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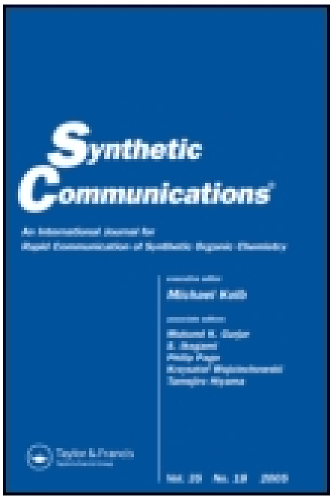

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CATALYTIC OLEFIN EPOXIDATION WITH MOLECULAR OXYGEN OVER SUPPORTED AMIDATE-BRIDGED PLATINUM BLUE COMPLEXES

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CATALYTIC OLEFIN EPOXIDATION WITH MOLECULAR OXYGEN OVER SUPPORTED AMIDATE-BRIDGED PLATINUM BLUE COMPLEXES

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ABSTRACT

The platinum complexes, $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4]$-$(NO_3)_5$ and $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2](NO_3)_4$, supported on a surface of silica gel, Al_2O_3, activated carbon, and poly-(4-vinylpyridine) are active heterogeneous catalysts for the liquid phase epoxidation of various olefins under 1 atm of dioxygen in the presence of isobutyraldehyde.

There has recently been enormous interest in the coordination and organometallic chemistry of platinum(III) complexes, because of their fascinating reactivity resulting from the electron deficiency of the high-valent metal centers. We have reported several novel reactions, i.e. activation of

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C-H bonds of ketones by amidate-bridged Pt(III) complexes to give the ketonyl-platinum(III) dinuclear complexes and coordination of olefins in water to give β-hydroxyalkyl-platinum(III) complexes.[1,2] It was also found that amidate-bridged Pt(III) complexes catalyze the oxidation of terminal olefins to ketones and promote dihydroxylation of olefins in acidic aqueous solutions.[3,4]

Transition-metal complex-catalyzed epoxidation of olefins has been of great interest due to the importance of epoxides as valuable synthetic intermediates. Various soluble metal complexes have been reported to be effective expoxidation catalysts, for instance, ruthenium[5] and manganese[6] porphyrins, Mn and Fe triamidoamine complexes,[7] and Ru-phosphine complexes[8] together with peroxides or molecular oxygen. Heterogeneous catalysts based on metals, metal ions or metal complexes adsorbed on supports such as carbon, aluminas, silicas, zeolites, and clays, polymer-supported Ru-porphyrin complexes have been used for liquid phase oxidation together with oxidant such as H_2O_2, $KHSO_5$, NaClO or organic peroxides.[9–14] A simple catalytic system using sacrificial aldehydes as the oxygen-acceptor agent and dioxygen as the source of oxygen, which was first reported by Mukaiyama,[15] have also been employed in other laboratories.[8,13]

Although amidate-bridged platinum(III) complexes catalyze the oxidation of olefins in biphasic aqueous-organic solutions, only cyclic olefins can be epoxidized with low turnover number (less than 25 moles of epoxides per mole of platinum blue complexes).[16] The true active catalyst in the reactions was found to be the platinum(III) dimer complex produced from the oxidation of the platinum blue complex.[2] By extending these our earlier results on the organometallic and catalytic chemistry of platinum blue complexes, here we report the immobilization of the platinum blue complexes on SiO_2, Al_2O_3, activated carbon, and poly(4-vinylpyridine), and their catalytic properties for the expoxidation of various olefins in the presence of a sacrificial aldehyde under atmospheric pressure of molecular oxygen at room temperature.

Five solid catalysts were prepared from $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ or $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2](NO_3)_4$, and are abbreviated as Pt_2/C, Pt_2/Al_2O_3, Pt_2/SiO_2, Pt_2/PVP (PVP = poly(4-vinylpyridine) 2% cross-linked), and Pt_4/C.

