

Application of Niobic Acid Catalysts towards the One-Step Synthesis of Methyl Isobutyl Ketone (MIBK) from Acetone and Hydrogen

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Introduction

The development of a highly efficient one-step process for MIBK synthesis is of industrial significance. MIBK production involves three major steps. First, acetone is dimerized to give diacetone alcohol (DAA). Second, DAA is dehydrated to produce mesityl oxide (MO) and water. Third, MO is selectively hydrogenated to produce MIBK. It is of interest to ascertain whether this complex synthesis may benefit from the application of catalytic distillation (CD) technology. Previously, the authors have benchmarked the performance the one step synthesis of MIBK via CD using commercially available catalysts and found that the process capability was limited by poor catalyst performance [1]. Consequently, improved catalysts for MIBK synthesis are needed. Niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) has a very strong acidity ($H_0 = -5.6$), excellent thermal stability and maintains its activity and stability when exposed to water [2]. $\text{Pd}/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and $\text{Pd}/\text{Nb}_2\text{O}_5/\text{SiO}_2$ have been identified as promising catalysts for MIBK synthesis [3-5]. However, the influence of the catalyst parameters such as the catalyst composition, calcination temperature, acidity and the type of the oxide support remain unexplored. In this work, the activity and selectivity of niobium oxide dispersed onto various transition metal oxide supports and the effects of the catalyst parameters were investigated for the synthesis of MO. The liquid phase kinetics of the one-step synthesis of MIBK over a promising $\text{Pd}/\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst were also studied.

Materials and Methods

Various transition metal oxides were pretreated in dry air at predetermined temperatures and impregnated with $\text{Nb}(\text{OC}_2\text{H}_5)_5$ in n-hexane for two hours at ambient temperature. The catalysts were separated from the supernatant liquid without exposure to the atmosphere and dried under vacuum for 24 hours followed by a thermal treatment at 200°C or 400°C in nitrogen and calcination in air at temperatures ranging from 100 to 500°C. The Nb_2O_5 loading (wt%) were determined by XRF. Selected catalysts were impregnated for 2 hours at 81°C with solutions of Pd(II) acetate dissolved in glacial acetic acid, then filtered and reduced with hydrogen at 100°C for 2 hours. The activity and selectivities of these catalysts for MO and MIBK syntheses from acetone were assessed at various temperatures in a 300 mL Parr autoclave. The liquid samples were analyzed by GC/FID and GC/TCD to determine the concentrations of organic species and water respectively. The nature and strength of the acidity of these catalysts were determined by FTIR and by ammonia TPD analysis.

Results and Discussion

The results show that the type of support had a large influence on the activity of the catalyst for the synthesis of MO with the following trend observed $\gamma\text{-Al}_2\text{O}_3 \approx \text{SiO}_2 \gg \text{TiO}_2 \approx \alpha\text{-Al}_2\text{O}_3 \gg \text{MgO}$. Niobia supported on SiO_2 and Al_2O_3 , which exhibit both Lewis and Bronsted acidity, were the most active. In contrast, niobia supported on MgO and TiO_2 , which only exhibit

Lewis acidity, showed low activity for MO synthesis. The calcination temperature of the $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 catalysts had a profound influence on the activity and particularly the acetone conversion for MO synthesis with the lower calcination temperature giving the superior catalyst performance as illustrated in Figure 1. It is known that the Bronsted acidity of niobic acid catalysts are maximized at calcination temperatures of about 100°C and decrease with increasing calcination temperature whereas the Lewis acidity becomes more prominent at higher calcination temperatures [6]. Thus the results suggest that Bronsted acidity plays an important role in the activity and stability of niobia catalysts for MO synthesis. The kinetics of the one step synthesis of MIBK over a multifunctional $\text{Pd}/\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst were studied over a broad range of temperatures (127°C to 183°C) and hydrogenation pressures (1.5 to 5.4 MPa). The kinetic analysis suggests that the dehydration of DAA is the rate determining step.

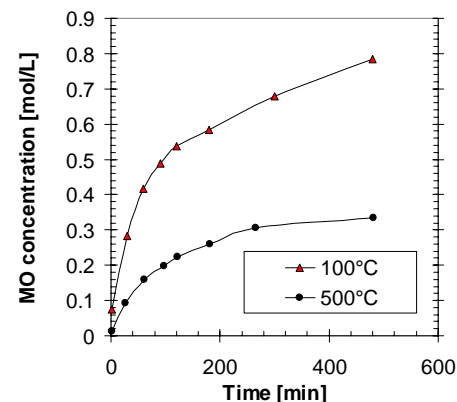


Figure 1 Effect of calcination temperature on the production of MO from acetone at 160°C and > 2 MPa (N_2) using 12.4 wt% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst calcined at 100°C and 500°C

Significance

This work demonstrates that niobia catalysts allow higher operating temperatures in contrast to cation exchange resins, thereby enabling a chemistry that is more favourable to DAA dehydration and MIBK productivity and may be used to develop a new CD process for MIBK synthesis. The results have also provided insight into the fundamental relationships between the nature and strength of the acid sites and the resultant kinetic behaviour.

References

1. O'Keefe, W.K., Ng, F.T.T. and Rempel, G.L. *Ind. Eng. Chem. Res.* (in press)
2. Tanabe, K. *Cat. Today*, 78, 65 (2003).
3. Maki, T., Yokoyama, T. and Sumino, Y., Japanese Patent 6396147 (1986).
4. Higashio, Y. and Nakayama, T. *Cat. Today*, 28, 127 (1996).
5. Chen, Y.Z., Liaw, B. J., Tan, H. R. and Shen, K. L., *Appl. Cat. A.*, 205, 61, (2001).
6. Iizuka, T., Ogasawara, K. and Tanabe, K., *Bull. Chem. Soc. Jpn.*, 56, 2927, (1983).