Zn/Al/Pb Mixed Oxides as Efficient Heterogeneous Catalysts for the Synthesis of Methyl N-Phenyl Carbamate

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ABSTRACT: Dimethyl carbonate aminolysis is an effective and green pathway for the synthesis of methyl N-phenyl carbamate (MPC), which is an important intermediate for the synthesis of polyurethanes and many other chemicals. In this work, we demonstrate the fabrication of Zn/Al/Pb mixed oxides as efficient and stable heterogeneous catalysts for MPC synthesis. The catalysts are prepared via facile coprecipitation and subsequent thermal annealing. Their micromorphology and physical–chemical properties are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and NH₃-TPD. The results show that rather than being doped into ZnO and/or Al₂O₃, PbO is highly dispersed in the ZnO/Al₂O₃ base forming ultrafine nanoparticles. Despite the weak interactions within the mixed oxides, the high density of active sites generates outstanding catalytic activity and cycling stability for MPC synthesis, with an aniline conversion of almost 100% and MPC yield of up to 90% during six repeated tests, providing great potential for their further application.

1. INTRODUCTION

Organic carbamates, such as methyl N-phenyl carbamate (MPC), dimethylhexane-1,6-dicarbamate (HDC), methylene diphenyl-4,4′-dicarbamate (MDC), etc., are generally used as raw materials for the synthesis of pharmaceuticals, pesticides, herbicides, insecticides, fumigicides, and so on. Carbamates can also be used for the synthesis of isocyanates, which are raw materials for the production of polyurethane foam and elastomers. Unfortunately, industrial isocyanate synthesis has been mainly focused on the phosgene path, and thus, serious environmental pollution and safety issues may occur during the process.1−4 Hence, efficient synthesis of carbamates is of great significance, especially for the non-phosgene synthesis of isocyanates.

As one of the important carbamates, MPC could be synthesized via the oxidative carboxylation of aniline with CO and O₂ and the reductive carbonylation of nitrobenzene with methanol and CO.3,4 Nevertheless, the above two synthesis routes are restricted by the high reaction temperature and pressure, the requirement of noble metal catalysts, and the high toxicity of CO. MPC could be synthesized via the reactions of phenylurea and methanol,5 aniline and dimethyl carbonate (DMC),4,5,6 methyl carbamate (MC)7 and even some C₂ sources (e.g., CH₃OH and CO₂),8,9 etc., which are ecologically and green. Among these reactions, aminoysis of DMC is very attractive due to its high economy, since the byproduct CH₃OH could be used as a raw material for DMC synthesis.2,3 However, different intermediates with high activity may form via several possible dissociation paths of DMC.5,9 Accordingly, N-methyl Aniline (NMA) and N,N′-dimethylaminopyridine (DMA) could also be produced as byproducts via the simultaneous methylation of aniline (Scheme S1).4,13 As a result, high-performance catalysts are quite necessary with the aim of enhancing the conversion of aniline, the selectivity, and the yield of MPC.

Despite the high activity of various homogeneous catalysts, such as the metal salts of Zn,16,17 Pb,18,19 Na,20 K,11 etc., and even ionic liquids,10 for the synthesis of MPC and other carbamates, these catalysts are also confined by the common problems of homogeneous catalysts, such as product purification and catalyst recovery. Thus, it is of great significance to develop high-performance heterogeneous catalysts via facile methods for the synthesis of carbamates. So far, various kinds of heterogeneous catalysts have been developed for the synthesis of carbamates, such as PbO,18,21 CuO−ZnO,22 AlSBA-15,23 Au/Fe₃O₄,24 CeO₂,13,25−28 Au/CeO₂,29 MnO₂−CeO₂,30 TiO₂−Cr₂O₃/SiO₂,31 zinc alkyl carbonate covalently bonded on silica,3 and so on. Some of the catalysts exhibit excellent reactivity and recyclable stability. For example, zinc alkyl carbonate covalently bonded on silica could give the MPC yield of 91.6%, whose activity did not change for 12 cycles.5 In our previous work, we found that Zn/A
Al/AlCe oxides derived from calcined Zn/Al/Ce hydroxide-like compound (HTlc) precursors showed efficient MPC synthesis activity and cyclic stability, which could give the aniline conversion of 95.8%, MPC selectivity of 81.6%, and MPC yield of 78.2%.22

Layered double hydroxides (LDHs), also known hydroxide clays, are excellent precursors for preparing mixed oxide catalysts because LDHs, with the general formula $M_{x/2}^{2+}M_{y/3}^{3+}(OH)_zA_{n/-m}+n_2H_2O$, possess the superior properties of high dispersion of metallic active sites and adjustable metal cations within LDHs.33 Herein, in the present work, we fabricate a series of Zn/Al/Mn mixed oxides via calcination of divalent metal cation doped Zn/Al LDHs for MPC synthesis via DMC aminolysis, where M represents the divalent metal cation. We find that the ZnO/Al2O3/PbO (Zn/Al/Pb) mixed oxide is highly active and stable for MPC synthesis, which holds great potential for its industrial application. The excellent performances of the Zn/Al/Pb mixed oxide mainly originate from the high density of active sites generated by the uniform dispersion of ultramine PbO nanoparticles with the size of ca. 1 nm in the ZnO/Al2O3 base.

