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Author(s)	Suzuki, Kenzi
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Application to catalyst of mayenite consisting of ubiquitous elements[†]

SUZUKI Kenzi^{*}

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1. Introduction

The effective utilization of the tar discharged from gasification of biomass is required. By the steam reforming reaction of the tar using a Ni catalyst, it is possible to produce synthesis gas such as H₂ and CO. One of the problems of this reaction is the degradation of the catalytic activity by the coking. Mayenite, Ca₁₂Al₁₄O₃₃, is the material which occludes oxygen radicals in the structure, and it is known to have the function of an oxidation catalyst [1]. In addition, the composition of the mayenite consists of only ubiquitous elements. In this study, the coking protective effect by using mayenite for a catalyst support of the Ni catalyst is presented.

2. Experimental

Catalysts preparation

Mayenite (Ca₁₂Al₁₄O₃₃) was prepared by solid mixing of Ca(OH)₂ and Al(OH)₃ in stoichiometric ratio, grinding and calcination at 1000°C for 4 hours in an air environment, followed by crushing and sieving to obtain particle sizes between 212-425µm. Ni/Mayenite (Ni = 1, 3, 5wt%) was prepared by mixing Mayenite with NiO in different

stoichiometric ratios, grinding without water, calcining at 600°C in air environment for 4 hours, using a temperature increase rate 3°C/min, lastly crushing and sieving to 212-425µm. The commercial-like Ni/Al₂O₃ (5wt%) was prepared by an impregnation method.

2) Catalyst performance examination

Toluene was selected as the biomass tar model compound. Experiments were carried out at atmospheric pressure in a fixed-bed reactor. All the catalysts were initially activated under the reduced gas mixture (<5% H₂ diluted by Ar) for 1.5 hours at 650°C, then tested at the given operation parameters. Two conditions of toluene concentration around 2000 and 4000ppm were studied.

3. Results and discussion

Figure 1 showed Raman spectra of Mayenite and Ni/Mayenite before reaction. The Raman band at 1090cm⁻¹ was O₂⁻ species, and an additional band assignable to the O₂²⁻ species appeared at 880cm⁻¹.

Experiments of steam reforming for toluene were carried out on Mayenite and Ni/Mayenite with a temperature range of 550-850°C for a S/C ratio of 1.9 and

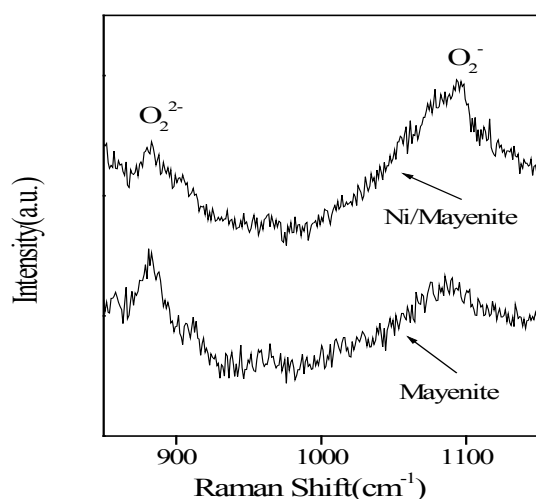
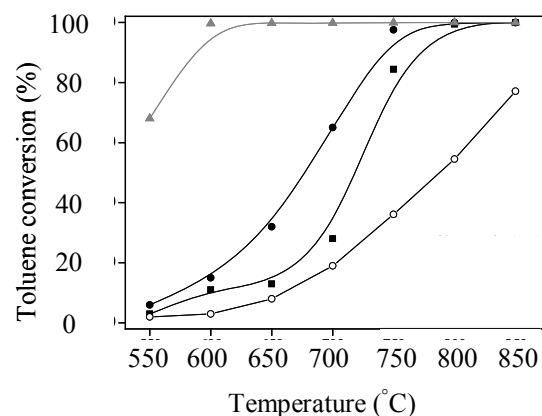


Fig. 1 Raman spectra of Mayenite and Ni/Mayenite before reaction.



▲: Ni/Mayenite(5%), ●: Ni/Mayenite(3%),
■: Ni/Mayenite(1%), ○: Mayenite

Fig. 2 Toluene conversion vs. Reaction temperature for Mayenite and Ni/Mayenite.

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^{*} EcoTopia Science Institute, Nagoya University, Nagoya, Japan

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space velocity of 6000h^{-1} at 25°C . No catalyst deactivation was observed after 24 hours of time on stream. Toluene conversion on different catalysts is shown in Fig. 2. From Fig. 2, Ni/Mayenite exhibited excellent performance. For all Ni/Mayenite catalysts, the toluene conversion reached nearly 100% at the temperature 800°C , even though the concentration of Ni metal was only 1%. Results were compared to that obtained with Mayenite alone. The latter showed almost no activity ($<6\%$) until 650°C , moderate (50% at 800°C) and weaker activity than with Ni/Mayenite (5wt%) catalyst at 550°C . And also for Mayenite, additionally to CO , CO_2 and H_2 , significant selectivity toward benzene (22% at 850°C) was observed, but for Ni/Mayenite, almost no benzene was observed.

