

Research Progress of Gold Catalysts

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Abstract: The other reason why the possibility of gold as a potential catalyst has been overlooked is its extremely high value, which has led scientists to deduce that the cost of using gold as a catalyst would be unaffordable. Coupled with other factors, over the past few years, an overall chain of gold substances has resulted in a range of gold substances that are even much cheaper than other metals (such as platinum, germanium, and puts) that have been used in large-scale technology catalysis. Unlike the latter, thousands of tons of gold can be recovered from stoichiometry applications, and the mine also produces thousands of tons of gold per year. Therefore, the price of gold is relatively more stable than that of platinum, which is very advantageous if gold is applied to industrial channels. In addition, we need to remember that the price of catalysts is generally determined by ligands, not metals. Gold catalyst is also a nice choice in the field of catalyst, it has the four main reasons.

Gold is also a nice choice for environment, because it is innocuous, and can not soluble in the water.

Keywords: Gold Catalysis; Lewis Acid; Optimization Conditions; Preparation Method

1. Lewis acid

When the gold be the catalyst, it is a kind of Lewis's acid, and it also has a lot of advantages and features of Lewis acid.

Lewis acids are atoms, molecules, or ions that can act as electron recipients. Structurally, it is a class of matter with empty orbitals. Lewis acid is electrophilic. Common Lewis acids include the following two: molecules that can act as electron recipients such as BF_3 , ZnCl_2 , AlCl_3 , FeCl_3 et al. Accepts electron ions such as Ag^+ , Au^+ , Cu^{2+} etc. Lewis acid has attracted the attention of chemists because of its good catalytic activity, small dosage, short reaction time, low cost, etc., and more and more Lewis acid is used as a catalyst for the synthesis of organic compounds. An illustration detailing the reaction between a Lewis acid and base leading to the formation of a coordinate covalent bond between them is given below.

Lewis acids and bases are named after the American chemist Gilbert Newton Lewis, who also made invaluable contributions in the fields of thermodynamics and photochemistry.

2. An introduction to the catalytic

Firstly, I'll talk something about catalyst.

The Catalysis can be divided into homogeneous catalysis and heterogeneous catalysis.

Homogeneous catalysis Homogeneous Catalysts.

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

There is liquid phase and gas phase homogeneous catalysis. Liquid acid-base catalysts, catalysts for soluble transition metal compounds and catalysts for gaseous molecular catalysts such as iodine and nitric oxide belong to this category. The active center of homogeneous catalyst is relatively uniform, the selectivity is high, the side reaction is less, and it is easy to

use spectroscopy, spectroscopy, isotope tracing and other methods to study the role of the catalyst, and the reaction kinetics are generally not complicated.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction: $3\text{O}_2(\text{g}) \xrightarrow{h\nu} 2\text{O}_3(\text{g})$ $3\text{O}_2(\text{g}) \xrightarrow{h\nu} 2\text{O}_3(\text{g})$ (a)

Gold as a homogeneous catalyst

Gold-catalyzed [2+2] cyclo-added to form cyclobutene.

In 2011, Chan's group reported the use of vinegar alkyne propyl benzoate for molecules under gold-catalyzed conditions.

The [2+2] ring addition within the synthesis of nitrogen heterocyclic [[4.2.0] octan-5-one-one. Pairs have Aphene, cyclopropane, OTBS and MeSO₂.

Some of the various 1,7-1-olene substrates have good.

Gold-catalyzed [3+2] ring addition reaction.

In recent years, gold complexes have been widely used to activate the carbon-carbon triad and promote the attack of nucleophilic reagents. Based on This reactivity, under the catalysis of gold containing alkyne groups and oxygen and nitrogen atoms of the substrate is more likely to be converted into amphoteric separation Sub-intermediates, with alkynes, olefins, etc. for cyclic addition reactions.

In 2006, Iwasawain's research group used the catalytic amount to obtain an AuBr₃ catalytic N-alkylphenylimide substrate and the [3+2] ring addition reaction with external olefins and prepared a three-ring noise derivation with a yield of 60-95%.

Gold-catalyzed 3+2 ring addition reaction to form a picarian derivative With the development of gold-catalyzed tandem cyclization isomerization reactions, a-c group carbene has also been proposed for the synthesis of complex molecules.

In 2008, Seunghoon's group published that alkyne hydrocarbons are activated under the catalytic action of AuCl₃, form a-group carbene through internal redox reaction, and finally form azabicyclic [3.2.1] octanes with [3+2] ring addition.

2.1 Heterogeneous catalysis

Heterogeneous catalysts are chemical catalysts whose physical phase is different from the physical phase of the reactants and/or products that take part in the catalyzed chemical reaction. Typically, solid phase heterogeneous catalysts are employed in order to facilitate the chemical reaction between two gaseous reactants. In such reactions, the catalysis takes place over the following three steps:

- The adsorption of the gaseous reactants on the surface of the solid heterogeneous catalyst.
- The chemical reaction between the adsorbed reactants, results in the formation of the product.
- Desorption of the product compound from the surface of the catalyst, results in the regeneration of the active catalytic surface.

This is a basic example of the heterogeneous catalysis.

(a) Hydrogen and ethene adsorb on to the metal surface by donating electron density into vacant d orbitals on the catalyst metal atoms. (b) and (c) Hydrogen atoms (radicals) interact with the electron density in the ethene double bond, and bond with the carbon atoms. (d) The product ethane desorbs from the surface of the catalyst.