2. RESULTS AND DISCUSSION

The catalytic performances of a series of Zn/Al/M5 catalysts are presented in Table 1. In accordance with the literature, we fabricate a series of Zn/Al/M mixed oxides via calcination of divalent metal cation doped Zn/Al LDHs for MPC synthesis via DMC aminolysis, where M represents the divalent metal cation. We find that the ZnO/Al2O3/PbO (Zn/Al/Pb) mixed oxide is highly active and stable for MPC synthesis, which holds great potential for its industrial application. The excellent performances of the Zn/Al/Pb mixed oxide mainly originate from the high density of active sites generated by the uniform dispersion of ultramine PbO nanoparticles with the size of ca. 1 nm in the ZnO/Al2O3 base.

| catalysts | aniline conv. (％) | MPC yield (％) | selectivity (%) |
|-----------|------------------|---------------|----------------|
| Zn/Al/Mg5 | 91.7             | 33.9          | 36.9 8.7 54.3 0 |
| Zn/Al/Ca5 | 86.5             | 59.1          | 68.4 11.7 17.6 2.3 |
| Zn/Al/Ba5 | 87.9             | 44.4          | 50.5 12.6 36.9 0 |
| Zn/Al/Co5 | 95.5             | 77.3          | 80.9 5.9 13.2 0 |
| Zn/Al/Ni5 | 93.1             | 69.6          | 74.7 7.7 16.0 1.6 |
| Zn/Al/Cu5 | 91.1             | 65.1          | 71.4 10.4 18.1 0 |
| Zn/Al/Mn5 | 72.4             | 18.2          | 25.1 50.9 24.0 0 |
| Zn/Al/Pb5 | 100              | 94.0          | 94.0 1.7 4.2 0 |

Al/Pb5 could be ascribed to the presence of Pb in Zn/Al mixed oxides. Since Zn/Al/Pb5 displays the highest catalytic performances, MPC synthesis via DMC aminolysis is further investigated over Zn/Al/Pb0, Zn/Al/Pb2.5, Zn/Al/Pb10, and pure PbO (Table 2). Similar to our previous results, Zn/Al/Pb0 exhibits limited activity, which might originate from the surface acid sites and zinc element within Zn/Al mixed oxides.32 With the addition of Pb, the catalytic activity of Zn/Al/Pb catalysts is enhanced significantly as compared with that of Zn/Al/Pb0. Particularly, Zn/Al/Pb catalysts generally exhibit high carbamoylation and low methylation activities, which lead to the high selectivity and yield of MPC. It should be noted that the activity of Zn/Al/Pb catalysts is comparable with and/or remarkably higher than that of pure PbO, especially for Zn/Al/Pb5. Thus, the results shown in Table 2 suggest that adding a small amount of PbO in ZnO/Al2O3 could generate heterogeneous catalysts possessing excellent activity for MPC synthesis via DMC aminolysis, which is of great significance due to the high toxicity of Pb.

X-ray diffraction (XRD) patterns of the Zn/Al/Pb precursors containing different contents of Pb are displayed in Figure 1a. Apparently, all samples show the typical diffraction peaks of Zn/Al-(NO3−)-LDHs, where the (003), (006), and (110) reflections can be perfectly indexed.33–35 Moreover, the peak intensities (e.g., (003)) of LDHs increase with increasing content of Pb, revealing the enhanced crystallinity of the precursors. This might originate from the high Al3+/Zn2+ ratio with the addition of more Pb.35 In addition, a series of strong diffraction peaks ascribed to ZnO (JCPDS: 79-0205) can also be identified.32,35 This might be caused by the relatively high aging temperature (80 °C), which could produce a weak hydrothermal condition and then lead to the slight dehydration and condensation of the precursors.

