Partial oxidation reforming catalyst for fuel cell-powered vehicles applications

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Transition metal oxide formulations for the partial oxidation (POX) reforming of isooctane were investigated for an onboard gasoline fuel processor. Ni/M/MgO/Al_2O_3 systems are more active than a commercial ICI catalyst. These catalysts showed better sulfur tolerance over the commercial ICI catalyst in the POX reforming of isooctane containing sulfur ($Cs = 100$ ppm). There was no apparent deactivation or modification of structure during 770 h onstream. It was found that Ni/(Fe,Co)/MgO/Al_2O_3 catalyst is a promising candidate as POX reforming catalyst for gasoline fuel processor applications.

KEY WORDS: PEM fuel cell; POX reforming; Ni/(Fe,Co)/MgO/Al_2O_3 catalyst; fuel cell-powered vehicles; gasoline fuel processor.

1. Introduction

All fuel cells currently being developed for near term use in the fuel-powered vehicles require hydrogen as a fuel. Recently, proton exchanged membrane (PEM) fuel cells operating with hydrogen from hydrocarbon reforming technologies are being increasingly accepted as the most appropriate power source for future generation vehicles. Catalytic partial oxidation (POX) of hydrocarbons for generating hydrogen has gained much attraction in recent years owing to its direct application in PEM fuel cells for generating clean electrical energy. The successful development of a fuel cell-powered vehicle is dependent on the development of a fuel processor. Hydrogen is an ideal fuel for a PEM fuel cell because it simplifies system integration [1]. However, since no hydrogen fuel supply infrastructure currently exists, fuel supply for fuel cell vehicles is directed at developing onboard fuels such as methanol and gasoline. The lower efficiency of gasoline in comparison with methanol can be compensated by the much higher energy density of gasoline compared to methanol and also by the well-developed infrastructure for gasoline [2–3]. Therefore, gasoline is recommended as the best candidate fuel for the fuel cell-powered vehicles.

Major process technologies for reforming hydrocarbons and alcohols into hydrogen, carbon monoxide and carbon dioxide are steam reforming (SR), partial oxidation and partial oxidation reforming (autothermal reforming, ATR) [4,5]. Steam reforming of hydrocarbon usually takes place at temperatures around 700 °C. These temperatures guarantee high reforming efficiencies. The drawback is that this reaction is endothermic and therefore the reactor needs to be heated by combustion of fuels itself. So far, no sulfur tolerance steam-reforming catalyst has been founded, resulting in the need for a very efficient and therefore probably large unit for removing the sulfur from fuels [4]. Partial oxidation reforming of fuels for vehicles applications was first proposed by Argonne National Laboratory (ANL) several years ago. It has been widely accepted as the most promising process to meet the efficiency, volume and cost goals of the transportation application [5,6]. For vehicle applications, the advantage of catalytic POX reforming over SR is a low energy requirement, sulfur tolerance of catalyst and more rapid and controlled response to the transient power requirements [6–8]. Commercial SR catalysts have been used for POX reforming of aliphatic and aromatic hydrocarbon liquids. A number of problems were identified, including the tendency to deactivate because of the formation of nickel aluminate spinals, excessive coking and susceptibility to sulfur poisoning, which preclude their use for vehicles applications [6,7]. In previous works [9,10], we have pointed out the necessity for developing a high performance POX reforming and low temperature shift (LTS) catalysts with coke- and sulfur-resistance, the various experimental features of the gasoline processor as well as the goals to be achieved in the near future.

To overcome these problems, this work was focused on the development of a more effective POX reforming catalyst for gasoline fuel processor applications. A Ni-based multimetal oxide catalyst was developed on the basis of our previous works [9,10,13,14,18,19].

2. Experimental

2.1. Chemical

The isooctane used as the fuel source was supplied from J.T. Baker. The standard isooctane feed containing

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100 ppm of sulfur was prepared by mixing isooctane with thiophene (99%+, Acros Organics). Hydrogen (99.999%), air (99.999%), and nitrogen (99.999%) were used in the reaction and the pretreatment of catalysts. Nickel nitrate, cobalt nitrate, ferric nitrate, ammonium molybdate and magnesium hydrate were provided by Sigma-Aldrich Co. Also, γ-alumina (2–3 μm) was obtained from High Purity Chemicals.

