ABSTRACT

The oxidation of cyclohexene with molecular oxygen, in the presence of hydrophobic niobium oxide/silica as catalysts, has been investigated. The catalysts have been prepared by impregnation of niobium penta-ethoxide on the silica surface followed by attachment of alkylsilyl groups from octadecyltrichlorosilane (ODS) on the surface with partial coverage. Cyclohexene was oxidized to 2-cyclohexene-1-ol, 2-cyclohexene-1-one and 7-oxabicyclo[4.1.0]hepane by molecular oxygen at atmospheric pressure in the presence modified Nb$_2$O$_5$/silica particles without any solvent at 70°C. These catalysts are efficient for the oxidation of cyclohexene with molecular oxygen which probably occurs with Mars-van Krevelen type mechanism. Based on these results, a catalyst design for liquid-gas reaction system is proposed.

1.  INTRODUCTION

Solid-gas catalyzed-liquid reactions are often encountered in the chemical process industry, most frequently in hydroprocessing operations and in the oxidation of liquid phase organic [1-4]. In respect of the latter reaction type, the system usually has been applied for mineralization of toxic organics in wastewaters. However, synthesis of useful organic materials with this system is also one of particular field of application. Along this line, we have attempted to make an effective heterogeneous catalytic system for this application.

Recent results about the evidence for a Mars-van Krevelen type mechanism for oxidation with molecular oxygen in the liquid phase have been reported in several journals [5-7], making this system a good starting point for further extensive research on this kind of mechanism in liquid system. Those are the only reports on the liquid-phase Mars–van Krevelen mechanism-type oxidation in liquid phase system. This is interesting because by controlling the lattice oxygen diffusion, an effective catalyst for liquid-gas system could be obtained with a proper selection of oxide (as catalyst/active site).

Recently, we proposed a novel concept of "phase-boundary catalysis (PBC)" in order to utilize the immiscible liquid-liquid reaction system with solid catalysts [8-12]. In the PBC system, it was demonstrated that the bimodal amphiphilic zeolite particles could be placed at the liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic phases and act as efficient catalyst for epoxidation reaction. In this paper, it is demonstrated that the phase-boundary catalysts not only show catalytic activity in liquid-liquid boundary, but also in liquid-gas system. For this purpose, the oxidation of cyclohexene with molecular oxygen using hydrophobic niobium oxide/silica particles is chosen as a reaction model. Creating active sites which is suitable for Mars-van Krevelen mechanism is proposed in this paper.

Despite the numerous reports on selective oxidation of hydrocarbons using niobium oxide, the oxidation of alkenes by molecular oxygen using Nb$_2$O$_5$/silica system has never been reported. The use of molecular oxygen as the oxidant makes the reaction interesting from both economic and environmental points of view.

2.  EXPERIMENTAL

Catalyst preparation
Silica sol with a primary particle size of 500 nm (Nissan Chemical Industries), was used after evaporation of water in order to get dry powder. Partially modified silica, whose surface was partly covered with alkylsilyl, was prepared in two steps. First, niobium penta-ethoxide Nb(OC$_2$H$_5$)$_5$; Wako Pure Chemical) in ethanol solution was impregnated into silica powder and heated at 383 K
overnight. After this treatment, it is believed that the niobic acid (\( \text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O} \)) is formed [12]. At this stage, the modified silica is called Nb-silica. The molar amount of Nb was 500 \( \mu \text{mol g}^{-1} \) of silica. In the second step, the Nb-silica powder in water (20 wt%) was immersed in 10 cm\(^3\) toluene containing 500 \( \mu \text{mol} \) of \( n\)-octadecyltrichlorosilane (ODS, ShinEtsu), and the suspension was shaken for ca. 5 min at room temperature. Then, the solid was collected by centrifugation and dried at 383 K overnight. Due to the hydrophilicity of the Nb-silica, the addition of a small amount of water led to aggregation by the capillary force of water among particles. Under these conditions, it is expected that only the outer surface of aggregates, being in contact with the organic phase, could be modified with ODS. The partially modified sample was labeled as part-Nb-silica.

Fully modified Nb-silica (full-Nb-silica) was prepared as follows. ODS (500 \( \mu \text{mol} \)) was dissolved in a mixed solution of toluene (80 vol\%) and CCl\(_4\) (20 vol\%). A dried sample of Nb-silica (1 g) was added to the solution, and the mixture was stirred overnight at room temperature. A solid sample was collected by centrifugation, washed with CCl\(_4\) and then ethanol, and dried at 383 K overnight.

**Reaction conditions and analytical method**

Oxidation of cyclohexene was carried out in the presence of air and oxygen under atmospheric pressure. Typically, cyclohexene (2 cm\(^3\), Wako), and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with stirring at 1000 rpm for 20 h at 70°C. Because of the presence of an appreciable amount of impurities, cyclohexene was purified by passing through column of basic alumina (Merck). The reaction products were analyzed by gas chromatography (a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and DB-1 column) and GC/MS.

