Epoxidation of Simple Alkenes with O₂ and Isobutyraldehyde Catalyzed by Ni Catalysts Deposited on Nanoporous Carbon

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Novel nickel catalyst deposited on nanoporous carbon was found to be an efficient catalyst for the epoxidation of simple alkenes with O₂ and isobutyraldehyde under mild conditions. Alkenes exhibited different reactivities towards Ni-catalyst and epoxidation with stilbene proceeds stereospecifically. This may be rationalized with the mechanism involving coordinated acylperoxy radical intermediate. Nickel contents depend on the preparative methods and the KNI-3 catalyst, which was synthesized by wet impregnation of Ni(NO₃)₂ into nanoporous carbon, shows the highest activity. The activity of the catalyst is well correlated with contents of nickel. Recycled catalysts suffer considerable loss of activity due to leaching of catalytic active species, nickel.

Key Words : Alkene epoxidation, Ni catalyst, Nanoporous carbon, Oxygen, Isobutyraldehyde

Introduction

The epoxidation of olefins have attracted much attention since epoxides, especially propylene oxide, are key intermediates in chemical industry and synthetic organic reactions.[1,2] Recent interests also arise in asymmetric synthesis.[3] The main process for propylene oxide, Halcon-Arco process consumes a considerable amount of Cl₂ and the impact on environment is not considered benign.[2] Therefore, many efforts have been done to develop environment-friendly processes employing H₂O₂ or O₂.[4,5,6] Also epoxidation of olefins in the aqueous solution has attracted much attention.[7] Many systems have been reported and various mechanisms have been proposed and this is well documented in the recent review.[8]

The epoxidation with molecular oxygen as the oxidant is much more benign than the processes with expensive and toxic organic peroxides or peroxyacids. Mukaiyama reported that transition metal β-diketonate complexes function as efficient catalysts for the aerobic epoxidation of unfunctionalized alkenes with isobutyraldehyde as the reductant under mild conditions.[9] Various transition metal β-diketonate complexes such as Ni(II)(acac)₂,[10] Co(II)(acac)₂,[11] Co(II)(thd)₂,[12] Mn(II)(acac)₂,[11,13] and Fe(III)(acac)₃[14] have been reported. In addition to transition metal β-diketonate complexes, Co(II) complexes containing Schiff bases[15] were also employed for the aerobic epoxidation of alkenes. Furthermore, Co(II) salen derived Jacobsen type complexes[16] and chiral Mn β-diketonate and salen complexes[17] were used as catalysts for aerobic asymmetric epoxidation. Ru(II) complexes[18,19] also catalyzed simple olefins successfully, utilizing molecular oxygen as oxidant.

However, homogeneous catalysts mentioned above are difficult to recover from the reaction mixture after reaction. Thus, the efforts to prepare heterogeneous catalysts have been continued. The heterogeneous catalysts are easily

separable and reusable with little loss of activity if there is no leaching problem. The aerobic epoxidation with catalysts supported on organic polymer would be one of the solutions and these efforts are recently reviewed.[20] A polyaniline-supported Co(II) acetate and Co(II) salen complexes,[21,22] a polystyrene-bound nickel complex,[23] and nickel acetylacetonate[24] which were supported on polybenzimidazole catalyzed alkenes efficiently under O₂. Moreover, nanostructured amorphous CoO deposited inside the pores of mesoporous silica (MCM-41) was found to be an efficient catalyst for the aerobic epoxidation of alkenes with isobutyraldehyde as reductant.[25] MgO-polysilazane-metal complexes (M = Fe, Co, Ni, Cu) were also active in aerobic epoxidation of olefins.[26]

Here we present Ni catalysts deposited on nanoporous carbon as another example of the efficient heterogeneous catalyst for the aerobic epoxidation with isobutyraldehyde as reductant under mild conditions.

Experimental Section

The All reagents, purchased from Aldrich Chemical Co., were used as supplied commercially without further purification. Solvents and isobutyraldehyde were used after distillation under nitrogen atmosphere.

