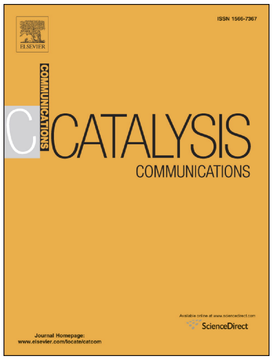

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Atomic Layer Deposition of Aluminium on Anatase: A Solid Acid Catalyst with Remarkable Performances for Alcohol Dehydration

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Notes

The authors declare no competing financial interest.

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Abstract: Here we reported the synthesis of Al sites with ultra-high dispersion on anatase by an atomic layer deposition (ALD) method (ALD-Al/TiO_2), which exhibits Brønsted acidity and satisfactory activity in the dehydration of alcohols, a key step in the deoxygenation of biomass. More importantly, the ALD-Al/TiO_2 catalyst has good stability, which is sintering-resistant and gives constant catalytic performances after treatments at high temperature.

Keywords: biomass • atomic layer deposition • solid acid catalyst • dehydration

1. Introduction

Biomass, which is regarded as renewable energy source, has attracted much attention for producing alternative fuels and fine chemicals [1-4]. Compared with crude oil, the biomass has high oxygen content, which makes it difficult for directly using the biomass to partly replace the crude oil feedstocks [5-7]. In order to solve this problem, upgrading the biomass-based molecules by deoxygenation is critically important [8-10]. In the deoxygenation process with multiple steps, the acid catalysts are generally necessary for the cleavage of carbon-oxygen bonds, a key step for the deoxygenation [11-16]. Therefore, synthesizing efficient acid catalyst is of great importance for the deoxygenation of biomass-based molecules.

Many homogeneous acids (e.g. H_2SO_4, HCl) are regarded as active catalysts for the deoxygenation, but their homogeneous feature creates difficulty in separation and regeneration from the reaction system [17-20]. Additionally, the corrosivity of these acids also leads high-cost and environmentally unfriendly problems. The heterogeneous acids could easily solve the problems of catalyst separation, exhibiting significant advantages compared with the homogeneous ones. Particularly, the acidic resins, which are synthesized by functionalizing acidic groups (e.g. $-SO_3H$) on the mesoporous organic polymers, are attractive because of their Brønsted acidity and high activity for conversion of bulky molecules. However, the low stability of acidic resins limited their wide application, especially for the reactions of high temperature [21-23]. Aluminosilicate zeolites with highly dispersed Al atoms in the silica framework (e.g. as ZSM-5, Y and Beta), which have significantly higher stability than the resins, are regarded as one of the most promising catalysts for biomass deoxygenation. [24] Nevertheless, for the reaction at high temperature (>200 °C) in water solvent, the stability of most aluminosilicate zeolites is still unsatisfactory, the Si-O-Al linkage in the zeolite framework could be destroyed, leading to lose of acid sites [11]. Additionally, the small micropore size of zeolite also limited their application in the conversion of bulky molecules. Therefore, development of solid acid with ultrahigh stability and favorable efficiency is still challenging.

It is generally known that highly dispersed metals (e.g. Al, Zr, Sn) oxides within several nanometers could efficiently produce rich Brønsted acid sites compared with the bulky ones [25, 26-37]. In these cases, many methods, such as the impregnating, grafting, chemical vapor depositing, have been employed for achieving highly dispersed metal species. However, we have to note that these methods are still unsatisfactory, where the aggregation of metal species usually occurs, causing the decreased number of acid centers. Recently, atomic layer deposition (ALD), which is atom controllable technique through self-limiting binary reactions between gaseous precursors and the substrate with significant advantages compared with the conventional chemical vapor deposition (CVD) technique, has been widely used for synthesizing various metal catalysts with distinguishable catalytic performances [38-39]. Although much success has been gained in synthesizing metal catalysts by ALD, to the best of our knowledge, synthesizing solid acids by ALD is rarely achieved.

Herein, we reported the synthesis of Al sites with ultra-high dispersion on anatase by an ALD method. The obtained catalyst, denoted as ALD-Al/TiO_2, exhibits Brønsted acidity and satisfactory activity in the dehydration of alcohols, which is employed as a model reaction for the deoxygenation of biomass-derived alcohols in water solvent. Furthermore, by combining ALD-Al/TiO_2 with the Pd/C, the mixed catalysts exhibit good performances in the upgrading of phenolic bio-oil by hydrodeoxygenation. Moreover, the ALD-Al/TiO_2 catalyst has outstanding stability, which gives constant catalytic performances after harsh treatments.

