国外催化剂专利大全

下 册

抚顺市科技情报研究所

《国外催化剂专利大全》　下　册

目　录

注：上述带"※"的专利提供专利号。

明 細 書

1. 発明の名称

　触媒組成物

2. 特許請求の範囲

　ランタン，セリウムおよびチタンの酸化物の少なくとも1種を活性成分・して含有してなる芳香族または芳香脂肪族カルボン酸と低級脂肪酸とを反応させてケトン化合物を製造するための触媒組成物。

3. 発明の詳細な説明

　本発明は、芳香族または芳香脂肪族カルボン酸と低級脂肪酸から芳香族または芳香脂肪族ケトン化合物を製造するための触媒組成物に関する。

　フェニル酢酸と酢酸からメチルベンジルケトンを製造する触媒として、および2−エチル安息香酸と酢酸から2−エチルアセトフェノンを製造する触媒として、トリウムの酸化物を磁石に担持させた触媒〔オーガニツク シンセシス Ⅱ．389（1943）およびヘミツシエ・ベリヒテ，81，258（1948）〕がそれぞれ提案されている。

しかし、トリウム化合物は、稀厚料物質であり、且つ核燃料物質であるため、その使用にあたつては、監督官庁の許可や使用上の規制があり、また放射性にもとづく危険性等から、触媒原料とする場合、種々のわずらわしさが伴う。

　そこで、トリウム酸化物に代わる触媒の開発を鋭意行なつた結果、セリウム，ランタンおよびチタンの酸化物の少なくとも1種を活性成分として含有してなる触媒組成物を用いると、芳香族または芳香脂肪族カルボン酸と低級脂肪酸から芳香族または芳香脂肪族ケトン化合物が高収率で得られ、トリウム酸化物触媒にかえうることに成功した。

　本発明触媒組成物は、自体公知の固体触媒の調製法に従つて得られるが、たとえば以下のようにして調製することができる。

　すなわち、化学反応や加熱により酸化物に変りうるセリウム，ランタン，チタン含有化合物を、必要により、たとえばケイ素，ジルコニウム，アルミニウム含有化合物など担体あるいは助触媒となりうる成分とともに水，アルコールなど適当な

低温に溶かし、酸、アルカリ、塩などを添加して加水分解し、乾燥後、たとえば300〜800℃で焼成することにより調製することができる。また、たとえば、ケイ素、チタン、ジルコニウム、アルミナなどの酸化物に、ランタン、セリウム、チタン含有化合物の水溶液を含浸あるいは沈着させた後、焼成することによっても調製できる。

上記ランタン含有化合物としては、酸化ランタン、水酸化ランタン、ランタン塩（硝酸ランタン、蟻酸ランタン、塩化ランタン、硫酸ランタンなど）など、セリウム含有化合物としては、酸化セリウム、水酸化セリウム、セリウム塩（硝酸セリウム、蟻酸セリウム、塩化セリウム、硫酸セリウム、炭酸セリウムなど）などいずれも容易に酸化物に導きうるものがあげられるが、ランタンおよびセリウム等の稀土類元素の混合物であるミッシュメタルの化合物を用いてもよい。

また、チタン含有化合物としては、酸化チタン、水酸化チタン、チタン酸塩、チタン塩（塩化チタン、硫酸チタンなど）などがあげられる。

本発明触媒組成物の調製は、上記各金属含有化合物を原料として用い、自体公知の触媒調製法、たとえば共沈法、含浸法、混練法、酸化物混合法などの手段により得ることができる。

本発明の触媒は活性成分だけからなるものであってもよいが、活性成分を通常の触媒に用いられる担体に担持させたものでもよい。担体として、特にケイ素、チタン、ジルコニウム、アルミニウムの酸化物を用いると、助触媒作用が発現し、目的物であるケトン化合物の収率が向上する。

ランタン、セリウム、チタンの酸化物を混合して使用する場合の混合比は全く任意にとることができる。

担体を用いる場合、担体に対するランタン、セリウムおよび／またはチタン酸化物の添加割合は原子比で0.001〜100、好ましくは0.01〜50、最も好ましくは0.03〜30である。

本発明触媒組成物のより具体的な調製法としては、たとえば硝酸ランタンまたはセリウムの水溶液に、酸化チタンの微粉末およびシリカのヒドロ

ゾルを加え、湯浴上で混合しながら水分などをとばし蒸発乾固した後、500℃程度で焼成する方法などがあげられる。

本発明による触媒組成物を用いて芳香族ケトン化合物を製造するにあたり、一方の原料である芳香族カルボン酸としては、たとえば、メチル、エチル、プロピルなどの低級アルキル基、メトキシ、エトキシ、プロポキシなどの低級アルコキシ基、クロル、ブロムなどのハロゲン、ニトロ基などの置換基をベンゼン環の任意の位置に1以上有していてもよい安息香酸があげられ、芳香脂肪族カルボン酸としては、前述と同じく、ベンゼン環の任意の位置に、たとえば低級アルキル、低級アルコキシ、ハロゲン、ニトロ基などの置換基の1個以上を有していてもよいフェニル酢酸があげられる。他方の原料である低級脂肪酸としては、炭素数2〜4程度の飽和脂肪酸、すなわち酢酸、プロピオン酸、酪酸等があげられる。これら芳香族または芳香脂肪族カルボン酸に対する、低級脂肪酸の供給モル比は、理論的には1：1であるが、実際に

は低級脂肪酸過剰の方が、目的とする芳香族または芳香脂肪族ケトンの収率は高い。しかし、低級脂肪酸があまり過剰に存在すると、低級脂肪酸同志が反応してアセトンやジエチルケトン等を生成するので、低級脂肪酸／芳香族または芳香脂肪族カルボン酸の供給モル比は1：1〜10間で選ぶのがよい。

原料である芳香族または芳香脂肪族カルボン酸、低級脂肪酸の他に、窒素、二酸化炭素、水蒸気、水素、ヘリウム、アルゴン、一酸化炭素、メタンなどの不活性ガスが共存しても構わない。

原料ガスの供給速度は、空間速度として100〜10000（1／hr）（NTP換算）がよい。反応圧は常圧、加圧および減圧下のいかなる条件でもよい。反応温度は、300〜500℃、好ましくは350〜430℃である。

生成した芳香族または芳香脂肪族ケトンは、冷却して捕集したり、適当な溶媒に吸収して捕集後、とくに精製しなくてもよいが、蒸留などの手段により、より高純度のケトン化合物とすることがで

きる。

このようにして得られたケトン化合物は、医薬、染料、工業薬品の原料として有用である。たとえば、特開昭55-151570号公報に記載されているピリミジン化合物の合成中間体となりうる。

実施例1.

