Epoxidation of Styrene using Nanosized γ - Al_2O_3 /NiO Heterogeneous Catalyst Derived from the P123 Surfactant

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ABSTRACT

Al_2O_3 /NiO powder was obtained through hydrolysis-condensation reactions and thermal treatments. An organic additive, triblock copolymer surfactant P123, was added to the starting materials to control the surface area and morphology. The synthesized powder was characterized by X-ray diffractometry (XRD), field-emission scanning electron microscopy (FE-SEM) and a Brunner-Emmett-Teller surface analysis (BET). The heterogeneous catalytic activity of this powder was applied to an epoxidation reaction of styrene and was monitored using a gas chromatograph with mass spectrophotometry (GC/MS).

Key words : Al_2O_3 /NiO, P123, Epoxidation, GC/MS

1. Introduction

There are several transitions of alumina that can be accomplished by a heat treatment. Alumina can be transformed by changing the temperature via the boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ phases and different phases can be obtained depending on the processes used. Mesoporous γ - Al_2O_3 is usually prepared by heating to 673~773 K from boehmite. γ - Al_2O_3 among the transition phases of alumina has especially remarkable textural and acid-base properties; therefore, it has been used as a type of ceramic support and as a heterogeneous catalyst.¹⁻³⁾ Moreover, it has the potential for broad application as an adsorbent catalyst, a catalytic support and an advanced ceramic owing to the thermal and chemical stability of its optical characteristics.

NiO is also considered as a catalyst because it is highly active and selective not only in hydrogenation but also catalytic reactions. It is used as a supporting co-catalyst with ceramic substrates such as silica and alumina.^{4,5)}

Molecular templates and several types of surfactants have been used to synthesize many types of organic and inorganic materials. To prepare mesoporous nano-crystalline γ - Al_2O_3 with a high surface area and a specific pore morphology, pluronic triblock P123 copolymer (Poly(ethylene oxide)20-poly(propylene oxide)70-poly(ethylene oxide)20 as a surfactant has been used. It serves to increase the thermal stability and to ensure a uniform form of the mesoporous γ - Al_2O_3 intermediate phase.^{6,7)} The P123 template is known as an active organic additive that can improve the specific surface area and textural properties of mixed oxides by forming

meso-structured materials with the template by means of surfactant micelles.

Styrene oxide is a commercially useful intermediate for organic reactions. It is used in the processing of fine chemicals and pharmaceuticals. Recently, many attempts have been made regarding the epoxidation of alkenes using environmentally friendly reusable heterogeneous catalysts such as Ti-SiO₂, TS-1, and Ti-MCM-41; noble-metal-based catalysts; and catalysts based on transition-metal oxides. Wang et al.⁸⁾ reported that various transition-metal oxide species supported on γ - Al_2O_3 could be used for the epoxidation process.

The synthesis of γ - Al_2O_3 with a uniformly ordered mesoporous structure is a long-standing goal for a variety of uses. Combinations of silica and γ - Al_2O_3 with transition metals are known to be very effective catalysts that have metal oxides dispersed onto the matrix. These can be prepared by a sol-gel process. The purpose of this study is to improve the catalytic effect so that it is highly efficient and economical for the epoxidation of styrene by controlling the surface area and morphology of these mixed oxides. Al_2O_3 /NiO powder was prepared by a hydrolysis and condensation technique with and without the P123 surfactant. The modified processes using a nonionic surfactant as used here can change the microstructure of homogeneous γ - Al_2O_3 precisely to obtain a uniform mesoporous distribution and morphology of the condensation materials. γ - Al_2O_3 with NiO powder was used in the epoxidation reaction, which was monitored by GC/MS.

