₂O₃ or Pd/SiO₂ as the catalyst, and the selectivity of the reaction to provide the desired product, cyclohexane, was 100% (Table 2, entries 2 and 4) with a carbon balance of >99%. In contrast, when Pd/C was used as the catalyst, byproducts were produced after addition of AlCl₃ (Table 2, entry 6). This finding is consistent with the result reported by other researchers.^[11] The reason is that the carbon

Table 2. Catalytic performance of different catalysts with or without a Lewis $\operatorname{acid}^{\operatorname{[a]}}$						
Entry	Catalyst	Lewis acid	H ₂ [Mpa]	Time [min]	Conv. [%]	Yield ^[b] [%]
1	Pd/Al ₂ O ₃	-	1	320	2.1	2.1
2	Pd/Al_2O_3	AICI ₃	1	320	100	100
3	Pd/SiO ₂	-	1	400	2.0	2.0
4	Pd/SiO ₂	AICI ₃	1	400	100	100
5	Pd/C	-	1	300	2.3	2.3
6	Pd/C	AICI ₃	1	300	80.1	68.2 ^[c]
7	SiO ₂	-	1	400	0	0
8	SiO ₂	AICI ₃	1	400	0	0
9	-	AICI ₃	1	400	13.2	0
10	Pd/Al_2O_3	-	0.1	300	0	0
11	Pd/Al_2O_3	AICI ₃	0.1	300	20.6	20.6
12	Pd/Al_2O_3	AICI ₃	0.5	300	62.9	62.9
13	Pd/Al ₂ O ₃	AICI ₃	1	300	97.0	97.0
14 ^[d]	Pd/Al_2O_3	AICI ₃	1	300	100	53.0
[a] Reaction conditions: benzene (2 mL), catalyst Pd/Al ₂ O ₃ , Pd (1 mol% of						

[a] Reaction conditions: benzene (2 mL), catalyst Pd/Al₂O₃, Pd (1 mol% of benzene), AlCl₃ (2 mol% of benzene), 30 °C, H₂ pressure 1 MPa. [b] The yield of cyclohexane. [c] The selectivity towards cyclohexane was low because a large number of byproducts were formed. [d] AlCl₃ (20 mol% of benzene).

support could not prevent the formation of byproducts formed by Lewis acid catalyzed side reactions, such as the Scholl reaction.^[9] GC-MS analysis (see the Supporting Information) indicated that the reaction catalyzed by Pd/C–AlCl₃ (Table 2, entry 6) contained many byproducts, such as bicyclohexyl, cyclohexylbenzene, and 1,4-dicyclohexylbenzene.

The effect of various Lewis acids on the hydrogenation of benzene catalyzed by Pd/Al_2O_3 was investigated, and the results are shown in Figure 1. All of the Lewis acids tested pro-



Figure 1. Hydrogenation of benzene in the presence of various Lewis acids. The reaction conditions were the same as those in Table 2, entry 2.

moted the reaction and the selectivity towards cyclohexane was 100%. In general, the efficiency of the Lewis acids for the hydrogenation of benzene followed the order of $AlCl_3 \gg FeCl_3 > LaCl_3 > CrCl_3 > CeCl_3 > AlCl_3 \cdot 6H_2O > Cu(OTf)_2 > CrCl_2 > Sc(OTf)_3 > FeCl_2 > CuCl_2$ (OTf=triflate). Anhydrous $AlCl_3$ was much more efficient than all of the other Lewis acids, mainly

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because the benzene ring is very stable and only strong Lewis acids, such as $AICI_3$, can activate the aromatic ring.

Control experiments using SiO₂ (with and without AlCl₃) were also conducted (Table 2, entries 7 and 8), indicating that the reaction did not occur in the absence of Pd. Pure AlCl₃, in the absence of the supported Pd catalyst, did not catalyze the hydrogenation reaction, but instead lead to the formation of various byproducts owing to condensation reactions between the aromatic compounds (Table 2, entry 9). Further studies showed that AlCl_3 could accelerate the reaction effectively over a wide range of hydrogen pressures (Table 2, entries 10-13). The cyclohexane selectivity was 100% in all cases. Interestingly, 20.6% yield of product could be obtained in 300 min at ambient pressure (0.1 MPa, Table 2, entry 11), whereas the amount of product was negligible in the absence of the Lewis acid (Table 2, entry 10). The reaction rate increased on increasing the amount of Lewis acid (Table S1) or increasing the reaction temperature (Table S2), and the selectivity towards cyclohexane remained 100% for all reaction conditions. The reaction was proven to be catalyzed in a heterogeneous manner because the reaction did not proceed if the supported Pd catalyst was excluded during the middle of the reaction (Figure S4). Moreover, the reaction also proceeded smoothly if H₂ was replaced by D_2 [the product was confirmed as $C_6H_6D_6$ by ¹H NMR analysis (Figure S5)], indicating that the H atoms of the hydroxyl groups on the support are not the hydrogen source in the hydrogenation reaction.