General Procedure for Preparing Ni/nano C Catalysts. The synthesis of mesoporous silica template, SBA-15[27] and CMK-3[27,28] were performed following the procedures described in the literature.

Three kinds of CMK-3 materials containing Ni species were prepared. First sample was prepared by wetness impregnation of Ni(NO₃)₂ into the CMK-3. Typically, 5 g of the CMK-3 was slurried in the aqueous solution containing 2.49 g of Ni(NO₃)₂·6H₂O for about 30 min at room temperature. Subsequently, the water was completely evaporated at 333 K by using a rotary evaporator and dried in an

oven for 24 hrs at 373 K. The sample thus obtained are denoted Ni/CMK-3-imp (abbreviated as ANI-3), where the imp means the impregnation method. Second Ni/CMK-3 material was obtained with the following procedure. 2.49 g of Ni(NO$_3$)$_2$·6H$_2$O was first impregnated into 10 g of the calcined SBA-15. After drying for 24 hrs at 373 K, the Ni/SBA-15 was directly used as the template for CMK-3 materials. The preparation method for the CMK-3 was the same as the above procedure. This sample is referred to as Ni/CMK-3-pre (abbreviated as ANI-1), where the pre means the pre-impregnation of Ni species. The procedure for the synthesis of the third Ni/CMK-3 sample was very similar with that of CMK-3 materials, except that the Ni(NO$_3$)$_2$·6H$_2$O were mixed with the carbon source. The mesopores of the SBA-15 were filled with the mixture of the sucrose, sulfuric acid and Ni(NO$_3$)$_2$·6H$_2$O by impregnation method. Remaining procedure for the carbon materials was the same as the above method. Third sample is designated Ni/CMK-3-com (abbreviated as ANI-2), where the com indicates composite material of mesoporous carbon and Ni species.

Instrumentation. The GC analyses were performed on a Varian 3300 instrument. The instrument was equipped with a flame ionization detector and coupled to a Varian 4400 integrator.

^{1}H NMR spectra were recorded by using 5 mm tube on a Varian Unity Inova 400 (400.265 and 100.657 MHz, respectively) or Varian Gemini 2000 (199.976 and 50.289 MHz, respectively) spectrometer and were referenced to tetramethylsilane (TMS). NMR was used to characterize the epoxidation products.
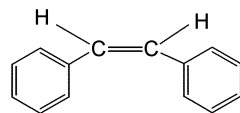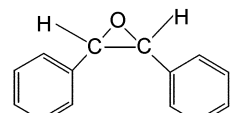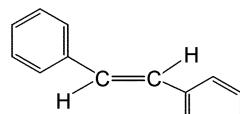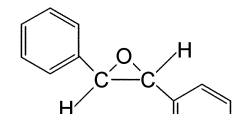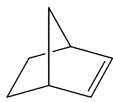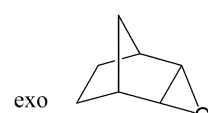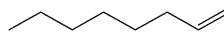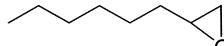
Reaction Conditions. In a glove box, Ni catalyst (6 mg, 10% Ni content, 1.00 mol%) was placed in a Schlenk flask with a magnetic stir bar. Then it was connected to a vacuum and evacuated and filled with nitrogen. 1 mmol of alkene and 3 mmol of isobutyraldehyde in CH$_3$CN (10 mL) were added to a flask. 200 μ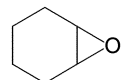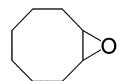L of decane was added as the internal standard. The reaction mixture was evacuated and stirred under an air balloon at room temperature for 4 hours. The GC analyses were performed at 0 h, 0.5 h, 1 h, 2 h and 4 h. The progress of the reaction was monitored by following the disappearance of the substrate.

Determination of Metal Contents by Atomic Absorption (AA) Spectroscopy. After weighing the sample to 0.1mg, about 10 mg of sample was completely dissolved in 10 ml of aqua regia while stirring vigorously at 70 °C. Then the solution was used to determine the metal content by AA spectroscopy (Spectr AA 220FS, Varian).

