Summary

The present inventors selected and screened several hundred promoter compositions and identified trends in catalyst activity and catalyst selectivity using regression models to fit the experimental data. It was discovered that through the use of carefully tailored amounts of certain alkali and oxyanion promoters, lower amounts of silver can be used without unduly sacrificing either the activity or selectivity of such catalysts. Relative to catalysts with silver content of about 33 percent by weight, the invented catalysts with silver less than about 25 percent by weight actually have higher levels of promoters. This was a surprising result because increasing promoter levels by linear scaling tends to decrease the catalyst activity (see US9649621B2 and US9908861B2). For catalysts with less than 25 percent silver, it was expected that promoter levels would need to be decreased in order to compensate for the expected activity penalty on decreasing the silver content from about 33 percent by weight to less than 25 percent by weight. Therefore, the disclosure relates to a supported silver catalyst prepared on an alumina-containing carrier. The carrier is a high-purity alumina carrier, having greater than about 80 weight percent alpha-alumina and less than about 30 parts per million acid-leachable alkali metals selected from lithium, sodium, potassium, and mixtures thereof, by weight, the weight percent of the alumina and the concentration of the acid-leachable alkali metals being calculated on the weight of the carrier. Onto this carrier is deposited: (A) silver in an amount of from 16 to 25 percent by weight of the catalyst; and (B) a solid promoter package comprising cesium, sulfate, rhenium, sodium and optionally lithium. Preferably manganese in an amount of 20 to 300 ppm is also deposited on the catalyst. For promoters other than manganese, the loadings are expressed in units of millimoles of promoter per kilogram of catalyst, and the loadings are scaled by a factor of Q, where Q is a unitless or dimensionless scaling factor equal to the surface area of the alumina-containing carrier prior to deposition of silver and promoters in units of square meters per gram divided by one square meter per gram.

The amounts of the components in the solid promoter package deposited on the catalyst are: C_{Cs}/Q in a range of from 3.1 to 8.7 mmol/kg catalyst; C_{Na}/Q in a range of 0.5 to 7.5 mmol/kg catalyst; C_S/Q in a range of 0.3 to 3.2 mmol/kg catalyst; C_{Re}/Q in a range of 2.4 to 6.9 mmol/kg catalyst; and C_{Li}/Q in a range of 0 to 35 mmol/kg catalyst, where C_{Cs}, C_{Li}, C_{Na}, C_S, and C_{Re} are the amounts of cesium, lithium, sodium, sulfate, and rhenium,

respectively, deposited on the carrier expressed in units of mmol promoter per kg of catalyst. Furthermore, these amounts are balanced in such a manner that F1/Q is in a range of from 0.3 to 5.2 mmol/kg catalyst; and F2/Q is in a range of from -5.1 to 6.3 mmol/kg catalyst, where F1 and F2 are linear combinations of the promoter deposited loadings as defined by the following equations:

$$F1 = C_{Cs} + 0.032 \cdot C_{Li} + 0.47 \cdot C_{Na} - (0.72 \cdot C_S + 0.94 \cdot C_{Re}); \quad \text{eq. 1}$$

$$F2 = C_{Cs} - 0.24 \cdot C_{Li} - 0.27 \cdot C_{Na} + 0.3 \cdot C_S. \quad \text{eq. 2}$$

In one aspect, there is provided a supported silver catalyst prepared on an alumina-containing carrier, the carrier comprising greater than 80 weight percent alpha-alumina and less than 30 parts per million acid-leachable alkali metals by weight, the weight percent of the alumina and the concentration of the acid-leachable alkali metals being calculated on the weight of the carrier, wherein the acid-leachable alkali metals are selected from lithium, sodium, potassium, and mixtures thereof, the carrier having deposited thereon: (A) silver in an amount of from 16 to 25 percent by weight of the catalyst; and (B) a solid promoter package comprising cesium, sodium, sulfate, rhenium, and optionally lithium, wherein for these promoters, the amounts are expressed in units of millimoles of promoter per kilogram of catalyst, and the amounts of these promoters in the solid promoter package deposited on the catalyst are such that: C_{Cs}/Q is in a range of from 3.7 to 8.7 mmol/kg catalyst; C_{Na}/Q is in a range of from 0.5 to 7.5 mmol/kg catalyst; C_S/Q is in a range of from 0.3 to 3.2 mmol/kg catalyst; C_{Re}/Q is in a range of from 2.4 to 6.9 mmol/kg catalyst; and C_{Li}/Q is in a range of from 0 to 35 mmol/kg catalyst; and F1/Q is in a range of from 0.3 to 5.2 mmol/kg catalyst; and F2/Q is in a range of from -5.1 to 6.3 mmol/kg catalyst; where Q is a unitless scaling factor equal to the surface area of the alumina-containing carrier prior to deposition of silver and promoters expressed in units of square meters per gram divided by one square meter per gram; where F1 and F2 are defined by the following equations:

