Preparation of large surface area nickel magnesium silicate and its catalytic activity for conversion of ethanol into buta-1,3-diene

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The ternary oxide catalysts of nickel magnesium silicate with a large surface area (498–784 m^2/g) can be obtained by calcining a mixture of $Ni(NO_3)_2$, $Mg(OH)_2$ and SiO_2. The large surface area of the catalyst is attributed to its layer structure. The selectivity for buta-1,3-diene formation from ethanol on the catalysts was 90% or more and the yield of buta-1,3-diene was 53 mol%.

Keywords: catalyst preparation; large surface area; acid–base bifunctional catalyst; nickel magnesium silicate; conversion of ethanol into buta-1,3-diene.

1. Introduction

Two-step reactions, such as dehydration and dehydrogenation processes, can be performed with one reactor by making use of acid–base bifunctional catalysts. Catalytic conversion of ethanol into buta-1,3-diene has been carried out on metal oxide supported on sepiolite [1], silica magnesia ($MgO\cdot SiO_2$) [2] and other binary metal oxides such as $Al_2O_3\cdot MgO$ and $Al_2O_3\cdot ZnO$ [3]. The reaction proceeds via dehydrogenation (acetaldehyde formation) and dehydration processes [2,3]. Dehydrogenation takes place at the base sites while dehydration takes place at the acid sites of the catalyst. Therefore, an acid–base bifunctional catalyst is essential for the conversion of ethanol into buta-1,3-diene. On the catalysts reported previously, the selectivity for buta-1,3-diene formation was low, because considerable amount of ethylene was produced as by-product due to the strong acid sites on the catalyst [1,2]. Nickel supported on SiO_2 alone (NiO/SiO_2) and nickel supported on MgO alone (NiO/MgO) are both base catalysts since only acetaldehyde is obtained and no buta-1,3-diene is produced by catalytic conversion of ethanol on them. Therefore, if an addition of acidic property to these catalysts is possible, an acid–base bifunctional catalyst will be obtained. It has been reported that the $MgO\cdot SiO_2$ catalyst exhibits the acidic properties attributed to unsaturated bonds of silicon and its acid strength is not so strong [4].

The present authors have tried to prepare ternary oxide catalyst of nickel, magnesium and silicon to obtain an acid–base bifunctional catalyst and have succeeded in the synthesis of a nickel magnesium silicate catalyst with high surface area. The catalysts obtained in this study showed high activity and high selectivity for the conversion of ethanol into buta-1,3-diene catalyzed by both acid and base sites.

2. Experimental

Samples of nickel magnesium silicate ($NiO/MgO\cdot SiO_2$) were prepared as follows; silica (Aerosil 380) and magnesium hydroxide were mixed with various molar ratios of $SiO_2/Mg(OH)_2$. The powder mixtures were impregnated with an aqueous solution of $Ni(NO_3)_2$. The samples were dried at 393 K and subsequently calcined in air at 673 K for 2 h.

Nickel supported on SiO_2 (NiO/SiO_2) and nickel supported on MgO (NiO/MgO) were prepared by impregnating silica (Aerosil 380) and magnesium hydroxide respectively with an aqueous solution of $Ni(NO_3)_2$. The obtained materials were dried at 393 K and were calcined at 673 K for 2 h.

Reactions were carried out in a fixed-bed continuous flow reactor at 553 K and atmospheric pressure. The internal diameter of the pyrex glass tube reactor was 8 mm. One gram of the catalyst was packed into the reactor and was preheated at the reaction temperature (553 K) in a nitrogen stream. Ethanol was kept in an evaporator maintained at constant temperature and introduced into the catalyst bed with nitrogen as the carrier gas at the space velocity $12.5\ h^{-1}$. Reaction products were analyzed by on-line gas chromatography. Selectivy was defined by the following equation:

$$\text{selectivity (\%)} = (\text{mol of product/mol of consumed ethanol}) \times 100.$$

Surface areas of the catalysts were measured by the conventional BET method using nitrogen gas.