2. Experimental

2.1 Sample preparation

All reagents were of analytical grade and used as purchased without further purification. The reference catalysts of H_3PO_4, H_2SO_4, and Amberlyst-15 were commercially obtained from Aladdin Chem. Co.

Synthesis of TiO₂. As a typical run, 20 g of tetrabutyl titanate was dropwised into 1 L of water under stirring. Then the mixture was stirred for 5 h at room temperature, and the white precipitate was separated by centrifugation. After calcining the precipitate at 600 °C in air, the nanosized TiO_2 was obtained.

Synthesis of ALD-Al/TiO_2-5C. The ALD experiment was performed on a LabNano-PE Atomic Layer Deposition System (Ensure Nanotech, China). The Al species were loaded on TiO_2 by using Trimethylaluminum (TMA) and H_2O as precursors of Al and O, respectively. Ultrahigh purity argon was used as carrier gas to pass through the reactor continuously at a mass flow rate of 15 sccm and a pressure of

0.4 Torr. Al_2O_3 coating was performed at 150 °C and the sequence of pulse for one cycle deposition is H_2O (0.02 s)/Ar_2(20 s)/TMA(0.02 s)/Ar_2(20 s). The samples after ALD were calcined in oxygen at 400 °C for 1 h. Five cycles were performed for obtaining enough Al sites.

Synthesis of IM-Al/TiO$_2$. As a typical run, 1 g of TiO_2 was dispersed in 30 ml of $Al(NO_3)_3$ solution. After ultrasonic treatment at room temperature for 1 h. the water was removed under vacuum. After calcining the obtained sample at 500 °C in oxygen for 3 h, the IM-Al/TiO_2 catalyst was obtained.

Synthesis of ZSM-5 zeolite. As a typical run, 3 ml of tetrapropyl ammonium hydroxide (TPAOH, 30 *wt*%) and 0.09 g of sodium aluminate ($NaAlO_2$) were added into 15 ml of water. After stirring at room temperature for 1 h, 7 ml of TEOS was added and the resulted mixture was stirred for 40 h. Then the gel was transferred into an autoclave to crystallize at 180 °C for 3 days. After filtrating, drying, and calcining at 550 °C for 4 h in oxygen, the ZSM-5 zeolite was obtained.

Synthesis of Al-SBA-15. As a typical run, 1.5 g of P123 and 1.18 g of NaCl were dissolved in 70 g of water at 40 □C. Then, 4.2 g of TEOS was added, and the mixture was stirred for another 4 h. 10 ml of $AlCl_3$ aqueous solution (0.76 mmol of $AlCl_3$) was added, and then the mixture was continuously stirred at 40 □C for 24 h, and hydrothermally treated at 90 □C for 24 h in an autoclave. After filtrating, washing, drying, and calcination at 500 °C for 4 h in oxygen, Al-SBA-15 with Si/Al atomic ratio at 55 was finally obtained.

2.2 Sample characterization

X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2550 diffractometer with Cu KR radiation (λ=1.5418 Å). Al loadings were determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Nitrogen sorption isotherms were measured using a Micromeritics ASAP Tristar, the solid samples were degased at 180 °C under vacuum for 14 h before the test. NMR experiments were performed on a BrukerAscend-500 spectrometer with a 4 mm triple-resonance MAS probe at a spinning rate of 10 kHz. Prior to the adsorption of the probe molecules, the acid samples were placed in glass tubes and connected to a vacuum line for dehydration. The temperature was gradually increased at a rate of 1 °C/min, and the samples were kept at a final temperature of 400 °C and a pressure below 10^{-3} Pa over a period of 10 h and were then cooled. After the samples were cooled to ambient temperature, a known amount of probe molecule was introduces to the samples. The samples were frozen by liquid N_2, followed by elimination of the physically adsorbed probing molecules by evacuation at room temperature for 10 min. Finally, the sample tubes were flame-sealed. The preparation of the acetone adsorbed samples was performed according to the prior to the NMR experiments. Scanning transmission electron microscopy and energy dispersive X-ray spectroscopy elemental maps were collected using a JEOL ARM 200F microscope operated at 200 kV. The samples were ultrasonically dispersed in ethanol and then a drop of the solution was deposited onto a holey C/Cu grid for STEM characterization and EDX elemental mapping.