$$F1 = C_{Cs} + 0.032 \cdot C_{Li} + 0.47 \cdot C_{Na} - (0.72 \cdot C_S + 0.94 \cdot C_{Re});$$

$$F2 = C_{Cs} - 0.24 \cdot C_{Li} - 0.27 \cdot C_{Na} + 0.3 \cdot C_S; \text{ and}$$

where C_{Cs}, C_{Li}, C_{Na}, C_S, and C_{Re} are the amounts of cesium, lithium, sodium, sulfate, and rhenium, respectively, deposited on the carrier expressed in units of mmol promoter per kg of catalyst.

The aforementioned catalyst of this disclosure exhibits utility in a continuous process for manufacturing an alkylene oxide directly from an olefin and oxygen or an oxygen-containing gas. Advantageously, the catalyst of this disclosure exhibits comparable levels of activity and/or efficiency, as compared with previously reported catalysts having higher levels of silver.

In another aspect, there is provided use of the catalyst as defined herein in the manufacture of ethylene oxide.

Brief Description of the Drawing

Figure 1 is a graph depicting the selectivity and the activity of catalysts 11-45.

Figure 2 is a graph depicting the selectivity and the activity of catalysts 46-57.

Detailed Description of the Invention

The invention described herein provides for a novel supported silver catalyst which finds utility in the direct oxidation of an alkylene (olefin), such as ethylene, with oxygen or an oxygen-containing gas to form an alkylene oxide, such as ethylene oxide, and which has a silver content of 25 percent by weight or less, preferably 24 percent or less , 23 percent or less, or even 22 percent or less. It has been found that good results in terms of ethylene oxide production can be obtained when the silver content is at least 16 percent, preferably 17 percent, 18 percent or even 19 percent by weight. More specifically, the supported silver catalyst of this invention comprises an alumina carrier comprising less than about 30 parts per million, preferably less than 25 parts per million acid-leachable alkali metals by weight, the concentration of the alkali metals being calculated on the weight of the carrier, wherein the alkali metals are selected from lithium, sodium, potassium, and mixtures thereof.

It is preferred that the supported silver catalyst comprises an alumina carrier comprising at least about 80 percent or greater, preferably at least 90 percent, 95 percent or even 98 percent alpha-alumina.

WHAT IS CLAIMED IS:

1. A supported silver catalyst prepared on an alumina-containing carrier, the carrier comprising greater than 80 weight percent alpha-alumina and less than 30 parts per million acid-leachable alkali metals by weight, the weight percent of the alumina and the concentration of the acid-leachable alkali metals being calculated on the weight of the carrier, wherein the acid-leachable alkali metals are selected from lithium, sodium, potassium, and mixtures thereof, the carrier having deposited thereon:

(A) silver in an amount of from 16 to 25 percent by weight of the catalyst; and

(B) a solid promoter package comprising cesium, sodium, sulfate, rhenium, and optionally lithium, wherein for these promoters, the amounts are expressed in units of millimoles of promoter per kilogram of catalyst, and the amounts of these promoters in the solid promoter package deposited on the catalyst are such that:

C_{Cs}/Q is in a range of from 3.7 to 8.7 mmol/kg catalyst;

C_{Na}/Q is in a range of from 0.5 to 7.5 mmol/kg catalyst;