Results and Discussion

The Aerobic Epoxidation of Simple Alkenes with ANI-3 catalyst. The epoxidation of simple alkenes has been performed with air in the presence of isobutyraldehyde at room temperature and 1 atm for 4 hrs. As shown in Table 1, various kinds of alkenes exhibited different reactivities towards the Ni/nano C catalyst, ANI-3 but this system generally showed moderate activity. As was expected from

**Table 1**. The aerobic epoxidation of alkenes with ANI-3 catalyst under aerobic condition at room temperature

Entry	Alkenes	Conversion (%)	Epoxides
1		14	
2		51	
3		98	exo
4		27	
5		65	
6		53	

other reports,[10,11,29] norbornene showed very good yield. Substrates such as *trans*-stilbene, cyclohexene and cyclooctene gave moderate yields. The epoxidation of *trans*-stilbene and *cis*-stilbene exclusively yielded *trans*-stilbene oxide and *cis*-stilbene oxide, respectively but yield is greatly stereodependent (51% vs. 14%). This stereodepedence is frequently observed but formation of stereospecific product is rather surprising. Journoux[30] reported the formation of trans isomer during the epoxidation of cis-stilbene and this ascribed to the formation of radical intermediates as proposed by Nam.[31]

Since peracid without transition metal complexes yielded the same stereospecific products as observed in this study,[10] peracids mechanism instead of oxo-metal pathway appears to work. Ni may only catalyze the formation of peracids because there are no other ligands that can control the geometry of the products. Without catalysts, no epoxidation reaction proceeds. However, direct reaction of aldehydes with Ni(II) to produce acyl radical (RC(O)•) and formation of metal oxides by *in-situ* formed peracids, proposed in the generally accepted mechanism[31] cannot be assumed due to unstable Ni(III) and Ni(IV) oxidation states.

As an alternative, the mechanism (Scheme 1) involving Ni-coordinated acylperoxy radical (RC(O)OO•) is proposed to rationalize the experimental results obtained in this study.

Epoxidation of internal alkene proceeds more rapidly than that of terminal one. In this reactivity difference, the electronic factors appear to be more important than steric
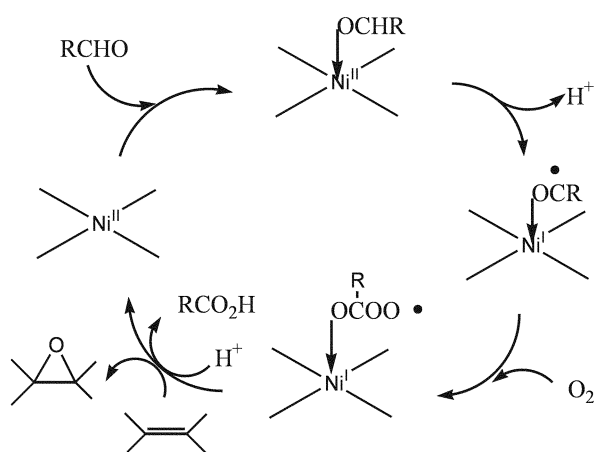
Scheme 1. Proposed mechanism for the epoxidation of Olefins with O_2 and an aldehyde, catalyzed by Ni(II) species.[10]

ones. Increased coordination ability of internal alkenes over terminal ones may lead to faster reaction rates due to increased π basicity. The reactivity differences among internal alkenes can be rationalized by considering the steric factor.

The aerobic epoxidation results of simple alkenes were also analyzed kinetically (Figure 1). As expected, norbornene gave the steepest slope at early stage. Substrates with respectable reactivities such as *trans*-stilbene, cyclohexene and cyclooctene yielded moderate slopes. An alkene with long-chain alkyl group, 1-octene exhibited very low slope at early stage and almost constant rate thereafter. *cis*-Stilbene, which displayed the poorest yields, did not even start the

epoxidation reaction after 1 h.

In order to investigate temperature effect, the epoxidation of norbornene was performed at room temperature, 50 °C and reflux temperature, respectively. GC analyses were done 1 and 4 h. As the temperature increases, the yields decrease; 82% (RT), 58% (50 °C), 33% (reflux) after 1 h, and 98%, 68%, 40% after 4 h. Volatility of the substrates, norbornene and isobutyraldehyde, or decomposition of coordinated acylperoxy radical, an initially formed intermediate, might be responsible for such a difference in reactivities.

