Oxidation of Aldehydes to Carboxylic Acids in Water Catalyzed by Cobalt(II) Schiff-Base Complex Anchored to SBA-15/MCM-41¹

Wei-Dong Zhang, Lin-Xian Xu, Wei Shi, Chang-Chun Wang, Yong-Hai Hui, and Zheng-Feng Xie

Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education & Xinjiang Uyghur Autonomous Region, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China e-mail: xjuwshi@gmail.com; xiezhf72@gmail.com

Received March 7, 2014

Abstract—Cobalt(II) Schiff-base complexes were successfully anchored to SBA-15/MCM-41 and used as a catalyst for the oxidation of aldehydes to afford carboxylic acids in water under the action of hydrogen peroxide. Reaction conditions, such as different catalyst type, reaction temperature, reaction time, solvents media, and catalyst amount were studied systematically. High yield (up to 98%) of the process was reached. Such substrate-supported catalyst can be reused up to five times without significant loss of its catalytic activity which is not lower than 85%.

Keywords: SBA-15, MCM-41, Schiff-base, aldehyde, carboxylic acids, oxidation

DOI: 10.1134/S1070363214040306

Anchoring of homogeneous catalysts onto solid supports is a long standing objective of studies aiming to facilitate the recovery and reuse of catalysts [1, 2]. Due to their well-defined uniform mesopores structure and ability to surface modification, structured mesoporous solids like MCM-41 and SBA-15, have displayed promising perspective for the heterogeneous high-performance catalysis [3-5]. Moreover, properties like highly developed surface area, large pore volume, well-defined hexagonal arrays of channels and cavities of mesoporous silica make it possible to act as an ideal support for anchoring metal complexes [6-8].

The oxidation of benzaldehyde to carboxylic acids is an important synthetic transformation in terms of its extensive application in modern industry. Over recent years, the most popular and widely used reagent for oxidation of benzaldehyde is Jones reagent [9]. However, the reaction must be performed under highly acidic conditions that may be not applicable to the substrates with efficient tolerance to acid. Application of another type of catalysts such as Cr-based reagents, is limited by the formation of significant amounts of side products in the reaction process. Compared to other commonly used oxidizing agents, including oxone [10], NaClO [11], H₅IO₆ [12], BuOOH [13], H_2O_2 the system under discussion is the most reasonable choice from an environmental viewpoint [14]. Benzaldehyde could not be oxidized by H_2O_2 without a catalyst [11]. We have successfully synthesized the cobalt Schiff-base complexes and blend them with immobilized siliceous MCM-41 and SBA-15 and studied their activity as catalysts. It had been reported [15–19] the application of a Schiff base or Schiff-base anchored to MCM-41 as the highly efficient organic catalyst for several classical reactions such as Henry reaction, Friedel-Crafts reaction, Knoevenagel condensation, etc. Due to high potential and good catalytic activity MCM-41/Schiff base composite catalysts, it was interesting to study such systems applied to oxidation of benzaldehyde.

The successful preparation of Cobalt Schiff-base complex anchored by SBA-15/MCM-41 composites and the application of these catalysts in the oxidation of aldehydes to carboxylic acids in water with the coexistence of hydrogen peroxide is presented.

EXPERIMENTAL

Analytical thin-layer chromatography (TLC) was performed on silica gel GF254 (Qingdao, China) with

¹ The text was submitted by the authors in English.

Scheme 1. Synthetic route to the catalysts.



Co-Schiff base-SBA-15, Co-Schiff base-MCM-41

ethyl acetate and petroleum ether eluents at 60–90°C and with a UV detector. The structure of the catalyst was determined using X-ray diffraction (Rigaku R-axis Spider, Japan). IR spectra were recorded with EQUINOX 55 FT-IR spectrophotometer (KBr). ¹H NMR and ¹³C NMR spectra were accumulated with VARIAN INOVA-400 spectrometer, 400 MHz (for ¹H) and 100 MHz (for ¹³C), in CDCl₃ solution with SiMe₄ as reference, SEM (LEO1430VP, Germany) techniques.

The mixture of aldehydes (1 mmol) and the catalyst 0.01 g (10 wt %) with 0.3 mL H_2O_2 was stirred at 70°C in water (1 mL) for an appropriate time. Upon completion (TLC monitoring) of the process, the reaction mixture was extracted repeatedly with EtOAc (3 × 10 mL) and filtered off. The extract was dried over anhydrous sodium sulfate and concentrated by

rotary evaporation. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether eluent. The residue (recovered catalyst) was treated with EtOAc (3×5 mL) and dried at 80°C for 2 h and reused for subsequent reactions.