Sample Pretreatment for ICP Analysis. The solid samples were dried at 120 °C under vacuum overnight, then ~15 mg of the sample (the amount was precisely measured) was digested in a mixed aqueous solution of HF and HNO_3. The suspension was heated at 100 °C for completely dissolving the sample. Then the solution was diluted to 100 ml. For each sample, the Al content was tested at least three times. The Al and Ti content were calculated by the mean value.

The Al content in the solid sample was calculated from the concentration according to the following equation:

$$P_{Al} = [(C_{Al}*V_{solution})/W]*100\%$$

Where P_{Al} is the weight percentage of Al in the solid sample, C_{Al} is the concentration of Al measured by ICP, $V_{solution}$ is 100 mL, and W is the amount of solid sample for preparing the solution.

2.3 Catalytic tests

The dehydration reactions were performed in a 40-mL high-pressure autoclave with a magnetic stirrer (1100 rpm). The substrate and powder catalyst were mixed in the reactor, then N_2 was introduced and kept at desired pressure. The reaction system was heated to a given temperature. After the reaction, the product was taken out from the system and analysed by gas chromatography (Fuli, using a flame ionization detector) with a flexible quartz capillary column. The recyclability of the catalyst was tested by separating it from the reaction system by centrifugation, washing with large quantity of ethanol and drying under vacuum.

3. Results and Discussion

The ALD was carried out in a viscous flow reactor by alternately exposing the sample to cycles of trimethylaluminum at room temperature. ALD with 5 cycles were applied to a nanosized anatase (10-20 nm), followed by calcination at 350 °C in air. By Inductively Coupled Plasma (ICP) analysis, the Al loading on the final sample (ALD-Al/TiO_2-5C, 5C means 5 ALD cycles in synthesizing the catalyst) was established to be 2.9%.

Figure S1 shows the XRD patterns of TiO_2 and ALD-Al/TiO_2-5C, which exhibit similar peaks assigning to typical anatase structure. Notably, the peaks of Al_2O_3 are completely absent in the pattern of ALD-Al/TiO_2-5C, suggesting the high dispersion of Al species. Figure S2 gives the N_2 sorption isotherms of ALD-Al/TiO_2-5C, which exhibits significant hysteresis loop at relative pressure of 0.6 to 0.9, indicating the presence of rich mesoporosity. The surface area and pore size were established at 98 cm^2/g and 8.2 nm, respectively. The nanoporous structure of ALD-Al/TiO_2-5C should be favorable for the Al sites accessing to the molecules, because catalysis is well known as a surface phenomenon.

Electron microscopy images were employed to characterize the Al species on TiO_2. Figure 1a shows high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) by the Z-contrast. This image exhibits aggregation of nanosized anatase crystals with mesoporosity, in good agreement with the results of N_2 sorption isotherms. Notably, it is difficult to distinguish Al_2O_3 from TiO_2 in the HAADF-STEM image, which might be due to the high dispersion of Al_2O_3 on anatase. EDX mapping analysis could directly observe the Al species. As shown in Figures 1b and 1c, the distribution of Al element is consistent with that of Ti element, indicating the uniform distribution of Al. Although it is difficult to directly observe Al_2O_3, it is reasonably to propose that this structure with high Al distribution is favorable to form small size Al_2O_3 clusters on TiO_2.

The acidity of ALD-Al/TiO_2-5C was studied by the TMP-adsorption ^{31}P NMR spectroscopy, which is a practical technique to characterize the acid strength based on the host-guest interaction between solid acid and basic probe molecules [40-41]. As shown in Figure 2, the ALD-Al/TiO_2-5C gives two obvious signals at -29 and -3 ppm, which are assigned to TMP adsorbed at relatively weak and strong acid sites on the ALD-Al/TiO_2-5C. Additionally, the TiO_2 support without Al species only gives at signal at -33 ppm. These results indicate that the weak acid sites are from the TiO_2 support (-29 to -33 ppm), while the Al on ALD-Al/TiO_2-5C could form strong acid sites (-3 ppm). It is worth emphasizing that ALD is critically important for creating the strong acid sites. For example, when Al was loaded on TiO_2 by conventional impregnation method, the obtained sample (IM-Al/TiO_2) still exhibits a signal at -33 ppm, the signals of strong acid sites are completely undetectable. This phenomenon is reasonably attributed to the uniformly distributed Al species on TiO_2 by ALD, where the Al_2O_3 clusters is favorable to produce rich hydroxyl groups, thus leading to the formation of strong acid sites.