2.2. *Catalyst preparation*

The commercial reforming catalyst was obtained from ICI Co., in the form of pellets. However, for the experiments, the catalyst was used in the form of powder with a mesh size of 120/230 after crushing.

Several compositions of oxide-based formulations, represented as $M/MgO/Al_2O_3$ and $M/M/MgO/Al_2O_3$, (where M = Ni, Fe, Co, Mo) have been prepared for the POX reforming of isooctane. The catalyst formulations prepared in this work were summarized in table 1 [14]. The various catalyst formulations were prepared by the method of incipient wetness of the γ-alumina with aqueous solutions of the corresponding metal nitrates. The solution containing the metal salts was added dropwise to precalcined alumina until incipient wetness was reached. The resulting materials were slowly dried at 80 °C for about 6 h and then calcined for 5 h at 650 °C in dry air.

2.3. *Catalyst characterization*

BET surface area and total pore volume of catalysts before and after the POX reforming reaction of isooctane ($Cs = 5$ ppm) and sulfur-containing isooctane ($Cs = 100$ ppm) were determined from N_2-adsorption isotherm measured at 77 K with a sorption analyzer (Quantachrome Co., Autosorb-1C). Active metal surface area of catalysts before and after the reaction was calculated by CO chemisorption at 400 °C using the sorption analyzer. The contents of carbon and sulfur before and after the reaction were analyzed by elemental inorganic analyzer (Lego Co., CS-344). X-ray diffraction (XRD) patterns of the catalysts obtained using a Shimazdu XRD-6000 diffractometer with Cu Kα radiation at 30 kV and 20 mV were used to identify the major phase present in the catalysts before and after the reaction.

2.4. *Catalytic activity*

The catalytic reforming reaction was carried out under atmospheric pressure in a gasoline POX reforming system. The gasoline POX reforming system consists of four sections: feed supply, preheater, POX reforming reactor and GC analysis sections. The gases were delivered by mass flow controllers, and H_2O and isooctane were fed by liquid delivery pumps (Young Lin Co. Model M930). The preheater and the POX reforming reactor were made of an Inconel 600 tube (0.095 m I.D. and 0.20 m length). The reaction temperature was controlled by a PID temperature controller and was monitored by a separated thermocouple in the catalyst bed. This arrangement was capable of ensuring an accuracy of ± 1 °C for the catalyst bed temperature. The unreacted H_2O was removed by an ice trap and the gas effluent was analyzed by GC.

One gram of POX reforming catalyst was charged to the Inconel reactor and was pretreated for 1 h at 700 °C under a H_2 flow of 60 cc/min. All runs were conducted under atmospheric pressure, temperature range of 550–750 °C, space velocity of 4000–50 000 h^{-1} and feed molar ratios of $H_2O/C = 0.5$–3.0 and $O/C = 0.5$–2.0. The vaporized fuel and water were mixed with oxygen and then passed over the heated catalyst zone. We have also carried out the stability test of the reforming catalyst to check carbon deposition and sulfur tolerance. The gas effluent was analyzed by an on-line gas chromatograph (HP-5890 Series II, TCD) equipped with a Carbosphere column (0.0032 m o.d. and 3.048 m length, 80/100 mesh). Each component in the product stream was identified by GC/MS (HP5890/5971) with an HP-1 capillary column (0.0002 m o.d. and 50 m length).

