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ARTICLE TYPE

Efficient Fenton-like La-Cu-O/SBA-15 catalyst for the degradation of organic dyes under ambient conditions

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Fenton-like La-Cu-O/SBA-15 catalyst is highly efficient for dye degradation, due to a synergistic effect between La-Cu-O and SBA-15, in which La-Cu-O is the active site of the reaction and SBA-15 acts as a gallery to adsorb and transport the organic dyes from solution to the surface of La-Cu-O.

Perovskite-type oxides with ABO_3 or A_2BO_4 structure are one class of promising materials in heterogeneous catalysis because of their structural features, such as exchangeable cations at A and B positions, controllable oxidation state of the B-site cation, and generation of oxygen vacancies.[1] They can be applied to gas or solid reactions carried out at high temperatures, or liquid-phase reactions carried out at low temperatures, due to their highly thermal and hydrothermal stability.[2] So far, these oxides have not gained applications in practice and their catalytic efficiency need to be improved before the possibility of industrialization.

One application of perovskite-type oxides is to catalyze the oxidative degradation of organic dyes in aqueous solution,[3] which are discharged from industrial plants and are destructive to aquatic life.[4] In this regard, these oxides can be classified as "Fenton-like" catalyst according to the description of Walling.[5] Comparing to the classic homogeneous Fenton catalysts,[6] the perovskite-type catalyst has wide working pH range, and is more operable in practice because of the facile separation and recovery of catalyst from industrial wastewater.[7] However, the oxidative efficiency of these catalysts is low and the use of ultrasonic and/or UV light irradiation is essential to accelerate reaction rate for better catalytic performance,[8] since the surface area of these oxides is low and the interaction between the substrates and the active sites (metal cations) is limited.

In this work, in order to increase the surface area and improve the catalytic efficiency of perovskite-type oxide catalysts, we attempt to synthesize them on a high-surface-area mesoporous silica SBA-15 support.[9] In detail, we synthesized a La-Cu-O mixture, which are composed of perovskite-type oxide La_2CuO_4 and a few amount of CuO, on a SBA-15 support, defined as La-Cu-O/SBA-15. This way the La-Cu-O can be well dispersed and more active sites can be exposed, relative to that of the bulk one. Furthermore, because of the large surface area and pore volume, SBA-15 shows good adsorption capacity for Rhodamine B (RhB) and thus has the potential to transport the adsorbed RhB to the active sites, guaranteeing the sufficient supply of RhB to the active sites and reaching the objective of improving the catalytic efficiency.

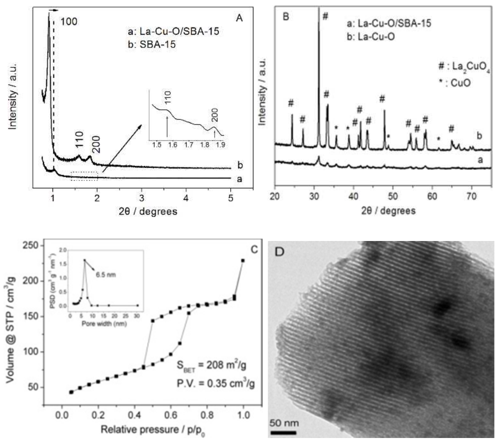


Figure 1. (A) small-angle XRD patterns for SBA-15 and La-Cu-O/SBA-15; (B) wide-angle XRD patterns for La-Cu-O/SBA-15 and bulk La-Cu-O; (C) N_2physisorption isotherms and (insert) the corresponding pore size distribution for La-Cu-O/SBA-15; (D) TEM image for La-Cu-O/SBA-15.