After calcination at 500 °C for 4 h, the Pb-containing precursors transform into light-yellow mixed oxides. As shown in Figure 1b, the LDH phase within the precursors completely disappears and only ZnO can be identified (JCPDS: 79-0205). The narrow sharp peaks suggest the high crystallinity of ZnO within the resulting Zn/Al/Pb catalysts. No crystalline Al2O3, PbO (Figure S2), and PbO2 can be observed in all XRD patterns, indicating that Al and Pb oxides may exist in the amorphous phase and/or cannot be detected by XRD due to the ultrasmall particle size. Moreover, the diffraction peaks of ZnO show no apparent shift with the addition of different contents of Pb, suggesting that Pb is not doped into the crystal lattice of ZnO. This might be ascribed to the significantly larger ionic radius of Pb2+ (0.112 nm)41 as compared to that of Zn2+ (0.074 nm).42 However, the introduction of Pb still

Table 2. Activities of Catalysts Containing Different Contents of Pb for MPC Synthesis

| catalysts | aniline conv. (％) | MPC yield (％) | selectivity (%) |
|-----------|------------------|---------------|----------------|
| Zn/Al/Pb0 | 76.6             | 34.1          | 44.5 10.9 24.3 0.7 |
| Zn/Al/ Pb2.5 | 95.5             | 77.9          | 81.6 5.0 13.4 0 |
| Zn/Al/Pb5 | 100              | 94.0          | 94.0 1.7 4.2 0 |
| Zn/Al/Pb10 | 95.7             | 84.6          | 81.0 4.2 11.1 0 |
| PbO      | 93.6             | 78.7          | 84.1 11.3 4.6 0 |

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results in the gradual increase of the average crystallite size of ZnO calculated from the Scherrer equation, which is 23.6, 32.1, 39.5, and 46.5 nm, respectively, for Zn/Al/Pb0, Zn/Al/Pb2.5, Zn/Al/Pb5, and Zn/Al/Pb10.

Scanning electron microscopy (SEM) images of the precursors for Zn/Al/Pb0, Zn/Al/Pb2.5, Zn/Al/Pb5, and Zn/Al/Pb10 are displayed in Figures 2a and S3. As can be seen, Zn/Al/Pb0 is aggregated into nanoplates, which is the typical morphology of Zn/Al LDHs (Figure S3a). With the addition of Pb, the precursors are then composed of a large number of nanoparticles and a few nanoplates (Figures 2a and S3b,c). After calcination, all four precursors are broken into much smaller nanoparticles, as shown in Figures 2b,c and S3d–f. Transmission electron microscopy (TEM), high-angle annular dark-field (HAADF)-TEM, and TEM energy-dispersive spectroscopy (EDS)-mapping images of the resulting Zn/Al/Pb2.5, Zn/Al/Pb5, and Zn/Al/Pb10 catalysts are displayed in Figures 2d–f and S4. TEM images also show that the above three Pb-containing catalysts are composed of ultrasmall nanoparticles, and the diameter of some particles is even smaller than 10 nm. A few nanoplates can also be distinguished from the TEM images, as illustrated in Figure 2d. Moreover, HAADF-TEM and TEM EDS-mapping images of Zn-K, Al-K, Pb-L, and O-K suggest the homogeneous
dispersion of Zn, Al, Pb, and O throughout the three Pb-containing catalysts, even for Zn/Al/Pb10 that contains the highest content of Pb.

To verify the distribution of lead oxide on the atomic scale, Zn/Al/Pb5 is also characterized by HAADF-STEM and STEM EDS-mapping (Figures 2g–i and S5b–d). In accordance with XRD results, the lattice fringes distinguished from high-resolution TEM (HRTEM) images could be ascribed to well-crystallized ZnO (Figures 2g and S5a), and no crystallized Al2O3 and PbO could be identified. The contrast of the HAADF image depends on the atomic number, and hence, it can be effectively used to illustrate the possible position and particle size of Pb oxide. As a consequence, the large number of bright contrast spots distinguished from the HAADF-STEM images (Figure 2h) suggest the high dispersion of PbO in the ZnO/Al2O3 base. Surprisingly, the diameter of PbO nanoparticles is as small as ca. 1 nm, which is expected to give a high density of active sites. For comparison, pure PbO and its precursor prepared under the same conditions possess significantly larger size (Figure S6).

Zn/Al/Pb catalysts are further characterized by means of X-ray photoelectron spectroscopy (XPS). It is found that both the binding energies of Zn 2p and Al 2p exhibit no apparent shift after the introduction of Pb, as shown in Figure S7. The Zn 2p1/2 and Zn 2p3/2 peaks of Zn/Al/Pb catalysts are centered at 1021.2 and 1044.2 eV (with a splitting of 23.0 eV), respectively, suggesting the +2 state of Zn atoms within the catalysts (Figure S7a). Moreover, the Al 2p spectra can be resolved with only one peak centered at 73.9 eV, suggesting the presence of Al3+ that is substitutionally incorporated into Zn2+. As for the Pb 4f core level, the intensities of XPS signals increase gradually from Zn/Al/Pb2.5 to Zn/Al/Pb10, suggesting the increased content of Pb (Figure 3).

