Excellent low temperature toluene oxidation over hollow NiCo-MMO derived from LDH @ ZIF-67

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Abstract: A facile and controllable method through *insitu* growing for nickel-cobalt layered double hydroxide (Ni-Co LDH) with a highly surface area is presented, in which hollow rhombic dodecahedron structured zeolitic-imidazolate-framework-67 (ZIF-67) nanocrystals as template. Ni_2Co-6h-350-MMO sample obtained from the calcination of LDH@ZIF-67 precursor, possesses much higher activity with 90% toluene conversion at 229 ℃ at a high space velocity (SV=60 000 ml g^{-1} h^{-1}) than other catalysts with different reaction time and calcination temperature. Abundant high valence Co ions are the key role for the best catalytic activities, together with adsorbed oxygen species and abundant medium-strength surface acid sites.

Keywords: ZIF-67, LDH, toluene oxidation.

1. Introduction

Catalytic oxidation has been generally considered as one of the most effective methods for VOCs treatment because of high efficiency and complete destruction of VOCs rather than transferring it to another phase. One of the main challenges of catalytic oxidation of VOCs is the selection of the proper catalysts from the large number of available catalysts. Mixed metal oxides derived from LDHs as VOCs oxidation catalysts are widely studied recently for increasing the synergistic effect.[1-3] Co is reported as one of the most active element for VOCs oxidation. In order to prepare a hollow structure catalyst with highly surface area and small size, we use ZIF-67 (as a sacrificial template and cobalt source) with ethanol and nickel nitrate to fabricate hollow rhombic dodecahedron structured Ni-Co LDHs precursor, which around the surface of the ZIF-67. A series of porous $NiCo_2O_4$/NiO hollow dodecahedron catalysts can be obtained by calcined of LDH@ZIF-67. Meanwhile, the effect of reaction time and calcination temperature on catalytic activities for degradation of toluene was further investigated.

2. Experimental

The synthesis of LDH precursor samples (with $Ni(NO_3)_2•6H_2O$/ZIF-67 mass ratios of 3/1, 2/1, 1/1) is based on the hydrothermal method with different reaction time, denoted as Ni_xCo-yh LDHs@ZIF-67. The catalysts NiCo-MMO are obtained through the calcination of corresponding LDH@ZIF-67 precursors by different temperatures.

3. Results and discussion

The fabrication process for NiCo-MMO is shown in Figure 1, the pure ZIF-67 single crystals were firstly fabricated with hollow rhombic dodecahedron structure. Then the obtained Ni-Co LDHs well inherited the polyhedral structure of the ZIF-67 template after hydrothermal treatment with $Ni(NO_3)_2•6H_2O$ in absolute ethanol solution. Driven by hydrolysis of $Ni(NO_3)_2$ in absolute ethanol, ZIF-67 slowly dissolves and the released Co^{2+} ions may be partially oxidized by dissolved O_2 and NO_3^- ions in the solution. Then the Co^{2+}/Co^{3+} ions will co-precipitate with Ni^{2+} ions to form NiCo-LDH nanosheets on the template. [4,5]

The TEM images in Figure 2a and e for Ni_2Co-6h LDH show the curved LDH platelets evenly distributed on the surface of ZIF-67 with polycrystal structures. After calcination in different temperatures, as shown in Figure 2, the catalysts all show hollow interior with around 500 nm. The Ni_2Co-6h-350-MMO shows typical $NiCo_2O_4$ and NiO phases. Increasing the calcination temperature from 350 to 500 ℃, the

LDHs platelet structure collapsed to small nanoparticles, which maybe affect the toluene oxidation performance.

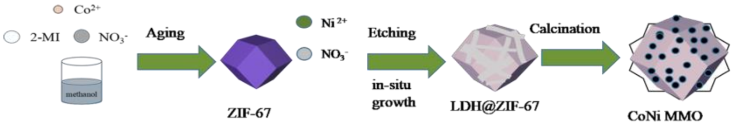

Figure 1. Synthesis of Ni-Co MMO Catalyst derived by ZIF-67.