Next, I'll show some application which is the gold as the heterogeneous catalyst.

>H₂O₂ is synthesized by direct method

>Au/Al₂O₃ is an effective catalyst for the direct oxidation of hydrogen to H₂O₂.

>The key to direct synthesis of H₂O₂ reactions is to improve reaction selectivity. In a short reaction time and low

concentration, the reaction selectivity can reach more than 95%.

Gold-catalyzed alkynylcyclopropane ketone [4+3] cycloaddition reaction In 2011, Zhang Junliang's research group reported that under the conditions of gold catalysis, the [4+3] ring addition reaction of 1,4-dipoles and nitrates formed by alkynyl cyclopropyl ketone was achieved for the first time.

Gold-catalyzed other ring addition reactions.

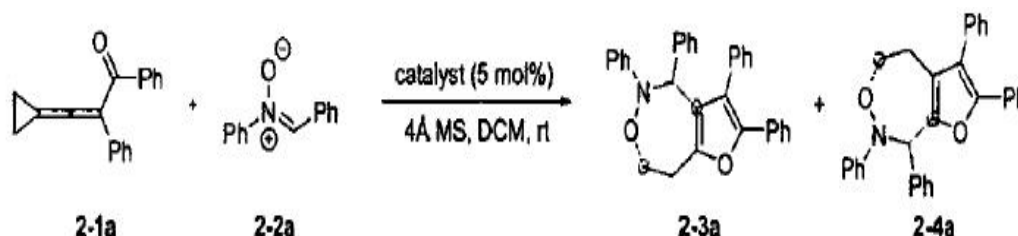
In addition to the ring addition reactions described above, other types of cyclization patterns can occur under gold catalytic conditions.

In 2008 and 2009, Nevado and Goek published a study of the cyclization reaction of 1-cyclopropyl propyne, respectively, which can generate different gold-containing intermediates according to the different substrate substituents to obtain cyclopentene and cyclohexene derivatives.

3. Optimization of reaction conditions when gold as the catalyst

The effect of reaction temperature and catalyst usage on the reaction First, the conditions of product 2-3a were optimized: it was found experimentally that increasing the temperature would reduce the yield and selectivity, while lowering the temperature would improve the regional selectivity; Experiments on the amount of gold catalysts found that 10 mol% PPh₃AuOTf had better reactivity; Further reducing the temperature to one 5 0C increases yield while remaining selective.

4.1 The effect of the catalyst on the reaction



Firstly, reaction experiments were conducted on different catalysts, and various representative metal catalysts were found, such as Pd(OAc)₂, CuCl₂, CuOTf₂, Zn(OTf)₂ and PdCl₂ are not conducive to the generation of 2-4a.

4.3 Some preparations of gold catalyst

Cool down R₁AuCy₂H_z0 (R₁: Na, I) (1 ec) dissolved in water and ethanol only water blade = 2:3 at a concentration of 10 mL/mmol R₁AuCl₄. 0C, followed by slow addition of the corresponding sulfur reagent (2-5, 2-6 or 2-7) under the stirring of ice bath for 45 minutes, followed by triphenylglycombyl 1 ec dissolved in absolute ethanol (10 mL/mxnol R₁AuCl₄), slowly added dropwise to the above reaction system, restored to 3h after warm stirring. Stop stirring, filter the reaction system, wash the solids with a small amount of cold methanol, and then recrystallize with dichloromethane/n-hexane to give PPh₃AuCl.

KAuCl₄·2H₂O (200 mg, 0.48 mmol) was dissolved in a water/ethanol (2 mL/3 mL) mixed solvent, cooled down to 0 degrees Celsius, and then slowly added 4, 4'-thiodiphenol 2-7 (316 mg, 1.44 mmol) under ice bath stirring within 45 minutes, followed by 1, 2-bis (diphenyllinyl) ethane (92 mg, 0.24 mmol) dissolved in chloroform / methanol ((1.4 mL / 1.4 mL) mixed solvent, Added to the previous reaction system, restored to room temperature stirred for 3 hours, after the end of the reaction added methanol (13.8 mL), filtered, washed solids with methanol (13.8 mL), dried to give a pale pink product (177 mg, 86%) 0 1H NMR (400MHz, CDCl₃) 8 7.66 to 7.61 (m, 8 H), 7.58-7.48 (m, 12 H), 2.63 (s, 4 H); 31P NMR (162MHz, CDCl₃) 8 31.8.

KAuCl₄·2H₂O (200 mg, 0.48 mmol) was dissolved in a water/ethanol (2 mL/3 mL) mixed solvent, cooled to 0 degrees Celsius, and then slowly added 4, 4, 4, monothiodiphenol 2-7 (316 mg, 1.44 mmol) under the stirring of ice bath

within 45 minutes, and then 1, 1'-bis (diphenyl) ferrocene ((134 mg, 0.24 mmol) dissolved in chloroform (1.4 mL), added to the above reaction system, Restore to room temperature and stir for 3h, filter, wash the filter cake with cold methanol, recrystallize with CH₂Cl₂/n-hexane to give a yellow solid product (158 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.53 to 7.42 (m, 20 H), 4.72 (m, 4 H), 4.27 (m, 4 H), ³¹P NMR (162 MHz, CDCl₃) δ 27.7.

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