Moreover, all of the Pb 4f core-level spectra of Zn/Al/Pb catalysts exhibit two main peaks at ca. 138.9 and 143.8 eV, which are ascribed to Pb 4f7/2 and Pb 4f5/2 of PbO, respectively. In addition, the peaks ascribed to Pb2O3 and/or PbO2 cannot be identified from all Zn/Al/Pb catalysts even for Zn/Al/Pb10 containing the highest content of Pb, implying that all Pb ions are in the form of PbO. For comparison, a couple of new strong peaks at 137.4 and 142.2 eV attributed to PbO2 can be identified for pure PbO, suggesting that the surface of pure PbO is almost completely oxidized to PbO2. Furthermore, the binding energy of Pb 4f for Zn/Al/Pb catalysts shows no obvious shift, which also reveals that PbO only locates on solid ZnO/Al2O3 base in the form of ultrafine particles rather than being doped into the crystal lattice. As a result, XPS results confirm the formation of ZnO/Al2O3/PbO mixed oxides, and the ZnO/Al2O3 base could stabilize the ultrafine PbO nanoparticles and prevent the surface from deep oxidation during thermal annealing.

It was reported that acid sites could effectively activate DMC and then favor the synthesis of MPC. Thus, the NH3-TPD technique is used to analyze the surface acidity and chemical interactions of the Zn/Al/Pb catalysts (Figure 4). Apparently, all Zn/Al/Pb catalysts exhibit three distinct ammonia desorption peaks labeled α, β, and γ, which could be ascribed to weak, medium, and strong surface acid sites, respectively. The temperature and desorption intensities of weak and strong acid sites show no substantial change after the introduction of PbO. For comparison, the medium acid sites of the Pb-containing catalysts slightly shift to lower temperatures, especially for Zn/Al/Pb5. As a result, similar to XRD and XPS results, NH3-TPD curves also confirm the weak chemical interactions between PbO and ZnO/Al2O3 for the Pb-containing catalysts. Accordingly, the substantial difference of catalytic activity between the catalysts with and without PbO suggests that the excellent performances of Zn/Al/Pb mixed oxides have hardly any relation to the surface acid sites.

Based on the above characterizations, it is confirmed that Zn/Al/Pb mixed oxides with PbO uniformly dispersed in the ZnO/Al2O3 base are prepared via a facile coprecipitation method combined with long-time aging at relatively high temperatures. The weak interactions between the oxides and the low catalytic activity of ZnO/Al2O3 reveal the crucial role of PbO in the extraordinary high activity. Thus, the variation of catalytic performances over the different Zn/Al/Pb catalysts (Table 2) might be attributed to the content and particle size of PbO. Particularly, Zn/Al/Pb5 possesses more active sites than Zn/Al/Pb2.5, and the particle size of PbO within Zn/Al/Pb is about 1 nm, which is expected to give a high density of active sites for the adsorption and selective dissociation of DMC. The as-formed –COOCH3 fragment reacts with aniline, leading to the appreciable catalytic activity for MPC synthesis (Figure 5). Moreover, the ZnO/Al2O3 base could immobilize the ultrafine PbO nanoparticles, preventing their aggregation during thermal annealing and dissolution under reaction conditions, which is essential for its long-term stability. Meanwhile, PbO nanoparticles in the present Zn/Al/Pb catalysts exhibit the trend of surface enrichment (Table S1). Particle agglomeration is thus expected with the addition of a large amount of PbO (such as Zn/Al/Pb10), which would result in relatively more inhomogeneous dispersion, larger size of PbO nanoparticles, and lower activity, as compared to Zn/Al/Pb5.
Stability and recyclability are key parameters for heterogeneous catalysts for industrial application. In the present work, the cycling stability was investigated over Zn/Al/Pb5 in the same manner as described in our previous work.32 The excellent activity of Zn/Al/Pb5 is maintained after six repeated tests, as displayed in Figure 6. The conversion of aniline is almost approaching 100%, and MPC selectivity and yield are in the range of 89.3–94.0% with a slight fluctuation. The average selectivity of the methylation byproducts, namely, NMA and DMA is 2.2 and 5.3%, respectively, and almost no DPU could be detected. As a heterogeneous catalyst, the present Zn/Al/Pb5 exhibits excellent catalytic performances and cycling stability, which are superior to those of many reported catalysts (Table S2), such as Zn(OAc)2/SiO2,4 ZnO−TiO2,7 ordered AlSBA-15,8 zinc alkyl carboxylate covalently bonded on silica,5 mixed oxide would dissolve, since the ZnO/Al2O3 base is very stable. Thus, the excellent stability of Zn/Al/Pb5 might be ascribed to the well-crystallized ZnO that could prevent the ultrafine PbO particles from dissolving under the harsh MPC synthesis conditions. As a result, it can be concluded that the present Zn/Al/Pb5 catalyst possesses the advantages of feasible preparation, low cost, environmental benignity, convenient recovery, outstanding catalytic performance, and cycling stability.

