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# RESTORING OR PRESERVING METAL ALKOXIDES

Maurice M. Mitchell, Jr., Wallingford, Pa., assignor to Atlantic Richfield Company, New York, N.Y., a corporation of Pennsylvania

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## ABSTRACT OF THE DISCLOSURE

Water contamination in alcoholic solutions of metal alkoxides can be prevented or removed by contacting the solution with a zeolitic material which selectively adsorbs the water and does not react with the metal alkoxide.

This is a continuation-in-part of application Ser. No. 640,557, filed May 23, 1967 in the name of Maurice M. Mitchell, Jr., and now U.S. Pat. No. 3,479,381.

## BACKGROUND OF INVENTION

Metal alkoxides find application as strong base catalysts, for example, in Meerwein-Ponndorf reductions, etc. The normal method of making these alkoxides is illustrated by the preparation of sodium methoxide by reaction of metallic sodium and methyl alcohol at room temperature. The alkoxides are normally stored as solutions in alcohol. During storage they are susceptible to being hydrolyzed by water which contaminates the system. This hydrolysis destroys the activity of alkoxide.

## SUMMARY OF THE INVENTION

It has now been discovered that this problem is overcome in accordance with the novel process of the present invention by combining the metal alkoxide solution with a zeolitic material. In general, the invention comprises contacting a metal alkoxide solution with a zeolitic molecular sieve adsorbent which selectively adsorbs the water and does not react with the metal alkoxide, said metal alkoxide having the structural formula $M(OR)_X$ wherein M is a Group I, II or III metal, R is an aliphatic hydrocarbon containing from 1 to 18 carbon atoms and X ranges from 1 to the valence number of the metal.

In general, any of the known metal alkoxides, including alkali metal alkoxides, such as lithium, sodium, potassium, rubidium or cesium alkoxide, magnesium alkoxide, aluminum alkoxide, etc. can be restored or preserved in accordance with the present invention. They have the general formula $M(OR)_X$ wherein M is a Group I, II or III metal, R is an aliphatic hydrocarbon containing from 1 to 18 carbon atoms and X ranges from 1 to the valence number of the metal. Most preferably R contains from 1 to 6 carbon atoms.

These alkoxides can be prepared by any of art recognized methods, for example, by reaction of the respective metal hydroxide of Group I, II or III metals of the periodic table of elements with an alcohol having the empirical formula $C_nH_{2n+2}O$, wherein $n$ is 1 to 18. The applicability of this process with respect to higher molecular weight alcohols is limited only by the solubility of the metal hydroxide in the particular alcohol employed. Normally, this reaction is conducted at a temperature between ambient temperature and a moderately elevated temperature which is below the boiling point of the alcohol employed. As set forth in application Ser. No. 640,557 previously referred to, a zeolite material can be added to this process to selectively adsorb the water produced by the reaction. Cooling is not detrimental to the reaction,



but heating to a temperature sufficient to force a portion of water away from the zeolitic material employed tends to reduce the yield of alkoxide produced. A preferred operating temperature range is between about 20 and about 60° C. When heating or cooling is required, the desired adjustment in temperature may be accomplished by the use of a jacketed vessel to either supply heat to the reactants or cool the reactants. Agitating the reactants with either mechanical agitators or a non-reactive gas medium tends to reduce the time needed to reach equilibrium. The use of zeolitic material in finely divided form also tends to decrease the time required to reach equilibrium. However, neither agitation nor the use of zeolitic material in finely-divided form is essential to this process. The reaction can be effected in a fixed bed.

Suitable zeolitic material for use in the present invention includes natural or synthetic molecular sieves. Included among these are such natural zeolitic molecular sieves as chabazete, faujasite, eironite, mordenite and gemilite and such synthetic zeolitic molecular sieves as types A and X. Zeolites possess the characteristic of being able to undergo dehydration with little, if any change in crystal structure. Preferably, the zeolitic molecular sieve is the synthetic type A or X.

The most preferred synthetic zeolitic molecular sieves are the type A zeolites, which are truncated cubo-octahedra with about 48 tetrahedra, and particularly, types 3A and 4A in which the numbers correspond approximately to the nominal pore size openings in angstrom units. Type 5A is a suitable molecular sieve when higher molecular weight alcohols are employed. Type 3A and type 4A sieves are dehydrated potassium and sodium zeolites, respectively, and type 5A is dehydrated calcium zeolite—the three zeolites having the same crystalline structure and being readily interchangeable by simple basic change procedures. Type A zeolites are represented by the following approximate empirical formula:

$$M_{2/v}OAl_2O_32SiO_2YH_2O$$

wherein M represents a metal in Groups I, II of the periodic table such as potassium, sodium, calcium, and strontium; transition metals of the periodic table such as nickel; hydrogen or ammonium; $v$ represents the value of M and Y may be any value between 1–6 depending on the nature of M. The transition metals are those whose atomic numbers are from 21–28, from 39–46 and from from 72–78 inclusive. Thus, for example, the empirical formula for type 4A zeolite is $Na_2OAl_2O_32SiO_24–5H_2O$.