‥‥‥‥‥‥‥‥‥‥‥‥‥‥‥た液に、20重量%のSiO₂を含むシリカコロイダルゾル75部を加え、温浴上で加熱してゲル化させる。このヒドロゲルを100℃で一夜乾燥し、キセロゲル化させた後、10～20メッシュに破砕し、500℃で4時間焼成してLa₂O₃/SiO₂触媒を調製した。

このようにして調製した触媒を、通常の流通式固定相反応装置に充填し、o-トルイル酸と酢酸のモル比1：5の混合液を240（mol/hr. g触媒）および窒素ガスを25（mol/hr. g触媒）で供給した。反応温度が400℃のとき、o-メチルアセトフェノンの収率は、供給o-トルイル酸基準で、54モル%であった。

酢酸セリウムを用いた以外、実施例1と同じ方法で触媒調製を行ない、La₂O₃・CeO₂/SiO₂触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、412℃におけるo-メチルアセトフェノン収率は56モル%であった。

実施例5.

実施例1における水20部に400部の硝酸ランタンを溶解させた液に代えて、20部のエタノールに356部の四塩化チタンを溶解させた液および、20部の水に153部の酢酸セリウムを溶解させた液を用いた以外、実施例1と同じ方法で触媒調製を行ない、TiO₂・CeO₂/SiO₂触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、379℃におけるo-メチルアセトフェノンの収率は64モル%であった。

実施例6.

水30部に306部の酢酸セリウムを溶解させた液に酸化アルミニウム微粉末（岩谷産業製RA

実施例2

実施例1における400部の硝酸ランタンに代えて、306部の酢酸セリウムを用いた以外、実施例1と同じ方法で触媒調製を行ない、CeO₂/SiO₂触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、410℃におけるo-メチルアセトフェノンの収率は55モル%であった。

実施例3.

実施例1における水20部に400部の硝酸ランタンを溶解させた液に代えて、エタノール30部に7.12部の四塩化チタンを溶解させた液を用いた以外は、実施例1と同じ方法で触媒調製を行ない、TiO₂/SiO₂触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、399℃におけるo-メチルアセトフェノンの収率は64モル%であった。

実施例4.

実施例1における400部の硝酸ランタンに代えて、200部の硝酸ランタンおよび153部の

-30-13．α-アルミナ，比表面積5.3 m²/g）を加え、温浴上でよく混ぜながら水の一部を蒸発させてペースト状にし、2mm径×5mm長に湿式成形した。100℃で一夜乾燥後、500℃で4時間焼成してCeO₂/Al₂O₃触媒を調製した。

実施例1と同じ条件でo-トルイル酸と酢酸を反応させた結果、430℃におけるo-メチルアセトフェノンの収率は52モル%であった。

実施例7.

実施例6における酸化アルミニウム微粉末に代えて、酸化チタン微粉末を用いた以外、実施例6と同じ方法で触媒調製を行ない、CeO₂/TiO₂触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、450℃におけるo-メチルアセトフェノンの収率は59モル%であった。

実施例8.

39.2部のオキシ塩化ジルコニウム（ZrOCl₂・8H₂O）を、60部の濃アンモニア水を含む540部のアンモニア水溶液を加え、水酸化ジル

コニウムのゲルをつくつた。306部の酢酸セリウムを含む水溶液に上記ゲルを加え、湯浴上で水の一部を蒸発させ、ペースト状にし、2mm径×5mm長に湿式成形した。100℃で一夜乾燥後、500℃で4時間焼成しCeO$_2$/ZrO$_2$触媒を調製した。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、458℃におけるo-メチルアセトフエノンの収率は50モル％であつた。

実施例9

実施例6における306部の酢酸セリウムに代えて、200部の硝酸ランタンを用いた以外、実施例6と同じ方法で触媒調製を行ない、La$_2$O$_3$/Al$_2$O$_3$触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、408℃におけるo-メチルアセトフエノンの収率は52モル％であつた。

実施例10.

実施例6における水30部に306部の酢酸セリウムを溶解させた液に代えて、エタノール30

部に7.12部の四塩化チタンを溶解させた液を用いた以外、実施例6と同じ方法で触媒調製を行ない、TiO$_2$/Al$_2$O$_3$触媒を得た。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、415℃におけるo-メチルアセトフエノンの収率は62モル％であつた。

実施例11

200部の硝酸ランタンを含む水溶液に20重量％のSiO$_2$を含むシリカコロイダルゾル75部および15部の酸化チタン微粉末を加え、湯浴上で加熱ゲル化させた。水分の一部を蒸発させペースト状にし、5mm径×5mm長に湿式成形した。100℃で一夜乾燥後、500℃で4時間焼成し、La$_2$O$_3$/SiO$_2$・TiO$_2$触媒を調製した。

実施例1と同じ条件で、o-トルイル酸と酢酸を反応させた結果、385℃におけるo-メチルアセトフエノンの収率は68モル％であつた。

実施例12

実施例11と同じ触媒を用いて、フエニル酢酸と酢酸のモル比1:2の混合液を1.35(mol/

hr.触媒)および窒素ガスを25(mol/hr.)で供給した。反応温度377℃におけるメチルベンジルケトンの収率は、供給フエニル酢酸基準で82モル％であつた。

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United States Patent [19]

Chang

[54] **METHOD OF REACTIVATING GROUP VIII ANIONIC HYDROFORMYLATION CATALYSTS**

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[73] Assignee: Ashland Oil, Inc., Ashland, Ky.

[21] Appl. No.: 600,437

[22] Filed: Apr. 16, 1984

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 414,565, Oct. 2, 1982, , and a continuation-in-part of Ser. No. 414,382, Oct. 2, 1982, , said Ser. No. 414,565, is a continuation-in-part of Ser. No. 332,558, Dec. 21, 1981.

