Synthesis of Primary Amines with OMS-2

Synthesis of amides from primary alcohols:

\[ R\text{-}\text{OH} + \text{aq NH}_3 \xrightarrow{(1), 1.4\text{-dioxane, 130 °C, O}_2 (3 \text{ atm})} R\text{-}\text{NH}_2 \]

Results:

- 3 h, 96% yield
- 3 h, 97% yield
- 3 h, 95% yield
- 3 h, 99% yield

Selected examples:

- 3 h, 89% yield (X = CHO)
- 3 h, 91% yield (X = CN)
- 3 h, 87% yield (X = CHO)
- 3 h, 93% yield (X = CN)

Syntheses of amides from aldehydes and nitriles:

\[ R\text{-}X + \text{aq NH}_3 \xrightarrow{(2), 1.4\text{-dioxane, 130 °C, O}_2 (3 \text{ atm, } X = \text{CHO})} R\text{-}N\text{H}_2 \]

Results:

- 3 h, 87% yield (X = CHO)
- 3 h, 93% yield (X = CN)
- 1 h, 94% yield (X = CHO)
- 1 h, 96% yield (X = CN)
- 24 h, 77% yield (X = CHO)
- 24 h, 98% yield (X = CN)

Significance: Manganese oxide based octahedral molecular sieves (OMS-2) catalyzed the reaction of primary alcohols with aqueous ammonia to give the corresponding amides in 65–99% yield under molecular oxygen (10 examples, eq. 1). The reactions of aldehydes and nitriles with aqueous ammonia also proceeded in the presence of OMS-2 to give the corresponding amides in 77–99% yield (16 examples, eq. 2). In the formation of 2-pyridinecarboxamide from 2-pyridinemethanol, the catalyst was recovered by filtration and reused eleven times without significant loss of its catalytic activity (1\textsuperscript{st} reuse: 93% yield, 11\textsuperscript{th} reuse: 85% yield).

Comment: Suib and co-workers have previously reported the preparation of OMS-2 (Chem. Mater. 1994, 6, 815). In the formation of benzamide from benzyl alcohol, the catalytic activity of OMS-2 was superior to that of precursors of OMS-2 (KMnO\textsubscript{4}, MnSO\textsubscript{4}\cdot\textsubscript{H}_2\text{O}), other manganese-based oxides (MnO\textsubscript{2} and Mn\textsubscript{3}O\textsubscript{4}) and other metal oxides (Co\textsubscript{3}O\textsubscript{4}, CeO\textsubscript{2}). After the reaction of benzyl alcohol with aqueous ammonia, no leaching of manganese species was observed by ICP-AES analysis.