Synthetic zeolitic molecular sieves of type X are truncated octahedra, with access to the inner cavity by four 12-sided windows each having a diameter of about 8–9 angstroms. Type 10X and type 13X sieves are calcium and sodium zeolites, respectively. The empirical formula for type 13X zeolite is

$$0.83\pm0.05Na_2O\cdot1.00Al_2O_3\cdot248\pm0.03SiO_2\cdot xH_2O$$

Regardless of whether natural or synthetic zeolite material is employed, the particles of material utilized are preferably regular in shape and size and must be sufficiently hard or attrition-resistant that they do not wear away during use, regeneration or other handling. The zeolitic material is activated or regenerated by heating to effect the loss of the water of hydration. For efficiency and economy, dehydration at a temperature of 150–320° C. is generally used. It might occasionally be necessary for the regeneration temperature to be taken above 320° C., but not above the thermal stability temperature of the material which is about 565° C. Above the latter temperature the essential crystalline structure will begin to suffer destruction. As an alternative to providing a kiln for regeneration, spent or hydrated material may be discarded.

The zeolitic materials contemplated herein exhibit adsorptive properties that are unique among known adsorbents. The common adsorbents, such as charcoal and silica gel, show adsorption selectivities based primarily on the boiling point or critical temperature of the adsorbate. The aforementioned zeolitic materials, on the other hand, exhibit a selectivity based on the size and shape of the adsorbate molecules. Among those adsorbate molecules whose size and shape are such as to permit adsorption by the contemplated zeolites, a very strong preference is exhibited toward those that are polar, polarizable and unsaturated. For example, at 25° C. and 0.2 mm. Hg of pressure, 22.1 wt. percent of water is adsorbed by type A zeolite whereas only 0.1 wt. percent is adsorbed by charcoal and only 1.6 wt. percent is adsorbed by silica gel.

The invention is illustrated by the following specific examples, it being understood that there is no intention to be necessarily limited by any details thereof since variations can be made within the scope of the invention.

## EXAMPLE I

To restore a 0.2 molar alcoholic solution of aluminum t-butoxide and t-butyl alcohol containing 1.08 grams of water, 10.8 grams of type 13X dehydrated molecular sieve are added to the solution. The restored alcoholic solution thus obtained can be preserved by adding additional molecular sieve to the solution.

## EXAMPLE II

To restore one liter of a 0.2 molar solution of aluminum t-butoxide in t-butyl alcohol containing 1.08 grams of water, 10.8 grams of type 10X dehydrated molecular sieve are added to the solution. The restored alcoholic solution thus obtained can be preserved by adding additional molecular sieve to the solution.

## EXAMPLE III

To restore 1 liter of a 0.2 molar sodium isopropoxide solution containing 1.0 gram of water, 10 grams of 4A dehydrated molecular sieves are added. The restored alcoholic solution thus obtained can be preserved by adding additional molecular sieve to the solution.

## EXAMPLE IV

To restore one liter of a 0.5 molar potassium ethoxide solution in ethyl alcohol containing 1.5 grams of water, 15 grams of 3A molecular sieve are added. The restored alcoholic solution thus obtained can be preserved by adding additional molecular sieve to the solution.

## EXAMPLE V

To restore one liter of a 0.3 molar solution of lithium methoxide in methyl alcohol containing 4 grams of water, 40 grams of 5A dehydrated molecular sieve are added. The restored alcoholic solution thus obtained can be preserved by adding additional molecular sieve to the solution.

## EXAMPLE VI

To preserve a freshly prepared, anhydrous, 0.1 molar solution of sodium ethoxide in ethyl alcohol, 1 to 2 grams of 13X dehydrated molecular sieve are added per liter of solution. The solution thus obtained will remain free of water contamination.



I claim:

1. A method for removing water from alcoholic solutions of metal alkoxides which comprises contacting the water contaminated metal alkoxide solution with a zeolitic molecular sieve adsorbent which selectively adsorbs the water and does not react with the metal alkoxides, said metal alkoxides having the structural formula $M(OR)_x$ wherein M is a metal selected from a group consisting of alkali metals, aluminum and magnesium, R is an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms and X ranges from 1 to the valence number of the metal.

2. A method according to claim 1 wherein the adsorbent is a natural zeolite.

3. A method according to claim 1 wherein the adsorbent is a synthetic zeolite.

4. A method according to claim 3 wherein the zeolite is either a Type A or Type X zeolite.

5. A method according to claim 4 wherein the zeolite is Type A zeolite.

6. A method according to claim 5 wherein the zeolite is either Type 3A or Type 4A zeolite.

7. A method according to claim 4 wherein the zeolite is a Type X zeolite.

8. A method according to claim 1 wherein the metal alkoxide is an alkali metal alkoxide.

9. A method according to claim 1 wherein R contains from 1 to 6 carbon atoms.

10. A composition comprising an alcoholic solution of a metal alkoxide and containing therein a zeolite molecular sieve adsorbent which selectively adsorbs water and does not react with the metal alkoxide, said metal alkoxide having the structural formula $M(OR)_x$ wherein M is a metal selected from the group consisting of alkali metals, aluminum and magnesium, R is an aliphatic hydrocarbon radical containing from 1 to 18 carbon atoms and X ranges from 1 to the valence number of the metal.

11. A composition according to claim 10 wherein the adsorbent is a synthetic zeolite.

12. A composition comprising an alcoholic solution of a metal alkoxide and containing therein a zeolite molecular sieve adsorbent which selectively adsorbs water and does not react with the metal alkoxide, said metal alkoxide having the structural formula $M(OR)_x$ wherein M is an alkali metal, R is a aliphatic hydrocarbon radical containing from 1 to 18 carbon atoms and X ranges from 1 to the valence number of the metal.


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TOBIAS E. LEVOW, Primary Examiner

H. M. S. SNEED, Assistant Examiner

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