RESULTS AND DISCUSSION

Schiff-base supported metal complexes were prepared according to the following pathway (Scheme 1).

FT-IR spectra of the parent SBA-15 and MCM-41 are displayed in Figs. 1a, 1b. The bands at ca. 3415 and 3446 cm⁻¹ can be attributed to the surface hydroxyl groups and the bands at ca. 1084, 803 and 459 cm⁻¹ are attributed to the asymmetric and symmetric Si–O–Si stretching bonds of the support frameworks. For the silane-containing catalysts, curves 2, distinct bands at 2961 and 2958 cm⁻¹ [not present in



Fig. 1. (a) FT-IR of (*1*) SBA-15, (*2*) SAB-15-NH₂, (*3*) Schiff base-SAB-15, and (*4*) Co-Schiff base-SBA-15. (b) FT-IR of (*1*) MCM-41, (*2*) MCM-41-NH₂, (*3*) Schiff base-MCM-41, and (*4*) Co-Schiff base-MCM-41.

the IR spectra of pristine SBA-15 (Fig. 1a, curve *I*) and MCM-41 (Fig. 1b, curve *I*)], are attributed to the v(CH₂) of the propyl group attached to the silylating agent. This suggests the successful modification of the support material. The bands of SBA-15 (Fig. 1a, curve *3*) and MCM-41 (Fig. 1b, curve *3*) at about 1648 and 1659 cm⁻¹ are attributed to the stretching vibrations of the C=N bond of the attached Schiff base, and these bands shifted further 1565 cm⁻¹ (Fig. 1a, curve *4*) and 1572 cm⁻¹ (Fig. 1b, curve *4*) after the immobilization of Co(OAc)₂ complex (Figs. 1a, 1b curves *4*), confirming the successful grafting of Co-Schiff base onto MCM-41/SBA-15.

The successful grafting of the Schiff base unit onto modified SBA-15 and MCM-41 was confirmed also with X-ray diffraction (Fig. 2) and the scanning electron micrograph (SEM) (Fig. 3). The bands in the range of $2\theta = \sim 15^{\circ} - 30^{\circ}$ appear in all spectra, which suggests that the basic hexagonal pore arrangement was preserved. For Co-Schiff base containing composites (curves 4), three distinct peaks appear between $2\theta = \sim 5^{\circ} - 15^{\circ}$, indicating that Co-Schiff base has been successfully anchored onto SBA-15/MCM-41 substrates. The SEM micrographs reveals that SBA-15



Fig. 2. (a) XRD of (*1*) SBA-15, (*2*) SAB-15-NH₂, (*3*) Schiff base-SAB-15, and (*4*) Co-Schiff base-SBA-15. (b) XRD of (*1*) MCM-41, (*2*) MCM-41-NH₂, (*3*) Schiff base-MCM-41, and (*4*) Co-Schiff base-MCM-41.

(Fig. 3a) and MCM-41 (Fig. 3c) samples consist of small agglomerates whose morphology did not alter in the supported catalysts (Figs. 3b, 3d).

The study targeting optimization of the reaction conditions was carried out and the corresponding results are listed in Table 1. It was determined that undetectable carboxylic acid product was obtained upon using pure SBA-15 or MCM-41 as the catalysts. Under the same reaction conditions, yield of the process increased significantly, up to 83% and higher (Table 1, entries 7–8), in the case of cobalt Schiff base complex modification under the action of MCM-41/ SBA-15 catalysis. Influence of various oxidants (Air, t-BuOOH and H_2O_2) (entry 11, 12) upon the product yield was also studied. H₂O₂ Proved to give better results than the other reagents (entry 7). Furthermore, to evaluate the solvent effect, the oxidation of benzaldehyde was carried out using different organic solvents (ethanol, acetonitrile, THF, toluene, CH₂Cl₂ and water) (entry 17-22) under the same reaction conditions (catalyst and oxidant). Among these solvents, water was found to be the most suitable solvent for the process. The reaction temperature and quantity of oxidants also had significant influence



Fig. 3. SEM of (a) SBA-15, (b) Co-Schiff base-SBA-15, (c) MCM-41, and (d) Co-Schiff base-MCM-41.

upon the yield. It was determined that the reaction that involved 0.3 mL H₂O₂ under 70°C afforded better yield than the other processes (entries 13–16, 29–30). Yield of the process improved from 80% to 98% with the longer reaction time (from 2 to 5 h). Further increase of time to 6 h did not influence upon the yield (entries 23–26). When the catalyst quantity was increased from 5 to 15 wt% (entries 27–28), the yield improved from 65 to 98% (entry 25).