3. Results and discussion

In our previous works [9,10,13,14,18,19], the heat of reaction for the POX reforming reaction of isooctane is calculated by the Gibbs free energy minimization method [11,14]. We found that the heat of reaction for the POX reforming reaction of isooctane can be

Table 1
The characteristics of the prepared and the commercial catalysts [14]

Catalyst code	Catalyst formulation (mol%)						Surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (Å)
	Ni	Fe	Co	CaO	MgO	Al_2O_3			
KIST-A	14.7				11.5	31.5	28.90	0.2067	286.0
KIST-B	11.76	2.94			11.5	31.5	73.55	0.2116	115.1
KIST-C	11.13	5.75	2.94		5.75	31.5	66.19	0.1836	126.3
ICI	12			10		43	35.32	0.0850	96.26

properly controlled by varying the O/C molar ratio and the H_2O/C. Reactor temperature required to prevent the formation of carbon during reforming of isooctane was estimated by a PRO-II simulation program, assuming thermodynamic equilibrium [11,12]. We identified the problems of catalyst deactivation by carbon deposition and sulfur poisoning in the POX reforming reaction of isooctane over the commercial reforming catalyst. We found that a reaction temperature of 700 °C, feed molar ratios of $H_2O/C = 3$ and $O/C = 1$ are identified to be ideal for operating the system [9–14,18].

In this work, we investigated various supported transition metal formulations for POX reforming of isooctane in order to develop a high-performance catalyst with high activity and stability. The performance of the prepared catalysts was compared with the commercial reforming catalyst. Many of the experimented catalyst formulations displayed reasonably good activity toward the POX reforming of isooctane.

Figure 1 shows the comparison of the product composition for POX reforming reaction of isooctane over KIST catalysts. The POX reforming reaction was performed at a temperature of 700 °C with a space velocity of 8776 h^{-1} and using the feed molar ratios of $H_2O/C = 3$ and $O/C = 1$. Conversions of isooctane over all catalysts under tested conditions were above 99.9%. The KIST-B and KIST-C catalysts showed higher H_2 selectivity than the KIST-A catalyst. Ni-supported systems (KIST-A catalyst) displayed substantially low H_2 selectivity and high CO selectivity. However, the systems possessing Ni as the major component, and both Fe and Co are very effective components, which in very small amounts can considerably enhance the performance of the Ni-based systems. The considerable enhancement of the H_2 selectivity over the nickel-based systems doped with small amounts of other active components may be caused by a synergistic effect of the active components and of the supports, resulting in the proper dispersion of the active components and thereby providing more active sites for the reaction. The characteristics of the prepared and the commercial ICI catalyst are summarized in table 1. The prepared catalysts showed higher BET surface area than the commercial ICI catalyst. However, there is no correlation between catalytic activities with BET surface area.

Comparison of the performances of KIST-C catalyst with that of commercial ICI catalyst is shown in figures 2 and 3, respectively. The POX reforming reaction of isooctane is carried out in the temperature range of 550–750 °C at the fixed reaction conditions of space velocity = 8776 h^{-1}, O/C molar ratio = 1.0 and $H_2O/C = 3.0$. It was found that KIST-C catalyst showed a little higher H_2 selectivity than the commercial ICI catalyst. The selectivities of H_2 and CO increased progressively with increasing reaction temperature. Hydrogen selectivities over KIST-C and ICI catalysts were obtained from 65 and 64% at 700 °C respectively, and CO selectivities were obtained from 11.3 and 13.4%, respectively.

Figure 4 shows the catalytic stability for the POX reforming of isooctane containing sulfur of less than 5 ppm at the reaction temperature of 700 °C and molar ratios of $H_2O/C = 3$ and $O/C = 1$ over 770 h. Conversion of isooctane was more than 99.9% for 770 h. It was found that there was no change in the product distributions for POX reforming of isooctane over the ICI and KIST-C catalysts during the time period investigated. To elute the effect of sulfur impurities on the catalytic deactivation, POX reforming reaction of isooctane containing sulfur of 100 ppm was investigated.