When the catalyst was recovered after the first run and reused for the second run, some loss of activity of the catalyst was observed due to leaching of the metal ions and the conversion rate became much slower. For 90% conversion, 4 h is required with a fresh catalyst while 19 hr is required with a recycled catalyst.

Dependence of Catalytic Activities of Ni/nano C Catalysts on Preparative Methods. Ni-catalysts deposited on nanoporous carbon were prepared in three different ways; the introduction of metal ion occurred before (ANI-1), during (ANI-2) and after carbonization step (ANI-3). In order to compare the activities of three different Ni/nano C catalysts, the aerobic epoxidation of norbornene was performed. As shown in Table 2, activity order is as follows; ANI-3 > ANI-2 > ANI-1. Reaction profiles of the aerobic epoxidation of norbornene with Ni/nano C catalysts also supported the order of epoxidation activity (Figure 2). As shown in Table 3, this order is well correlated with the initial Ni contents in the catalysts but inversely correlated with the leaching amounts of Ni. This may indicate that Ni in solution contributes little to the epoxidation and the
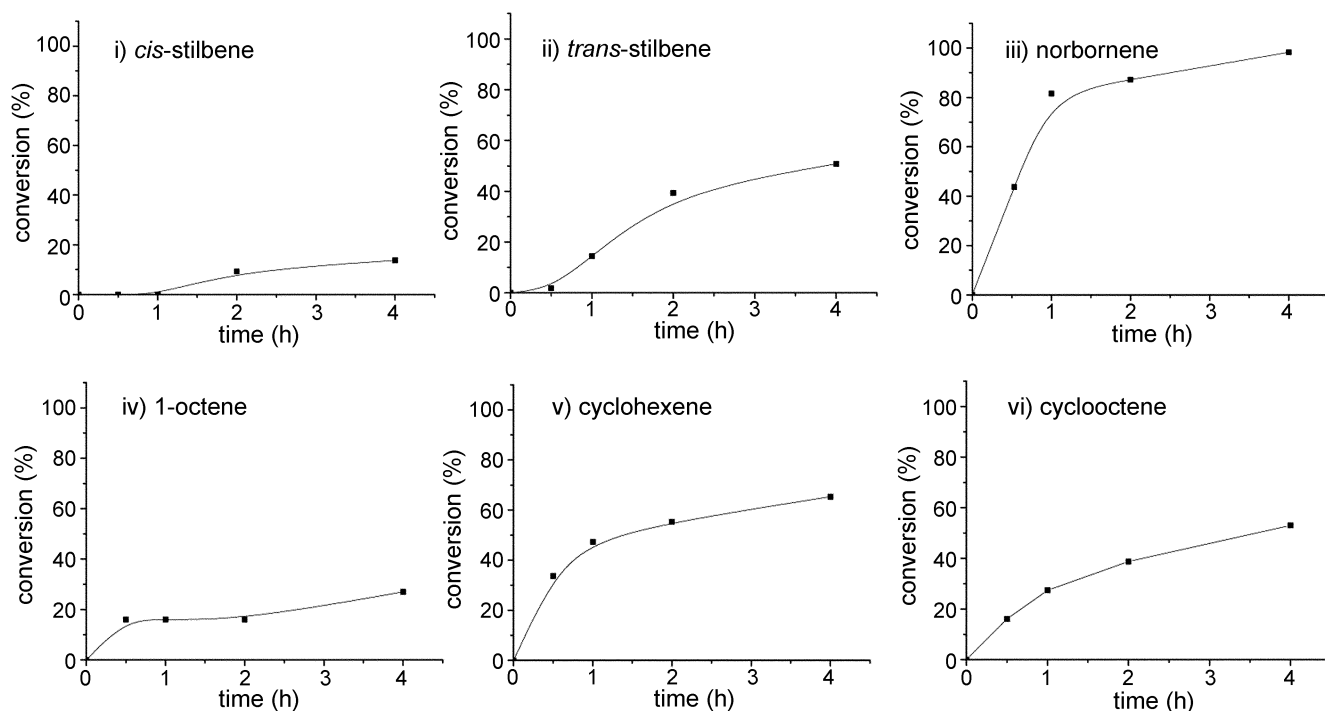

