

Highly Efficient Procedure for the Synthesis of Schiff Bases Using Hydrotalcite-like Materials as Catalyst

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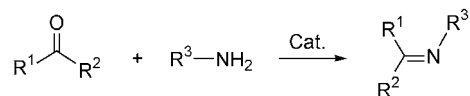
The novel efficient procedure has been developed for the synthesis of Schiff bases. The results showed that the 5% Fe(III)MgAl-LDH was very efficient for the reactions with the excellent yields in several minutes. Operational simplicity, no need of any solvent, low cost of the catalyst, high yields, reusability, wide applicability are the key features of this methodology.

Keywords hydrotalcite-like material, conjugate addition, solvent-free

Schiff base ligands, as variety of compounds with an imine group, have gained importance because of physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordinating metal ion given complexes, which serves as models for biological system.^{1,2} Also these complexes have many important catalytic applications, such as catalysts for epoxidation of olefins,³ alkene cyclopropanation,⁴ trimethylsilylcyanation of aromatic aldehydes,⁵ borohydride reduction of aromatic ketones,⁶ asymmetric oxidation of methyl phenyl sulfide,⁷ enantioselective epoxidation of silyl enol,⁸ ring opening polymerization of lactide,⁹ application of ion-selective electrodes,¹⁰⁻¹⁴ determination of heavy metal ions in environment samples,¹⁵ extraction of metal ions,¹⁶ etc. A lot of investigations have been made concerning the synthesis of Schiff bases,¹⁷⁻²¹ but these procedures have some limitations such as low yield, long reaction time, high environmental pollution regarding to solvent, and hardness reaction work up. These are once again topical in connection with a diverse range of applications in organic synthesis, bioorganic and medicinal chemistry. Many suffer from limitations such as the requirement for a large excess of reagents, long reaction time, harsh terms and also involvement of toxic solvents. Hence, the development of less expensive, simpler, 'green' catalysts for the reactions is still highly desirable. Aiming to these advantages, we developed a solvent-free procedure for the synthesis of Schiff bases using hydrotalcite-like materi-

als as catalyst. The results showed that the catalysts were efficient for the reactions with the excellent yields.

Scheme 1 Synthesis of Schiff bases



Experimental

All organic reagents were commercial products with the highest purity available (>98%) and used for the reaction without further purification.

Synthesis of the catalyst

All the hydrotalcites were prepared by a co-precipitation method. An aqueous solution (80 mL) containing various Mg(NO₃)₂•6H₂O, Al(NO₃)₃•9H₂O, Zn(NO₃)₂ or Fe(NO₃)₃•9H₂O (total metal nitrates, 1.0 mol), was added slowly to a second solution (80 mL) containing NaOH (0.16 mol) and Na₂CO₃ (0.01 mol) under vigorous mechanical stirring, maintaining the pH between 9 and 10. The addition took nearly 0.5 h at 70 °C. The mixture was kept at this temperature for 3 h under stirring, after that the product was left for 15 h at 353 K. The resulting white precipitate was filtered, washed to eliminate the alkali metal ions and the nitrate ions until the pH of the washing water was 7. Then the formed hydrotalcite was dried at 353 K for 24 h.

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Synthesis of Schiff bases

Typical procedure for the synthesis of Schiff base: A mixture of amine (24 mmol), aldehyde or ketone (20 mmol) and the catalyst (20 mg) was stirred in a three-necked round bottom flask (50 mL) at room temperature for the certain time as shown below. The process of the reaction was monitored by GC analysis [Shimadzu (GC-14B)]. On completion, the catalyst was recycled by filtration and washed with ether.

Results and discussion

Characterization of the catalyst

The XRD patterns (see Figure 1) with sharp and symmetric reflections for the (003), (006), (110) and (113) planes and broad symmetric peaks for the (102), (105), and (108) planes are characteristics of well-crystallized hydrotalcite-like materials.

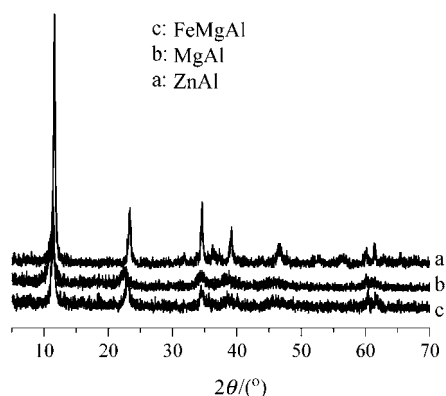


Figure 1 XRD patterns of LDHs.