C_S/Q is in a range of from 0.3 to 3.2 mmol/kg catalyst;

C_{Re}/Q is in a range of from 2.4 to 6.9 mmol/kg catalyst; and

C_{Li}/Q is in a range of from 0 to 35 mmol/kg catalyst; and

F1/Q is in a range of from 0.3 to 5.2 mmol/kg catalyst; and

F2/Q is in a range of from -5.1 to 6.3 mmol/kg catalyst;

where Q is a unitless scaling factor equal to the surface area of the alumina-containing carrier prior to deposition of silver and promoters expressed in units of square meters per gram divided by one square meter per gram;

where F1 and F2 are defined by the following equations:

$F1 = C_{Cs} + 0.032 \cdot C_{Li} + 0.47 \cdot C_{Na} - (0.72 \cdot C_S + 0.94 \cdot C_{Re})$;

$F2 = C_{Cs} - 0.24 \cdot C_{Li} - 0.27 \cdot C_{Na} + 0.3 \cdot C_S$; and

where C_{Cs}, C_{Li}, C_{Na}, C_S, and C_{Re} are the amounts of cesium, lithium, sodium, sulfate, and rhenium, respectively, deposited on the carrier expressed in units of mmol promoter per kg of catalyst.

2. The catalyst of claim 1 wherein the carrier further has deposited thereon manganese in an amount of from 20 to 300 ppm by weight of the catalyst.

3. The catalyst of claim 1 or 2 wherein the amount of cesium deposited on the catalyst is such that C_{Cs}/Q is in a range of from 4.2 to 7.8 mmol/kg catalyst.

4. The catalyst of any one of the preceding claims wherein the amount of lithium deposited on the catalyst is such that C_{Li}/Q is in a range of from 6 to 30 mmol/kg catalyst.

5. The catalyst of any one of the preceding claims wherein the amount of sodium deposited on the catalyst is such that C_{Na}/Q is in a range of from 1.2 to 7.5 mmol/kg catalyst.

6. The catalyst of any one of the preceding claims wherein the amount of rhenium deposited on the catalyst is such that C_{Re}/Q is in a range of from 3.0 to 6.8 mmol/kg catalyst.

7. The catalyst of any one of the preceding claims wherein the amounts of promoters deposited on the catalyst are such that F1/Q is in a range of from 1.5 to 4.1 mmol/kg catalyst.

8. The catalyst of claim 7 wherein the amounts of promoters deposited on the catalyst are such that F1/Q is in a range of from 1.9 to 3.7 mmol/kg catalyst.

9. The catalyst of any one of the preceding claims wherein the amounts of promoters deposited on the catalyst are such that F2/Q is in a range of from -2.5 to 3.5 mmol/kg catalyst.

10. The catalyst of claim 9 wherein the amounts of promoters deposited on the catalyst are such that F2/Q is in a range of from -1.8 to 2.7 mmol/kg catalyst.

11. The catalyst of claim 1 or 2 wherein the amounts of promoters in the solid promoter package deposited on the catalyst are such that:

C_{Cs}/Q is in a range of from 4.7 to 7.3 mmol/kg catalyst; and

C_{Li}/Q is in a range of from 10 to 26 mmol/kg catalyst; and

C_{Na}/Q is in a range of from 2.5 to 7.5 mmol/kg catalyst; and

C_{Re}/Q is in a range of from 3.3 to 6.7 mmol/kg catalyst; and wherein F1/Q is in a range of from 1.9 to 3.7 mmol/kg catalyst; and F2/Q is in a range of from -1.8 to 2.7 mmol/kg catalyst.

12. The catalyst of any one of the preceding claims wherein the catalyst is prepared using a calcination step which is carried out at a temperature within a range of 480-550 °C.

13. The catalyst of claim 12 wherein the calcination is carried out on a roasting belt, wherein the catalyst is in a hot zone at a temperature within a range of 480-550 °C for a duration not greater than 5 minutes.

14. The catalyst of any one of the preceding claims wherein the alumina-containing carrier has a surface area in the range of 0.7 to 1.5 m^2/g.

15. The use of the catalyst of any one of the preceding claims in the manufacture of ethylene oxide.