The hydrogenation of toluene and naphthalene was also performed in the presence of $AlCl_3$ under mild conditions by using Pd/Al₂O₃ as the catalyst; the results are listed in Table 3.

Table 3. Hydrogenation of different arenes						
Entry	Substrate	Lewis acid	Time [min]	Product	Conv. [%]	Selectivity [%]
1 ^[a] 2 3		– AICI₃ AICI₃	300 300 550	\frown	3.0 60.2 100	100 100 100
4 ^[b] 5 6		– AICI₃ AICI₃	60 30 60		0.3 52.8 100	100 100 99.9 ^[c]
[a] Hydrogenation of toluene: toluene (2 mL), catalyst Pd/Al ₂ O ₃ (1 mol%), AlCl ₃ (2 mol% of toluene), 30 °C, H ₂ pressure 1 MPa. [b] Hydrogenation of naphthalene: substrate (1 mmol), catalyst Pd/Al ₂ O ₃ (5 mol%), AlCl ₃ (10 mol% of naphthalene), dichloromethane (2 mL), 30 °C, H ₂ pressure 1 MPa. [c] 0.1% decalin, which is the product of complete hydrogenation of naphthalene was obtained. For all the reactions, the carbon balance was >99%.						

For all of the reactions studied, there was no byproduct, showing that the Al_2O_3 -supported catalyst could inhibit side reactions completely. $AlCl_3$ could also accelerate the reactions significantly. Toluene was hydrogenated to methylcyclohexane with 100% selectivity. Compared with the reactivity in the absence of $AlCl_3$, the hydrogenation reactivity increased more than twenty-fold on the addition of $AlCl_3$ (Table 3, entries 1–3). For the hydrogenation of naphthalene, the reaction rate in the presence of the Lewis acid was 333 times higher than that without the Lewis acid (Table 3, entries 4–6); naphthalene was selectively hydrogenated to tetralin, which is an important intermediate in chemical industry.

The experimental results described above clearly demonstrate that $AlCl_3$, Pd, and the support with abundant surface hydroxyl groups (Al_2O_3 or SiO_2) display excellent cooperative effects to promote hydrogenation reactions. $AlCl_3$ accelerated the hydrogenation catalyzed by Pd significantly, while Al_2O_3 or SiO_2 inhibited the side reaction initiated by $AlCl_3$.

To study the mechanism of the effect of the Lewis acid and the influence of the surface hydroxyl groups on the reaction, we used density functional theory (DFT)^[16] to perform ab initio calculations in a similar manner to that previously described.^[17] The theoretical calculations employed the Becke's three parameterized Lee–Yang–Parr exchange correlation functional (B3LYP)^[18] with 6-31 + +G(d,p) basis sets.^[19] All of the calculations were performed with the Gaussian 09 package.^[20]

Theoretical calculations revealed that there is a strong interaction between benzene and AlCl₃ that forms a σ complex, benzene–AlCl₃ ($\Delta H_1 = -5.1 \text{ kcal mol}^{-1}$). The optimized structure is shown in Figure 2a, and is similar to that reported previous-



Figure 2. The optimized structures of a) benzene–AlCl₃ complex; b) charge distribution of the benzene ring in (a); c) benzene–AlCl₃–H₇Si₈O₁₂(OH) complex; d) charge distribution of the benzene ring in (c).

ly.^[7] This interaction leads to the uneven distribution of the charge on the benzene ring (Figure 2b). The charge density on the carbon atom (C1) closest to the Al atom is higher than that on the other carbon atoms, and a partial positive charge was induced at the carbon atom (C4) in the *para* position. However, the benzene molecules activated by $AlCl_3$ react easily with each other to form oligomers, mainly by the Scholl reaction.^[21]

We also conducted calculations to elucidate the influence of the surface hydroxyl groups of SiO₂ on the reaction. The unit $H_7Si_8O_{12}(OH)$ was used to represent SiO₂. This unit is commonly used as the model for SiO₂ in theoretical calculations.^[22] Various

structures for the interaction between benzene, AlCl₃, and SiO₂ were studied. It was found that the formation enthalpy (ΔH_2) of the complex benzene–AlCl₃–H₇Si₈O₁₂(OH) shown in Figure 2 c is -9.1 kcalmol⁻¹. In the complex, there are hydrogen bonds between a Cl atom (Cl1) of AlCl₃ and a H atom (H7) of an OH group of SiO₂ (Cl···H–O), and between a H atom (H1) of benzene and a O atom (O1) of an OH group of SiO₂ (H···O–H). Importantly, the formation of the complex also results in an uneven distribution of charges in the benzene ring, as shown in Figure 2 d. This is favorable for the hydrogenation of benzene because the stable structure of the benzene is destroyed.