Table 1 shows the representative results for the epoxidation of cyclohexene and styrene catalyzed by various supported platinum complexes in the presence of a sacrificial aldehyde and molecular oxygen. Although it is known that alkenes can be epoxidized only with molecular oxygen and isobutyraldehyde in the absence of a metal complex,[17,18] the data listed in Table 1 obviously demonstrate that supported platinum blue complexes afford higher yield of epoxides. Simultaneously, isobutyric acid was also

Table 1. Catalytic Epoxidation of Olefins by Various Supported Platinum(III) Complexes*

Catalyst	Substrate	Product	Time (h)	Epoxide Yield (%)
Carbon	Cyclohexene	1,2-epoxycyclohexane	24	49.0
Pt_2/C	Cyclohexene	1,2-epoxycyclohexane	6	99.0
Pt_2/C	Styrene	2-phenyloxirane	6	52.6
Pt_4/C	Cyclohexene	1,2-epoxycyclohexane	8	99.0
Pt_4/C	Styrene	2-phenyloxirane	14	83.7
SiO_2	Cyclohexene	1,2-epoxycyclohexane	24	36.6
Pt/SiO_2	Cyclohexene	1,2-epoxycyclohexane	15	43.8
Pt_2/SiO_2	Styrene	2-phenyloxirane	15	19.4
Al_2O_3	Cyclohexene	1,2-epoxycyclohexane	24	22.5
Pt_2/Al_2O_3	Cyclohexene	1,2-epoxycyclohexane	14	52.6
Pt_2/Al_2O_3	Styrene	2-phenyloxirane	14	10.7
Pt_2/PVP	Cyclohexene	1,2-epoxycyclohexane	8	12.2
Pt_2/PVP	Styrene	2-phenyloxirane	14	26.7

*The reaction conditions are given in the experimental section.

formed as the side-product from the oxidation of isobutyraldehyde. In order to test the efficiency of the supported metal complexes, the reactions in the presence of Al_2O_3, SiO_2 and carbon were performed respectively. The results demonstrate that platinum complexes apparently facilitate the epoxidation. All the supported catalysts showed much higher catalytic activity than those of our earlier reported soluble platinum complexes in aqueous-organic biphasic solutions.[2,16] It is especially noteworthy that styrene was not epoxidized in the previous biphasic solution reactions, but is epoxidized in the present supported system in good yield. And also the reaction proceeds much faster in the present system.

It can be seen from Table 1 that the catalyst activity is dependent upon the catalyst carriers. The two activated carbon supported catalyst, Pt_2/C and Pt_4/C, did not show significant difference in the cyclohexene epoxidation. Higher conversions were achieved with Pt_2/C and Pt_4/C for the epoxidation of cyclohexene with 99% yield of 1,2-epoxycyclohexane within 6 h, which corresponds to a frequency of 71 turnovers h^{-1} per mole of the platinum. Both $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ and $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2](NO_3)_4$ supported on carbon afforded better yield for cyclohexene and styrene than Pt_2/Al_2O_3, Pt_2/SiO_2, and Pt_2/PVP. Probably the interaction between the platinum complexes with the hydroxyl groups or adsorbed water molecules on the surface of SiO_2 and Al_2O_3, and the nitrogen on the pyridine rings of poly(4-vinylpyridine) prevents the approaching of olefins to the platinum complexes and therefore lower their catalytic activities.

Catalyst leaching was observed when Pt_2/PVP was employed after long time running, and the reaction mixture turned to be slightly yellow. Although the catalyst leaching in other cases was not found during the reaction courses, the side-product, isobutyric acid, induced metal loss is expected.