The detailed results obtained at 800°C are presented in Fig. 3. H_2 and CO_2 yields increased but CO yield decreased when the S/C ratio increased. These gas yield evolutions with the S/C ratio can be explained by the reactions involved in toluene steam reforming ($\text{C}_7\text{H}_8 + 7\text{H}_2\text{O} \rightarrow 7\text{CO} + 11\text{H}_2$, $\text{C}_7\text{H}_8 + 14\text{H}_2\text{O} \rightarrow 7\text{CO}_2 + 18\text{H}_2$). The water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) produced more H_2 and CO_2 at higher values of S/C ratios, so the increase in the CO selectivity at the same time less H_2 and CO_2 yield could be explained, as a high steam partial pressure made the water gas equilibrium shift toward hydrogen formation. However, the partial pressure of the organic compound in the gas stream will be lower due to the dilution as the S/C ratio rises. All of these will affect the apparent kinetic constant.

From the above results, Ni/Mayenite (5wt%) exhibited excellent steam reforming activities above 600°C . To confirm the practical applicability of this promising industrial catalyst, long-term durability tests were conducted at the condition of 800°C , space velocity of 6000h^{-1} at 25°C and inlet toluene concentration of 4000ppm, S/C is 1.15. The results are shown in Fig. 4, which illustrates that Ni/Mayenite maintains more than 98% of

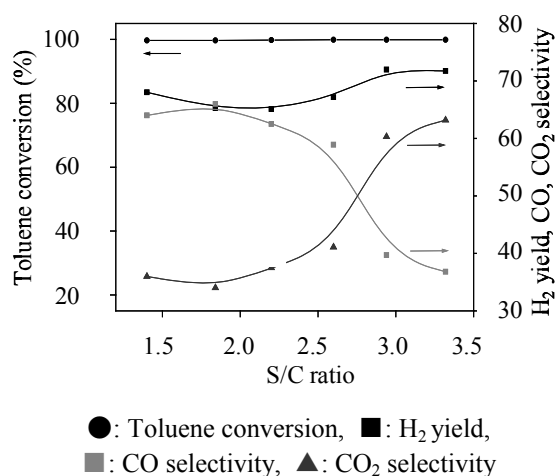


Fig. 3 The influence of S/C on toluene conversion and products composition for Ni/Mayenite (5%).

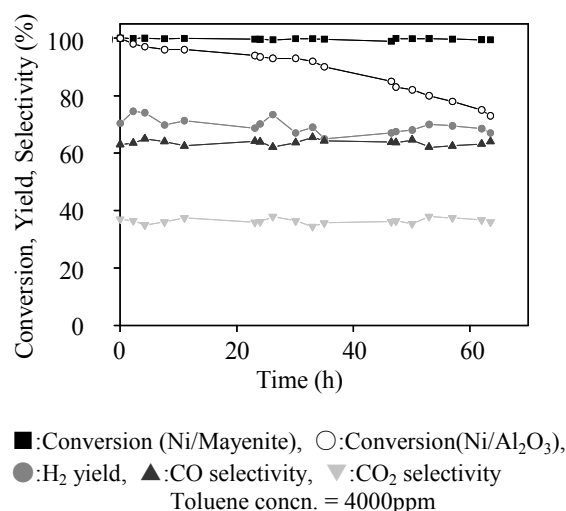


Fig. 4 Toluene conversion, H_2 yield, CO and CO_2 selectivity vs. Time.

toluene reforming for more than 60 hours at 800°C , more stable than that of traditional $\text{Ni}/\text{Al}_2\text{O}_3$.

The observed promotion of catalysts such as dolomite, olivine by loading Ni metal for hydrocarbon reforming was justified, but also easily devitalized because of carbon formation on the nickel metal surface [2, 3]. However, no obvious decrease of activation was observed for our catalyst based on the above results. At least three possible reasons to account for such unexpected observation may be considered. The first possibility is that the excess S/C ratio can prevent or reduce the formation of coke on the catalyst, especially the ratio above 1.2 [4], but the long-time evaluation of our experiments was carried out on the smaller S/C (1.15). A second possibility is that the formation of coke deposits on the surface of Mayenite not nickel metal. In some cases, most of the formation of coke deposited on the supported surface, but only a small amount on the activity component surface [5]. The quantitative analysis of coke amount on the after reaction catalyst performed with the TG analyzer. The sample of 50-70mg was heated from 30 to 1000°C with a heating rate of $10^\circ\text{C}/\text{min}$ in air. The weight loss due to the combustion of deposited carbon less than 0.1% was observed, which indicated nearly no carbon deposition on Ni/Mayenite.

For the third possibility is the “free” oxygen in the special structure of Mayenite, which was attributed to the presence of hydroxide, peroxide and superoxide radicals in the cages. So the super oxide radicals in the cages will transfer to nickel sites to gasify the surface carbon on nickel metal to CO , which is the reasonable explanation for the excellent performance of Ni/Mayenite [5].

4. Conclusion

The newly synthesized nickel mayenite catalysts ($\text{Ni}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) is developed and studied. It was observed that $\text{Ni}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ showed excellent sustainability against coke formation due to the “free oxygen” in the catalysts.

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