

New Catalysts for Selective Oxidation of p-Xylene to Terephthalaldehyde (TPAL)

Won-Ho Lee,*, Hyun K. Yoon, Ji H. Shon, Dong I. Lee, Jong H. Chae,
In K. Park and Won J. Lee

*LG Chem.Ltd./Research Park, Moonji-dong, Yuseong-gu., Daejeon 305-380 (Korea)

*whlee@lgchem.com (corresponding author designated with a star)

Introduction

The selective oxidation of p-xylene to terephthalaldehyde (TPAL) has been one of challenges in the selective oxidation catalysis. The current commercial TPAL production involves Cl_2 and HCl in the process, which is not environmentally favored (Fig. 1). There have been efforts [1-4] to develop the selective oxidation process from p-xylene and air as an oxidant using heterogeneous catalysts (Fig. 2). However, catalysts developed so far had either low selectivity toward to TPAL or low thermal stability of metal oxide components, which makes the selective oxidation process to be commercialized. In this presentation, we introduce new high performance catalysts for the selective oxidation of p-xylene to TPAL, which we recently have discovered. Alkali-metal doped tungsten oxide catalysts show excellent thermal stability too.

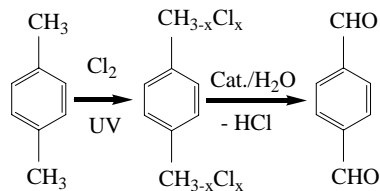


Fig. 1. The current commercial process for TPAL production ($x = 1$ or 2).

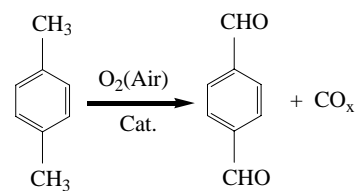


Fig. 2. The process of selective oxidation of p-xylene to TPAL.

Materials and Methods

W_{12}M_x ($x = 0 \sim 0.03$, $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) were prepared by doping metal nitrate solution of alkali-metal on WO_3 made by thermal decomposition of $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$. Alkali-metal doped WO_3 catalysts were dried at 120°C overnight and then calcined at 650°C in air for 2 hr. Characterization of catalysts was made using SEM, XRD, NH_3 -TPD and H_2 -TPR. Selective oxidation was carried out using an 8-channel tubular reactor system at an atmospheric pressure.

Results and Discussion

Fig. 3 summarizes performance of catalysts, alkali-metal doped tungsten oxide catalysts. WO_3 is not selective for TPAL formation producing only CO and CO_2 . However, a little amount alkali-metal doping on WO_3 enhances TPAL selectivity significantly with the

activity being decreased. While the selectivity was maximum at alkali-metal content $x = 0.02 \sim 0.03$, the maximum TPAL yield was obtained at $x = 0.01$ except for $\text{W}_{12}\text{Na}_{0.02}\text{O}_x$. We have tried to elucidate the role of alkali-metal for enhancing the selectivity using various characterization tools as well as theoretical modeling study.

Significance

We have developed catalysts based on alkali-metal doped WO_3 which is active and selective for the selective oxidation process for TPAL production from p-xylene. Our catalyst system shows excellent thermal stability. Based on the new catalyst we developed the entire process including separation and purification steps. The pilot scale test is being under study.

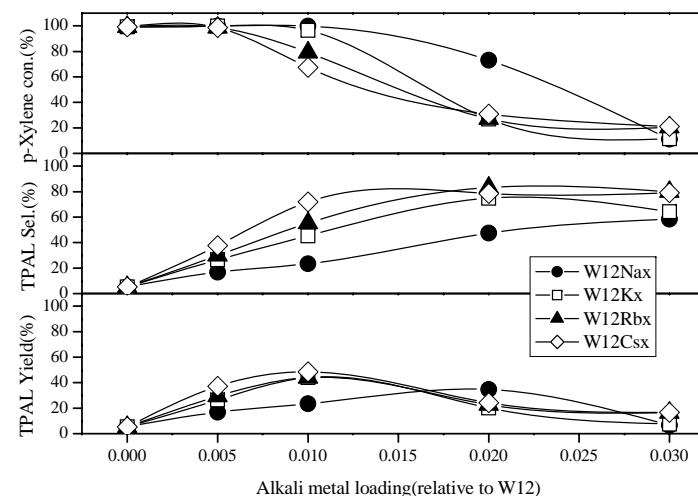


Fig. 3. p-Xylene conversion, TPAL selectivity and TPAL yield as a function of alkali metal content.

References

1. Simmons, Kenneth E., Williams, James E., US Patent No. 4 017 547 (1977), to Eastman Kodak Company.
2. J.S. Yoo, J.A. Donohue, M.S. Kleefisch, P.S. Lin, S.D. Elflin, Appl. Catal. A 105 (1993) 83.
3. J.S. Yoo, M.S. Kleefisch, J.A. Donohue, US Patent 5 324 702 (1994), to Amoco Corporation.
4. N. Kishimoto, I. Nakamura, Y. Nagamura, A. Nakajima, M. Hashimoto, K. Takahashi, US patent 6 458 737 (2002), to NiPPon Shokubai Company Limited.