The above reaction conditions were applied to the oxidation of other aromatic aldehydes containing both





Fig. 4. Reusability of catalyst; Co-Schiff base-SBA-15 (1), Co-Schiff base-MCM-41 (2), reaction conditions: aldehyde (1 mmol), H_2O_2 0.3 mL, catalyst 0.01 g (10%) in water at 70°C.

 Table 1. Optimization of the reaction conditions^a

Entry	Catalyst	Solvent	Oxide	Temperature, °C	Time, h	Yield, % ^b
1	SBA-15 (10 wt %)	H ₂ O	H ₂ O ₂ (0.3 mL)	70	3	Traces
2	MCM-41 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	3	Traces
3	SAB-15-NH ₂ (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	3	Traces
4	MCM-41-NH ₂ (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	3	Traces
5	Schiff base-MCM-41(10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	3	Traces
6	Schiff base-MCM-41 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	3	Traces
7	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	3	85
8	Co-Schiff base-MCM-41 (10 wt %)	H ₂ O	H ₂ O ₂ (0.3 mL)	70	3	83
9	Co(OAc) ₂ (10 wt %)	H ₂ O	H ₂ O ₂ (0.3 mL)	70	3	78
10	None	H ₂ O	H_2O_2 (0.3 mL)	70	3	Traces
11	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	TBHP(0.3mL)	70	3	43
12	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	Air	70	3	30
13	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	25	36	55
14	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	50	3	50
15	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	60	3	57
16	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	80	3	75
17	Co-Schiff base-SBA-15 (10 wt %)	EtOH	H_2O_2 (0.3 mL)	70	3	_
18	Co-Schiff base-SBA-15 (10 wt %)	CH ₃ CN	H_2O_2 (0.3 mL)	70	3	42
19	Co-Schiff base-SBA-15 (10 wt %)	THF	H_2O_2 (0.3 mL)	66	3	_
20	Co-Schiff base-SBA-15 (10 wt %)	Tolune	H_2O_2 (0.3 mL)	70	3	43
21	Co-Schiff base-SBA-15 (10 wt %)	CH_2Cl_2	H_2O_2 (0.3 mL)	40	3	60
22	Co-Schiff base-SBA-15 (10 wt %)	None	H_2O_2 (0.3 mL)	70	3	76
23	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	2	80
24	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	4	91
25	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	5	98
26	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	6	98
27	Co-Schiff base-SBA-15 (5 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	5	65
28	Co-Schiff base-SBA-15 (15 wt %)	H ₂ O	H_2O_2 (0.3 mL)	70	5	98
29	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.1 mL)	70	5	81
30	Co-Schiff base-SBA-15 (10 wt %)	H ₂ O	H_2O_2 (0.2 mL)	70	5	90
31	Co-Schiff base-MCM-41 (10 wt %)	H ₂ O	H ₂ O ₂ (0.3 mL)	70	5	96

^a Reaction conditions (unless noted otherwise): aldehyde (1 mmol), H₂O₂ 0.3 mL, catalyst 0.01 g (10%) in water at 70°C. ^b Yield of the pure product.

 Table 2. Reagents ratio effect on the reaction^a

Entry	Catalyst	R	Product	Time, h	Yield, % ^b
1	Co-Schiff base-SBA-5 Co-Schiff base-MCM-41	C_2H_5	а	5	<u>98</u> 96
2	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$4-FC_6H_4$	b	5	<u>99</u> 97
3	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$4-ClC_6H_4$	с	5	<u>93</u> 90
4	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$4\text{-BrC}_6\text{H}_4$	d	5	<u>80</u> 77
5	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$4-CH_3C_6H_4$	e	5	<u>81</u> 76
6	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$4-NO_2C_6H_4$	f	5	Trace
7	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$4\text{-OCH}_3\text{C}_6\text{H}_4$	g	5	$\frac{81}{80}$
8	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	2,4-Di-ClC ₆ H ₃	h	5	<u>85</u> 84
9	Co-Schiff base-SBA-5 Co-Schiff base-MCM-41		i	8	<u>81</u> 73
10	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41		j	8	$\frac{40}{36}$
11	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41		k	8	<u>51</u> 50
12	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$2\text{-OHC}_6\text{H}_4$	1	5	Trace
13	<u>Co-Schiff base-SBA-5</u> Co-Schiff base-MCM-41	$2\text{-OCH}_3C_6H_4$	m	5	Trace
14	Co-Schiff base-SBA-5 Co-Schiff base-MCM-41	2-CIC ₆ H ₄	n	5	Trace

