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Effect of modified-alumina supports on propane–hydrogen-SCR over Ag/alumina

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Abstract

The effect of supports on the selective catalytic reduction (SCR) of NO by propane and hydrogen over Ag/alumina catalysts was investigated by using alumina supports modified by incorporation of various additives (Zn, Mg, Y, P and Na). The doping of Zn and Mg into alumina support enhanced the conversion of NO to N_2, while that of Na and P significantly decreased the NO conversion. The Zn-doping also increased the selectivity, while other additives decreased the selectivity. Comparing the rate of NO reduction and acid amount determined by NH_3-TPD, the contribution of surface acid sites of alumina supports to the promotion of the SCR activity of Ag was indicated. As an exception, although the P-doping increased the acid amount of alumina, Ag/P-alumina only showed poor SCR activity. By using in situ FT/IR spectra, the poor SCR activity of Ag/P-alumina was explained by very low surface concentration of adsorbed nitrates and acetate under the reaction conditions. It was also suggested that the acid sites of alumina effectively stabilize $Ag_n^{\delta+}$ clusters in the hydrogen containing atmospheres, which results in the high activity and selectivity on the SCR reaction.

Keywords: Selective reduction of NO; Silver; Alumina; Support; Hydrogen

1. Introduction

Selective catalytic reduction of NO by hydrocarbons (HC-SCR) in the presence of excess oxygen is thought to be a potential method for removing NO_x from lean-burn and diesel exhausts. In 1990, Iwamoto et al. [1] and Held et al. [2] discovered that NO_x reduction under excess oxygen could be accomplished using unburned hydrocarbons as the reducing agents. Through the extensive research on development of SCR catalysts up to the present, many types of catalyst have been reported [3–5].

Among a number of catalysts reported, supported Ag catalysts have attracted much attention after the finding of the high activity of SCR with ethanol over Ag/alumina by Miyadera and co-workers [6,7]. The higher hydrocarbons such as octane also act as effective reductant for HC-SCR over Ag/alumina [8–11]. Actually, good performances of Ag/alumina catalysts have been confirmed by engine bench tests using secondary fuel injection [12,13] and the use of ethanol as a reductant [14]. As for the catalyst design, the addition of metal additives, such as Pd and Rh, are reported to be effective for the enhancement of the SCR activity of Ag/alumina [14,15].

The reaction atmospheres significantly affect the SCR activity of Ag/alumina. The most significant and surprising promotion effect can be obtained by the addition of small amount of H_2. As Satokawa reported, the addition of 909 ppm of H_2 into C_3H_8-SCR atmosphere boosted the NO conversion at 673 K from nearly zero to ca. 50% [16,17]. A similar promotion effect of H_2 can be observed over Ag-zeolite catalysts [18–20]. This discovery on the remarkable positive effect of reaction atmosphere may provide a novel approach to the design of SCR systems for lean-burn and diesel exhausts. From scientific points of view, the roles of H_2 are still under debate, and various roles of H_2 addition have been proposed, i.e., the promotion of oxidation of NO to NO_2 and the activation of hydrocarbons to surface oxygenates [21], formation of partially charged $Ag_n^{\delta+}$ cluster [19,20,22], contribution of gas phase radical reaction [23], and generation of peroxide species [24]. From engineering points of view, various researchers in this field are focused on enhancement of SCR activity at low temperatures [25–27]. Breen et al. [25] and Burch [27] demonstrated further activity enhancement by using octane as reductant.

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As for catalyst design, the effect of H_2 on the SCR activity is strongly affected by supports. The promotion effect of H_2 on HC-SCR activity was significant on Ag/alumina, Ag/MFI and Ag/BEA, while that was not observed when TiO_2, ZrO_2, SiO_2, or Ga_2O_3 were used as supports [17]. Furthermore, in the case of Ag-zeolites, the strong dependence of the H_2 effect on the strength of zeolite acid sites was observed [19,28]. These facts imply strong interaction between Ag and supports, and the clarification of the controlling factor of support properties for the SCR activity may open up further improvement of Ag/alumina catalysts. In this paper, the controlling factor of alumina support on the HC-SCR activity of Ag/alumina was investigated by using alumina modified with various additives (Zn, Mg, Y, P, and Na).

2. Experimental

The modified-alumina supports were prepared by impregnating aqueous solutions of nitrates or ammonium salts of promoter, shown in Table 1, into boehmite followed by evaporation to dryness and calcination at 873 K for 4 h in air. The content of promoters is 5 wt.% in the obtained modified alumina. A series of 2 wt.% Ag/alumina catalysts were prepared by impregnating an aqueous solution of $AgNO_3$ to the pure or modified alumina followed by evaporation to dryness and calcination at 873 K for 4 h. Table 1 shows the surface area of the alumina supports and the Ag/alumina catalysts. The changes of the surface area by the addition of promoters were not significant.

