Upcycling degraded Li(Ni-Co-Mn)O_2 cathodes to highly active thermal catalyst via lithium pre-extraction method for air pollutant abatement

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Significance and Relevance

This study presents a novel upcycling strategy of NCM622 ($Ni_{0.6}Co_{0.2}Mn_{0.2}O_2$) layered transition metal oxide (LTMO) into highly active thermal catalyst for numerous pollutant abatement. Unlike conventional recycling methods mainly focused on metal recovery, our approach provides an upcycling pathway of direct transformation of NCM to thermal catalyst via simple selective Li pre-extraction followed by heat-treatment. This process significantly enhances catalytic performance by increasing surface area and generating new active sites, well-suited for environmental catalysis. This innovative strategy significantly reduces the need for chemical processing while enabling complete recycling of valuable metals, offering dual benefits of environmental protection and resource sustainability.

Preferred and 2nd choice for the topic: 1st Automotive and stationary emission control, 2nd Air cleaning and combustion
Preferred presentation: Oral only

Introduction and Motivations

Given the rapid growth of the broader electrical industries, recycling massive volume of LTMO cathode material in spent lithium-ion batteries presents a significant challenge for both environmental protection and resource sustainability[1]. To date, numerous researchers have proposed solutions for closed-loop and sustainability to address these demands. Mature strategies in industrial scale including pyrometallurgy and hydrometallurgy would somewhat meet this requirement through high-temperature combustion or chemical leaching[2]. As known, however, these are severely limited by low metal recovery rates, toxic by-products, and most critically, extremely low energy efficiency. Under these constraints, research on the recycling of spent cathode materials has expanded beyond closed-loop recycling to explore the potential of the upcycling.

The spent NCM can be upcycled into various high-value products including catalyst; Indeed, NCM holds significant potential as it is composed of transition metals widely used as active metal in thermal catalyst. However, considering the environmental catalysts under actual operating conditions, the low surface area (~4 m^2/g) and the non-reducible, super-stable structure of NCM shows significant limitations to the catalysis. Herein, our study demonstrates a direct upcycling pathway of spent NCM cathodes into superior environmental catalyst through simple Li pre-extraction and oxidative heat-treatment. Through comprehensive catalytic characterization, we identified that delithiated NCM622 undergoes aggregation via oxidative heat treatment, leading to the formation of novel pore structures and active sites derived from thermal stabilization. The upcycled NCM catalyst demonstrated outstanding performance in diverse reactions including CH_4/NH_3/CO oxidation and CO_2 utilization etc., highlighting the potential as versatile environmental catalyst. This work highlights a sustainable and efficient pathway for resource recovery and air pollutant abatement, addressing key challenges in conventional recycling.

Materials and Methods

The NCM622 used in this study was purchased from commercial LIBs cathode. The delithiation process was conducted in two steps: first, NCM622 was stirred in a solution of ACN and NO_2BF_4. Then, the sample was carefully recovered through vacuum filtration followed by repeated washing. All catalytic reaction and heat-treatment were performed in a packed-bed reactor equipped with in-situ FT-IR. Prior to each reaction, catalyst was pretreated at 500 °C for 1 hour under a gas flow consisting of 5% O_2, 5% H_2O with balance N_2.

Results and Discussion

The pristine NCM622 sample (namely, LNCM622) was converted into delithiated NCM622 through the above-mentioned process. The Li removal efficiency was confirmed via ICP analysis, >98% of Li was removed in all NCM622 samples (from 1.01 to 0.02 wt.%). Figure 1 (a) shows the difference of CH_4 oxidation performance between LNCM622 and NCM622 catalyst. Clearly shown, LNCM622 exhibited no CH_4 oxidation activity at all, whereas delithiated NCM622 demonstrated a dramatic improvement in catalytic oxidation performance. As known, CH_4 oxidation is typically challenging on non-PGM based catalyst, especially in the presence of H_2O. However, the delithiated NCM622 showed complete CH_4 oxidation at 600 °C and T_{50}=480 °C, outperforming most of the previously reported non-PGM based catalyst. Beyond CH_4 oxidation, we also applied NCM622 catalyst to various reactions, including CO and NH_3 oxidation, CO_2 hydrogenation, and NH_3 decomposition. The reaction results demonstrated that NCM622 achieved superior catalytic performance for all these reactions.

To investigate the origins of this enhanced catalytic performance, comprehensive characterizations including BET, TEM, EXAFS and series of temperature programmed experiments were conducted. Two key insights emerged from these characterizations: 1) the pre-extraction of lithium contributes to the thermal destabilization of the LTMO structure in NCM622. 2) the defects induced by Li pre-extraction act as vacancies over the LTMO framework, inducing enhanced surface area and redox properties during thermal stabilization. The most pronounced result of the NCM622 during the delithiation and heat-treatment is shown in Figure 1(b); the BET isotherm data. Both LNCM622 and NCM622 exhibit the typical N_2 adsorption-desorption trends of mixed metal oxide, with extremely low specific surface areas. However, the 500 °C heat-treated NCM622 sample show significant changes, including nearly tenfold increase in S_{BET} (3.9 to 41.2 m^2/g) and the formation of mesopore structure, indicating notable morphological transformation. These porous structure via top-down approach is regarded as an essential characteristic for environmental catalysts, which must handle large-scale continuous pollutant streams. Moreover, characterizations including H_2-TPR, XRD, and EXAFS, revealed that during the heat-treatment of NCM622, nickel undergoes controlled aggregation into well-dispersed NiO. These NiO species serve as newly formed active sites, substantially contributing to enhanced redox property. These findings not only establish a framework for the sustainable upcycling of NCM but also guide a pathway for the development of cost-effective, high-performance environmental catalyst.

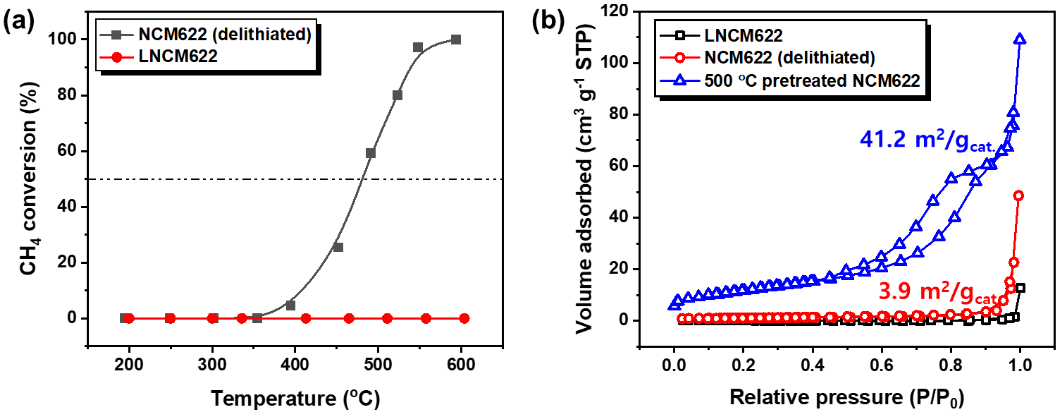

Figure 1. (a) catalytic CH_4 oxidation activity of LNCM622 and NCM622. Reaction conditions: 2000 ppm CH_4, 5% O_2, 5% H_2O in balance N_2, S.V.: 100,000 hr^{-1}. (b) BET analysis of N_2 adsorption-desorption isotherm of LNCM622, NCM622 and 500 °C pretreated NCM622

References

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