[51] Int. Cl.^{4} C07C 45/50
[52] U.S. Cl. 568/454; 502/514; 568/909
[58] Field of Search .... 502/514; 568/451, 454, 568/456, 909; 260/429 R

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Primary Examiner—Werren B. Lone
Attorney, Agent, or Firm—Wood, Herron & Evans

[57] **ABSTRACT**

A method of reactivating anionic Group VIII hydroformylation catalysts to maintain high selectivity towards linear products. In the process of manufacturing aldehydes and alcohols from olefins, hydrogen, carbon monoxide and a catalyst, the selectivity for linear products is extremely high when an anionic Group VIII catalyst is used. This selectivity, after prolonged use of a catalyst, falls off along with the turnover number. The catalyst is reactivated to increase the selectivity towards linear products as well as the turnover number by subjecting the catalyst to a reducing agent which is strong enough under treatment conditions to reduce the anionic Group VIII catalyst. Reactivation of anionic iron, ruthenium, osmium, and mixed transition metal complex catalysts are particularly described and claimed.

16 Claims, No Drawings

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METHOD OF REACTIVATING GROUP VIII ANIONIC HYDROFORMYLATION CATALYSTS

RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 414,565, filed Oct. 2, 1982, entitled Process For the Hydroformylation of Olefins to Produce Linear Aldehydes and Alcohols, which is a continuation-in-part of application Ser. No. 332,558, filed Dec. 21, 1981, entitled Process For the Hydroformylation of Olefins Using an Improved Ruthenium Catalyst and Improved Hydroformylation Catalyst. This application is also a continuation-in-part of application Ser. No. 414,382, filed Oct. 2, 1982, entitled Use of Mixed Metal Catalysts in The Hydroformylation of Olefins to Produce Linear Aldehydes and Alcohols.

BACKGROUND OF THE INVENTION

The present invention relates to a process for the hydroformylation of olefins to produce aldehydes and alcohols. The present invention more particularly relates to such a process in which anionic Group VIII and mixed transition metal complex catalysts are used which are extremely selective toward straight chain products. The present invention more particularly relates to the regeneration of these hydroformylation catalysts to maintain this high selectivity toward straight chain aldehydes and alcohols.

BACKGROUND OF THE INVENTION

Aldehydes and alcohols are extremely useful as general purpose solvents, as surfactants and as precursors to many other useful chemicals. Due to the extent to which these compounds are used, it is important that such compounds be biodegradable. It is known that linear aldehydes and alcohols are more easily biodegraded than branch-chain aldehydes and alcohols.

Further, certain straight chain aldehydes and alcohols are extremely useful in particular applications. One particular straight chain aldehyde which has particular utility is n-butyraldehyde. This aldehyde can be dehydrated to form 2-ethyl hexanol which is useful as a gasoline additive or the alcohol can be esterified with phthalic anhydride to produce dioctylphthalate which is used for plasticizing polyvinyl chloride resins.

One method of producing aldehydes and alcohols is the hydroformylation of olefins. Hydroformylation is an old reaction and is used commercially to prepare both straight and branch-chain aldehydes and alcohols. In this reaction, an olefin is reduced by the addition of carbon monoxide and hydrogen to form an aldehyde. This reaction can be carried further until the aldehyde is reduced to an alcohol. This is further explained in U.S. Pat. No. 3,876,672 which is incorporated herein by reference.
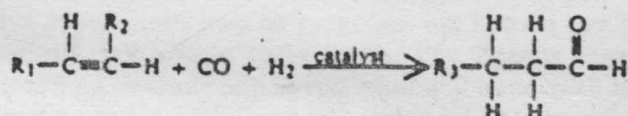
The hydroformylation reaction generally requires a catalyst. In the past, typical catalysts have included cobalt carbonyl, rhodium carbonyl, nickel, and platinum complexes. Although anionic metal catalysts are known, it has never been appreciated that the anionic character of the catalyst improves selectivity toward linear products. A problem encountered with the most commonly used prior art catalysts was the low percentage of linear aldehydes or alcohols produced. A reason for this is that the most commonly used catalysts were either cationic metal complexes or neutral or weakly anionic complexes.

In the co-pending application, particular anionic Group VIII metal catalysts have been disclosed which are very selective toward straight products. These include anionic ruthenium and iron compounds wherein the anionic moiety has at least a -2 charge as well as anionic osmium compounds and anionic mixed metal compounds.

SUMMARY OF THE INVENTION

The present invention involves the catalytic reaction or method in which aldehydes or alcohols are formed according to the following reaction:

$$R_1-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle R_2}{|}}{C}-H + CO + H_2 \xrightarrow{\text{catalyst}} R_1-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$
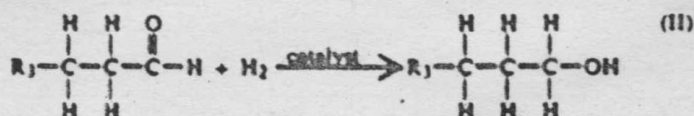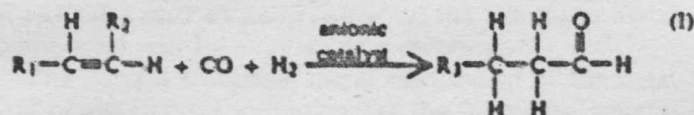
The reaction can be continued, reducing the aldehyde to linear alcohol. As the reaction continues, the catalyst tends to lose its selectivity. According to the present invention, the catalyst is reactivated, i.e., selectivity is improved by treating the catalyst with a reducing agent. The reducing agent must be strong enough to reduce the catalyst under treatment conditions.

DETAILED DESCRIPTION OF THE INVENTION

The hydroformylation reaction is an addition reaction in which carbon monoxide and hydrogen are reacted with an olefin to produce a saturated aldehyde. In other words, carbon monoxide and hydrogen are added to the olefin and the olefin reduced. The olefin can be reacted with carbon monoxide in the presence of hydrogen and a catalyst, or the olefin can be reacted with an excess of carbon monoxide and water in the presence of a catalyst. When carbon monoxide and water are used in the reaction, the water is simply a source of hydrogen, reacting with the carbon monoxide to form hydrogen and carbon dioxide. Hydrogen is thereby provided to react together with additional carbon monoxide upon the olefin. In either case, there is a hydrogen source available to react in combination with carbon monoxide upon the olefin. This reaction can be continued and available hydrogen would react with the aldehyde to produce an alcohol. The formation of the alcohol is encouraged by altering reaction conditions such as reaction time, pressure and temperature.

