

APPENDIX A

Co Catalyst Formulations

Co.064: 20 wt% Co
 8.5 wt% Zr
 0.5 wt% Ru
 γ -alumina

Ru- and Zr-promoted alumina-supported catalyst similar otherwise to Co.041. One-step impregnation of alumina with zirconium nitrate followed by one-step impregnation with cobalt nitrate and Ru nitrosil nitrate solution.

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Zr Oxonitrate [$\text{ZrO}(\text{NO}_3)_2$] using an appropriate quantity to get incipient wetness with the desired loading of Zr.

Dry the Zr-loaded Al_2O_3 in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried support in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Impregnate the Zr-loaded Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and Ru nitrosil nitrate using an appropriate quantity to get incipient wetness with the desired loadings of Co and Ru.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

Co.065: 20 wt% Co
 8.5 wt% Zr
 0.5 wt% Ru
 0.3 wt% K
 γ -alumina

Ru-, K- and Zr-promoted alumina-supported cobalt catalyst similar otherwise to Co.048. One-step impregnation of alumina with zirconium nitrate followed by one-step impregnation with cobalt nitrate, potassium nitrate and Ru nitrosil nitrate solution.

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Zr Oxonitrate [$\text{ZrO}(\text{NO}_3)_2$] using an appropriate quantity to get incipient wetness with the desired loading of Zr.

Dry the Zr-loaded Al_2O_3 in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried support in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Impregnate the Zr-loaded Al_2O_3 with an aqueous solution of Co nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], K nitrate and Ru nitrosil nitrate using an appropriate quantity to get incipient wetness with the desired loadings of Co, K and Ru.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

Calcine the dried catalyst in air by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.

CAL.11-CAL13:

**20 wt% Co
0.5 wt% Ru
0.3 wt% K
 γ -alumina**

Ru/K-promoted catalyst similar to Co.047 calcined in N₂ prepared by Calcicat for reproducibility study.

Preparation Procedure:

Calcine the γ -alumina at 500°C for 10 hrs. Use Vista B alumina. Presieve to >38 microns (400-0 mesh).

Impregnate the support with an aqueous solution of Co nitrate [Co(NO₃)₂·6H₂O] an Ru nitrosil nitrate and K nitrate using an appropriate quantity to get incipient wetness (ca. 1.2 ml/g) with the desired loading of Co, Ru, and K.

Dry the catalyst precursor in an oven for 5 hrs at 115°C with moderate stirring.

The dried catalyst is then calcined in nitrogen by raising its temperature at a heating rate of ca. 1°C/min to 300°C and holding for 2 hrs.

Reduction Procedure before Reaction:

Reduce the catalyst in a pure hydrogen flow of 3000 cc/g/hr by heating at 1°C/min to 350°C and holding for 10 hrs.