3. CONCLUSIONS

In conclusion, herein, Zn/Al/MII mixed oxides are prepared and used as heterogeneous catalysts for MPC synthesis via DMC aminolysis. Particularly, the Zn/Al/Pb5 mixed oxide shows extraordinarily high activity giving the aniline conversion of almost 100% and MPC yield of 94%, whose catalytic performances do not show any apparent decrease during repeated tests. Characterization results suggest that PbII ions are not doped into ZnO and/or Al2O3, generating weak interactions between the oxides. However, ultrafine PbO nanoparticles with the size of ca. 1 nm are uniformly dispersed in the ZnO/Al2O3 base, which results in a high density of active sites, appreciable catalytic activity, and cycling stability. This work demonstrates the feasibility of fabricating heterogeneous catalysts with outstanding catalytic performances and cycling stability for MPC synthesis. The advantages of feasible preparation, low cost, and environmental benignity of the catalysts suggest that they are highly promising for further application.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. Catalysts were prepared via conventional coprecipitation and subsequent thermal annealing. Typically, Zn/Al/MII precursors were prepared as follows: a calculated amount of Zn(NO3)2·6H2O, Al(NO3)3·9H2O, and M(NO3)2·yH2O (with the Zn/Al/MII atomic ratio of 75-x/25/x) were dissolved in distilled water to form solution A. Then, NaOH was dissolved in distilled water to form solution B with the concentration of about 0.1 M. Solutions A and B were added dropwise into another beaker that contained 100 mL of distilled water under vigorous stirring. During coprecipitation, the solution pH was maintained at 10 ± 0.5. After being aged for 24 h at 80 °C, the suspension was filtered and completely washed. The filter cake was then dried at 80 °C and calcined at 500 °C for 4 h.

The resulting catalysts were denoted as Zn/Al/Mx, where M and x represent the divalent metal cation and its calculated content in the starting mixed solution, respectively. For instance, Zn/Al/Pb5 denoted that the atomic ratio of Zn/Al/Pb in the mixed nitrate solution was 70:25:5 but not the real composition of the resulting catalyst (Table S1).

4.2. Materials Characterization. The precursors and catalysts were characterized by X-ray diffraction (XRD) on a Rigaku D/max-rB diffractometer with Cu Kα radiation. The morphology of samples was observed by scanning electron microscopy (SEM, Scios, FEI) and transmission electron microscopy (TEM, JEM 2100F, JEOL) coupled with an energy-dispersive spectroscopy (EDS) analyzer. A scanning transmission electron microscope (STEM, Themsis Z, FEI) equipped with a probe monochromator and a probe spherical aberration corrector was further used to observe the high-angle annular dark-field (HAADF) image and EDS-mapping so as to identify the dispersion of elements more clearly. X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB250Xi spectrometer (Thermo Fisher Scientific). All of the binding energies were calibrated internally by the adventitious carbon deposit C 1s peak at 284.8 eV. The liquid products were analyzed by inductively coupled plasma (ICP) emission spectrometry using a Perkin-Elmer ICP OPTIMA-
3000 to determine the soluble behavior of catalysts during repeated tests.

Temperature-programmed desorption of ammonia (NH3-TPD) was performed on an AutoChem II 2920, a Micro-meritics, automatic chemical adsorption instrument to investigate the surface acidity of catalysts. NH3-TPD was conducted as follows: 100 mg of catalyst was pretreated under Ar (40 mL/min) at 400 °C for 1 h. After being cooled to 50 °C, the catalyst was saturated with NH3 for 1 h and then flushed with Ar (40 mL/min) for 1 h. Finally, the samples were heated up to 650 °C with a heating rate of 5 °C/min, and the NH3 signal was detected continually.