### 3. RESULTS AND DISCUSSION

As shown in Fig. 1a, in the mixture of cyclohexene and air, the catalyst exhibits an interesting activity during the catalytic oxidation of cyclohexene. The catalytic reaction was carried out in the absence of solvent at 70°C without the use of any special oxidant or co-reductant, affording 2-cyclohexen-1-ol and 2-cyclohexen-1-one as the major products. No products of the oxidation of double bond was observed in the organic phase.

When molecular oxygen was used as oxidant, a similar product selectivities were obtained and the activities were higher compared with those obtained by using air. It was observed that 2-cyclohexen-1-ol and 7-oxabicyclo[4.1.0]hexane were the major products in the conversion of cyclohexene over modified Nb-silica catalysts (Fig. 1b).

Figures 1 and 2 show the trend of the yield of the oxidation products in the presence of modified Nb-silica. The results suggest that all the part-Nb-NaY showed higher activity in liquid-gas system. Interestingly, when the reaction was performed in strictly anaerobic condition, after molecular oxygen is completely removed and replaced by bubbling Argon, and in the presence of part-Nb-silica, the oxidation products observed; were 2-cyclohexen-1-ol (8.2 \( \mu \text{mol} \)), 7-oxabicyclo[4.1.0]hexane (4.1 \( \mu \text{mol} \)) and 2-cyclohexen-1-one (0.5 \( \mu \text{mol} \)). None of these products were observed in the presence of only silica and without catalyst. This suggests that the oxidation of cyclohexene may be occurs with Mars-van Krevelen mechanism, in which the lattice oxygens transferred from the oxide (Nb\(_2\)O\(_5\)) to yield the reaction products. This phenomenon is also supported by the fact that the amount of the oxidation product is larger than the amount of oxygen in the system. In the system containing part-Nb-silica (see Fig. 1b), it is calculated that the amount of products (1.00 mmol) is larger than the amount of molecular oxygen (0.98 mmol). Due to the low activity of the system containing Nb-silica and full-Nb-silica, the evidence of the Mars-van krevelen mechanism is not observed.

Silica particles are dry particles. They become hydrophobic after their surface silanols are replaced by alkylsilyl groups. In order to show the hydrophobicity/hydrophilicity character of Nb-silica, part-Nb-silica and full-Nb-silica, the dispersibility of these particles in the immiscible mixture of cyclohexene and water was compared. It was observed that the part-Nb-silica particles were effectively located at liquid-liquid boundary of water and cyclohexene mixtures, whereas Nb-silica and full-Nb-silica were well-dispersed in the aqueous and organic phases respectively, due to their hydrophilicity and hydrophobicity. The reason why part-Nb-silica was effectively located at liquid-liquid boundary is due to its surface structure. Recently, it has been clarified that the methods used here for making part-Nb-silica could produce bimodal particles, i.e., one side is covered with hydrophobic alkylsilyl groups and the other is kept hydrophilic [8].
Based on the above discussions, it can be proposed that the higher activity of part-Nb-Silica is due to the stabilization of liquid-gas system by bimodal amphiphilic particles as shown in Fig. 2. The use of hydrophilic catalyst (Nb-silica) decreases the wetting efficiency. Although the wetting efficiency could be increased by attachment of the alkylsilyl groups with full coverage (full-Nb-silica), the gaseous reactant is difficult to reach the catalyst surface, because it has to overcome gas-liquid and liquid-solid mass transfer resistance. According to the model, there is a path for $O_2$ to reach the niobium oxide active sites: from the gas bulk towards the “dry” catalyst surface, for which $O_2$ has to overcome only the gas-solid mass transfer resistance. This should lead to changes in catalytic properties; demonstrated by higher catalytic activity of part-Nb-silica compared to full-Nb silica and

![Diagram](image)

**Fig. 1** The yield of 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 7-oxabicyclo[4.1.0]hexane on the oxidation of cyclohexene using various modified Nb-silica under stirring condition at 1000 rpm. All reactions were carried out at 70°C for 20 h: 50 mg catalyst, 2 cm$^3$ cyclohexene and 11 cm$^3$ oxygen (a) and 11 cm$^3$ oxygen (b) at atmospheric pressure.
Fig. 2 The stabilization of amphiphilic solid particles containing niobium oxide as actives sites on liquid-gas (cyclohexene-O₂) for oxidation of cyclohexene with Mars-van Krevelen Mechanism.

Nb-silica. Although all the results mentioned above seem consistent with a Mars-van Krevelen mechanism; some products of the reaction leave the solid catalysts’ surface with one or more constituents of the catalysts’ lattices [13], a detail mechanism such as catalyst regeneration is not known. This study is now underway in Solid State Chemistry laboratory, Universiti Teknologi Malaysia.

In conclusion, the results described above demonstrate the feasibility and possibility of the amphiphilic niobium oxide-silica working as catalyst for oxidation of cyclohexene with molecular oxygen with Mars-van Krevelen type mechanism.

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