The hydroformylation reaction is shown by the following reaction formulas (I) and (II):

$$R_1-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle R_2}{|}}{C}-H + CO + H_2 \xrightarrow[\text{catalyst}]{\text{anionic}} R_1-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad \text{(I)}$$

$$R_1-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2 \xrightarrow{\text{catalyst}} R_1-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \qquad \text{(II)}$$

wherein R_1 represents alkyl, substituted alkyl, aryl or substituted aryl and R_2 represents hydrogen, alkyl, substituted alkyl, aryl or substituted aryl.

If R_2 is not hydrogen, the anionic catalyst used in the present invention will tend to cause the double bond in

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the olefin to migrate to form a linear aldehyde. R_1 or R_2 must, however, be either hydrogen or an unsubstituted alkyl group or the reaction will proceed at a very slow rate. R_3 will represent alkyl, substituted alkyl, aryl or substituted aryl and its formula will be determined by the make-up of R_1 and R_2. Thus, for example, if R_1 and R_2 are methyl groups, the hydroformylation will produce an aldehyde in which R_3 is an ethyl group. The double bond in the olefin will have migrated one carbon atom to form n-pentaldehyde.

The hydroformylation reaction is applicable to a wide variety of unsaturated compounds, including compounds containing more than one ethylenic group. Since difficulty has been experienced where the olefin is highly branched, two substituents of the olefinic group should be hydrogen as is shown in formula I. Hydroxyl or halogen substituents must be removed from the double bond by at least two carbon atoms and preferably not be present at all since they inactivate the catalyst in some situations.

Substituents which do not substantially interfere with the hydroformylation reaction include alkyl, aryl carbonyl, aryl C_1–C_9 alkoxycarbonyl, aralkyl, C_1–C_9 alkaryl, C_1–C_9 alkoxy and aryloxy. Aryl groups present may also be substituted by any of the other non-interfering substituents. The unsaturated compounds may contain up to 20 carbon atoms.

In order to obtain the full benefit of the present invention, R_1 and R_2 should be a straight chain C_1–C_9 alkyl group or R_1 or R_2 should be hydrogen. If R_1 and R_2 would be hydrogen, the product must necessarily be straight chain, i.e., propanal. Therefore, if ethylene is the olefin reactant, no benefit is derived from using the anionic catalysts of the present invention. When ethylene is the olefin reactant, a more reactive catalyst which is not necessarily selective toward linear products should be used.

The preferred olefin of the present invention should have the following general formula:

$$\begin{matrix} & H & H \\ & | & | \\ R_4 & -C = C - H \end{matrix} \qquad (III)$$
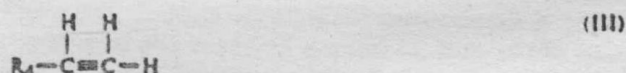
wherein R_4 is a straight chain C_1–C_{18} alkyl. This olefin should react quickly with high selectivity toward linear product.

In the event a di-olefin were reacted to form a dialdehyde or dialcohol, the olefin should have the following general Formula IV.

$$\begin{matrix} & H & & H \\ & | & & | \\ CH_2 = C & - R_5 - & C = CH_2 \end{matrix} \qquad (IV)$$

wherein R_5 is an alkyl, substituted alkyl, aryl or substituted aryl, and preferably, a straight chain C_1–C_9 or higher alkyl.

Preferred olefins include: propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, eicosene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, and 1,11-dodecadiene.

CATALYSTS

The catalysts for use in the present invention are anionic Group VIII transition metal compounds. A

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general formula of one preferred anionic transition metal complex for use as hydroformylation catalysts in the present invention is:

$$M^{+n}[H_yA_xL_z]^{-n}$$
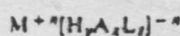
wherein A represents Fe, Ru and Os, M is a cationic species, n is an integer greater than or equal to 2 when A is Fe or Ru and n is an integer greater than n equal to 1 when A is Os; x is an integer greater than or equal to 1; y is an integer greater than or equal to 0, and z is an integer less than or equal to the available coordination bonding sites of the transition metal complex represented by A_x.
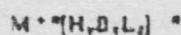
Typically, n will not exceed 6, y will not exceed 4 and is usually 2 or less, x will not exceed about 6. In theory, these upper limits may be exceeded, but known species generally fall within these limits. The ligands represented by L include any ligand whih will bond with the transition metal complexes and which will not interfere with the hydroformylation reaction. Ligands specifically suitable for use in the present invention include: trialkyl phosphines, trialkyl arsines, trialkyl antimonies, trialkyl bismuths, triaryl phosphines, triaryl arsines, triaryl antimonies, triaryl bismuths, carbon monoxide, cycloalkyldienes, isonitrile, isocyanide, acetylenes, crownethers, nitriles, such as phenyl nitrile, tertiary amines and halides. The choice of a ligand is critical in practicing the present invention. Those of ordinary skill in the art are well aware of many other suitable ligands.

M can represent any cationic species which will bond to the transition metal anionic complex and will not interfere with the hydroformylation reaction. Generally, M will be a metal and preferably selected from Group IA and Group IIA or an organic cation such as iminium, ammonium, phosphonium or arsenium. Again, one of ordinary skill in the art will be well aware of many other suitable cationic species. The above list is by no means meant to be exhaustive.

The hydroformylation catalysts may also be mixtures of transition metals wherein two transition metal compounds are combined in the reaction vessel. The first transition metal compound is a neutral or anionic transition metal compound selected from Group VIII of the Periodic Table. Preferably, these should be halides or carbonyls of the transition metals. Included are mono-, di- and multinuclear transition metal compounds as well as organotransition metal compounds.