2. Experimental Procedure

2.1. Preparation of mesoporous γ - Al_2O_3 /NiO powders

Aluminum isopropoxide $\text{Al}(\text{OC}_3\text{H}_7)_3$ (CAS No. 555-31-7, Aldrich) was dissolved in distilled water at a mole ratio of

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$\text{Al}(\text{OC}_3\text{H}_7)_3 : \text{H}_2\text{O}=1:100$ at 353 K. 20wt% of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (CAS No. 13478-00-7, Aldrich) to $\text{Al}(\text{OC}_3\text{H}_7)_3$ was added and refluxed for 3 h. Nitric acid (HNO_3) as an acid catalyst was added to this reaction mixture for peptization to obtain a homogeneous sol. 10wt% of P123 surfactant was used for the powder with P123. This sol solution was stirred overnight and kept for 24 h to obtain a gel sample after quenching. This gel sample was washed with water and alcohol, followed by drying at 393 K for 24 h. The obtained samples were heat-treated with powders with and without the P123 surfactant at temperatures ranging from 773 K to 1473 K.

2.2. Characterization and catalytic test

The structural change and phase transformation of the $\text{Al}_2\text{O}_3/\text{NiO}$ powder with and without P123 were characterized by X-ray diffraction measurements (XRD, Bruker D8 Focus, 40 kV, 40 mA, $0.2^\circ/\text{min}$, $10\text{--}80^\circ$) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$) and Rietveld structure refinement for a quantitative analysis. The morphology and microstructure of these powders, heat-treated at 973 K, were analyzed by field-emission scanning electron microscopy (FE-SEM, JEOL-JMS 7500F). The specific surface area and pore size of the powders were measured by a Brunauer-Emmett-teller surface analyzer (BET, BELSORP-mini).

The catalytic reaction was carried out using 5.2 g of styrene, 6.7 g of TBHP (tert-butyl hydroperoxide) and 0.1 g of $\gamma\text{-Al}_2\text{O}_3/\text{NiO}$ with P123 as a catalyst. The reaction was held at around 353–368 K and was measured at 1, 3, 5, 7 and 10 h. The styrene oxide reaction products as obtained from the epoxidation of styrene were analyzed by a gas chromatograph with mass spectrophotometry (GC/MS, HP 6890 series Injector/5973 Mass Selective Detector, HP-1MS column and He as a carrier gas).

3. Results and Discussion

Fig. 1(a) and (b) show XRD patterns of the obtained powders with and without P123 after being heat-treated at various temperatures. The XRD patterns in (a) and (b) are similar, suggesting that they possess close crystallinity and the same phase patterns. Weak metastable peaks of $\gamma\text{-Al}_2\text{O}_3$ started to appear at 773 K and were developed at 973 K. A trace of newly formed nickel aluminum oxide ($\text{Ni}_{0.94}\text{Al}_{2.09}\text{O}_{3.09}$, JCPDS file No. 01-078-2180, cubic) starts to appear at 973 K. The major peaks at 38.1, 46.0 and 66.3 correspond to the

Fig. 1. XRD patterns of $\text{Al}_2\text{O}_3/\text{NiO}$ powders (a) with (b) without P123 heat-treated at various temperatures.

[331], [400] and [440] reflections of α -alumina, respectively (JCPDS file No. 50-0741, cubic). The major phase of $\alpha\text{-Al}_2\text{O}_3$ and the new spinel structure of the $\text{Ni}_{0.94}\text{Al}_{2.09}\text{O}_{3.09}$ phase were clearly observed at 1173 K. Eventually, most (96.85%) of the nickel aluminum oxide peaks and a trace (3.15%) of the $\alpha\text{-Al}_2\text{O}_3$ peaks were obtained at 1373 K from Rietveld structural refinement (Table 1). The major peaks were com-

Table 1. Quantitative Analysis of the XRD Results by Rietveld Structure Refinement*

Heat-treatment temperature (K)			1373 K		1473 K			
phase			$\gamma\text{-Al}_2\text{O}_3$		$\text{Ni}_{0.94}\text{Al}_{2.09}\text{O}_{3.09}$		$\alpha\text{-Al}_2\text{O}_3$	
			Amount	Crystallite size	Amount	Crystallite size	Amount	Crystallite size
with P123			3.15%	44.8 nm	96.8%	56.8 nm	64.66%	79.9 nm
without P123			1.23%	45.5 nm	98.77%	47.8 nm	55.08%	92.1 nm

