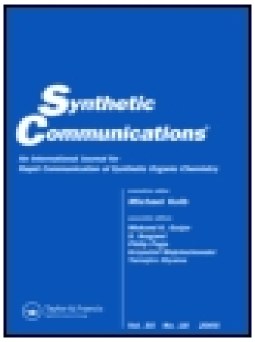

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EPOXIDATION OF OLEFINS BY MOLECULAR OXYGEN OVER SUPPORTED METAL HETEROGENEOUS CATALYSTS

Hanrong Gao and Robert J. Angelici*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011-3111, USA

Abstract: Molecular oxygen (1 atm) conveniently reacts with olefins in the presence of simple supported metal heterogeneous catalysts and aldehydes (e.g., isobutyraldehyde and benzaldehyde) at room temperature to give epoxides in good yields.

Selective oxidation of organic substrates is important in the chemical and petrochemical industries.[1,2] The epoxidation of olefins is one such useful reaction which yields epoxides as useful synthetic intermediates.[3,4] Epoxidations using peracids, hydrogen peroxide, alkyl peroxide or molecular oxygen and metal complex catalysts of ruthenium, molybdenum and titanium have been reported.[1] One of the main disadvantages of most of these systems is poor selectivity to the epoxide. The use of heterogeneous catalysts and air/oxygen in place of homogeneous oxidants is clearly preferred on economic, safety and environmental

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* To whom correspondence should be addressed

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grounds.[5,6] Although air/oxygen is a weak, non-selective oxidizing agent, it has been used as the oxygen source in oxidations involving a sacrificial aldehyde as an oxygen transfer agent.[7-12] Heterogeneous catalysts that have been used in epoxidations include titanium-silica materials (using hydroperoxides as the oxidizing agents),[13,14] a cobalt-substituted Keggin-type heteropolytungstate [8] and a clay-supported nickel complex [9] (both using molecular oxygen and a sacrificial aldehyde). Recently, Clark et al. reported that metal ions, such as Cu^{2+}, Cr^{3+} and Mn^{2+}, supported on a surface-functionalized silica gel are efficient catalysts for the liquid phase, room temperature epoxidation of olefins by molecular oxygen in the presence of aldehyde.[15,16] Here we report the epoxidation of olefins by molecular oxygen in the presence of aldehyde over silica (or carbon)-supported metal heterogeneous catalysts (Pd/SiO_2, Pd/C, Pt/SiO_2, Ru/SiO_2 and Ir/SiO_2) under 1 atm of O_2 and at room temperature. The catalysts are robust, easily separated and give excellent yields and selectivity for epoxides. To our knowledge, these are the first systems to use simple supported metal heterogeneous catalysts for the epoxidation of olefins by molecular oxygen in the liquid phase.

Results of the epoxidation of cyclohexene at room temperature under 1 atm of O_2 with various supported metal heterogeneous catalysts and in the presence of isobutyraldehyde are shown in Table 1. Although cyclohexene is epoxidized by molecular oxygen without using a metal catalyst (entry 6),[17] the reactions carried out in the presence of Ir/SiO_2, Pd/SiO_2 and Pd/C gave much higher conversion. The conversions of cyclohexene with the five supported metal catalysts decrease

Table 1 Epoxidation of Cyclohexene by Molecular Oxygen over Supported Metal Heterogeneous Catalysts[a]

Entry	Catalyst	Time (h)	Conversion (%)[b]	Epoxide yield (%)[c]
1	Ir/SiO_2	4.0	100	100
2	Pd/SiO_2	6.5	98.0	98.0
3	Pd/C	6.0	74.0	73.6
4	Pt/SiO_2	6.5	42.0	42.0
5	Ru/SiO_2	6.5	33.1	33.0
6	none	6.0	32.0	32.0

[a] Reaction conditions: 50 mg of catalyst; 3.0 mL of isobutyraldehyde; 1.0 mL of cyclohexene; 10 mL of 1,2-dichloroethane solvent; 1 atm of O_2, room temperature.

[b] Determined by GC.

[c] Determined by GC-MS.

in the order: Ir/SiO_2 > Pd/SiO_2 > Pd/C > Pt/SiO_2 > Ru/SiO_2. All the catalysts gave excellent selectivity for cyclohexene oxide (> 99%). Isobutanoic acid was also formed as a by-product from the starting isobutyraldehyde; it can be simply removed by extraction with aqueous base.[9]

The supported metal heterogeneous catalysts, Pd/SiO_2, Pd/C, Ir/SiO_2 and Pt/SiO_2, were also used to catalyzed the epoxidation of other olefins in the presence of isobutyraldehyde or benzaldehyde under the mild conditions of room temperature and 1 atm of O_2 (Table 2). The data in Table 2 show that with the