4.3. Catalytic Evaluation. MPC synthesis was carried out under the same reaction conditions described in our previous work. Typically, 19.35 g of DMC, 0.8 g of aniline, and 0.253 g of catalyst were loaded into a Teflon-lined autoclave (50 mL) equipped with a magnetic stirrer. After substitution of air by a flow of nitrogen, MPC synthesis was carried out at 200 °C for 7 h. After reaction, the solid catalyst was carefully collected by centrifugation and successively washed with methanol. The liquid products were qualitatively analyzed by liquid chromatography–mass spectrometry (LC–MS, UltiMate 3000-MSQ Plus, Thermo Fisher Scientific). Moreover, quantitative analysis was performed on a Shimadzu LC-20A high-performance liquid chromatograph (H PLC), which was equipped with a Shimadzu C-18 (4.6 mm × 150 mm, 5 μm) column. The flow rate of mobile phase CH3OH/H2O (70/30, volume-to-volume) was 0.4 mL/min. The column temperature was 40 °C, and the detection wavelength was 254 nm (Figure S1). The selectivity of products was calculated on the basis of aniline.

conversion (%) = \frac{\text{amount of aniline consumed}}{\text{amount of aniline charged}} \times 100%

selectivity (%) = \frac{\text{amount of each product}}{\text{amount of aniline consumed}} \times 100%

AUTHOR INFORMATION

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03137.

Schematic pathways of DMC aminolysis of aniline, HPLC and LC–MS analyses of liquid products, atomic ratio of Zn/Al/Pb catalysts, XRD pattern of PbO, morphologies of Zn/Al/Pb and PbO catalysts, Zn 2p and Al 2p core-level spectra of Zn/Al/Pb catalysts, XRD pattern of cycled Zn/Al/Pb5, ICP test of liquid products, and catalytic performances of various catalysts (PDF)