3. Results and discussion

Fig. 1 shows the relationship between BET surface

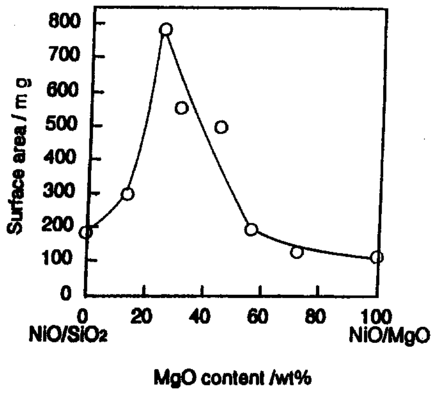

Fig. 1. Dependence of the surface area on MgO content in the catalysts.

area and the MgO content in the NiO/MgO·SiO_2 catalysts prepared at fixed NiO content (10 wt%). The surface area drastically increased from 183 to 784 m^2/g with increasing MgO content from 0 to 25 wt%. At above 31 wt% of MgO content, the surface area significantly decreased. A large surface area of 496–784 m^2/g was obtained at the MgO content in the range of 25–40 wt%. Manganese or Zn supported on sepiolite gave only 260 m^2/g at the most, as shown in a previous report [1]. The nickel magnesium silicate catalyst obtained by the present method showed two- or three-fold increase of surface area. Powder X-ray diffraction (XRD) patterns of the catalysts are shown in fig. 2. Only XRD peaks due to NiO were observed at $d = 0.2088$ and 0.2412 nm in the NiO/SiO_2 catalyst (MgO content = 0%). However, after the additon of MgO to NiO/SiO_2, new broad peaks appeared at $d = 0.256$ and 0.45 nm while the NiO peaks disappeared. Similar XRD peaks have been observed in natural aquacreptite [5] and layered magnesium silicate [6] which has been synthesized by the hydrothermal reaction of $Mg(OH)_2$ and SiO_2 at the atomic ratio of Si/Mg = 1.5. A layered structure may be formed in the three-component oxide up to 31 wt% MgO content (atomic ratio of Si/Mg = 1.5). No peaks due to MgO were observed in the sample whose MgO content was less than 25 wt%. At 31 wt% MgO content, a small XRD peak due to MgO (d_{200}) was observed at 0.2106 nm in addition to the new peaks. Above 57 wt% MgO content (atomic ratio of Si/Mg = 2) in the sample, the XRD peak due to MgO (d_{200}) increased and a peak due to MgO (d_{111}) appeared at 0.2431 nm. These results show that the layered structure of the ternary oxide of nickel, magnesium and silicon is formed in the range of MgO content from 14 to 31 wt% by mutual interaction during calcination of $Ni(NO_3)_2$, $Mg(OH)_2$ and SiO_2 in air at 673 K. The large surface area of NiO/MgO·SiO_2 catalyst is considered to result from the layered structure of the ternary oxide. The interlayer of the brucite structure of $Mg(OH)_2$ may contribute to the formation of the layer structure. Significant decreases in the surface area of the samples containing more than 57 wt% of MgO as shown in fig. 1 are attributed to the MgO phase formation in the layered ternary oxide of the catalyst. Narayanan et al. [7] have reported that the dispersion and diffusion of Ni^{2+} ions into the MgO lattice was observed in nickel supported on magnesia prepared by impregnating $Mg(OH)_2$ with an aqueous solution of $Ni(NO_3)_2$. The disappearance of NiO peaks from the XRD patterns of the samples is attributed to the diffusion of Ni^{2+} ion into the magnesium silicate lattice.

