Summary

The present disclosure provides a method for improving the activity of a Ziegler-Natta (ZN) catalyst. Specifically, it has been discovered that removing excess aluminum alkyls during the partial modification of the ZN catalyst helps to mitigate losses in activity, such as losses during the storage of the modified ZN catalyst. In one aspect, the present disclosure refers to a method of forming a modified precursor composition of a Ziegler-Natta (ZN) catalyst, comprising: providing a precursor composition of the ZN catalyst for treatment with an aluminum alkyl compound in a liquid organic solvent, where the precursor composition of the ZN catalyst includes at least one titanium compound, wherein providing the precursor composition includes precipitating at least one magnesium compound with the at least one titanium compound on a carrier material; treating the at least one titanium compound in the precursor composition with the aluminum alkyl compound in the liquid organic solvent, where the aluminum alkyl compound converts the at least one titanium compound in the precursor composition into a modified state of the ZN catalyst; and removing at least a portion of the aluminum alkyl compound in the liquid organic solvent not consumed in converting the at least one titanium compound in the precursor composition into the modified state from the precursor composition to form the modified precursor composition of the ZN catalyst, wherein precipitating the at least one magnesium compound with the at least one titanium compound on the carrier material includes: dissolving the at least one magnesium compound and the at least one titanium compound in a mole ratio of 3:1 to 5:1 (mole the at least one magnesium compound: mole at least one titanium compound) in tetrahydrofuran to form a Magnesium compound/Titanium compound solution; and remove the tetrahydrofuran and to form the precursor composition of the ZN catalyst. To this end, the present disclosure provides a method of forming a modified precursor composition of a ZN catalyst that includes providing a precursor composition of the ZN catalyst for treatment with an aluminum alkyl compound in a liquid organic solvent. The precursor composition of the ZN catalyst includes at least one titanium compound that is treated with the aluminum alkyl compound in the liquid organic solvent. The aluminum alkyl compound converts the at least one titanium compound in the precursor composition into the modified precursor composition of the ZN catalyst. At least a portion of the aluminum alkyl compound not consumed in converting the at least one titanium compound in the precursor composition into the modified state from the precursor composition and reaction

by-product compounds in the liquid organic solvent are then removed to form the modified precursor composition of the ZN catalyst of the present disclosure.

Providing the precursor composition includes precipitating (or impregnating) at least one titanium compound on a carrier material. The at least one titanium compound has the formula $Ti(OR)aX_b$, wherein R is selected from the group consisting of: a C1 to C14 aliphatic hydrocarbon moiety, a C1 to C14 aromatic hydrocarbon moiety, and COR' where R' is a C1 to C14 aliphatic or aromatic hydrocarbon moiety; X is selected from the group consisting of Cl, Br, I and combinations thereof; a is selected from the group consisting of 0, 1 and 2; b is an integer of 1 to 4 inclusive; and a + b = 3 or 4. The at least one titanium compound is selected from the group consisting of: $TiCl_3$, $TiCl_4$, $Ti(OCH_3)Cl_3$, $Ti(OC_6H_5)Cl_3$, $Ti(OCOCH_3)Cl_3$ and $Ti(OCOC_6H5)Cl_3$.

The disclosure further includes precipitating (or impregnating) at least one magnesium compound with the at least one titanium compound on the carrier material. The at least one magnesium compound has the formula MgX_2, wherein X is selected from the group consisting of Cl, Br, I and combinations thereof. The at least one magnesium compound is selected from the group consisting of: $MgCl_2$, $MgBr_2$ and MgI_2. Precipitating the at least one magnesium compound with the at least one titanium compound on the carrier material: dissolving the at least one magnesium compound and the at least one titanium compound in a mole ratio of 3:1 to 5:1

(mole the at least one magnesium compound : mole at least one titanium compound) in tetrahydrofuran to form a Magnesium compound/Titanium compound solution; mixing the carrier material in the Magnesium compound/Titanium compound solution; and removing the tetrahydrofuran to form the precursor composition of the ZN catalyst. The precursor composition can contain between 8 and 35 weight percent (wt.%) of tetrahydrofuran (THF), where wt.% is based on the total weight of the precursor composition.

For the present disclosure, the aluminum alkyl is selected from the group consisting of tri-n-hexyl aluminum, triethyl aluminum, diethyl aluminum chloride, trimethyl aluminum, dimethyl aluminum chloride, methyl aluminum dichloride triisobutyl aluminum, tri-n-butyl aluminum, diisobutyl aluminum chloride, isobutyl aluminum dichloride, $(C_2H_5)AlCl_2$, $(C_2H_5O)AlCl_2$, $(C_6H_5)AlCl_2$, $(C_6H_5O)AlCl_2$, $(C_6H_{12}O)AlCl_2$ and combinations thereof. In a specific example, the aluminum alkyl is selected from the group consisting of tri-n-hexyl aluminum, triethyl aluminum, diethyl aluminum chloride and combinations thereof. The aluminum alkyl can be added separately or as a mixture in treating the at least one titanium compound in the precursor composition.

Converting the at least one titanium compound in the precursor composition with the aluminum alkyl compound includes providing a molar ratio of the aluminum alkyl compound to the at least one titanium compound in a range of 1:1 to 10:1. Converting the at least one titanium compound in the precursor composition with the aluminum alkyl compound can also include providing a molar ratio of the aluminum alkyl compound to THF in a range of 0.2:1 to 1:1. The liquid organic solvent is selected from the group consisting of isopentane, hexane, heptane, toluene, xylene, naptha and combinations thereof. In an additional example, the liquid organic solvent is an aliphatic mineral oil.