Figures 1A and 1B show the X-ray diffraction patterns of the samples conducted at small- and wide-angles. At small angles, the peak intensity is largely attenuated and the peak position is slightly shifted to higher angles from SBA-15 to La-Cu-O/SBA-15, indicating that the long-range order of the channels of SBA-15is decreased and the unit cell of SBA-15 is shrunk.[10] Whereas, the reserved (100), (110) and (200) faces (see the insert picture) suggest that the porous structure of SBA-15 is not destroyed after the loading of La-Cu-O. At wide angles, the predominant peaks of La-Cu-O/SBA-15 appear almost at the same position as those of La-Cu-O. By referring to the standard PDF card of copper compounds, we inferred that the La-Cu-O contains mainly ofLa_2CuO_4 (signal #) and few amount of CuO(signal *).[4d, 11] The peak intensity of La-Cu-O/SBA-15 is largely attenuated relative to that of La-Cu-O, which could be that the La-Cu-O mixture is well dispersed and has poorer crystallinity,[12] and/or a dilution effect of the SBA-15 support.

N_2 physisorption isotherms (Figure 1C) and TEM image (Figure 1D) of La-Cu-O/SBA-15 (more pictures can be found in Figure S4) confirms that the matrix structure of SBA-15 is maintained and demonstrates that the La-Cu-O mixture is highly dispersed on the surface of SBA-15, suggesting that the La-Cu-O/SBA-15 composite is successfully prepared. With this structure, it can be imaged that the organic dyes adsorbed on the pores of SBA-15 could be transported to the surface of La-Cu-O, and subsequently oxidized by H_2O_2. The good adsorption ability of SBA-15 to organic dyes would ensure the sufficient supply of organic dyes to the surface of La-Cu-O, improving the reaction rate and thus catalytic efficiency.

To verify the above speculation, we first measured the capacity of La-Cu-O, SBA-15 and La-Cu-O/SBA-15 for RhB adsorption. Results indicate that SBA-15 and La-Cu-O/SBA-15 exhibit 0.017 and 0.0076 mmol/g adsorption capacity for RhB, while negligible value is observed for La-Cu-O. This implies that the supply of RhB from solution to the surface of La-Cu-O/SBA-15 should be better than that to the surface of bulk La-Cu-O.

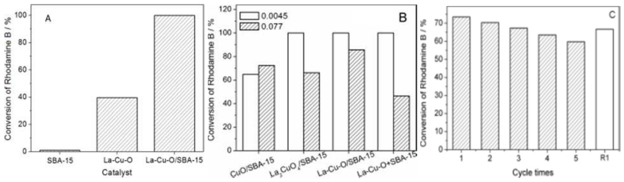
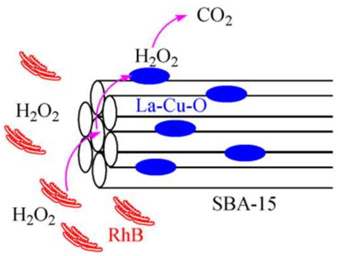


Figure 2. (A) and (B) RhB conversion measured on the specified samples and at different molar ratios of RhB to catalyst; (C) Reusability of La-Cu-O/SBA-15 for RhB oxidation; “R1” means that the activity was obtained from the used catalyst re-treated at 500 °C for 2 h. Data in Figure 2 (A) and (B) were measured at 60 min, while those in Figure 2 (C) were taken at 30 min. The molar ratio of RhB to catalyst is 0.0045, if not specified.

As expected, La-Cu-O/SBA-15 shows far higher activity for RhB oxidation than La-Cu-O, and no appreciable activity is detected on SBA-15, Figure 2A, indicating that SBA-15 is hard to catalyze the reaction while it can largely improve the catalytic performances of La-Cu-O. Considering that SBA-15 is a porous material and has strong ability to RhB adsorption, it is suggested that the contribution of SBA-15 in the reaction, on one hand, is to act as a support to improve the dispersion of La-Cu-O or the exposure of copper active sites; and on the other hand that is more crucial is to adsorb and transport RhB from solution to the surface of La-Cu-O, accelerating the reaction rate and improving the catalytic activity. Namely, there has a synergistic effect between La-Cu-O and SBA-15, in which La-Cu-O is the active site of reaction and SBA-15 acts as a gallery to adsorb and transport RhB from the solution to the surface of La-Cu-O, where the reaction occurs and CO_2 is produced, Scheme 1.