Examples of these compounds would include $RhCl_3$, $RuCl_3$, $(Rh)(CO)_2Cl_2$, $Co_2(CO)_8$, $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, $HRh(CO)(PPh_3)_3$, $H_2Ru_4(CO)_{13}$, $H_2Ru_6(CO)_{18}$, H_2PtCl_6, $H_4Ru_4(CO)_{12}$, $PdCl_2(PPh_3)_2$, $HCoRu_3(CO)_{13}$, and so on. Preferably, the transition metal compound will be a halide or a carbonyl.

The second transition metal component of the catalyst of the present invention has the following general formula:

$$M^{+n}[H_xB_yL_z]^{-n}$$

wherein B represents Fe, Ru, Os, W, Mo, Cr, Co, Rh and Ir;

M is a cationic species;

n is an integer greater than or equal to 2;

x is an integer greater than or equal to 1;

y is an integer greater than or equal to 0; and

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z is an integer less than or equal to the available coordination bonding sites of the transition metal complex represented by B_z. This catalyst is hereinafter referred to as the mixed metal catalyst.

Typically, n will not exceed 6, y will not exceed 4 and is usually 2 or less, x will not exceed about 36. In theory, these upper limits may be exceeded, but known species generally fall within these limits. The ligands represented by L include any ligand which will bond with the transition metal complexes and which will not interfere with the hydroformylation reaction. Ligands specifically suitable for use in the present invention include: trialkyl phosphines, trialkyl arsines, trialkyl antimonies, trialkyl bismuths, triaryl phosphines, triaryl arsines, triaryl antimonies, triaryl bismuths, tertiary amines, carbon monoxide, cycloalkyldienes, isonitrile, isocyanide, acetylenes, crownethers, nitriles, such as phenyl nitrile, and halides. This is by no means an exhaustive list. Those of ordinary skill in the art are well aware of different ligands which can be used in place of the ligands listed above.

M can represent any cationic species which will bond to the transition metal anionic complex and will not interfere with the hydroformylation reaction. Generally, M will represent one or more metals preferably selected from Group IA and Group IIA or an organic cation such as iminium, ammonium, phosphonium or arsenium. Again, this is not an exhaustive list of suitable cations. Those of ordinary skill in the art are well aware of different cations which can be used in place of those listed above.

HYDROFORMYLATION REACTION

The hydroformylation reaction is conducted by mixing the olefin, carbon monoxide, and a hydrogen source, i.e., hydrogen or water together with the catalyst, and optionally, a solvent in a continuous or batch-type reactor. Preferably, the solution is heated and maintained under increased pressure.

While the reaction will occur at room temperature, it is preferred to heat and maintain the solution at $120°$–$200°$ C. In general, if the temperature is decreased, the rate of the reaction decreases. But, as the temperature is increased above $200°$ C., the selectivity toward linear aldehydes and alcohols decreases. In addition, the increase in temperature increases the difficulty of controlling the reaction to obtain primarily aldehydes as opposed to alcohols should this be desired.

Preferably, for the production of straight chain aldehydes, the pressure of the reaction should be maintained at between 500 psi to 2500 psi. This combined with a mixing force causes the carbon monoxide to go into solution. The higher pressure also tends to increase both the reaction rate and the selectivity of the reaction toward linear products. However, increased pressure also promotes the continuation of the reaction to produce alcohols.

The reaction time will vary depending on the temperature and pressure. Generally, the reaction time is maintained between 0.5–10 hours. An increase in time will cause an increase in the production of alcohol. It should be noted that in order to obtain only linear aldehydes, the reaction time is kept to a minimum which in turn does not provide time for most of the olefin to react. This can be more fully appreciated by considering the examples provided below.

To increase the production of alcohol as opposed to the aldehyde, the reaction temperature should be above $160°$ C.; the pressure should be above 800 psi and the reaction time should be from 3–5 hours or longer. Analysis of the reaction products will enable one of ordinary skill in the art to select the preferred reaction conditions for a particular olefin and catalyst.

The reaction may be run with or without a solvent. Suitable solvents include aldehydes, alcohols, ethers, esters, ketones, nitriles, aromatic hydrocarbons, aliphatic hydrocarbons, and chlorocarbons. Particularly suitable solvents include tetrahydrofuran, dibutyl ether, diethyl ether, dioxane, 2-methoxyethyl ether, 1,2-dimethoxyethane, butyl alcohol, ethyl alcohol, ethylene glycol, isobutyl alcohol, n-butyraldehyde, ethyl acetate, amyl acetate, ethyl butyrate, methyl benzoate, acetone, methyl ethyl ketone, methyl isobutyl ketone, acetonitrile, propionitrile, benzonitrile, chloroform, ethylene dichloride, methylene chloride, chlorobenzene, the chlorotoluenes, benzene, toluene, xylene, hexane, heptane, octane, cyclohexane, and methylcyclohexane.

REACTIVATION OF THE CATALYST

After prolonged use of the catalyst, the selectivity towards linear products will tend to fall off. By monitoring the selectivity periodically, one can determine the point at which the reaction should be discontinued due to unsatisfactory selectivity towards linear products.

In order to reactivate the catalyst, the catalyst is treated with a reducing agent which under the reactivation or treatment conditions, is strong enough to reduce a neutral Group VIII metal. Reactivation conditions specifically refer to the temperature and pressure at which the catalyst is reactivated as well as the duration of the reactivation.

More specifically, in the reactivation procedure, the catalyst is removed from the reactor and placed in a separate container or flask. The solvent and aldehydes or alcohols present on the catalyst are removed by vacuum distillation. The catalyst residue is resolved in an anhydrous solvent, for example, 1,2-dimethoxymethane or tetrahydrofuran and treated with 1–15 molar equivalents of a reducing agent.

Suitable reducing agents would include alkali metal hydrides such as potassium hydride or sodium hydride, alkali metal benzaphenones, for example, potassium benzophenone, sodium benzophenone, alkali boron or aluminum hydrides, for example, potassium borohydride, and alkali metal naphthalene, for example, potassium naphthalene or sodium naphthalene.