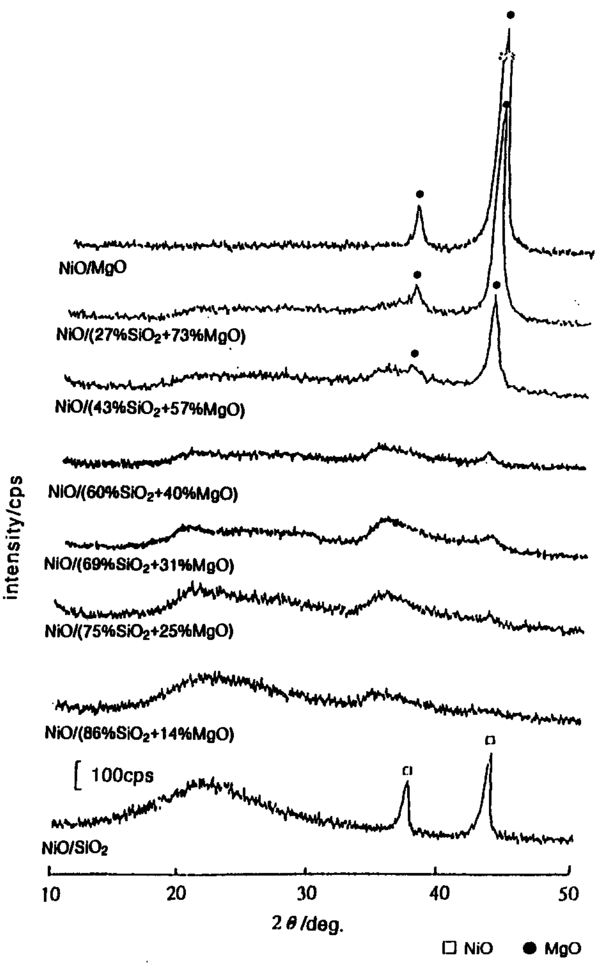

Fig. 2. XRD patterns of the catalysts with varying MgO content.

The catalytic activity in buta-1,3-diene formation from ethanol was studied. The relationship between the yield of buta-1,3-diene and the MgO content of nickel magnesium silicate at fixed nickel content (NiO = 10 wt%) is shown in fig. 3. The composition of MgO and SiO_2 in the NiO/MgO·SiO_2 affected the ability to form buta-1,3-diene. The selectivity for buta-1,3-diene formation was 90% or more on ternary oxides but not binary oxides (NiO/SiO_2, NiO/MgO). Nickel supported on SiO_2 or MgO (NiO/SiO_2 and NiO/MgO) was not active for buta-1,3-diene formation but active for acetaldehyde formation from ethanol. The yield of buta-1,3-diene increased with an increase of MgO content up to 31 wt% (atomic ratio of Si/Mg = 1.5). The atomic ratio of Si/Mg = 1.5 in NiO/MgO·SiO_2 will give the

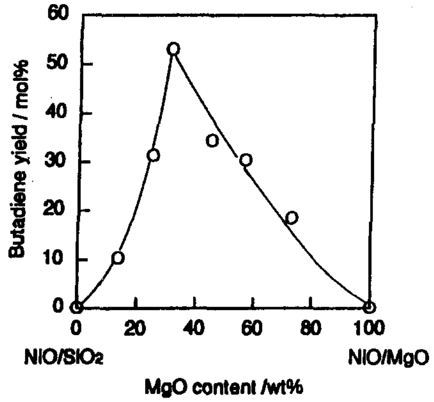

Fig. 3. Dependence of the butadiene yield on MgO content in the catalysts.

optimum acidic and basic properties for the formation of buta-1,3-diene formation from ethanol. The selectivity for ethylene formation was less than 0.5% on the ternary oxide catalysts prepared in this study. This may be attributed to a decrease of acid sites and acid strength in the ternary oxide catalysts. The activity of the catalysts for buta-1,3-diene was poisoned by the addition of NH_3 and phenol into the reactant. This is consistent with both acid and base sites playing an important role for the catalytic conversion of ethanol into buta-1,3-diene. The catalyst with 31 wt% MgO exhibited the maximum yield of buta-1,3-diene, while the catalyst with 25 wt% MgO exhibited the maximum surface area. This is consistent with the catalytic activity for the formation of buta-1,3-diene depending not only on the surface area but also on the basicity of the catalyst. The MgO obtained from $Mg(OH)_2$ showed a strong basicity [8]. The presence of a small amount of MgO phase in the catalyst gives rise to an increase in the basicity and a slight decrease in the surface area of the catalyst. This means that a well-matched state in acidic and basic properties of the catalyst is necessary for the activity of the buta-1,3-diene formation. The study of acidic and basic properties of the catalysts is now in progress.

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