ASSOCIATED CONTENT

Supporting Information

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REFERENCES

1. Chaturvedi, D. Perspectives on the synthesis of organic carbamates. Tetrahedron 2012, 68, 15–45.
2. Rokicki, G.; Parzuchowski, P. G.; Mazurek, M. Non-isocyanate polyurethanes: synthesis, properties, and applications. Polym. Adv. Technol. 2015, 26, 707–761.
3. Wang, J.; Li, Q.; Dong, W.; Kang, M.; Wang, X.; Peng, S. A new non-phosgene route for synthesis of methyl N-phenyl carbamate from phenyleurea and methanol. Appl. Catal., A 2004, 261, 191–197.
4. Li, F.; Li, W.; Li, J.; Xue, W.; Wang, Y.; Zhao, X. Investigation of supported Zn(OAc)2 catalyst and its stability in N-phenyl carbamate synthesis. Appl. Catal., A 2014, 475, 355–362.
5. Wang, Y.; Liu, B. Efficient and recyclable heterogeneous zinc alkyl carboxylate catalyst for the synthesis of N-phenyl carbamate from aniline and dimethylcarbonate. Catal.: Sci. Technol. 2015, 5, 109–113.
6. Juárez, R.; Pennemann, H.; García, H. Continuous flow carbamoylation of aniline by dimethyl carbonate using a microreactor coated with a thin film of ceria supported gold nanoparticles. Catal. Today 2011, 159, 25–28.
7. Li, F.; Wang, Y.; Xue, W.; Zhao, X. Clean synthesis of methyl N-phenyl carbamate over ZnO-TiO2 catalyst. J. Chem. Technol. Biotechnol. 2009, 84, 48–53.
8. Lucas, N.; Amrute, A. P.; Palraj, K.; Shanbhag, G. V.; Vina, A.; Halligudi, S. B. Non-phosgene route for the synthesis of methyl phenyl carbamate using ordered AlSBA-15 catalyst. J. Mol. Catal. A: Chem. 2008, 295, 29–33.
9. Han, B.; Zhao, W.; Qin, X.; Li, Y.; Sun, Y.; Wei, W. Synthesis of dimethyl hexane-1,6-diyldicarbonate from 1,6-hexamethylenediamineand methyl carbonate using lead dioxide as catalyst. Catal. Commun. 2013, 33, 38–41.
10. Zhang, Q.; Yuan, H.; Fukaya, N.; Yasuda, H.; Choi, J.-C. Direct Synthesis of Carbamates from CO2 Using a Task-Specific Ionic Liquid Catalyst. Green Chem. 2017, 19, 5614–5624.
11. Zhang, Q.; Yuan, H.; Fukaya, N.; Choi, J.-C. Alkali Metal Salt as Catalyst for Direct Synthesis of Carbamate from Carbon Dioxide. ACS Sustainable Chem. Eng. 2018, 6, 6675–6681.
12. Zhang, Z.; Liu, S.; Zhang, L.; Yin, S.; Yang, G.; Han, B. Driving dimethyl carbonate synthesis from CO2 and methanol and...
production of acetylene simultaneously using CaC2. Chem. Commun. 2018, 54, 4410–4412.
(13) Laursen, S.; Combita, D.; Hungria, A. B.; Boronat, M.; Corma, A. First-Principles Design of Highly Active and Selective Catalysts for Phosgene-Free Synthesis of Aromatic Polyurethanes. Angew. Chem. Int. Ed. 2012, 51, 4190–4193.
(14) Cabrero-Antonino, J. R.; Adam, R.; Junge, K.; Beller, M. A general protocol for the reductive N-methylation of amines using dimethyl carbonate and molecular hydrogen: mechanistic insights and kinetic studies. Catal. Sci. Technol. 2016, 6, 7966–7966.
(15) Cabrero-Antonino, J. R.; Adam, R.; Wärnå, J.; Murzin, D. Y.; Beller, M. Reductive N-methylation of amines using dimethyl carbonate and molecular hydrogen: Mechanistic insights through kinetic modelling. Chem. Eng. J. 2018, 351, 1129–1136.
(16) Reixach, E.; Haak, R. M.; Wershofen, S.; Vidal-Ferran, A. Alkoxy carbonylation of Industry Relevant Anilines Using Zn4O(OC2H5)6 as Catalyst. Ind. Eng. Chem. Res. 2012, 51, 16165–16170.
(17) Zhang, Q.; Yuan, H.; Fukaya, N.; Yasuda, H.; Choi, J.-C. A Simple Zinc Catalyst for Carbamate Synthesis Directly from CO2. ChemSusChem 2017, 10, 1501–1508.
(18) Pei, Y.; Li, H.; Liu, H.; Zhang, Y. A non-phosgene route for synthesis of methylene diphenyl dicarbamate from methylene dianiline and methyl carbonate. Catal. Today 2009, 148, 373–377.
(19) Wang, S.; Zhang, G.; Ma, X.; Gong, J. Investigations of Catalytic Activity, Deactivation, and Regeneration of Pb(OAc)2 for Methoxy carbonylation of 1,6-hexanedi amine by dimethyl carbonate to dimethylhexan-1,6-dicarbamate. Green Chem. 2010, 12, 483–490.
(20) Gao, J.; Li, H.; Zhang, Y.; Fei, W. Non-phosgene synthesis of isocyanates based on CO2: Synthesis of methyl N-phenyl carbamate through coupling route with lead compound catalysts. Catal. Today 2009, 148, 378–382.
(21) Li, Q.; Wang, P.; Liu, S.; Fei, Y.; Deng, Y. Catalytic degradation of polyurea: synthesis of N-substituted carbamates with CuO-ZnO as the catalyst. Green Chem. 2016, 18, 6091–6098.
(22) Li, H.; Cao, Y.; Li, X.; Wang, L.; Li, F.; Zhu, G. Heterogeneous Catalytic Methoxy carbonylation of 1,6-Hexanedi amine by Dimethyl Carbonate to Dimethylhexan-1,6-dicarbamate. Ind. Eng. Chem. Res. 2014, 53, 626–634.