The catalyst reducing agent mixture is then subjected to heat for a period of time. The temperature and duration of the reactivation procedure will depend upon the degree of deactivity (loss of selectivity) of the catalyst and strength of the reducing agent. A weaker reducing agent would require higher reactivation temperatures and/or a longer reactivation time. With the reducing agents listed above, the deactivation anionic Group VIII hydroformylation catalyst can be reactivated at a temperature from about $20°$ C. to about $150°$ C. in from about one minute to about 24 hours. Depending on the solvent systems used, the temperature may have to be maintained at less than about $100°$ C. or the reactivation may have to be conducted under elevated pressure conditions. Temperatures lower than $20°$ C., i.e., $0°$ C. or less may be used, but the reactivation would require more time than desirable. The $150°$ C. upper limit represents the approximate temperature at which the catalyst would revert to the neutral or metallic form. This tem-

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perature will vary depending on the particular catalyst. The reactivation should be conducted in a neutral atmosphere such as argon or nitrogen.

The resulting solution of catalyst can then be placed back into the reactor and once again used to produce linear aldehydes or alcohol.

These reactions can be further appreciated by reference to the examples provided below. Attention should be focused on the selectivity toward the linear product obtained. As can be seen by looking at these examples, the specificity toward a linear product is substantially improved after a deactivated catalyst has been reactivated using the method of the present invention. In each of these examples, the catalyst reactivated had been previously deactivated by using it to catalyze a hydroformylation reaction. The selectivity and turnover number of the deactivated catalyst is provided for each example.

EXAMPLE 1

A deactivated hydroformylation catalyst $(PNP)H_3Ru_4(CO)_{12}$ (83.9% selectivity toward linear product and turnover of 10.2) containing 0.20 mmol of ruthenium metal was placed in a flask. The solvent, aldehydes or alcohols produced during the hydroformylation reaction were removed by distillation under vacuum. The remaining catalyst residue was dissolved in 10 milliliters of anhydrous 1,2-dimethoxyethane and treated with 0.36 mmol of potassium tri-sec-butylborohydride. The reaction mixture was heated under argon at 60° C. for 24 hours.

Hydroformylation Reaction with Reactivated Catalyst

The resulting dark brown catalyst solution, 3 milliliters (19.1 mmol) of 1 octene and 70 milliliters of anhydrous 1,2-dimethoxyethane were placed in a 300 milliliter Hastelloy C autoclave. The reactor was sealed, flushed three times with carbon monoxide, pressurized with 860 psig of approximately equimolar mixture of carbon monoxide and hydrogen and heated to 180° C. with stirring. The pressure was maintained at 1,000 psig. The reaction proceeded for two hours. After the reactor cooled, the reaction products were drawn out and analyzed with gas chromatography. It was found that 23.7% of octene was converted into a mixture of n-nonanal (4.04 mmol, 95.7% selectivity) and branched aldehydes (0.18 mmol, 4.3% selectivity) with a total turnover of 17.7 mole of products produced to mole of ruthenium metal.

EXAMPLE 2

Partially deactivated $(PNP)_2Ru_6(CO)_{18}$ (83.9% selectivity with a turnover number of 10.2) hydroformylation catalyst solution containing 0.240 mmol of ruthenium metal was placed in a flask. Solvent, aldehydes or alcohols produced from the previous hydroformylation reaction were removed by distillation under vacuum. The catalyst residue left was reactivated by dissolving it in 10 milliliters of anhydrous 1,2-dimethoxyethane and treating the catalyst with 0.48 mmol of potassium-benzophenone. This reaction mixture was stirred under argon at room temperature for three hours.

Hydroformylation With Reactivated Catalysts

The resulting dark brown catalyst solution, together with 3 milliliters (19.1 mmol) of 1 octene, and 70 milliliters of anhydrous 1,2-dimethoxyethane were placed in a 300 milliliter Hastelloy C autoclave. The reactor was

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sealed, flushed three times with carbon monoxide, pressurized with 860 psig of approximately equimolar mixture of carbon monoxide and hydrogen and heated to 180° C. with stirring. The pressure was maintained at 1,000 psig. The reaction proceeded for two hours. The reactor was cooled and the reaction products drawn out and analyzed using gas chromatography. It was found that 31.4% of octene was converted into a mixture of n-nonanal (5.3 mmol, 94.1% selectivity) and branched aldehydes (0.33 mmol, 5.9% selectivity) with a total turnover number of 23.7 mole of product produced to mole of ruthenium metal.

EXAMPLE 3

A partially deactivated (PNP) $CoRu_3(CO)_{13}$ hydroformylation catalyst solution (58.2% selectivity and turnover of 4.3) containing 0.55 mmol of ruthenium metal and 0.18 mmol of cobalt was placed in a flask. The solvent and aldehydes or alcohols produced from the previous hydroformylation reaction were removed by distillation under vacuum. The catalyst residue left was dissolved in 10 milliliters of anhydrous 1,2-dimethoxyethane and treated with 1.1 mmol of potassium naphthalene. The reaction mixture was stirred under argon at room temperature for two hours.

Hydroformylation Reaction With Reactivated Catalyst

The resulting dark brown catalyst solution, 3 milliliters, (19.1 mmol) of 1 octene and 70 milliliters of anhydrous 1,2-dimethoxyethane were placed in a 300 milliliter Hastelloy C autoclave. The reactor was sealed, flushed three times with carbon monoxide, pressurized with 860 psig of approximately equimolar mixture of carbon monoxide and hydrogen and heated to 180° C. with stirring. The pressure was maintained at 1,000 psig. The reaction proceeded for three hours. The reactor was cooled and the reaction products drawn out and analyzed with gas chromatography. It was found that 44.2% of octene was converted into a mixture of n-nonanal (6.57 mmol, 96.4% selectivity) and branched aldehydes (0.25 mmol, 3.6% selectivity) with a total turnover number of 9.3 moles of products produced per mole of ruthenium metal.

EXAMPLE 4

A partially deactivated ruthenium carbonyl hydroformylation catalyst solution (84.1% selectivity, turnover 14) containing 0.270 moles of ruthenium metal was placed in a flask. The catalyst had been formed in situ by adding 3 equivalents of KH per mole of $Ru_3(CO)_{12}$ in the hydroformylation reaction vessel. Solvents and aldehydes or alcohols produced from the previous hydroformylation reaction were removed by distillation under vacuum. The catalyst residue left is dissolved in 10 milliliters of anhydrous 1,2-dimethoxyethane and treated with 0.49 mmol of potassium hydride. The reaction mixture was heated under argon at 65° C. for 24 hours.