The removing step separates the liquid organic solvent containing the at least a portion of the aluminum alkyl compound not consumed in converting the at least one titanium compound in the precursor composition to the modified precursor composition of the ZN catalyst and reaction by-product compounds. After removing, the portion of the aluminum alkyl compound not consumed in converting the at least one titanium compound in the precursor composition into the modified state can be recycled for use in treating at least one titanium compound in an additional precursor composition.

What is Claimed is:

1. A method of forming a modified precursor composition of a Ziegler-Natta (ZN) catalyst, comprising:

providing a precursor composition of the ZN catalyst for treatment with an aluminum alkyl compound in a liquid organic solvent, where the precursor composition of the ZN catalyst includes at least one titanium compound, wherein providing the precursor composition includes precipitating at least one magnesium compound with the at least one titanium compound on a carrier material;

treating the at least one titanium compound in the precursor composition with the aluminum alkyl compound in the liquid organic solvent, where the aluminum alkyl compound converts the at least one titanium compound in the precursor composition into a modified state of the ZN catalyst; and

removing at least a portion of the aluminum alkyl compound in the liquid organic solvent not consumed in converting the at least one titanium compound in the precursor composition into the modified state from the precursor composition to form the modified precursor composition of the ZN catalyst,

wherein precipitating the at least one magnesium compound with the at least one titanium compound on the carrier material includes:

dissolving the at least one magnesium compound and the at least one titanium compound in a mole ratio of 3:1 to 5:1 (mole the at least one magnesium compound: mole at least one titanium compound) in tetrahydrofuran to form a Magnesium compound/Titanium compound solution; and

remove the tetrahydrofuran and to form the precursor composition of the ZN catalyst.

2. The method of claim 1, wherein the aluminum alkyl is selected from the group consisting of tri-n-hexyl aluminum, triethyl aluminum, diethyl aluminum chloride, trimethyl aluminum, dimethyl aluminum chloride, methyl aluminum dichloride triisobutyl aluminum, tri-n-butyl aluminum, diisobutyl aluminum chloride, isobutyl aluminum dichloride, $(C_2H_5)AlCl_2$, $(C_2H_5O)AlCl_2$, $(C_6H_5)AlCl_2$, $(C_6H_5O)AlCl_2$, $(C_6H_{12}O)AlCl_2$ and combinations thereof; or

wherein the aluminum alkyl is selected from the group consisting of tri-n-hexyl aluminum, triethyl aluminum, diethyl aluminum chloride and combinations thereof.

3. The method of any one of claims 1-2, further including drying the modified precursor composition after the removing step to remove the liquid organic solvent from the modified precursor composition of the ZN catalyst.

4. The method of any one of claims 1-2, wherein treating the at least one titanium compound in the precursor composition with the aluminum alkyl compound includes providing a molar ratio of the aluminum alkyl compound to the at least one titanium compound in a range of 1:1 to 10:1; or

wherein treating the at least one titanium compound in the precursor composition with the aluminum alkyl compound includes providing a molar ratio of the aluminum alkyl compound to the at least one titanium compound in a range of 4:1 to 8:1; or

wherein treating the at least one titanium compound in the precursor composition with the aluminum alkyl compound includes providing a molar ratio of the aluminum alkyl compound to tetrahydrofuran in a range of 0.2:1 to 1:1.

5. The method of any one of claims 1-2, wherein the liquid organic solvent is selected from the group consisting of isopentane, hexane, heptane, toluene, xylene, naptha and combinations thereof; or

wherein the liquid organic solvent is an aliphatic mineral oil.

6. The method of any one of claims 1-2, further including recycling the portion of the aluminum alkyl compound not consumed in converting the at least one titanium compound in the precursor composition into the modified state for use in treating at least one titanium compound in an additional precursor composition.

7. The method of any one of claims 1-2, wherein the at least one titanium compound has the formula $Ti(OR)aX_b$, wherein R is selected from the group consisting of: a C1 to C14 aliphatic hydrocarbon moiety, a C1 to C14 aromatic hydrocarbon moiety, and COR' where R' is a C1 to C14 aliphatic or aromatic hydrocarbon moiety; X is selected from the group consisting of Cl, Br, I and combinations thereof; a is selected from the group consisting of 0, 1 and 2; b is an integer of 1 to 4 inclusive; and a + b = 3 or 4; or

wherein the at least one titanium compound is selected from the group consisting of: $TiCl_3$, $TiCl_4$, $Ti(OCH_3)Cl_3$, $Ti(OC_6H_5)Cl_3$, $Ti(OCOCH_3)Cl_3$ and $Ti(OCOC_6H5)Cl_3$.

8. The method of claim 7, wherein the at least one magnesium compound has the formula MgX_2, wherein X is selected from the group consisting of Cl, Br, I and combinations thereof; or

wherein the at least one magnesium compound is selected from the group consisting of: $MgCl_2$, $MgBr_2$ and MgI_2

or

where the carrier material is a non-porous silica support.

9. The method of any one of claims 1-2, further including removing the liquid organic solvent from the modified precursor composition of the ZN catalyst; or

wherein removing at least a portion of the aluminum alkyl compound in the liquid organic solvent not consumed in converting the at least one titanium compound in the precursor composition includes neutralizing the aluminum alkyl compounds in the liquid organic solvent with hydroxyl groups.