The investigation on the catalytic performances of ALD-Al/TiO_2-5C starts from the dehydration of cyclohexanol to cyclohexene, which is a key step in the hydrodeoxygenation of lignin-based phenolic molecules into alkane bio-oils [42-44]. Dehydration of cyclohexanol in water solvent has been regarded as challengeable topic. The reaction was carried out at 180 °C in autoclave with high-pressure nitrogen in water solvent. The catalytic data are shown in Table 1. The TiO_2 support without Al species is inactive for the reaction, giving cyclohexanol conversion lower than 1% (entry 1). Interestingly, the ALD-Al/TiO_2-5C is very active, exhibiting cyclohexanol conversion at 34.2% with cyclohexene as a sole product (entry 2). In contrast, other Al-based catalysts of IM-Al/TiO_2, γ-Al_2O_3, $AlCl_3$, and $NaAlO_2$ give very low conversion (<6.9%, entries 3-6), due to the lack of effective acid sites. When the reaction temperature decreased to 150 °C, ALD-Al/TiO_2-5C still gives cyclohexanol conversion at 22.4% (entry 7), higher than the homogeneous acids of H_3PO_4 and H_2SO_4 (entries 8-9). In comparison, Amberlyst-15 and Al-SBA-15, two widely used acid resin catalysts, catalyzed the cyclohexanol conversion at 9.4% and 2.2%, respectively (entries 10 and 11). Notably, the cyclohexanol conversion over ALD-Al/TiO_2-5C is even comparable to that over ZSM-5 zeolite (22.0%, entry 12). These results confirmed the high activity of ALD-Al/TiO_2-5C in the dehydration of cyclohexanol. Furthermore, similar results could also be obtained in the dehydration of cyclopentanol (entries 14-15) and phenylethyl alcohol (entries 16-17), where ALD-Al/TiO_2-5C exhibits much higher activity.

Further study was carried out to understand the stability of ALD-Al/TiO_2-5C. By a calcination treatment at 600 °C for 4 h, which is a harsh condition for most nanocatalysts, the calcined ALD-Al/TiO_2-5C still exhibits uniform distribution of Al, as confirmed by the electronic microscopy characterization (Figure S3). The TMP-adsorption ^{31}P NMR spectrum still exhibits the obvious signal at -3 ppm (Figure

2), assigning to the presence of strong acid sites. In the catalytic dehydration of cyclohexanol, the calcined ALD-Al/TiO_2-5C exhibits similar performances with the as-synthesized ALD-Al/TiO_2-5C catalyst (entry 13, Table 1). These results indicate the high stability of ALD-Al/TiO_2-5C catalyst, therefore, we can reasonably expect a good recyclability of the catalyst. We verified this by testing the dehydration of cyclohexanol in water solvent at 180 °C in 12 h to avoid the activity saturation. As shown in Figure 3, the conversion kept unchanged in a 5-recycle test over ALD-Al/TiO_2-5C, showing excellent recyclability. In contrast, the Amberlyst-15 resin lost most of the activity in the 2nd run due to its poor thermal stability. ZSM-5 zeolite exhibit constant conversion in the 4th run, but the conversion obviously decreases in the 5th run, which might be due to the coke formation blocking the micropores, and the activity can be regenerated by calcination in oxygen.

Furthermore, we also employed the ALD-Al/TiO_2-5C catalyst in the hydrodeoxygenation of phenolic molecules, which are employed as model bio-oil molecules. As presented in Table 2, by combining ALD-Al/TiO_2-5C with the commercial Pd/C as bifunctional catalysts, the mixed catalysts exhibit better performances (higher substrate conversions and higher alkane selectivities) in the hydrodeoxygenation of phenol and 2,6-dimethoxyphenol to cyclohexane than mixed catalysts of H_3PO_4 and Pd/C, which is important process in the upgrading of biomass-derived pyrolysis oil. All these data confirm the high performance and potential practical application of ALD-Al/TiO_2-5C developed from the ALD method.