Figure 1. Reaction profiles of the aerobic epoxidation of i) *cis*-stilbene, ii) *trans*-stilbene iii) norbornene, iv) 1-octene, v) cyclohexene, vi) cyclooctene with ANI-3 catalyst.
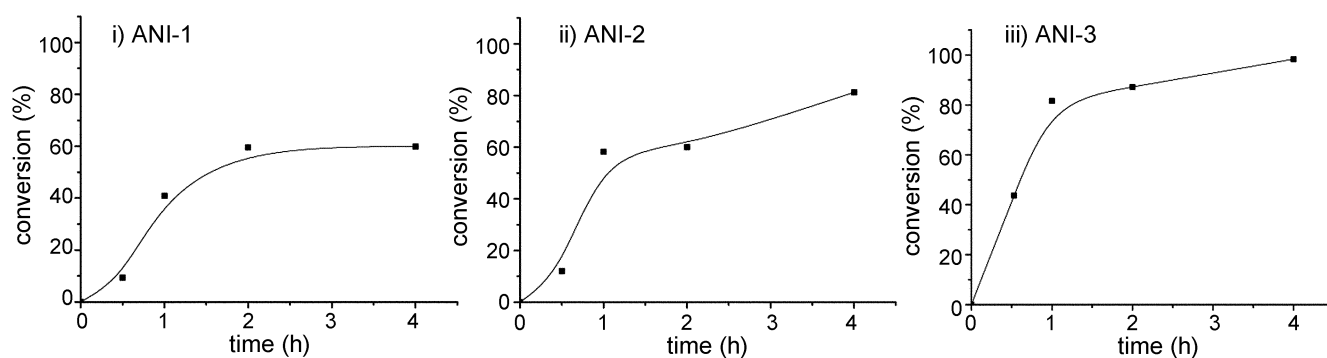
Figure 2. Reaction profiles of the epoxidation of norbornene with catalysts ANI-1, ANI-2, and ANI-3 under aerobic conditions at room temperature.

Table 2. Comparison of catalytic activities of ANI-1, ANI-2 and ANI-3 on the epoxidation of norbornene

Entry	Catalysts	Conversion (%)
1	ANI-1	60
2	ANI-2	81
3	ANI-3	98

Table 3. Ni contents in catalysts determined by Atomic Absorption Spectroscopy

		Ni	
	Type		wt %
As prepared	Ni(1)		6.00
	Ni(2)		6.11
	Ni(3)		6.28
After reaction	Ni(1)		2.05
	Ni(2)		2.39
	Ni(3)		2.66

formation of coordinated acylperoxy radical proceeds mainly on the Ni on the surface of carbon supporter. Much reduced reaction rate (around 5% yield at room temperature after 1 h) in the solution, obtained by filtration of catalysts and addition of another batch of norbornene after the 1st reaction, supports this conclusion.

Conclusion

Nickel catalyst deposited on nanoporous carbon was successfully employed as a heterogeneous catalyst for the aerobic epoxidation of simple alkenes with isobutyraldehyde as a reductant under mild conditions. It appears that the epoxidation proceeds via a coordinated acylperoxy radical intermediate. Internal alkenes exhibit higher reaction rates than terminal ones due to faster coordination onto metal ions and different reactivities among internal alkenes were rationalized by considering the steric factor. ANI-3 catalyst, which was synthesized by wet impregnation of $Ni(NO_3)_2$ into nanoporous carbon after carbonization, was found to be the most efficient catalyst among three different Ni/nano C

catalysts. Activity is well related with the amount of Ni on the catalyst. When the temperature increases, the epoxidation rate decreases, possibly due to decomposition of initially formed coordinated acylperoxy radical. Recycled catalysts show considerable loss of activity due to leaching of catalytic active species, Ni.

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