The catalytic test of the NO–C_3H_8–H_2–O_2 reaction (C_3H_8–H_2-SCR) was performed with a fixed-bed flow reactor by passing a mixture of 0.1%NO, 0.1%C_3H_8, 0.5%H_2, and 10%O_2 in He at $W/F = 0.06$ g s mL^{-1}. Prior to the experiment the catalyst was heated in O_2/He at 773 K for 1 h. After reaching a steady state, the effluent gas was analyzed by gas chromatography and NO_x analyzer (Best BCL-100 uH).

XRD patterns were obtained with a Rigaku RINT 1200 using Cu Kα radiation filtered by Ni. Diffuse reflectance UV–vis spectra of catalysts were measured with a JASCO V-570 [19]. The sample was exposed to various gas mixtures at 573 K for 0.5 h in quartz in situ cell, and quenched at room temperature. Then, UV–vis spectra of the quenched sample were measured after moving into the optical quartz cell without exposure to the air. In situ IR spectra were recorded on a JASCO FT/IR-620 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 0.080 g of self-supporting wafer and mounted into the quartz IR cell with CaF_2 windows. The spectra were measured at accumulating 100 scans at a resolution of 2 cm^{-1}. A reference spectrum of the catalyst wafer in He taken at 573 K was subtracted from each spectrum. Prior to each experiment, the catalyst was pretreated in O_2/He at 773 K for 1 h, followed by cooling to 573 K in He and purging at 573 K for 30 min in He. Then, the catalyst wafer was exposed to the reaction conditions at 573 K. The amount and strength of acid sites were determined from NH_3-TPD (Temperature Programmed Desorption) spectra by using a Bel Japan Malti-task TPD equipped with a quadruple mass spectrometer. After the evacuation at 773 K for 30 min, the catalyst was exposed to 13 kPa of NH_3 at 373 K, followed by evacuation at 373 K for 5 h. Then, the measurement was made from 373 K with a heating rate of 5 K min^{-1} in flowing He as a carrier gas at a flow rate of 60 cm^3 min^{-1} until ammonia was desorbed completely [29,30].

Table 1
List of pure and modified 2 wt.% Ag/alumina examined in this study

Catalyst	Promoters		Surface area (m^2 g^{-1})	
	Source	Amount (wt.%)	Support	Catalyst
Ag/Al_2O_3	–	–	187	180
Ag/Zn-alumina	$Zn(NO_3)_2$	5	192	167
Ag/Mg-alumina	$Mg(NO_3)_2$	5	182	166
Ag/Y-alumina	$Y(NO_3)_3$	5	207	220
Ag/P-alumina	$(NH_4)_3PO_4$	5	125	117
Ag/Na-alumina	$NaNO_3$	5	145	142

3. Results

3.1. C_3H_8–H_2-SCR

Fig. 1 shows temperature dependence of NO and C_3H_8 conversions of C_3H_8–H_2-SCR over Ag catalysts supported on pure and modified alumina in the range of 523–773 K. The conversions of NO and C_3H_8 monotonously increased with reaction temperature, being strongly affected by the doped elements. The NO conversion was clearly enhanced by the doping of Zn, and slightly increased with the doping of Mg. The Mg-doping increased the C_3H_8 conversion, while the Zn-doped catalyst showed lower C_3H_8 conversion than Ag/Al_2O_3. The P- and Na-doping significantly decreased both NO and C_3H_8 conversions. The doping of Y slightly decreased both NO and C_3H_8 conversions. The order of the NO reduction rate per surface area at 573 K was as follows: Zn-doped (1.53 nmol m^{-2} s^{-1}) > Mg-doped (1.27) > pure Ag/Al_2O_3 (1.18) > Y-doped (0.86) ≫ Na- and P-doped (∼0). Even if the surface area took into account, the SCR activity was promoted by the Zn- and Mg-doping, and suppressed by the Y-, Mg-, and P-doping.

In Fig. 2, the NO conversion to N_2 was plotted as a function of the C_3H_8 conversion to estimate the changes in the selectivity. The Zn-doped catalysts showed the higher NO conversion than pure Ag/alumina at the same C_3H_8 conversion, indicating improvement of the selectivity by Zn-doping. On the other hand, the doping of Mg and Y slightly, and that of Na and P significantly decreased the selectivity.

3.2. Characterizations

Fig. 3 shows XRD patterns of pure and modified Ag/alumina catalysts. The calcination of Ag impregnated pure boehmite (Ag/A_2O_3) results in the formation of γ-alumina phase. There were no other diffraction lines such as the lines assignable to Ag derived phases. The Ag/doped-alumina showed γ-alumina phase and some other additional phases. The formation of solid solution was suggested by the shifts of the line at $2\theta = 46.0$–45.7° for Ag/Zn-alumina and to 45.4° for Ag/Mg-alumina.