(23) Shang, J.; Guo, X.; Li, Z.; Deng, Y. CO2 Activation and Fixation: Highly Efficient Syntheses of Hydroxy Carbamates over Au/Fe3O3. Green Chem. 2016, 18, 3082–3088.
(24) Fan, G.; Luo, S.; Fang, T.; Wu, Q.; Song, G.; Li, J. Cerium dioxide catalyzed synthesis of methyl N-phenylcarbamate from carbon dioxide, aniline and methanol in the presence of n-butyllithium. J. Mol. Catal. A: Chem. 2015, 404–405, 92–97.
(25) Allerov, K. A.; Fu, Z.; Ye, S.; Han, D.; Wang, S.; Xiao, M.; Meng, Y. One-Pot Synthesis of Dimethyl Hexane-1,6-dicarbamate from CO2, Methanol, and Diamine over Co2O Catalysts: A Route to an Isocyanate-Free Feedstock for Polyurethanes. ACS Sustainable Chem. Eng. 2019, 7, 10708–10715.
(26) Tamura, M.; Ito, K.; Nakagawa, Y.; Tomishige, K. CeO2-catalyzed direct synthesis of dialkylureas from CO2 and amines. J. Catal. 2016, 343, 75–85.
(27) Puertolas, B.; Bellán-Piñeiro, M.; Núñez-Rico, J. L.; Amrute, A. Phosgene-Free Synthesis of Carbamates as Polyurethane Precursors. ACS Catal. 2019, 9, 7708–7720.
(28) Ruiz, R.; Concepción, P.; Corma, A.; Fornés, V.; García, H. Gold-Catalyzed Phosgene-Free Synthesis of Polyurethane Precursors. Angew. Chem. 2010, 122, 1308–1312.
(29) Zhang, R.; Guo, L.; Chen, C.; Chen, J.; Chen, A.; Zhao, X.; Liu, X.; Xie, Y.; Hou, Z. The role of Mn doping in CeO2 for catalytic synthesis of aliphatic carbamate from CO2. Catal. Sci. Technol. 2015, 5, 2959–2972.
(30) Wang, P.; Ma, Y.; Liu, S.; Zhou, F.; Yang, B.; Deng, Y. N-Substituted carbamate synthesis using urea as carbonyl source over TiO2-Cr2O3/SiO2 catalyst. Green Chem. 2015, 17, 3964–3971.
(31) Kang, M.; Zhou, H.; Tang, D.; Chen, X.; Guo, Y.; Zhao, N. Methyl N-phenyl carbamate synthesis over Zn/Al/Ce mixed oxide derived from hydrotalcite-like precursors. RSC Adv. 2019, 9, 42474–42480.
(32) Ahmed, A. A. A.; Talib, Z. A.; Hussein, M. Z. Thermal, optical and dielectric properties of Zn-Al layered double hydroxide. Appl. Clay Sci. 2012, 56, 68–76.
(33) Ahmed, A. A. A.; Talib, Z. A.; Hussein, M. Z.; Zakaria, A. Improvement of the crystallinity and photocatalytic property of zinc oxide as calcination product of Zn-Al layered double hydroxide. J. Alloys Compd. 2012, 53, 154–160.
(34) Medaglia, P. G. Emerging switchable ultraviolet photoluminescence in dehydrated Zn/Al layered double hydroxide nano platelets. Sci. Rep. 2019, 9, No. 11498.
(35) Li, F.; Miao, J.; Wang, Y.; Zhao, X. Synthesis of Methyl N-Phenyl Carbamate from Aniline and Dimethyl Carbonate over Supported Zirconia Catalyst. Ind. Eng. Chem. Res. 2006, 45, 4892–4897.
(36) Zhao, X.; Kang, L.; Wang, N.; An, H.; Li, F.; Yang, W. Synthesis of Methyl N-Phenyl Carbamate Catalyzed by Ionic Liquid Promoted Zinc Acetate. Ind. Eng. Chem. Res. 2012, 51, 11335–11340.
(37) Zhang, R.; Guo, L.; Chen, A.; Zhao, X.; Huang, L. Zn-Al hydrotalcite-derived Co/Zn/AlOx catalysts for hydrogen generation by autothermal reforming of acetic acid. Int. J. Energy Res. 2019, 43, 7075–7084.
(38) Faur-Braquet, C.; Reddad, Z.; Kadirov, K.; Cloirec, P. L. Modelling the adsorption of metal ions (Cu2+, Ni2+, Pb2+) onto ACCs using surface complexation models. Appl. Surf. Sci. 2002, 196, 356–365.
(39) Devi, L. G.; Kottam, N.; Murthy, B. N.; Kumar, S. G. Enhanced photocatalytic activity of transition metal ions Mn2+, Ni2+ and Zn2+ doped polycrystalline titania for the degradation of Aniline Blue under UV/visible light. J. Mol. Catal. A: Chem. 2010, 328, 44–52.
(40) Liu, J.; Wang, P.; Wang, M.; Xu, R.; Zhang, J.; Liu, J.; Li, D.; Liang, N.; Du, Y.; Chen, G.; Tang, G. Achieving ZT = 2.2 with Pb and Zn codoped polycrystalline SnSe via phase separation and nano-structuring strategies. Nano Energy 2018, 53, 683–689.
(41) Saáedi, A.; Yousefi, R.; Jamali-Sheini, F.; Zak, A. K.; Cheraghizadeh, M.; Mahmoudian, M. R.; Baghchesara, M. A.; Dezaki, A. S. XPS studies and photocurrent applications of alkali-metals-doped ZnO nanoparticles under visible illumination conditions. Phys. E: Low-dimens. Syst. Nanostruct. 2016, 79, 113–118.
(42) Li, Y.; Wang, J.; Kong, Y.; Zhou, J.; Wu, J.; Wang, G.; Bi, H.; Wu, X.; Qin, W.; Li, Q. Micro/Nano hierarchical peony-like Al doped ZnO superhydrophobic film: The guiding effect of (100) preferred seed layer. Sci. Rep. 2016, 6, No. 19187.
(43) Jin, J.; Chen, S.; Wang, J.; Chen, C.; Peng, T. One-pot hydrothermal preparation of PhO-decorated brookite/anatase TiO2 composites with remarkably enhanced CO2 photo reduction activity. Appl. Catal. B 2020, 263, No. 118353.