Scheme 1. Proposed reaction route for the oxidation of RhB with H_2O_2over La-Cu-O/SBA-15

Besides, considering that the real amount of La-Cu-O in the La-Cu-O/SBA-15 (loading: 55.6wt.%) is 0.056 g, while that for the bulk La-Cu-O is 0.1 g, and the fact that SBA-15 is inactive to the reaction, this means that 0.056 g supported La-Cu-O is more active than 0.1 g bulk La-Cu-O. Moreover, recalling that the total amount of RhB converted over La-Cu-O/SBA-15 contains both the pre-adsorbed RhB and those in the solution, while that over bulk La-Cu-O contains only the RhB in the solution as it shows no adsorption capacity for RhB. This suggests that the real ability of La-Cu-O/SBA-15 to RhB oxidation should be better than what observed in Figure 2A. Overall, La-Cu-O/SBA-15can show far high efficiency for dye degradation relative to the bulk La-Cu-O.

To ensure that the pre-adsorbed RhB is oxidized, we carried out an additional measurement: after the oxidation reaction, the catalyst was filtered and added to a new batch of RhB solution, to test if it could adsorb RhB again from the solution. Indeed, we found that the concentration of this new RhB solution decreased after addition of the used catalyst, confirming that there have refreshed space in the used La-Cu-O/SBA-15 and part of pre-adsorbed RhB is consumed. By calculation, the used La-Cu-O/SBA-15 shows capacity of 0.0036mmol/g for RhB adsorption, which is nearly half of the fresh one, confirming that the adsorbed RhB is indeed oxidized in the reaction.

In justifying the transport capacity of SBA-15, we tested the activity of a mechanically mixed “La-Cu-O+SBA-15” sample for RhB oxidation, finding that although its activity is lower than that of La-Cu-O/SBA-15, is far better than that of bulk La-Cu-O (see Figures 2A and 2B). This is interesting as SBA-15 itself is hard to catalyze RhB oxidation, while the physically mixed sample shows enhanced activity relative to the bulk La-Cu-O. The reason could be that when this mixture is added to and stirred in the RhB solution, some of SBA-15 powders are suspended and attached to the La-Cu-O mixture, forming a new composite (let define as La-Cu-O%SBA-15), which is similar to La-Cu-O/SBA-15 except that the interaction between La-Cu-O and SBA-15 is weaker. Hence, RhB will mobilize or be transported to the surface of La-Cu-O through SBA-15, and thus an increased activity is observed. This confirms that SBA-15 can absorb and transport RhB from solution to the surface of La-Cu-O. Otherwise, La-Cu-O%SBA-15 should behave as the bulk La-Cu-O, which is obviously contrary to the experimental results.

As demonstrated above that La-Cu-O is composed of La_2CuO_4 and CuO, we thus prepared La_2CuO_4/SBA-15 and CuO/SBA-15 and tested their activities for RhB oxidation, Figure 2B, to clarify which phase predominates the reaction. At molar ratio of RhB to catalyst equals to 0.0045, the RhB conversion measured over CuO/SBA-15, La_2CuO_4/SBA-15 and La-Cu-O/SBA-15 is 65%, 100%, 100%, indicating that La_2CuO_4 is more crucial to the reaction than CuO. To differentiate the oxidation ability of La_2CuO_4/SBA-15 and La-Cu-O/SBA-15, we increased the molar ratio of RhB to catalyst to 0.077 and found that the former shows lower activity than the latter (66% and 86%, respectively), suggesting that the La-Cu-O mixture is more favorable for the reaction than La_2CuO_4. The reason might be that there have more copper active sites exposed in La-Cu-O (molar ratio of La/Cu is 1) than that in La_2CuO_4 (molar ratio of La/Cu is 2).

Comparing with previously reported perovskite catalysts, the herein La-Cu-O/SBA-15 shows better turnover (TOF) for RhB oxidation, meanwhile requires fewer amount of H_2O_2, Table S1. This demonstrates that La-Cu-O/SBA-15 is indeed an efficient catalyst for RhB degradation. The strong ability of La-Cu-O/SBA-15 to RhB oxidation is further confirmed by applying it to high concentrated RhB solution. It is found that even at molar ratio of RhB to catalyst equals to 0.077, the RhB conversion can be reached up to 95% at reaction time of 3h, Figure S6.