4. Conclusion

In summary, the atomic dispersion of Al species on TiO_2 support was achieved by atomic layer deposition. The obtained catalyst, denoted as ALD-Al/TiO_2-5C, exhibits Brønsted acidity and much higher activity than the conventional Al_2O_3-based catalyst in the dehydration of alcohols. More importantly, the ALD-Al/TiO_2-5C exhibit outstanding stability and recyclability. The simple synthesis procedure and high activity combined with the excellent stability of ALD-Al/TiO_2-5C make it important for potential application. On the other hand, this work also demonstrates a very unique method for synthesizing solid acids by ALD, which might open a new route by employing ALD as efficient tools for atomically designing and synthesizing acid catalysts for biomass conversion in the future.

ASSOCIATED CONTENT

Supporting Information. XRD and N_2 sorption are available in Supporting Information.

Acknowledgements

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Captions

Table 1. Catalytic dehydration of alcohols to olefins over various catalysts in water solvent.[a]

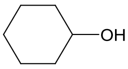
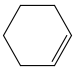
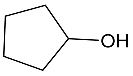
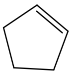
Table 2. Catalytic data in hydrodeoxygenation of phenol and 2,6-dimethoxyphenol over different catalysts.[a]

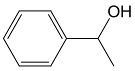
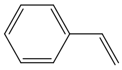
Figure 1. (a) HADDF-STEM images of ALD-Al/TiO_2-5C. (b, c) Ti, Al elemental maps by analysing the red-square region in (a).

Figure 2. TMP-adsorption ^{31}P NMR spectra of various samples. The calcined ALD-Al/TiO_2-5C is the sample after calcination treatment at 600 °C for 4 h.

Figure 3. Recyclable tests of various catalysts in the catalytic dehydration of cyclohexanol. Reaction conditions: 1 mmol of alcohol, 50 mg of catalyst, 5 ml of water, 3 MPa of N_2, reaction time of 12 h.

Table 1. Catalytic dehydration of alcohols to olefins over various catalysts in water solvent.^{a}

Entry	Catalyst	T (°C)	Conversion (%)	Selectivity (%)	C Balance^b (%)
					
1	TiO_2	180	<1.0	--^{c}	
2	ALD-Al/TiO_2-5C	180	34.2	>99.0	>99.0
3	IM-Al/TiO_2	180	6.9	>99.0	>99.0
4	$\gamma\text{-Al}_2\text{O}_3$	180	2.1	>99.0	98.0
5	AlCl_3	180	3.9	96.4	97.9
6	NaAlO_2	180	<1.0	--^{c}	
7	ALD-Al/TiO_2-5C	150	22.4	>99.0	>99.0
8	H_3PO_4^{d}	150	1.2	69.0	
9	H_2SO_4	150	19.9	97.5	82.1
10	Amberlyst-15	150	9.4	>99.0	>99.0
11	Al-SBA-15	150	2.2	>99.0	>99.0
12	ZSM-5	150	22.0	>99.0	>99.0
13	Calcined ALD-Al/TiO_2-5C^e	180	32.1	>99.0	>99.0
					
14	ALD-Al/TiO_2-5C	180	29.5	92.3^f	95.2
15	IM-Al/TiO_2	180	1.5	--^{c}	

					
16	ALD-Al/TiO_2-5C	180	38.8	>99.0	>99.0
17	IM-Al/TiO_2	180	5.4	>99.0	>99.0

[a] Reaction conditions: 1 mmol of alcohol, 50 mg of catalyst, 5 ml of water, 3 MPa of N_2, reaction time of 20 h.

[b] Calculated from the carbon atoms in the feed and products.

[c] Undetectable.

[d] The data are from Ref. [30].

[e] The calcined ALD-Al/TiO_2-5C is the sample after calcination treatment at 600 °C for 4 h.

[f] The by-product is ether.

Table 2. Catalytic data in hydrodeoxygenation of phenol and 2,6-dimethoxyphenol over different catalysts.[a]

	Substrate	Catalyst	Conv. (%)	Product selectivity (%)[b]			Carbon balance (%)
				cyclohexane	cyclohexanol	cyclohexanone	
1	Phenol	ALD-Al/TiO_2-5 C + Pd/C	>99.5	97.0	3.0	<1.0	>99.5
2	Phenol	H_3PO_4 + Pd/C	>99.5	92.0	8.0	<1.0	>99.5
				cyclohexane	others[c]		
3	2,6-dimethoxyphenol	ALD-Al/TiO_2-5 C + Pd/C	90.1	70.4	24.0		93.3[d]
4	2,6-dimethoxyphenol	H_3PO_4 + Pd/C	77.2	55.0	38.0		93.0[d]

[a] Reaction conditions: 150 °C, 4 h, 4.0 MP of H_2, 50 mg of catalyst, 1 mmol of phenolic molecules,10 ml of water;

[b] (C atoms in each product/total C atoms in all products)*100%; [c] Cyclohexanol-, cyclohexanone-derived molecules and some others; [d] The undetected carbon was mainly due to the volatilization of methanol product.

