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Heterogeneously Catalyzed Synthesis of Primary Amides Directly from Primary Alcohols and Aqueous Ammonia


Synthesis of Primary Amines with OMS-2

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 77–98% 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 (1st reuse: 93% yield, 11th 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 (KMnO4, MnSO4·H2O), other manganese-based oxides (MnO2 and Mn3O4) and other metal oxides (Co3O4, CeO2). After the reaction of benzyl alcohol with aqueous ammonia, no leaching of manganese species was observed by ICP-AES analysis.

Synthesis of amides from primary alcohols:

\[
\text{R-OH} \quad (0.5 \text{ mmol}) \quad + \quad \text{aq NH}_3 \quad (\text{2.6 equiv}) \quad \xrightarrow{\text{OMS-2 (100–200 mg, Mn component: 27–54 mol%)}} \quad \text{R-OCH}_2\text{NH}_2 \quad \text{21 examples} \quad 45–97\% \text{ yield}
\]

Results:

\[
\begin{align*}
\text{R-OH} & \quad \xrightarrow{1.4\text{-dioxane, 130 °C, O}_2 (3 \text{ atm})} \quad \text{NH}_2 \\
& \quad (\text{eq. 1}) \\
\text{3 h, 96% yield} & \quad \text{3 h, 97% yield} \\
\text{3 h, 95% yield} & \quad \text{3 h, 99% yield}
\end{align*}
\]

Selected examples:

\[
\begin{align*}
\text{R-OH} & \quad \xrightarrow{1.4\text{-dioxane, 130 °C, O}_2 (3 \text{ atm})} \quad \text{NH}_2 \\
& \quad (\text{eq. 2}) \\
3 h, 89\% \text{ yield} \quad (X = \text{CHO}) & \quad 3 h, 87\% \text{ yield} \quad (X = \text{CN}) \\
3 h, 91\% \text{ yield} \quad (X = \text{CN}) & \quad 3 h, 93\% \text{ yield} \quad (X = \text{CN}) \\
1 h, 94\% \text{ yield} \quad (X = \text{CHO}) & \quad 1 h, 96\% \text{ yield} \quad (X = \text{CN}) \\
24 h, 77\% \text{ yield} \quad (X = \text{CHO}) & \quad 24 h, 98\% \text{ yield} \quad (X = \text{CN})
\end{align*}
\]

Syntheses of amides from aldehydes and nitriles:

\[
\text{R-OH} \quad (0.5 \text{ mmol}) \quad + \quad \text{aq NH}_3 \quad (\text{2.6 equiv}) \quad \xrightarrow{\text{OMS-2 (100–200 mg, Mn component: 27–54 mol%)}} \quad \text{R-CONH}_2 \quad \text{16 examples} \quad 77–98\% \text{ yield}
\]

Results:

\[
\begin{align*}
\text{R=CHO} & \quad \xrightarrow{1.4\text{-dioxane, 130 °C, O}_2 (3 \text{ atm}, X = \text{CHO})} \quad \text{NH}_2 \\
& \quad (\text{eq. 1}) \\
3 h, 96\% \text{ yield} & \quad 3 h, 97\% \text{ yield} \\
3 h, 99\% \text{ yield} & \quad 3 h, 99\% \text{ yield}
\end{align*}
\]

Selected examples:

\[
\begin{align*}
\text{R=CHO} & \quad \xrightarrow{1.4\text{-dioxane, 130 °C, O}_2 (3 \text{ atm}, X = \text{CHO})} \quad \text{NH}_2 \\
& \quad (\text{eq. 2}) \\
3 h, 89\% \text{ yield} \quad (X = \text{CHO}) & \quad 3 h, 87\% \text{ yield} \quad (X = \text{CHO}) \\
3 h, 91\% \text{ yield} \quad (X = \text{CN}) & \quad 3 h, 93\% \text{ yield} \quad (X = \text{CN}) \\
1 h, 94\% \text{ yield} \quad (X = \text{CHO}) & \quad 1 h, 96\% \text{ yield} \quad (X = \text{CN}) \\
24 h, 77\% \text{ yield} \quad (X = \text{CHO}) & \quad 24 h, 98\% \text{ yield} \quad (X = \text{CN})
\end{align*}
\]