*Rietveld structure refinement could be done for a powder having reasonable crystallinity and could be obtained only the temperatures listed above

Fig. 2. (a) Pore size distribution and (b) nitrogen adsorption-desorption isotherms of the Al_2O_3 /NiO powders with and without P123 heat-treated at 973 K.

pletely changed from γ - Al_2O_3 to spinel $\text{Ni}_{0.94}\text{Al}_{2.09}\text{O}_{3.09}$ at this temperature. These peaks at this temperature could be analyzed by Rietveld structure refinement due to their remarkable crystallinity. The minor γ - Al_2O_3 peaks were transformed to α - Al_2O_3 phases (JCPDS file No. 5-0712, hexagonal) with very sharp peaks at a ratio of 64.66% at 1473 K.

Fig. 2(a) indicates the pore size distribution of Al_2O_3 /NiO powders heat-treated at 973 K by the BJH (Barrett-Joyner-Halenda) method. Fig. 2(b) shows nitrogen sorption isotherms heat-treated at 973 K. Comparing both samples, the powder with P123 has a more uniform pore size distribution and a higher total pore volume than that without P123. The pore diameter was also smaller, with a value of 5.7 nm in the case of P123 as compared to 6.1 nm without P123. These samples were mesoporous and had an S-shaped structure. Analyzing these diagrams in both cases, all of powders gave rise to a typical type IV H_2 hysteresis loop, as defined by IUPAC (International Union of Pure and Applied Chemistry). This type of H_2 hysteresis loop is commonly associated with ink-bottle pores or voids between close-packed spherical particles of the types in both (a) and (b). The adsorption occurred on a wide wall, whereas desorption was achieved at a small entrance, as the entrance and bottom sizes of the pores were different. The distribution of the pore morphology was uniform, and the pore volume was large in the sample with P123. It is known that the pore volume and the pore size distribution is important for an active catalyst life-time.⁹⁾

The surface morphology and surface area of Al_2O_3 /NiO powder with and without P123 heat-treated at 973 K are shown in Fig. 3. The morphology of the surface is shown in the shape expected from aggregation and is overlapped with a clustered rod form, as shown in Fig. 3(b). The surface area of the powder with P123 was slightly larger than powder without P123 (from 144.1 m^2/g to 134.1 m^2/g). The surface area is expected to be improved by the template/metal-

Fig. 3. FE-SEM micrographs and BET of the Al_2O_3 /NiO powders (a) with (b) without P123 heat-treated at 973 K.

Fig. 4. The yield of the obtained styrene oxide with the reaction time of the powder with P123 heat-treated at different temperatures.

oxides micelle formation process due to the induced non-covalent bonding interaction between the non-ionic block copolymer (P123) and the Ni/Al species.⁶⁾ The γ - Al_2O_3 formation of a high surface area is extremely beneficial for the dispersion of an active phase to increase the catalytic activity of the derived materials.

Fig. 4 shows the yield of the obtained product of styrene oxide from the catalytic reaction of the powder with P123 as a function of the reaction time. The best yield performance (38.45%) was the catalyst with using P123 after a heat-treatment at 973 K. It had more of the γ - Al_2O_3 phase with a higher surface area. On the other hand, the yield decreased with increase in the heat-treatment temperature due to the effect of the α - Al_2O_3 . The activity yield from this study was better than the conversion results using aluminium dawsonites.¹⁰⁾

4. Conclusion

In a result of a catalytic reaction, the best yield performance (38.45%) was gained with the $\text{Al}_2\text{O}_3/\text{NiO}$ catalyst prepared with the P123 surfactant after a heat-treatment at 973 K. The P123 surfactant was added to optimize the uniform meso-porous distribution of γ - Al_2O_3 and to maintain a high surface area. The γ - Al_2O_3 intermediate phase in the mixed oxides can be observed at 773 K, and it increases at 973 K. At 1173 K, the $\text{Ni}_{0.94}\text{Al}_{2.09}\text{O}_{3.09}$ peaks were increased more than the peaks of γ - Al_2O_3 . It is important for the catalyst to have a uniform meso-porous distribution and a high pore volume for the catalytic reaction.

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