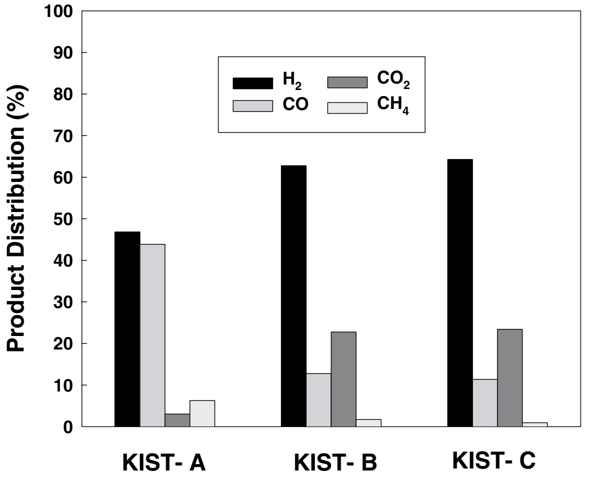

Figure 1. The comparison of product composition for POX reforming reaction of isooctane over KIST catalysts. Reaction temperature = 700 °C space velocity = 8776 h^{-1}; feed molar ratios of $H_2O/C = 3$ and $O/C = 1$.

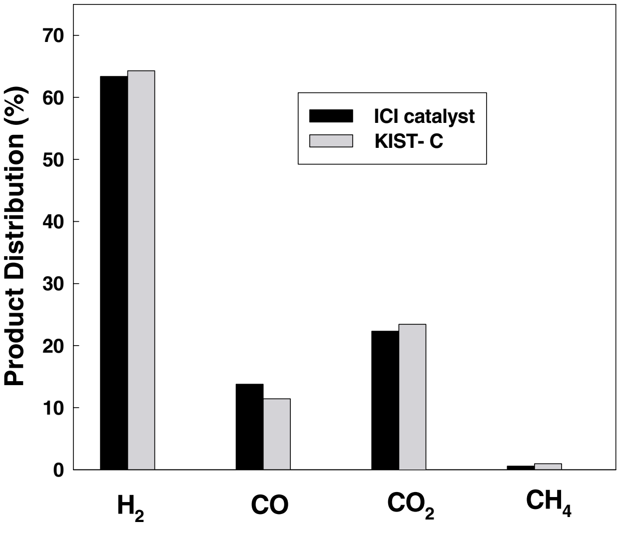

Figure 2. The comparison of the KIST-C with the commercial ICI catalyst for the product distribution in the POX reforming of isooctane. Reaction temperature = 700 °C; space velocity = 8776 h^{-1}; feed molar ratios of $H_2O/C = 3$ and $O/C = 1$.

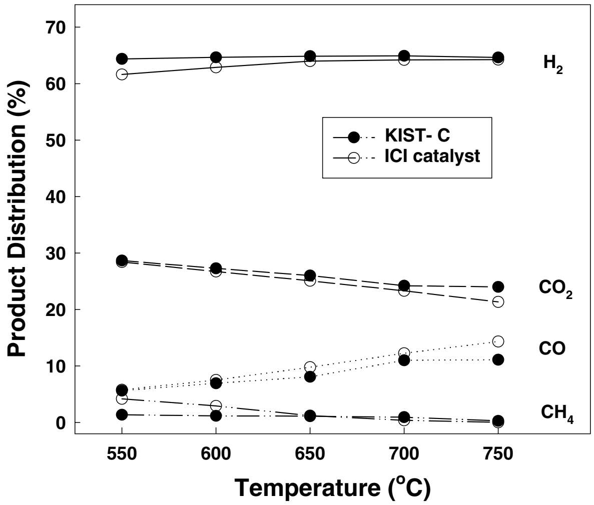

Figure 3. Product distribution as a function of reaction temperature for the POX reforming of isooctane over the KIST-C and ICI catalysts. Space velocity = 8776 h^{-1}; feed molar ratios of $H_2O/C = 3$ and $O/C = 1$.