Catalytic activities of various hydrotalcite-like materials

The catalytic activities of different hydrotalcite-like materials were first investigated (Table 1). As expected, the reaction took place and afforded the corresponding product in a high yield. From the results, it was found that the differences between these catalysts were very obvious. 5% Fe(III)MgAl-LDH (layered double hydroxides) showed the highest catalytic activity for the reaction with the conversion over 99% only within 5 min. ZnAl-LDH and MgAl-LDH were not so efficient for the selectivity of product. The self-condensation of valeraldehyde could also be promoted by the catalyst, which reduced the selectivity for the reaction. 5%

Table 1 Catalytic activities of various hydrotalcite-like materials

Catalyst	MgAl-LDH	ZnAl-LDH	5% Fe(III)MgAl-LDH
Conversion/%	92	98	99
Selectivity/%	93	90	99

^a The reaction conditions: propyl amine 24 mmol, valeraldehyde 20 mmol, catalyst 50 mg, r.t. (25 °C); ^b The conversion and selectivity were determined by GC based on valeraldehyde.

Fe(III)MgAl-LDH was very efficient for the acidic effect of the iron when the iron was added to the catalyst. So the results showed that 5% Fe(III)MgAl-LDH was the most efficient catalyst for the reaction.

Catalytic procedure for the synthesis of Schiff bases

The reactions between various amines and aldehyde or ketone under solvent-free condition were first investigated (Table 2). The results showed that the reactions underwent smoothly at room temperature within several minutes. Aldehydes showed much higher activities within 5 min for all kinds of amines than the ketones (Entries 1–4, 8–12). The carbonyl group of the aldehydes was more active than that of the ketones, which made the reactions of aldehydes undergo smoothly. But the carbonyl groups of aldehydes were very active and the self-condensation of the aldehydes would take place as the side-reactions in the reaction conditions, which

Table 2 Synthesis of various Schiff bases

Entry	Amine	Carbonyl compound	Conversion/%	Selectivity/%
1	<chem>CCCCN</chem>	<chem>CCCC=O</chem>	99	99
2	<chem>CCN</chem>	<chem>c1ccc(C=O)cc1</chem>	82	99
3	<chem>CCCCN</chem>	<chem>c1ccc(C=O)cc1</chem>	99	99
4	<chem>C1CCNCC1</chem>	<chem>c1ccc(C=O)cc1</chem>	99	99
5	<chem>CCN</chem>	<chem>C1CC(=O)CC1</chem>	44	99
6	<chem>CCCCN</chem>	<chem>C1CC(=O)CC1</chem>	76	99
7	<chem>C1CCNCC1</chem>	<chem>C1CC(=O)CC1</chem>	82	99
8	<chem>CCN</chem>	<chem>c1cc(C=O)oc1</chem>	85	96
9	<chem>CCCCN</chem>	<chem>c1cc(C=O)oc1</chem>	99	92
10	<chem>C1CCNCC1</chem>	<chem>c1cc(C=O)oc1</chem>	99	99
11	<chem>c1ccc(N)cc1</chem>	<chem>c1cc(C=O)oc1</chem>	98	99
12	<chem>OCCCN</chem>	<chem>c1cc(C=O)oc1</chem>	99	99
13	<chem>C1CCNCC1</chem>	<chem>CCCC=O</chem>	99	37

^a The reaction conditions: amine 24 mmol, aldehyde or ketone 20 mmol, catalyst 20 mg, r.t. (25 °C); ^b The conversion and selectivity were determined by GC based on aldehyde or ketone.

made the selectivity for the aldehydes very low (Entry 13). The conversions of the ethyl amine were much lower for the low boiling point (Entries 2, 5, 8). The ethyl amine was evaporated when the reaction took place, which made the conversion much lower. 2-Furaldehyde was extremely active here for the reactions with almost complete conversion and selectivity (Entries 8–12). Both the aliphatic and aromatic amines could be transferred to the corresponding products in high yields.

Reuse of the catalyst

One property of the catalyst is the heterogeneous catalytic process. Thus, recovery of the catalyst is very convenient. After reactions, the catalyst was recovered by filtration. The recovered activities were investigated through the reaction of propyl amine with valeraldehyde carefully (Figure 2). The yield remained unchanged even after the catalyst had been recycled for the sixth time.

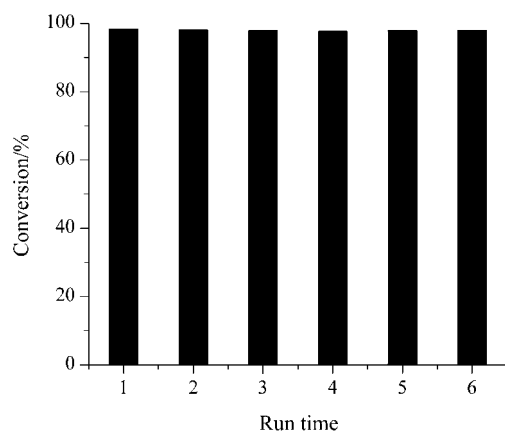


Figure 2 Reuse of the catalyst.

Conclusion

In conclusion, a novel efficient procedure has been developed for the synthesis of Schiff bases. Operational simplicity, no need of any solvent, low cost of the catalyst, high yields, wide applicability are the key features of this methodology.

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