On the basis of the above discussion, we propose a possible mechanism for the excellent cooperative effect of AICl₃ and Pd nanocatalysts on supports with abundant surface hydroxyl groups for the hydrogenation of aromatic compounds. This proposed mechanism is discussed by using benzene as an example. Firstly, the Lewis acid interacts with the benzene ring, leading to an uneven charge distribution over the benzene ring and making the aromatic ring more active. The Pd species is responsible for the activation of molecular hydrogen by dissociative adsorption,^[23] the H⁺/H⁻ pair resulting from the heterolytic cleavage of H₂ transfers to the polarized aromatic ring and the hydrogenation reaction occurs. These two effects work together to make the hydrogenation of benzene proceed smoothly. The surface hydroxyl groups play an important role in enhancing the selectivity of the reaction and preventing undesired reaction pathways.^[24] The hydroxyl groups prevent the side reactions initiated by Lewis acids in two ways. Firstly, for the formation of the structure shown in Figure 2c the amount of hydroxyl-group functionality needs to be much larger than that of AlCl₃. Hence, all of the AlCl₃ in the reaction system is bound on the support. Thus, the AlCl₃-activated benzene molecules are also bound on the solid particles, preventing efficient collision between AlCl3-activated benzene molecules for the Scholl reaction. Secondly, once a benzene molecule is activated it can be hydrogenated quickly because it is close to the Pd nanocatalysts on the surface of the support. Therefore, the Scholl reaction, or other side reactions, between benzene molecules is prohibited. To provide further evidence to support this argument, we carried out the reaction with an excess amount of AlCl₃ (Table 2, entry 14), so that free AlCl₃ existed in the reaction system. The results indicated that the byproduct was formed under these conditions.

In conclusion, it has been found that Al₂O₃ or SiO₂ solid oxide particles that have abundant surface hydroxyl groups can prevent undesirable reactions in benzene–AlCl₃, toluene– AlCl₃, and naphthalene–AlCl₃ mixtures, whereas the aromatic compounds condensed quickly to form oligomers in the absence of the solid oxide particles. Further studies showed that AlCl₃ can promote hydrogenation of the aromatic compounds, catalyzed by Pd/SiO₂ or Pd/Al₂O₃, very efficiently under mild and solvent-free conditions without forming any byproduct. The hydrogenation reactions catalyzed by Pd/C produce a large number of byproducts from side reactions owing to the lack of surface hydroxyl groups on the carbon support. DFT studies indicated that AlCl₃ interacts with benzene, making the benzene ring much more active. At the same time, benzene, AlCl₃, and the hydroxyl groups on the catalyst support form a complex, through hydrogen bonding, which prevents the side reactions. We believe that the excellent cooperative effect between AlCl₃ and the supports with surface hydroxyl groups provides new opportunities for the highly efficient transformation of nonpolar or weakly polar aromatic compounds under mild and solvent-free conditions.

Experimental Section

The chemicals used, the procedures for catalyst preparation, and the characterization details are described in the Supporting Information.

The reactions were performed in a 15 mL Teflon-lined stainlesssteel autoclave equipped with a magnetic stirrer. In a typical experiment, reactant, catalyst, Lewis acid, and solvent (if used) were loaded into the reactor. The autoclave was sealed and purged with hydrogen several times to remove the air at 0°C. The reactor was then placed into a water bath at the desired temperature. Hydrogen was introduced into the reactor after the desired temperature was reached and the stirrer was started with a rate of 400 rpm. After the reaction, the autoclave was cooled in ice water and the H₂ in the reactor was released. Then an internal standard (n-octane or *n*-decane, depending on the reactant) was added into the reactor. The product was analyzed by gas chromatography (Agilent 4890, equipped with HP-INNOWax capillary column and an FID). Identification of the products and reactant was achieved by GC-MS (SHIMADZU-QP2010, equipped with DB-5ms capillary column) analysis as well as by comparison of the retention times of the standards in the GC traces. The conversion and selectivity were calculated from the GC data.

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Keywords: arenes • hydrogenation • Lewis acids • palladium • surface hydroxyl groups

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