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WET METHOD FOR PREPARING ALKALI METAL COATED CARRIER PARTICLES

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This invention relates to a method for the disposition of sodium metal upon inert solid inorganic oxy-compound carriers. More particularly, it relates to the disposition of molten alkali metals having an atomic number below 12 upon inert solid oxy-compound in the presence of liquid aprotic hydrocarbon mediums and of a minor amount of molten potassium metal under dispersing conditions.

The disposition of sodium and lithium metals upon inert oxy-compound support materials as known in the art is both inconvenient and hazardous. One method, the so-called dry mix method, is accomplished by mechanically grinding together the solid supporting particles and molten alkali metal in an inert atmosphere. A fortuitous admission of oxygen, moisture, and the like, during a dry mix preparation is not only extremely harmful because of the highly reactive nature of the alkali metal, but fire and explosion are known to occur. Less desirable methods for the preparation of the desired alkali metal coated carrier particles are known, for example, U.S. Patent 2,818,350 describes an involved process which includes the vaporization of both the alkali metal and of a hydrocarbon diluent and the generation of a flowing stream at high velocity and turbulent flow as well as other inconveniences.

It has now been found that alkali metals having an atomic number below 12 may be safely and efficiently disposed upon solid, inert inorganic carrier oxy-compounds when applied to the carrier under dispersing conditions in the presence of an inert liquid hydrocarbon and from about .01 to 99 weight parts of molten potassium metal per part of molten sodium or lithium metal. This wet method disposition of sodium and lithium metals upon carrier particles is especially advantageous because equipment requirements are minimal, and in fact no particular concern need be had relative to the fortuitous presence of oxygen and water-vapor during the preparation so long as the inert hydrocarbon medium is one having a relatively low volatility (for example, one having a flash point above about 80° C.). The alkali metal and the alkali metal coated particles are effectively blanketed by a protective coating of the hydrocarbon medium.

The amount of potassium metal required to facilitate the disposition of sodium and lithium metals upon the solid carrier in the present process may be as little as 1 gram of potassium per 100 grams of the desired alkali metal, or as much as 49 grams of potassium per 51 grams of the alkali metal, or more. In the absence of any added potassium, there is for all practical purposes no disposition of sodium or lithium metal upon the solid when the contacting is effectuated in the presence of the inert liquid hydrocarbon medium. On the contrary, and under the same dispersing conditions, the addition of the potassium metal promotes a rapid and efficient disposition

of sodium and lithium or their mixtures upon the carrier particles.

The amount of alkali metal, sodium or lithium, plus potassium which may be disposed varies depending upon the oxy-compound. In general, the use of from about 0.5 to 100 weight parts of solid oxy-compound per weight-part of the alkali metals results in a satisfactory disposition and from about 1.0 to 10.0 part are preferred.

The wet method disposition of alkali metals upon solid carriers is applicable to a wide variety of solids. The solids must be essentially chemically inert towards the alkali metals, and, in addition, it must contain chemically bound oxygen. In general, therefore, solid oxy-compounds such as inert metal oxides, sulfates, carbonates, silicates, phosphates, and the like, and their mixtures, whether crystalline or amorphous, may be used. Particularly desirable are carrier materials comprising oxy-compounds in which the positive radical is the cation of an element having relative electronegativity below about 1.6 (see, for example, Nature of a Chemical Bond, Linus Pauling, Cornell Univ. Press, 1945, p. 65). Representative oxy-compounds include sodium carbonate, lithium sulfate, Al_2O_3, potassium phosphate, silica-alumina, talcs, aluminum silicate, magnesium oxide, calcium sulfate, kaolins, feldspars, micas, zeolites, glasses, and the like.

While a wide variety of temperatures may be employed, so long as it is high enough to ensure the melting of the alkali metals and not of such a degree as to make impossible the maintenance of the liquid hydrocarbon phase, the temperature will be effective. In general, temperatures in the range of the melting point of the particular alkali metal mixture employed up to about 50 degrees above the melting point are preferred. Useful temperatures are found in the range from about 50° to 200° C.

The size of the solid carrier particles, the dispersing means, and the time required for the preparation are inter-related. For the very small particles, for example, those of a size below about 100 microns in diameter, very high speed mechanical stirring may be used and only a few minutes up to about one-half hour is usually fully adequate for the disposition. Larger size carrier particles, for example, for use in fixed-bed reactors, and the like, require slower stirring speeds or even a different means of disposition such as an ultrasonic vibrator, or the like. Also, for the large particle sized carriers, it is frequently advantageous to disperse the alkali metal in the absence of the carrier particles using a high speed stirrer (10,000 r.p.m. plus) and then to subsequently contact the dispersion thus produced at temperature with the carrier compound after discontinuing the high speed stirring.

Example 1

Into a 500 ml. flask, containing a nitrogen atmosphere and equipped with a high-speed stirring means, 200 cc. of a high-boiling paraffinic oil, 23 grams of anhydrous magnesium silicate, and 11 grams of sodium metal were charged and heated at 110° C. The mixture was stirred at high speed (10,000 r.p.m. plus) for a short period. A cooled sample of the mixture was examined under a high power microscope. There was no disposition of the sodium metal upon the magnesium silicate carrier particles. About 0.6 gram of potassium metal was then added and the mixture was stirred at high speed for a

short period. The microscopic examination showed that the alkali metals were completely and efficiently disposed upon the carrier material.