Hydroformylation Reaction With Reactivated Catalyst

The resulting dark brown catalyst solution, 3 milliliters (19.1 mmol) of 1 octene and 70 milliliters of anhydrous 1,2-dimethoxyethane were placed in a 300 milliliter Hastelloy C autoclave. The reactor was sealed, flushed three times with carbon monoxide and hydrogen and heated to 180° C. with stirring while the pressure was maintained at 1,000 psig. The reaction was allowed to proceed for two hours. The reactor was then
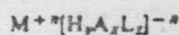
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cooled, and products drawn out and analyzed with gas chromatography. It was determined that 38.2% of the octene was converted into a mixture of n-nonanal (6.56 mmol, 97.3% selectivity) and branched aldehydes (0.18 mmol, 2.7% selectivity) with a total turnover number of 25.0 moles of product produced per mole of ruthenium metal.

These examples demonstrate that the anionic hydroformylation catalysts, once deactivated can be reactivated by subjecting them to a strong reducing agent.

I claim:

1. The method of reactivating an anionic Group VIII hydroformylation catalyst wherein said catalyst has the following general formula:

$$M^{+n}[H_yA_xL_z]^{-n}$$

wherein

A represents a metal selected from the group consisting essentially of Fe, Ru and Os;

n represents an integer greater than or equal to 1;

M represents a cationic moiety;

y represents an integer greater than or equal to 0;

x represents an integer greater than or equal to 1;

L is a ligand; and

z is an integer less than or equal to the available coordination bonding sites of A;

said method comprising reducing said deactivated catalyst by contacting said catalyst with a reducing agent strong enough to reduce said hydroformylation catalyst.

2. The method of reactivating an anionic Group VIII hydroformylation catalyst claimed in claim 1 wherein said deactivated catalyst is contacted with said reducing agent by mixing said catalyst with said reducing agent in an organic solvent solution and heating said solution for a period of time effective to reactivate said catalyst.

3. The method of reactivating an anionic Group VIII hydroformylation catalyst as claimed in claim 2 wherein said catalyst and reducing agent are heated for about one minute to about 24 hours at from about 20° C. to about 150° C.

4. The method of reactivating an anionic Group VIII catalyst claimed in claim 3 wherein said reducing agent and said catalyst are heated for about one minute to about 24 hours at from about 20° C. to about 100° C.

5. A method of reactivating an anionic Group VIII hydroformylation catalyst as claimed in claim 3 wherein said reducing agent is selected from the group consisting of alkali metal hydrides, alkali metal benzophenones, alkali boron hydrides, alkali aluminum hydrides and alkali metal naphthalenes and mixtures thereof.

6. A method of reactivating an anionic Group VIII hydroformylation catalyst claimed in claim 5 wherein said reducing agent is selected from the group consisting of potassium hydride, sodium hydride, potassium benzophenone, sodium benzophenone, potassium borohydride, sodium borohydride, sodium aluminum hydride, potassium aluminum hydride, sodium naphthalene, potassium naphthalene and mixtures thereof.

7. The method claimed in claimed in claim 1 wherein A represents Os.

8. The method claimed in claim 1 wherein A represents Ru and n is greater than or equal to 2.

9. The method claimed in claim 1 wherein A represents Fe and n is greater than or equal to 2.

10. The method of reactivating an anionic Group VIII hydroformylation catalyst wherein said catalyst is

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a composition comprising in admixture a first transition metal compound and a second transition metal compound wherein said first transition metal compound is selected from the group consisting essentially of anionic and neutral Group VIII transition metal compounds; and

wherein said second transition metal compound has the following general formula:

$$M^{+n}[H_yB_xL_z]^{-n}$$
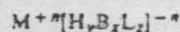
wherein

n is an integer greater than or equal to 2; p1 M is a cationic species;

B is a transition metal selected from the group consisting essentially of Ru, Os, Fe, Cr, Co, Rh, Ir, Mo and W;

x is an integer greater than or equal to 1;

L is a ligand;

z is an integer greater than or equal to the available coordination bonding sites of B; and

y is an integer greater than or equal to 0;

said method comprising reducing said deactivated catalyst by contacting said catalyst with a reducing agent strong enough to reduce said catalyst.

11. The method claimed in claim 10 wherein said first transition metal compound is a carbonyl.

12. The method claimed in claim 10 wherein said first transition metal is a halide.

13. The method claimed in claim 10 wherein said first transition metal compound includes a transition metal selected from the group consisting of Rh, Os and Ru.

14. The method claimed in claim 10 wherein the molar ratio of the transition metals of the first transition metal compound to said second transition metal compound is from about 1:10 to about 1:1.

15. The method of reactivating an anionic Group VIII hydroformylation catalyst wherein said catalyst comprises:

a first transition metal compound wherein said transition metal is selected from the group consisting essentially of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt, and wherein said first transition metal compound is a halide or a carbonyl compound;

a second transition metal compound having the following general formula:

$$M^{+n}[H_yB_xL_z]^{-n}$$
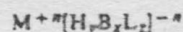
wherein

n is an integer greater than or equal to 2;

M is a cationic species;

B is a transition metal selected from the group consisting essentially of Ru, Os, Fe, Mo and W;

x is an integer greater than or equal to 1;

L is a ligand;

z is an integer less than or equal to the available coordination bonding sites of B; and

wherein the molar ratio of the transition metals of said first transition metal compound to said second transition metal compound is from about 1:1 to about 1:10 thereby providing an effective hydroformylation catalyst;

said method comprising contacting said catalyst with a reducing agent selected from the group consisting of alkali metal hydrides, alkali metal benzophenones, alkali boron hydrides, alkali aluminum hydrides and alkali metal naphthalenes and mixtures

thereof at a temperature from about 20° C. to about 100° C. for about one minute to about 24 hours.