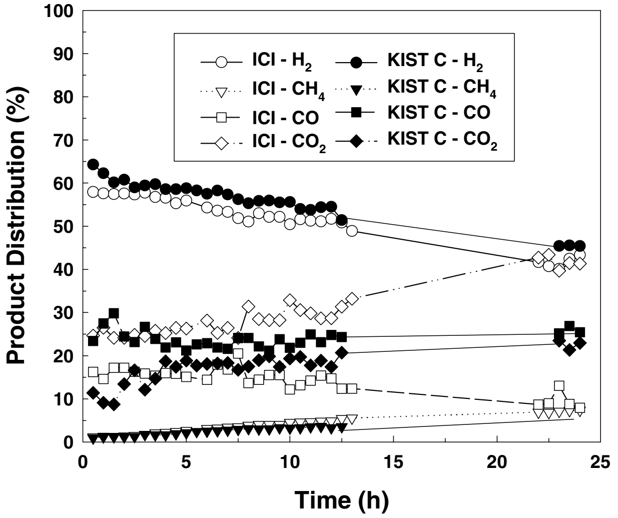

Figure 5. Sulfur tolerance for the KIST-C and commercial ICI catalysts in the POX reforming of isooctane containing sulfur ($Cs = 100$ ppm). Reaction temperature = 700 °C; space velocity = 8776 h^{-1}; feed molar ratios of $H_2O/C = 3$ and $O/C = 1$.

Figures 5 and 6 show the comparison of the KIST-B and KIST-C with the commercial ICI catalyst for sulfur tolerance in the POX reforming reaction of isooctane containing sulfur ($Cs = 100$ ppm) at the reaction conditions of 700 °C, space velocity 8776 h^{-1} and feed molar ratios of $H_2O/C = 3$ and $O/C = 1$. It was found that the KIST-B and KIST-C catalysts displayed better sulfur tolerance than the commercial ICI catalyst. The characteristics of catalysts after the reaction are summarized in table 2. To investigate the characteristics of catalysts under reaction conditions, active metal surface area of catalysts before and after the reaction was measured by CO chemisorption at 400 °C using the sorption analyzer, even though CO may be dissociated on Ni, Fe, MgO at 300 °C. Active metal was assumed as Ni + M in catalysts in this work. The surface area of ICI and KIST-B catalysts after the POX reforming reaction of isooctane ($Cs < 5$ ppm) decreased by 14 and 12%, respectively, and on the other hand, that of ICI and KIST-B catalysts after reaction of isooctane containing sulfur ($Cs = 100$ ppm) decreased by 34 and 17%, respectively. The active metal surface area of ICI and KIST-B catalysts after the reaction of isooctane ($Cs < 5$ ppm) decreased by 31 and 19.8% respectively, and that of ICI and KIST-B after reaction of isooctane containing sulfur ($Cs = 100$ ppm) decreased by 49.69 and 26.7%, respectively. These results were interpreted that KIST-B catalyst is more sulfur tolerant than ICI

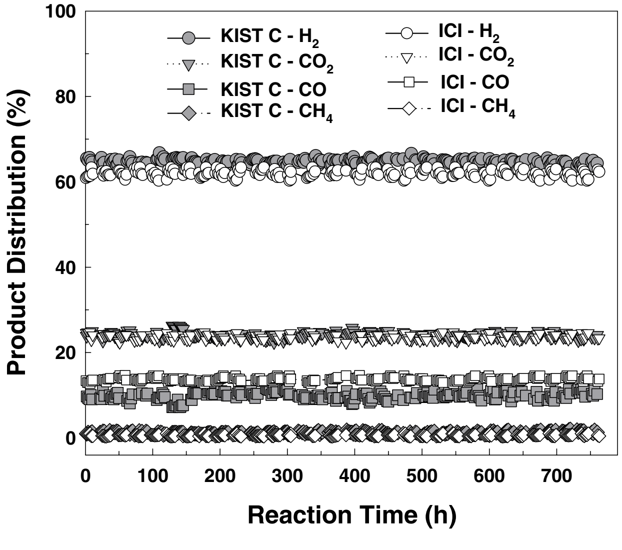

Figure 4. Long-term test of KIST-C and commercial ICI catalyst for the POX reforming of isooctane containing sulfur ($Cs < 5$ ppm). Reaction temperature = 700 °C, space velocity = 8776 h^{-1}, feed molar ratios of $H_2O/C = 3$ and $O/C = 1$.