Reusability tests indicate that an extent of ca. 14% decrease in

RhB conversion is observed after the fifth run, but the activity can be recovered after a treatment of the used catalyst in air at 500 °C for 2 h (see "R1" in Figure 2C). This indicates that the decrease in the activity is not attributed to the leaching of copper active site in the solution, but to the deterioration of active site. This is also confirmed by an atomic absorption spectrometry (Cu lamp, Shimadzu AA-6300), which shows that no leaching copper detectable in the filtered solution after reaction. Characterizations on the used La-Cu-O/SBA-15 (XRD, TEM, XPS, etc.) indicate no significant change in the textural structure relative to the fresh one (Figures S2 and S4), suggesting that the sample is stable in the reaction.

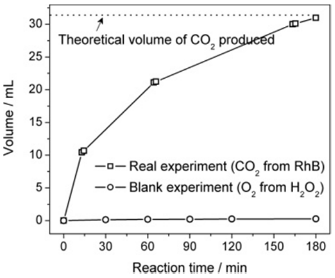


Figure 3.Volume of CO_2 and O_2 evolved from the real and blank experiments. Reaction conditions: molar ratio of RhB to catalyst is 0.077,H_2O_2 amount: 1 mL.

In order to test if RhB is completely converted into CO_2, that is the mineralization of RhB, we measured the volume of CO_2 evolved during the reaction, Figure 3. Results show that although some amounts of small organic molecules (Figure S12) exist at reaction time of 1h, where the colour of RhB solution is faded, they can be completely converted into CO_2 at reaction time of 3 h. Besides, blank experiment (no RhB is added to the solution with otherwise identical reaction conditions) shows that H_2O_2 is hardly decomposed into O_2 over the catalyst. This indicates that H_2O_2 can be mostly used for RhB oxidation and the gas evolved from the reaction is due to the yield of CO_2 degraded from RhB.

Finally, we also tested the applicability of La-Cu-O/SBA-15 to other organic dyes including reactive brilliant red X-3B, direct scarlet 4BS and methylene blue (MB), showing that the sample is the most active for RhB, meanwhile also shows considerable activities forMB, X-3B and 4BS, Figure S9. Moreover, like other perovskite catalysts[4d, 13] La-Cu-O/SBA-15 also endures wide working pH range (pH = 2-10) for the reaction, owing to the buffer function of the active compounds, see Figure S10 and S11.

In summary, we reported that Fenton-like La-Cu-O/SBA-15isa highly efficient catalyst for the oxidative degradation of organic dyes, in particular for RhB, which can be fully oxidized into CO_2at reaction time of 3h in the present reaction conditions. This is the best perovskite-type catalyst reported in literature for RhB degradation using H_2O_2 as oxidant to the best of our knowledge. The high efficiency is due to a support effect by increasing the exposure of copper active sites and, more crucial, to a synergistic effect between La-Cu-O and SBA-15, in which La-Cu-O is the active site and SBA-15 acts as a gallery to transport the organic dyes from solution to the surface of La-Cu-O. The high catalytic efficiency, wide working pH ranges, strong resistance to deactivation as well as the facile separation from aqueous solution enable La-Cu-O/SBA-15 to be a potential industrial catalyst for oxidative degradation of organic dyes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, additional characterizations, activity tests with reaction time and that for different dyes, and the HPLC-MS analysis on the intermediate products. See DOI: 10.1039/b000000x/

1 (a) D. Ferri and L. Forni, *Appl. Catal. B: Environ.*, 1998, **16**, 119; (b) R. F. Klie, Y. Ito, S. Stemmer and N. D. Browning, *Ultramicroscopy*, 2001, **86**, 289; (c) W. L. Warren, K. Vanheusden, D. Dimos, G. E. Pike and B. A. Tuttle, *J. Am. Ceram. Soc.*, 1996, **79**, 536; (d) J. Zhu and A. Thomas, *Appl. Catal. B: Environ.*, 2009, **92**, 225.