Example 2

Example 1 was repeated except that 16 grams of sodium and two grams of potassium were charged to the flask. The metals were heated to the fusion point and after the fusion was complete a slurry of 20 grams of powdered calcium silicate in 200 cc. of paraffinic white oil was charged to the flask. The mixture was stirred at high speed at a temperature of 100–110° C. Examination under the high-powered microscope revealed that the alkali metal mixture was efficiently disposed upon the solid oxy-compound which had taken on a black coloration.

In a similar manner, sodium metal was disposed upon a series of oxy-compounds including solids such as silica gel, alumina, kaolins, barium sulfate, calcium oxide, magnesium oxide, calcium carbonate, sodium carbonate, and the like. In every case, in the absence of the added potassium metal, there was essentially no disposition of the sodium metal upon the carrier material. On the other hand, the addition of a minor amount of potassium metal in a quantity even as small as 1 gram of potassium per 99 grams of sodium effectively promotes the disposition of the alkali metal upon the oxy-compound carrier materials.

Example 3

In a manner analogous to Example 1, a series of sodium-potassium alloys were disposed upon powdered calcium silicate. A slurry of 12 grams of the calcium silicate in 200 cc. of paraffinic white oil was added to the melted alloy maintained at a temperature of about 100° C. The mixture was vigorously stirred (10,000 r.p.m. plus) for 2–3 minutes at temperature. The amount of sodium (mol percent) was 5, 10, 30 and 50. In every case there resulted an excellent disposition of the alkali metal upon the solid carrier material, there being no apparent tendency of the alkali metal to leave the surface of the solid oxy-compound and to reagglomerate under continued and variable stirring temperature variations, and the like.

In a similar manner and in similar quantities, the addition of potassium to lithium promotes the disposition of lithium metal upon solid, oxy-carrier compounds whereas in the absence of the added potassium metal little, if any, lithium metal is effectively disposed upon the carrier.

The wet method disposed alkali metals of the present invention are especially useful as catalysts in organic synthesis. Handling, production, and transport thereof is convenient and safe.

When the solid oxy-compound is a water-soluble compound, such as an alkali metal carbonate, silicate, phosphate, and the like, the removal of the catalyst from polymers, for example, butadiene polymers, is greatly facilitated.

The disposition of sodium upon solid oxy-compounds in the presence of small amounts, 1–10 weight percent, of potassium yields useful olefin polymerization catalysts. Thus, when 1 gram of sodium was contacted with 2 grams of powdered calcium silicate in the presence of 1 gram of potassium metal and about 100 cc. of paraffinic hydrocarbon, under highly dispersing conditions, the sodium and potassium were rapidly disposed upon the solid.

The slurry thus produced was transferred to a 630 ml. dry oxygen-free autoclave and about 74 grams of propene were introduced. The autoclave and contents were heated under autogenous pressure in the range 177–200° C. for

103 minutes. Twenty cc. of propene dimer having the composition:

	Percent
4-methyl-1-pentene	4.5
4-methyl-2-pentene	5.6
2-methyl-2-pentene	58.4
n-Hexenes+2-methyl-1-pentene	28.7
Unknown	2.8

were recovered.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and the scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof set forth above, except as defined in the appended claims.

I claim:

1. In the disposition of molten alkali metals of atomic number below 12 upon solid, inert, inorganic, carrier compounds containing chemically bound oxygen, the improvement which comprises contacting said alkali metal and said compound within a stirred, inert liquid hydrocarbon medium at a temperature in the range from about 50°–200° C. in the presence of molten potassium metal wherein for each part by weight of said alkali metal of atomic number below 12, there is from about .01 to 99 parts of potassium and from about 0.5 to 100 parts of said carrier compound.

2. In the disposition of molten alkali metals of atomic number below 12 upon a solid compound, the improvement which comprises contacting within a stirred inert liquid hydrocarbon compound medium at a temperature in the range from about 50°–200° C., said alkali metal, and a compound selected from the group consisting of solid, inert, inorganic carrier compounds containing chemically bound oxygen whose positive radical is the cation of an element having a relative electronegativity below about 1.6 and whose negative radical is selected from the group consisting of carbonate, silicate, phosphate, sulfate and oxide, in the presence of molten potassium metal wherein for each part by weight of said alkali metal of atomic number below 12, there is from about .01 to 99 parts of potassium and from about 0.5 to 100 parts of said carrier compound.

3. The composition obtained by contacting within a stirred inert liquid hydrocarbon medium at a temperature in the range from about 50°–200° C. a solid, inert, inorganic, carrier compound containing chemically bound oxygen and molten alkali metal consisting essentially of potassium and an alkali metal having an atomic number below 12, said compound being selected from the group of compounds whose positive radical is the cation of an element having a relative electronegativity below about 1.6 and whose negative radical is selected from the group consisting of carbonate, silicate, phosphate, sulfate and oxide, said composition having for each part by weight of said alkali metal having an atomic number below 12 from about .01 to 99 parts of potassium and from about 0.5 to 100 parts of said carrier compound.

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