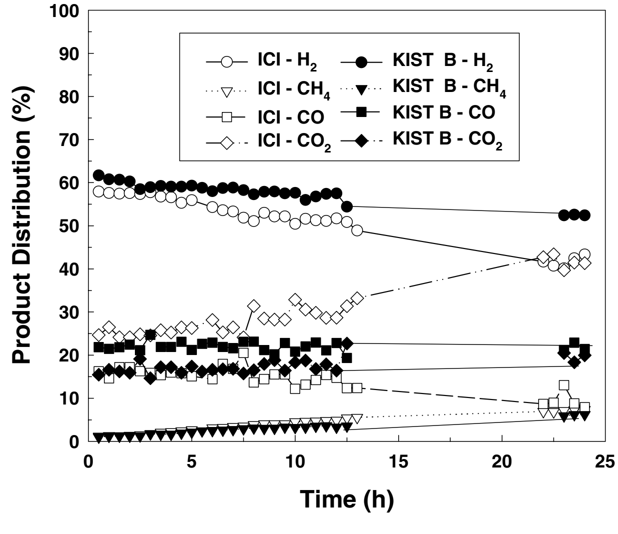

Figure 6. Sulfur tolerance for the KIST-B and commercial ICI catalysts in the POX reforming of isooctane containing sulfur ($Cs = 100$ ppm). Reaction temperature = 700 °C; space velocity = 8776h^{-1}; feed molar ratios of $H_2O/C = 3$ and $O/C = 1$.

Table 2
The characteristics of the catalysts before and after the reaction

Catalyst		S_{BET} (m^2/g)	$V_{total\ pore}$ (cc/g)	$S_{active\ metal}$ (m^2/g)	Carbon content (wt%)	Sulfur content (wt%)
ICI	Before the reaction	35.32	0.085	0.789	0.098	0.003
	After the reaction of isooctane ($Cs < 5$ ppm)	26.73	0.069	0.543	5.8	0.004
	After the reaction of isooctane ($Cs = 100$ ppm)	19.89	0.049	0.397	25.7	0.006
KIST-B	Before the reaction	73.55	0.212	1.906	0.098	0.003
	After the reaction of isooctane ($Cs < 5$ ppm)	61.91	0.185	1.528	4.9	0.004
	After the reaction of isooctane ($Cs = 100$ ppm)	49.38	0.166	1.397	19.6	0.005

catalyst, even though new high performance catalyst with coke- and sulfur-resistance are to be developed for applying in the POX reformer based on gasoline feed. It was found that the amount of carbon deposition increased with increasing sulfur content in isooctane under the same conditions, even though conversion of isooctane was more than 99.9%. These results were considered that carbon deposition on the catalyst surface was accelerated by increasing sulfur content in isooctane. However, there was no accumulation of sulfur in catalysts after the reaction of isooctane containing sulfur ($Cs = 100$ ppm). Recently, ANL research group [15] reported that the effect of sulfur impurities on the catalyst performance is dependent on the catalyst. Sulfur appears to improve the hydrogen yield for Pt-containing ANL catalyst, but appears to reversibly poison Ni-containing catalyst. Instances of sulfur acting as a promoter in catalytic reforming of *n*-heptane and oxidation reactions have been reported in the literature [16,17]. It was also reported that Pt pricing and loading are significant factors in the economics of fuel cell system [17,18]. Platinum is approximately 20% of the total system cost at present Pt loading and fuel cell performance. Therefore, the development of high performance catalysts based on transition metal oxide is desirable to commercialize the gasoline fuel processor.

X-ray diffraction patterns of the KIST-B and KIST-C catalyst before and after the reaction are presented in figures 7 and 8 respectively. The used catalysts were recovered after the POX reforming of isooctane ($Cs < 5$ ppm) and isooctane containing sulfur ($Cs = 100$ ppm) at 700 °C for 24 h. We could not observe any major changes in the phase pattern of the catalysts after the POX reforming reactions of isooctane and isooctane containing sulfur. It was found that XRD patterns of the KIST-B catalyst exist on the structure of NiO, $MgAl_2O_4$, and $FeAl_2O_4$ in the bulk. It was identified that XRD patterns of the KIST-C catalyst exist on the structure of NiO, $MgFe_2O_4$, $MgAl_2O_4$, and $FeAl_2O_4$ in the bulk. Metallic carbides such as nickel carbide and ferric carbide were not formed during the POX reforming of isooctane at 700 °C for 770 h. Although some graphitic carbon was deposited on the KIST-B catalyst, the formation of metallic carbides such as