2 (a) R. J. H. Voorhoeve, *Advanced Materials in Catalysis*, Academic Press, New York, 1977; (b) M. A. Pena and J. L. G. Fierro, *Chem. Rev.*, 2001, **101**, 1981; (c) L. G. Tejuca and J. L. G. Fierro, *Properties and Applications of Perovskite-type Oxides*, CRC Press, New York, 1993.

3 (a) P. Mahata, T. Aarthi, G. Madras and S. Natarajan, *J. Phys. Chem. C*, 2007, **111**, 1665; (b) S. Song, L. Xu, Z. He, H. Ying, J. Chen, X. Xiao and B. Yan, *J. Hazard. Mater.*, 2008, **152**, 1301; (c) J. Faye, E. Guélou, J. Barrault, J. M. Tatibouët and S. Valange, *Top. Catal.*, 2009, **52**, 1211.

4 (a) M. Ajmal and A. U. Khan, *Environ. Pollut. Biol.*, 1985, 37, 131; (b) M. P. Gupta and P. K. Bhattacharya, *J. Chem. Technol. Biot.*, 1985, **35**, 23; (c) W. Luo, L. Zhu, N. Wang, H. Tang, M. Cao and Y. She, *Environ. Sci. Technol.*, 2010, **44**, 1786; (d) L. Zhang, Y. Nie, C. Hu and J. Qu, *Appl. Catal. B: Environ.*, 2012, **125**, 418.

5 C. Walling, *Accounts. Chem. Res.*, 1975, **8**, 125.

6 (a) F. Haber and J. Weiss, *P. Roy. Soc. A: Math. Phy.*, 1934, **147**, 332; (b) S. Meriç, H. Selcuk, M. Gallo and V. Belgiorno, *Desalination*, 2005, **173**, 239; (c) D. L. Sedlak and A. W. Andren, *Environ. Sci. Technol.*, 1991, **25**, 777; (d) J. J. Pignatello, *Environ. Sci. Technol.*, 1992, **26**, 944.

7 S. Parra, I. Guasaquillo, O. Enea, E. Mielczarski, J. Mielczarki, P. Albers, L. Kiwi-Minsker and J. Kiwi, *J. Phys. Chem. B*, 2003, **107**, 7026.

8 (a) T. Soltani and M. H. Entezari, *Chem. Eng. J.*, 2013, **223**, 145; (b) S. Taherian, M. H. Entezari and N. Ghows, *Ultrason. Sonochem.* 2013, **20**, 1419.

9 D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.

10 (a) B. S. Liu, X. N. Wei, Y. P. Zhan, R. Z. Chang, F. Subhan and C. T. Au, *Appl. Catal. B: Environ.*, 2011, **102**, 27; (b) X.-K. Li, W.-J. Ji, J. Zhao, Z.-B. Zhang and C.-T. Au, *J. Catal.*, 2006, **238**, 232; (c) Y.-M. Liu, Y. Cao, S.-R. Yan, W.-L. Dai and K.-N. Fan, *Catal. Lett.*, 2003, **88**, 61.

11 M. L. Rojas and J. L. G. Fierro, *J. Solid State Chem.*, 1990, **89**, 299.

12 (a) L. F. Liotta, G. Carlo, G. Pantaleo, J. C. Hernandez Garrido and A. M. Venezia, *Top. Catal.*, 2012, 55, 782-791; (b) P. Xiao, J. Hong, T. Wang, X. Xu, Y. Yuan, J. Li and J. Zhu, *Catal. Lett.*, 2013, **143**, 887.

13 (a) S. Song, L. Xu, Z. He, J. Chen, X. Xiao and B. Yan, *Environ. Sci. Technol.*, 2007, **41**, 5846; (b) M. Y. Leiw, G. H. Guai, X. Wang, M. S. Tse, C. M. Ng and O. K. Tan, *J. Hazard. Mater.* 2013, **260**, 1