

산소 처리한 텅스텐 카바이드 촉매에 의한 헥산의 이성화반응

Senzi Lee, 송병준, 이재성
포항공과대학교 촉매기술연구센터

Oxygen-Treated Tungsten Carbide as a Catalyst for *n*-Hexane Isomerization

Senzi Lee, Byung Jun Song, and Jae Sung Lee

Center for catalytic Technology, Pohang University of Science and Technology,
San 31, Hyoja-dong, Pohang

Introduction

Recently, there have been interesting reports on catalysis by oxygen-modified molybdenum and tungsten carbides. Groups at Exxon and Stanford reported that oxygen treatment below 700 K of tungsten carbides (WC or β -W₂C) prepared from reduction/carburization of WO₃ inhibited hydrogenolysis rates of hydrocarbons and introduced surface sites active for isomerization⁸⁻¹⁰. Essentially the same results were reported by Ledoux and coworkers¹¹⁻¹² for oxygen-treated Mo₂C prepared by contact of MoO₃ vapor with activated charcoal. The results are intriguing because oxygen had been thought to be a poison for carbide catalysts that had to be avoided to obtain active catalysts. In order to understand better these interesting systems without complications that might arise due to different preparation procedures, we compared oxygen-treated WC and Mo₂C prepared by similar reduction/carburization procedures from their respective oxides. An attempt was made to correlate the kinetic behavior of these catalysts in *n*-hexane-H₂ reactions with their physical properties obtained from x-ray diffraction (XRD), CO chemisorption, temperature-programmed reaction (TPR) with flowing H₂ or He, temperature programmed desorption (TPD) of adsorbed NH₃, and x-ray photoelectron spectroscopy (XPS).

Experimental

WC powders were prepared by direct carburization of WO_3 in CH_4 (20%)- H_2 mixture at 1100 K for 6 h. Excess polymeric carbon deposited on WC during the preparation was removed by a hydrogen treatment at 973 K for 0.8 h. Mo_2C powders were prepared by temperature-programmed reaction between MoO_3 and CH_4 (20%)- H_2 mixture at increasing temperatures from 473 K to 973 K at a rate of 30 K h^{-1} . Reactions of *n*-hexane in the presence of excess H_2 were carried out at 623 K and atmospheric pressure. A saturator immersed in a constant temperature bath at 273 K was used to produce a reacting mixture of 6% *n*-hexane in H_2 . Reaction products were analyzed by an on-line gas chromatograph (HP-5890A) equipped with a flame ionization detector and an AT-1 (Alltech) capillary column.

Results and Discussion

Oxygen treatment of tungsten carbide WC improved both activity and selectivity to branched hexanes in *n*-hexane- H_2 reactions and the effects became greater as the treatment temperature was raised. A marked increase in isomerization rates and a small change in hydrogenolysis rates for oxygen-treated catalysts were responsible for this result. The selectivity remained invariant with the change in *n*-hexane conversion. The oxygen-treatment of molybdenum carbide Mo_2C , on the other hand, brought about isomerization activity by suppressing hydrogenolysis activity dominant over the untreated catalyst. The isomerization selectivity of Mo_2C catalysts was much less than that of WC and depended strongly on *n*-hexane conversion. The Mo_2C catalysts also showed rapid deactivation with time-on-stream. Several techniques (CO chemisorption, XRD, TPD/TPR and XPS) were employed to understand the effects of oxygen treatment on the catalytic behavior of WC and Mo_2C . The x-ray diffraction indicated that WC structure was maintained under oxygen below 673 K. The surface reactivity of oxygen-treated catalysts depended on parent metal (Mo or W), and treatment temperature. Treatment at higher temperatures not only deposited

more oxygen onto the carbides, but also increased its stability toward reduction. Also, a greater number and a higher strength of acid sites were generated by oxygen treatment at higher temperature as evidenced by TPD of adsorbed NH_3 . The presence of this stable oxygen as previous works⁸⁻¹² reported strikingly similar results over WC and Mo_2C which were appeared to be a prerequisite to the isomerization selectivity and activity maintenance for oxygen-treated WC or Mo_2C .

Two important results emerge from the present work in designing oxygen-treated carbide catalysts for the isomerization of alkanes. First, a balance is required between hydrogenolysis and isomerization activities. For WC and, especially Mo_2C , improvement in the density and activity of isomerization sites is needed while reducing the number of hydrogenolysis sites. The creation of isomerization sites by oxygen treatment at high temperatures, however, is limited by the reactivity of the carbide surface toward oxygen because bulk oxidation should be avoided. Second, the stability of isomerization sites under reducing atmosphere is critical to maintenance of activity and selectivity of the catalyst.

References

1. F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J.E. Baumgartner, E. Iglesia, *J. Catal.*, **130**, 86 (1991).
2. M.J. Ledoux, C. Pham-Huu, H. Dunlop, J. Guille, *Stud. Surf. Sci. Catal. (Proc. 10th ICC, Budafest)*, **75**, 955 (1993).
3. J.S. Lee, K. Imura, S. Yoshida, M. Boudart, *J. Catal.*, **103**, 30 (1987)

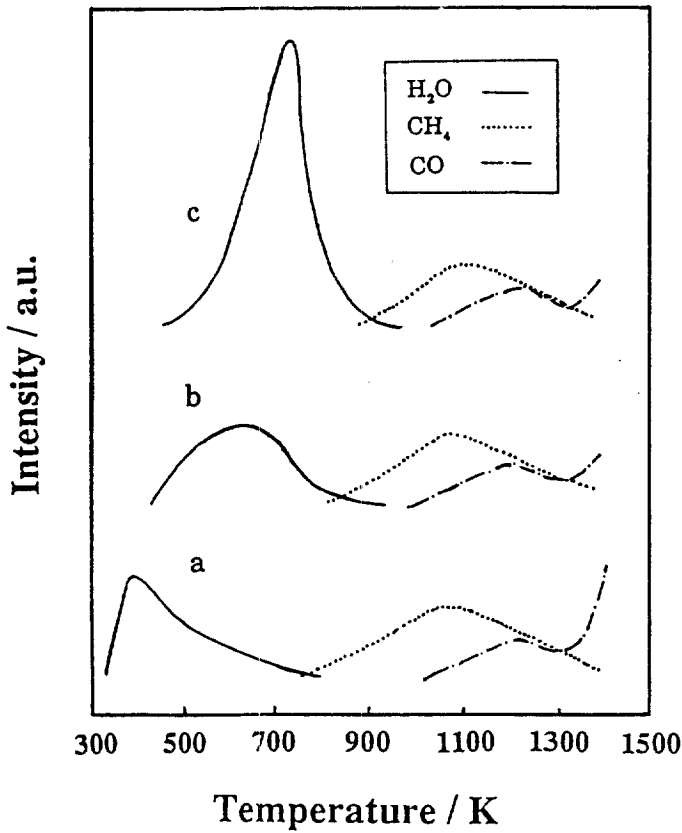


Figure 1. TPR of (a)WC/fresh, (b)WC/RT, (c)WC/473 and (d)WC/673 under H₂ flow.

Figure 2. TPD of NH₃ preadsorbed at RT on (a)WC/fresh, (b)WC/RT, (c)WC/473, and (d)WC/673. The samples were reduced in H₂ at 673 K for 1 h before the TPR.