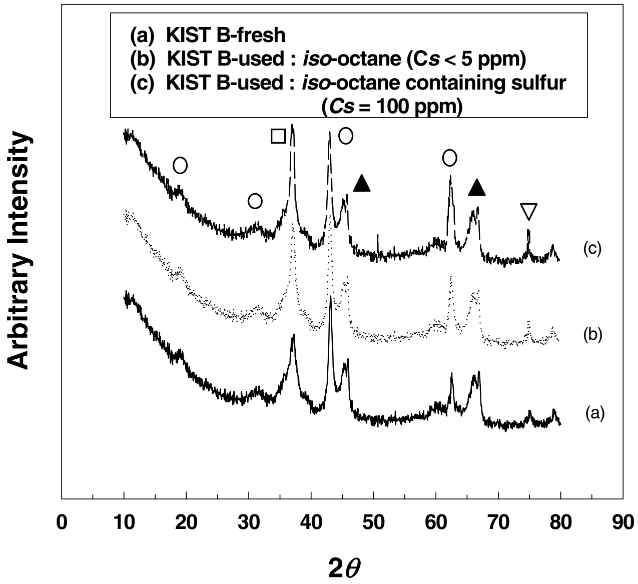

Figure 7. The XRD patterns of the KIST-B catalyst before and after the reaction. The used catalysts are recovered after the reaction for 24 h. ○ : NiO, ▲: $MgAl_2O_4$, □: $FeAl_2O_4$, ▽ : Ni.

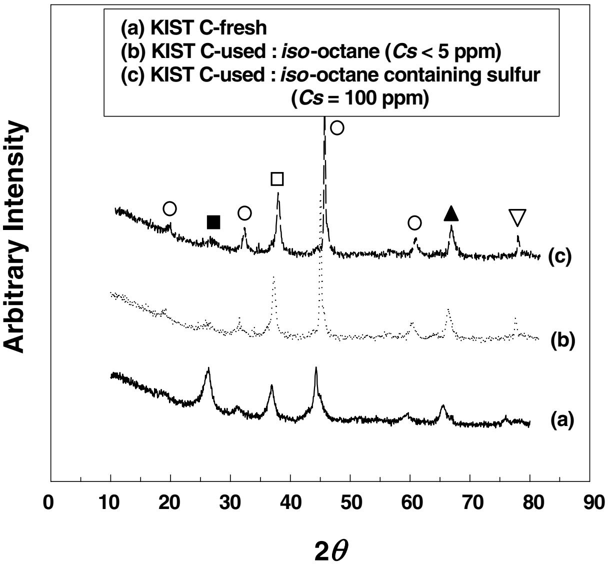

Figure 8. The XRD patterns of the KIST-C catalyst before and after the reaction. The used catalysts are recovered after the reaction for 24 h. ○ : NiO, ■: $MgFe_2O_4$, ▲: $MgAl_2O_4$, □: $FeAl_2O_4$, ▽ : Ni.

nickel carbide and ferric carbide were not formed during the POX reforming of isooctane under reaction conditions. This is evident from the identical nature of the XRD patterns of fresh and used systems.

Conclusions

The nickel-based systems doped with small amounts of Fe and/or Co displayed reasonably high H_2 selectivity for POX reforming of isooctane ($Cs < 5$ ppm). These catalysts showed higher H_2 selectivity and lower CO selectivity than a commercial ICI catalyst tested under the same conditions. These catalysts showed better sulfur tolerance over the commercial ICI catalyst in the POX reforming of isooctane containing 100 ppm of sulfur, even though none of the systems was found to be completely sulfur resistant. It was found that the conversion and selectivities were constant during the POX reforming of isooctane over KIST-C catalyst at 700 °C for 770 h. It was also found that metallic carbides such as nickel carbide and ferric carbide were not formed during the POX reforming reaction. It was suggested that modified $Ni/M//MgO/Al_2O_3$ systems may be used as the POX reforming catalyst for fuel cell-powered vehicles applications.

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