16. The method of reactivating an anionic Group VIII hydroformylation catalyst where said catalyst has been at least partially deactivated catalyzing the formation of linear alcohols and aldehydes from an olefin, carbon monoxide, and hydrogen source;

wherein said catalyst has the following general formula:
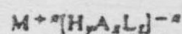
$$M^{+n}[H_yA_xL_z]^{-a}$$

wherein

A represents a metal selected from the group consisting essentially of Fe, Ru and Os;

n represents an integer greater than or equal to 1;

M represents a cationic moiety;

y represents an integer greater than or equal to 0;

x represents an integer greater than or equal to 1;

L is a ligand; and

z is an integer less than or equal to the available coordination bonding sites of A;

said method comprising reducing said deactivated catalyst by contacting said catalyst with a reducing agent selected from the group consisting essentially of alkali metal hydrides, alkali metal benzophenones, alkali metal boron hydrides, alkali metal aluminum hydrides and alkali metal napthalenes and mixtures thereof at about 20° C. to about 150° C. for about one minute to about 24 hours.

* * * * *

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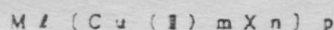
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明　細　書

1. 発明の名称

触媒の回収方法

2. 特許請求の範囲

1) 一般式

$Ml \, [Cu(I) \, mXn] \, p$

（結晶水を含んでも含まなくてもよい）（式中、Mは周期律表において1Aで表されるアルカリ金属またはアンモニウム、Cu（I）は二価の銅、Xはハロゲン、lは1～3の整数、mは1または2、nは3～8の整数、pは1または2）

で示される銅ハロゲノ錯体、又は該銅ハロゲノ錯体とアルカリ金属ハロゲン化物からなる触媒を用いて水及び炭素数5～10の脂肪族アルコール中で2,3,5-トリメチルフェノールを酸素又は酸素含有ガスと接触させ2,3,5-トリメチルベンゾキノンを製造する方法において、

反応後、分液された有機相より水を用いて抽出装置内のpHを1.5～2.5に保ちながら触媒を

抽出し、次いで抽出液内の水を蒸発させて触媒を回収することを特徴とする触媒の回収方法

2) 向流多段震拌槽を用い触媒を抽出する特許請求の範囲第1項記載の方法

3) 触媒を抽出するために用いる水の量を反応後分液された有機相に対して10～30wt%とする特許請求の範囲第1項記載の方法

4) 向流多段震拌槽を2～5段とする特許請求の範囲第2項記載の方法

5) 向流多段震拌槽の各層の間に沈降槽をおく特許請求の範囲第2項記載の方法

6) 向流多段震拌槽における有機相の滞留時間を10～60分とする特許請求の範囲第2項記載の方法

7) 震拌槽におけるpHを1.5～2.5に保つためにハロゲン化水素酸水溶液を添加する特許請求の範囲第2項記載の方法

8) ハロゲン化水素酸水溶液として1～10重量%の塩酸を用いるを添加する特許請求の範囲第7項記載の方法

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3) 抽出溶媒中の水を50〜200Torrの真空下、連続的に蒸発させる特許請求の範囲第1項記載の方法

3. 発明の詳細な説明
〔産業上の利用分野〕

本発明は触媒の回収方法に関するものであり、詳しくは2,3,6-トリメチルフェノール（以下、TMPと略する）を水及び炭素数5〜10の脂肪族アルコール類中で銅ハロゲノ錯体触媒の存在下、分子状酸素と接触させて2,3,5-トリメチルベンゾキノン（以下、TMBQと略する）を製造する方法における触媒の回収方法に関するものである。

TMBQはビタミンEの合成中間体として有用な物質である。

〔従来の技術〕

触媒の存在下、TMPを酸素で酸化してTMBQを得る方法としては種々の方法が知られている。例えば、特公昭53-17585号公報は銅及び

ハロゲンイオンの存在下、TMPを酸素で酸化する方法を開示し、特公昭49-2446号公報はコバルト錯体を触媒とする方法を開示している。

これらの方法は限定された条件下ではTMBQの収率が高く、優れた方法の一つと考えられるが、これらの方法が工業的製造法として成立するには触媒が反応系から容易に回収でき、回収された触媒の活性が常に維持されていることが必要である。しかしながら、上記した公報には触媒の回収は可能であるとの記載はあるものの具体的な回収方法および回収した触媒の活性についての記載はない。

例えば特公昭53-17585号公報では水に易溶な有機溶媒、例えばジメチルホルムアミド中で反応を行い、反応終了後に大量の水を導入し、次いで水に不溶な有機溶媒、例えば四塩化炭素で有機物を抽出して有機相と水相に分離し、分離された水相は触媒水溶液として次の反応に使用し得るとされている。しかしながら、回収触媒の活性についての言及はなく、また他の実施例

によれば水が存在しなかった下で反応を行った場合、触媒の活性は低く極めて効率の悪い反応になっている。したがって、水相に移行した触媒を触媒水溶液としてそのまま用いることは実際上、実施し得ないことである。

それ故に特公昭53-17585号公報においては回収触媒に十分な触媒活性を発揮させるためには触媒が移行した触媒水溶液から完全に水を蒸発させ、触媒を固体状で回収し反応に供しなければならない。しかしながら、この方法は大量の水を蒸発させる必要があるためエネルギー消費が大きくなると同時に反応溶媒と抽出溶媒の分離が必要である等、反応終了後から触媒を回収するまでの過程が複雑であり、工業的実施に当たっては多くの困難がある。

特公昭49-2446号公報の方法においても触媒の回収は可能であろうが上記と同様の理由により工業的実施に当たっては問題点が多いし、更に触媒寿命が短いという大きな欠点を有する。

本発明者らは先に銅ハロゲノ錯体又は銅ハ

ロゲノ錯体とアルカリ金属ハロゲン化物からなる触媒を用い、水および有機溶媒の共存下にTMPを酸化する方法を提案した。ここで用いる触媒は水媒体中で使用するものである。またこの方法では有機溶媒として水に殆ど不溶な C₅〜C₁₀ 脂肪族アルコールを用いる。従って反応は完全な殆々不均一系で行われるが反応は全く問題なく進行し、また反応終了後、触媒を含む水相と有機相とは容易に分離でき、したがって触媒の回収も容易であり相分離した触媒液はそのまま反応に供することができる。しかしながら分離された有機相中には若干量の水と共に触媒が存在しており相分離だけでは完全な触媒回収はできない。

有機相に存在している触媒量は使用する銅ハロゲノ錯体、アルカリ金属ハロゲン化物の種類、量、水相における濃度などによって異なるが、触媒回収操作を省略することは触媒の大きな損失となり好ましくない。

反応後、分離された有機相に存在している触