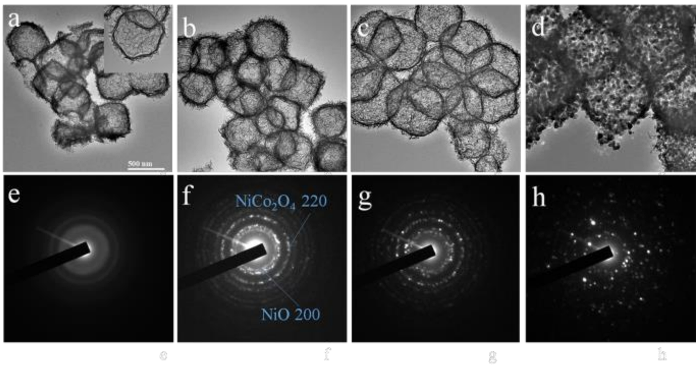

Figure 2. (a–d) TEM images of Ni_2Co-6h LDH precursor, Ni_2Co-6h-350-MMO, Ni_2Co-6h-400-MMO, Ni_2Co-6h-500-MMOcatalysts and (e–h) the corresponding SAED pattern in (a–d), respectively.

The catalytic performances of Ni_2Co-6h-MMO catalysts for the oxidation of toluene are shown in Figure 3. Ni_2Co-6h-350-MMO sample shows excellent catalytic performance (T_{50} = 220 and T_{90} = 229 ℃) for toluene combustion than other samples, which can be attributed to the high surface area, the rich adsorbed oxygen species, the lots of medium-strength acid sites, and the good low temperature reducibility developed from synergistic effect between Ni and Co, which proved by BET, XPS, NH_3-TPD and H_2-TPR, respectively. Furthermore, the sample shows good reproducibility by three repeated toluene oxidation tests.

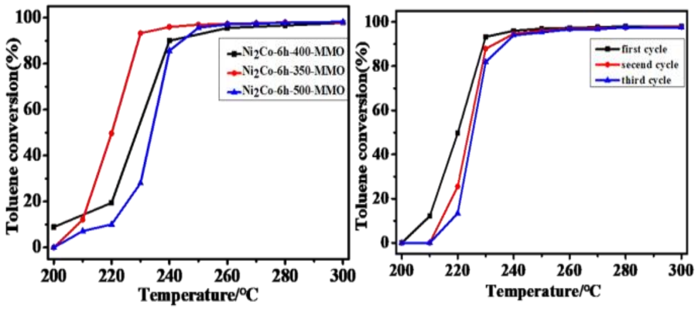

Figure 3. toluene conversion and reproducibility as a function of reaction temperature over Ni_2Co-6h-MMO catalysts under the conditions of toluene concentration 200 ppm in air, SV= 60,000mL g^{-1} h^{-1}.

4. Conclusions

In summary, a series of hollow structured NiCo-MMO with a highly surface area have been successfully fabricated on layered double hydroxide @ zeolitic-imidazolate-framework-67 (LDH@ZIF-67) precursors. Among the samples, Ni_2Co-6h-350-MMO shows best toluene oxidation reactivity with T_{90} at 229 ℃ under space velocity 60 000 ml g^{-1} h^{-1}. This is probably due to the better redox, the abundant surface Co^{3+}, and adsorbed oxygen species.

References

1. S. Li, H. Wang, W. Li, X. Wu, W. Tang and Y. Chen, Appl. Catal. B 166-167 (2015) 260.
2. S. Mo, S. Li, J. Li, Y. Deng, S. Peng, J. Chen and Y. Chen, Nanoscale 8 (2016) 15763.
3. S. Li, S. Mo, J. Li, H. Liu and Y. Chen, RSC. Adv 6 (2016) 56874.
4. G. Yilmaz, K. M. Yam, C. Zhang, H. J. Fan and G. W. Ho, Adv. Mater 29 (2017) 1606814,.
5. H. Hu, B. Guan, B. Xia and X. W. Lou, J Am. Chem. Soc 137 (2015) 5590.