^a Reaction conditions (unless noted otherwise): aldehyde (1 mmol), H₂O₂ 0.3 mL, catalyst 0.01 g (10%) in water at 70°C. ^b Yield of the pure product.

electron-withdrawing and electron-donating substitutents (Table 2). Aromatic aldehydes containing halogen atom, methoxy and cinnamaldehyde groups in *para*-position underwent oxidation efficiently under the action of Co-Schiff base-SBA-15 and Co-Schiff base-MCM-41 catalysts (entries 1–5, 7–9). However, in the case of β -chlorocinnamaldehydes, and aromatic aldehydes containing 2-nitro- and hydroxyl groups, poor results were achieved.

It is important that the catalyst could be reused up to five times without significant loss of its activity, confirming the strong association between Schiff base and substrates and high stability of the composite catalyst (Fig. 4).

CONCLUSIONS

In summary, MCM-41&SBA-15/Schiff base derivatized composites have been proven to be efficient catalysts for the oxidation of aldehydes by hydrogen peroxide to afford carboxylic acids in water with excellent yield (up to 98%). It is important that the catalyst could be reused (up to 5 times) without significant loss of activity.

ACKNOWLEDGMENTS

We appreciate the financial support of the National Natural Science Foundation of China (nos. 21262034, 21162026, and 20962018).

REFERENCES

- Hoffmann, F.M., Angew. Chem. Int. Ed., 2006, vol. 45, p. 3216.
- 2. Augustine, R., Tanielyan, S., Anderson, S., and Yang, H., *Chem. Commun.*, 1999, p. 1257.
- Kresge, C.T., Leonowicz, M.E., and Roth, W.J., *Nature* 1992, vol. 359, p. 710.
- 4. Wang, X.L., Wu, G.D., Wei, W., and Sun, Y.H., *Catal. Lett.*, 2010, vol. 136, p. 96.
- 5. Sugino, K., Oya, N., Yoshie, N., and Ogura, M., J. Am.

Chem. Soc. 2011, vol. 133, p. 20030.

- 6. Ravikovitch, P.I., Wei, D., and Chueh, W.T., J. Phys. Chem. B, 1997, vol. 101, p. 3671.
- Galo, J.D. and Eduardo, L.C.S., Curr. Opin. Colloid Interface Sci, 2003, vol. 8 p. 109.
- Flodstroem, K., Wennerstroem, H., and Alfredsson, V., Langmuir, 2004, vol. 20, p. 680.
- Bowers, A., Halsall, T.G., Jones, E.R.H., and Lemin, A.J., J. Chem. Soc, 1953, p. 2548.
- 10. Travis, B.R., Sivakumar, M., Hollist, G.O., and Borhan, B., Org. Lett. 2003, vol. 5, p. 1031.
- 11. Shi, D.P. and Ji, H.B., Chin. Chem. Lett. 2009, vol. 20, p. 139.
- 12. Hunsen, M., J. Fluorine Chem, 2005, vol. 126, p. 1356.
- 13. Sodhi, R.K., Paul, S., and Clark, J.K., *Green Chem*, 2012, vol. 14, p. 1649.
- 14. Joseph, J.K., Jain, S.L., and Sain, B., Catal. Commun. 2007, vol. 8, p. 83.
- 15. Zhou, G.P., Hui, Y.H., Wan, N.N., Xie, Z.F., and Wang, J.D., *Chin. Chem. Lett*, 2012, vol. 23, p. 690.
- Wan, N.N., Hui, Y.H., Xie, Z.F., and Wang, J.D., *Chin. J. Chem*, 2012, vol. 30, p. 311.
- 17. Yang, Y.L., Wan, N.N., Wang, W.P., Xie, Z.F., and Wang, J.D., *Chin. Chem. Lett*, 2011, vol. 22, p. 1071.
- 18. Hui, Y.H., Chen, C.M., and Xie, Z.F., *Chin. Chem. Lett*, 2012, vol. 23, p. 525.
- 19. Dong, X.Z., Hui, Y.H., Xie, S.L., Zhang, P., Zhou, G.P., and Xie, Z.F., *RSC Adv*, 2013, vol. 3, p. 3222.