Table 2 Epoxidation of Olefins in the Presence of Isobutyraldehyde and Benzaldehyde[a]

Entry	Catalyst	Substrate	Aldehyde	Time (h)	Yield (%)[b]	Selectivity (%)[c]
7	Pd/SiO$_2$	cyclohexene	Isobutyraldehyde	6.5	98.0	100
8		1-hexene	isobutyraldehyde	21	68.8	82.0
9		1-octene	isobutyraldehyde	22	57.6	83.2
10		1-decene	isobutyraldehyde	22	43.7	84.2
11		styrene	isobutyraldehyde	22	33.1	41.3
12		cyclohexene	benzaldehyde	12	11.1	100
13		1-decene	benzaldehyde	22	95.3	100
14	Pd/C	cyclohexene	Isobutyraldehyde	5.5	73.6	99.7
15		1-decene	isobutyraldehyde	20	46.7	100
16		1-dodecene	isobutyraldehyde	13	37.4	100
17		styrene	isobutyraldehyde	5.0	84.3	84.3
18		1-decene	benzaldehyde	22	90.1	100
19	Ir/SiO$_2$	1-decene	isobutyraldehyde	22	39.9	100
20		1-decene	benzaldehyde	22	59.1	100
21	Pt/SiO$_2$	1-decene	isobutyraldehyde	22	23.1	100
22		1-decene	benzaldehyde	22	35.7	100
23	none	1-decene	isobutyraldehyde	25	24.9	100
24		1-decene	benzaldehyde	26	27.0	100

[a] Reaction conditions and footnotes (*a* and *b*) are the same as those in Table 1.

[c] Selectivity for epoxide determined by GC.

Pd/SiO_2 and Pd/C catalysts and in the presence of isobutyraldehyde, the epoxidation of cyclohexene is faster than those of terminal alkenes. Rates for the epoxidation of terminal alkenes decrease as the length of the hydrocarbon chain increases, but selectivities for the epoxides are about the same. The selectivity of Pd/C for epoxide is higher than that of Pd/SiO_2. Although the epoxidation rate of styrene on both Pd/SiO_2 and Pd/C catalysts is higher than those of 1-decene and 1-dodecene, the selectivity for styrene oxide is the lowest (entries 11 and 17). For all four supported metal catalysts, Pd/SiO_2, Pd/C, Ir/SiO_2 and Pt/SiO_2, the epoxidation of 1-decene in the presence of isobutyraldehyde is slower than that with benzaldehyde. However, the epoxidation rate for cyclohexene on the Pd/SiO_2 catalyst with isobutyraldehyde is much higher than that with benzaldehyde (entries 7 and 12). When a mixture of cyclohexene and 1-decene was epoxidized by molecular oxygen with the Pd/SiO_2 catalyst and in the presence of benzaldehyde under the reaction conditions in Table 1, the only product observed before cyclohexene was completely converted was cyclohexene oxide. This result suggests that under these reaction conditions, cyclohexene completely inhibits the epoxidation of 1-decene. Thus, the epoxidation rate is strongly affected by the nature of both the olefin substrate and the aldehyde oxygen transfer agent.

In conclusion, the epoxidation of common olefins by molecular oxygen is efficiently performed using supported metal heterogeneous catalysts in the presence of an aldehyde and at room temperature and 1 atm of O_2. Besides the operational ease of these reactions, the catalysts are easily prepared or are commercially available.

EXPERIMENTAL

The silica-supported (silica gel 100 (Fluka); BET surface area, 400 m^2/g) metal catalysts, Pd/SiO_2,[18] Pt/SiO_2,[18] Ru/SiO_2[18] and Ir/SiO_2[19] were prepared by procedures similar to those described in the literature. The Pd/C catalyst was purchased from Aldrich. The metal loading in all the supported catalysts was 10 wt%. All the chemicals were commercial and used without further purification. A Varian 3400 GC interfaced to a Finnigan TSG 700 high-resolution magnetic sector mass spectrometer with electronic ionization (70 ev) was used for all GC-MS measurements. Gas chromatographic analyses were performed with a HP-6890 GC using a 25 m HP-1 capillary column with a FID detector. The epoxidation reactions were performed as follows: A 100 mL reaction flask containing an O_2 atmosphere was charged with 50 mg of catalyst, 10 mL of 1,2-dichloroethane solvent, 1.0 mL of olefin and 3.0 mL of aldehyde (isobutyraldehyde or benzaldehyde). The mixture was stirred under 1 atm of O_2 at room temperature. After completion or interruption of the reaction, the liquid mixture was analyzed by GC and GC-MS.

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first reduced under a H_2 flow at 200 °C for 3 h and then at 250 °C for 5 h to give the black Ir-SiO_2 (Ir, 10 wt%) powder.

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