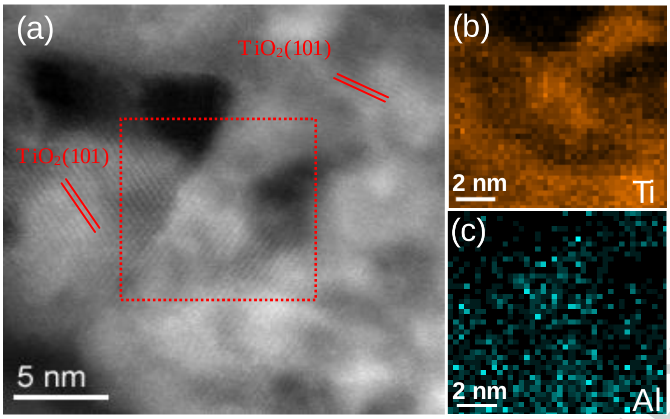


Figure 1. (a) HADDF-STEM images of ALD-Al/TiO_2-5C. (b, c) Ti, Al elemental maps by analysing the red-square region in (a).

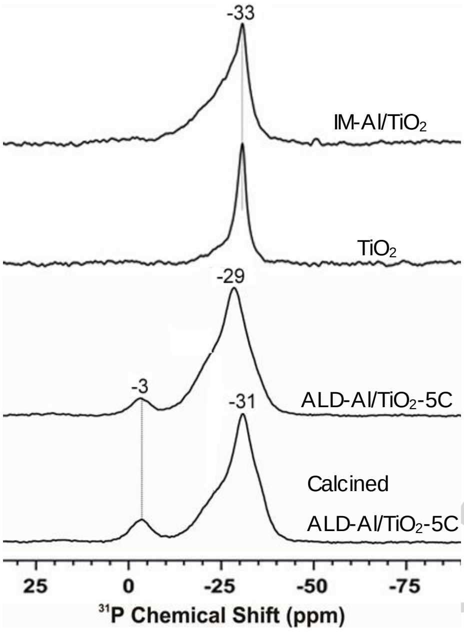


Figure 2 TMP-adsorption ^{31}P NMR spectra of various samples. The calcined ALD-Al/TiO_2-5C is the sample after calcination treatment at 600 °C for 4 h.

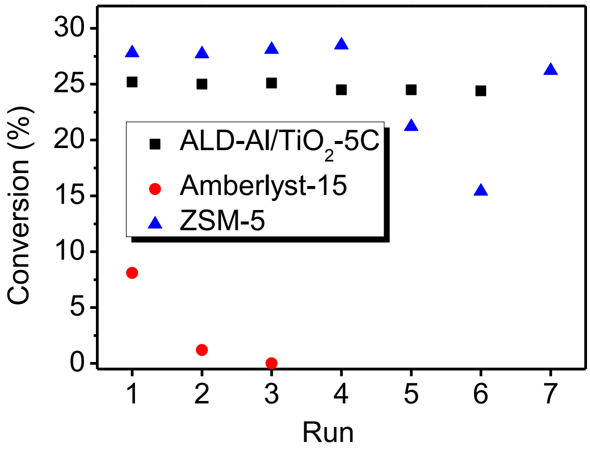


Figure 3. Recyclable tests of various catalysts in the catalytic dehydration of cyclohexanol. Reaction conditions: 1 mmol of alcohol, 50 mg of catalyst, 5 ml of water, 3 MPa of N_2, reaction time of 12 h. The ZSM-5 catalysts were calcined in oxygen at 450 °C for 4 h after the 6th run.

Research highlights

- Solid acid catalyst ALD-Al/TiO_2 is synthesized via atomic layer deposition (ALD) technique.
- ALD-Al/TiO_2 exhibits highly dispersed Al sites with Brønsted acidity.
- ALD-Al/TiO_2 catalysts are efficient for dehydration of alcohols.