Forced Dynamic Operation: Propene Ammoxidation over Bismuth Molybdate-based Catalysts

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Highlights

- Forced dynamic operation can enhance acrylonitrile production versus steady state operation
- Lattice oxygen in the catalyst surface plays a crucial role in the catalytic activity
- Forced dynamic operation facilitates the regeneration of the active oxygen species of the catalyst

1. Introduction

Ammoxidation (AMO) of propene over bismuth molybdate (BMO)-based catalysts to produce acrylonitrile (ACN) has been used since the 1950s[1]. Acrylonitrile is the precursor to polyacrylonitrile (PAN), which can in turn be manufactured into acrylic fiber or carbon fiber (CF). CF is used in applications such as sporting goods, automobiles, and aircraft materials, due to its lightweight and high tensile strength nature. As the demand for CF is predicted to grow at 10% per year, manufacturing capacity of ACN is bound to increase. Instead of building in traditional large-scale production, which is capital intensive and time consuming, modular, small-scale production could be more economic and provide quicker response to market demands for ACN.

Forced dynamic operation (FDO) utilizing feed concentration modulation is suitable for small-volume reactors. In FDO, the reactor is operated such that the composition is periodically changed to achieve enhanced product selectivity and yield. FDO has been explored in reactions like selective oxidation of hydrocarbons to maleic anhydride[2] and Fischer-Tropsch synthesis[3] and resulted in increased selectivity and yield. One intuitive aspect in improving yield via FDO is the utilization of lattice oxidation in the catalyst. BMO-based catalysts are well-known for their dynamic oxygen storage capacity (DOSC). However, exactly how DOSC impacts FDO for this reaction is not well-established. Write your introduction here.

2. Methods

In this work, we applied FDO for propene ammoxidation over transition metal promoted BMO (denoted HM-BMO, home-made BMO). A commercial BMO-based catalyst provided by INEOS Nitriles, USA LLC was also evaluated for comparison. FDO schemes with changing compositions of reactant gases (C_3H_6, NH_3 and O_2) and conditions (cycle period, duty cycle) were tested to identify the best pathway in improving ACN yield. Oxygen storage capacities were also characterized, using propene as the reductant, and measuring the O containing products.

3. Results and discussion

We found a higher than steady state ACN productivity with a periodic switch between the normal feed and an O_2 regen FDO scheme (Fig. 1a). The so-called ACN "spikes" indicate FDO parameters could be adjusted so that the time-averaged ACN yield can exceed those of steady-state operation. We also found that the DOSC of the BMO-based catalysts is correlated with ACN productivity in FDO. By tuning promoter element ratios, the FDO performance can be optimized (Fig. 1b). Our results show that FDO can provide promising ACN production rates compared with steady-state operation, potentially contributing to the pursuit of economic modular ACN manufacturing.

Using literature guidance, we synthesized a series of Ni-, Fe- and Co-containing catalysts (some shown in Figure 1b, labelled HM) that enabled us to tune the DOSC and therefore the response to FDO conditions. X-ray diffraction (XRD) was used to characterize different phases before and after reaction, in order to probe which might be the active phases in the reaction.

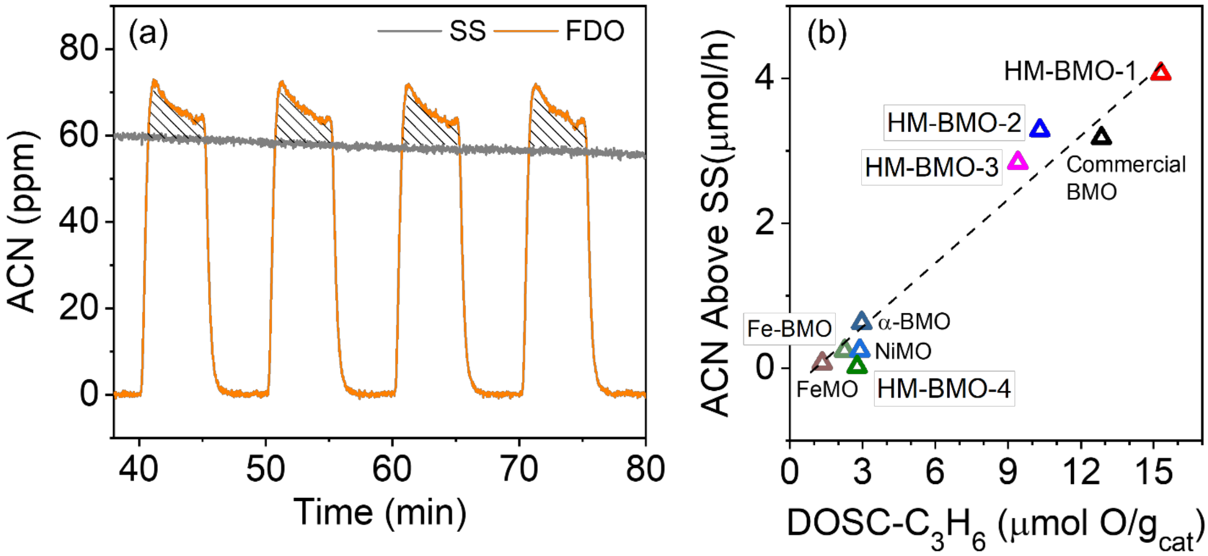

Figure 1. (a) ACN transient concentration in a normal feed/O_2 regen FDO experiment overlayed with those of steady state; the shaded area indicates ACN production that is above steady state. Normal fullfeed: C_3H_6:NH_3:O_2= 1500:1500:3000 ppm, O_2 regen: O_2 3000 ppm, balance N_2, total flowrate 50 sccm. The FDO tests were done with a cycle period = 10 min, 50% duty cycle, and at T = 330 °C. (b) DOSC vs ACN production above SS for home-made BMO samples, α-BMO, commercial BMO and other reference molybdates at 330 °C.

4. Conclusions

In this presentation, the results of using forced dynamic operation (FDO) to reactively produce acrylonitrile via ammoxidation of propene using an industrial multicomponent-promoted bismuth molybdate-based catalyst will be presented. An FDO scheme that leverages O_2 regeneration of lattice oxygen was utilized. Effects of cycle period, duty cycle, O_2 concentration during the regeneration phase, temperature and lattice oxygen were interrogated. Under certain conditions, ACN yield using FDO surpasses that obtained at steady state conditions. ACN production and ACN yield can both be enhanced by increasing O_2 concentration in the regeneration phase. At temperatures higher than 330 °C (360-380 °C) the ACN production and yield enhancement by FDO was not as pronounced because the rate of reoxidation was no longer as rate-limiting. The results show that the catalytic performance in forced dynamic operation can surpass that of the steady-state operation under certain conditions, i.e., when the catalyst is at some higher oxidation state or the active oxygen species is replenished, with that lattice oxygen availability appearing to play a crucial role in the FDO scheme employed.

References

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Keywords
Propene ammoxidation, forced dynamic operation, bismuth molybdate, lattice oxygen.