The activated carbon supported catalyst, Pt_2/C, was also employed to catalyze the epoxidation of other olefins under the mild conditions of room temperature and atmospheric pressure of dioxygen, and the data are collected in Table 2. In the epoxidation reactions of all olefins studied, the catalyst showed excellent selectivity for the epoxides, only trace amount of cyclohex-2-enone being detected by GC-MS in the case of cyclohexene. The formation of cyclohex-2-enone was previously also observed in large amount as by-product in the previous biphasic solution reaction under similar conditions. Generally, cyclic olefins and internal alkenes give better yield than terminal linear olefins; only 5% of 1,2-epoxyoctane was detected for 1-octene. Only one olefinic bond of cyclohex-1,4-diene was epoxidized under these mild conditions. It is noted that in the absence of isobutyraldehyde no cyclohexane oxide was observed by GC-MS for cyclohexene using Pt_2/C as catalyst. Although *trans*-cinnamaldehyde bears

Table 2. Epoxidation of Various Olefins Catalyzed by Pt_2/C*

Substrate	Product	Time (h)	Epoxide Yield (%)
Cyclopentene	1,2-epoxycyclopentane	6	92.2
Cyclohexene	1,2-epoxycyclohexane	6	99.0
Cyclooctene	1,2-epoxycyclooctane	14	35.5
Cyclohex-1,4-diene	1,2-epoxycyclohex-4-ene	14	55.7
1-methylcyclohexene	1,2-epoxy-1-methylcyclohexane	8	60.6
1-octene	1,2-epoxyoctane	14	5.0
2-octene	2,3-epoxyoctane	15	100
cis-stilbene	2,3-diphenyloxirane	14	88.0
trans-cinnamaldehyde	2,3-epoxy-3-phenylpropanal	15	69.1
trans-cinnamaldehyde	2,3-epoxy-3-phenylpropanal	48	No reaction[a]
Cyclohexene	1,2-epoxycyclohexane	24	No reaction[b]
Cyclohexene	1,2-epoxycyclohexane	24	No reaction[b]

*The reactions were carried out under atmospheric molecular oxygen in CH_2Cl_2 at room temperature in the presence of isobutyraldehyde. [a]No additive. [b]PhIO or Me_3NO was used as the oxidant instead of O_2.

potential oxygen-transferring group, it was not oxidized to its corresponding epoxide in the absence of the additional aldehyde; the –CHO group did not initiate efficiently the intramolecular oxidation reaction like the additional aldehyde. In the presence of isobutyraldehyde, however, the epoxide was obtained nearly in 70% yield. It illustrates that the additional oxygen-transferring agent plays a dominating role for the oxygenation reaction. PhIO and Me_3NO were also tested as oxygen-transferring agent, but no epoxidation reaction was observed.

The results presented above show that platinum blue complexes immobilized onto both inorganic and organic carriers catalyze the epoxidation of olefins smoothly with moderate to good yield under mild conditions. Although the heterogeneous catalysts have the advantage of recoverability and give much higher turnover than their soluble counterpart, the catalysts still suffer from the drawback of using a sacrificial aldehyde as the oxygen-transferring agent. Further improvement of the catalysts is required to avoid the use of sacrificial aldehyde and realizes a clean, economic route for the production of epoxides.

EXPERIMENTAL

Supported platinum catalysts were prepared by impregnation of each support with an aqueous solution of either $[Pt_4(NH_3)_8((CH_3)_3CCONH)_4](NO_3)_5$ or $[Pt_2(NH_3)_4((CH_3)_3CCONH)_2](NO_3)_4$, at room temperature. The mixtures were stirred until the impregnation solution turned to colorless. The supported catalysts were collected by filtration and washed with water and acetone successively, and then dried in vacuum. The loading of platinum was 2.3% for activated carbon and 1.2% for Al_2O_3, SiO_2 and PVP. The epoxidation of olefins was performed under room temperature and 1 atm of molecular oxygen, typically as follows. A reaction flask under O_2 atmosphere was charged with solid catalyst (in each reaction, the catalysts containing 0.024 mmol of platinum were used regardless of their loading), 10 ml of CH_2Cl_2, 10 mmol of substrate, and 3 ml of isobutyraldehyde. The reaction was run at room temperature with constant stirring by a magnetic stirrer. After completion or interruption of the reaction, the catalyst was filtrated off, and the solution was subjected to GC or ^1H NMR analysis.

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