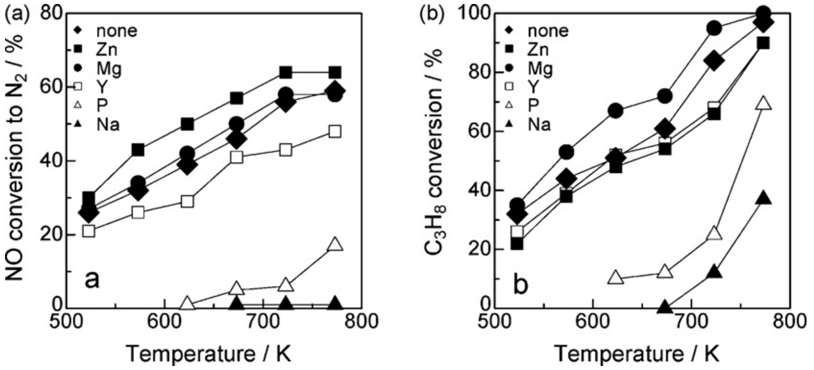

Fig. 1. NO conversion to N_2 (a) and C_3H_8 conversion (b) on C_3H_8–H_2-SCR over pure and modified Ag/alumina catalysts.

These line shifts can be attributed to the formation of $ZnAl_2O_4$ and $MgAl_2O_4$ spinel phases, respectively. The very weak diffraction of Ag/P-alumina and hollow line around 25° indicates abundance of amorphous phase, in other words, deformation of spinel structure of alumina supports. The diffraction lines of Ag metal were observed at $2\theta = 38.1°$ and 44.3° in Ag/Na-alumina. Other catalysts did not show any lines attributable to Ag derived phase, such as Ag metal, Ag_2O, and AgO.

The solid acid properties of alumina supports were characterized by means of NH_3-TPD. As shown in Fig. 4, a single broad desorption profile ranged 373–50 K was observed for pure alumina support. The Zn-, Mg-, and P-doped alumina showed larger desorption profiles than that of pure alumina. These desorption profiles terminated at around 700 K, which is slightly higher than that of pure alumina. On the other hand, the doping of Y and Na results in decrease of the NH_3 desorption. The desorbed amount of NH_3 per surface area, i.e., the surface concentration of acid sites, was in the order of Zn-alumina (2.7 μmol m^{-2}) > Mg-alumina (2.6) ~ P-alumina (2.6) > Al_2O_3 (1.9) > Y-alumina (1.3) ≫ Na-alumina (0.08). This order was in a good agreement with that of the HC-SCR activity on supported Ag catalysts, except P-alumina.

Fig. 5 shows in situ IR spectra of surface adsorbed species on pure and modified Ag/alumina catalysts under the C_3H_8–H_2-SCR at 573 K. On Ag/Al_2O_3, the bands assignable to bidentate nitrate (1247, 1590 cm^{-1}), monodentate nitrate (1294 and 1552 cm^{-1}), acetate on Ag (1458 and 1571 cm^{-1}), NCO on Ag or Al (2230 cm^{-1}) were observed [31–36]. The Zn-, Mg-, and Y-doped catalysts showed basically the similar spectra to pure Ag/Al_2O_3, while the band assignable to formate (1380 cm^{-1}) was also observed. From the detailed observation, monodentate

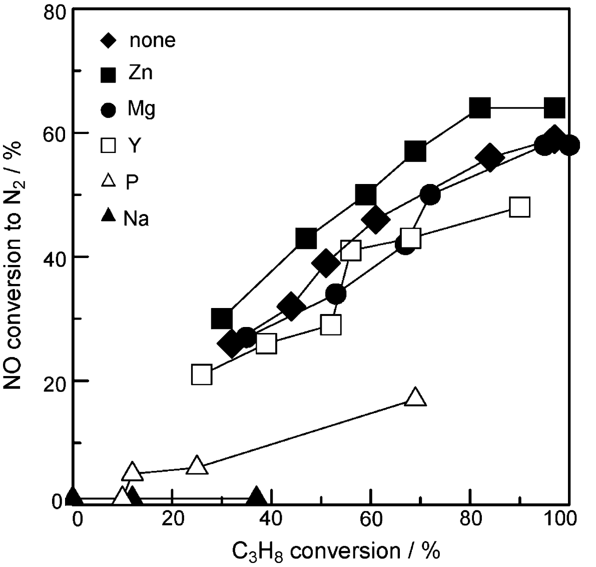

Fig. 2. NO conversion to N_2 as a function of C_3H_8 conversion on C_3H_8–H_2-SCR over pure and modified Ag/alumina catalysts at 523–773 K.

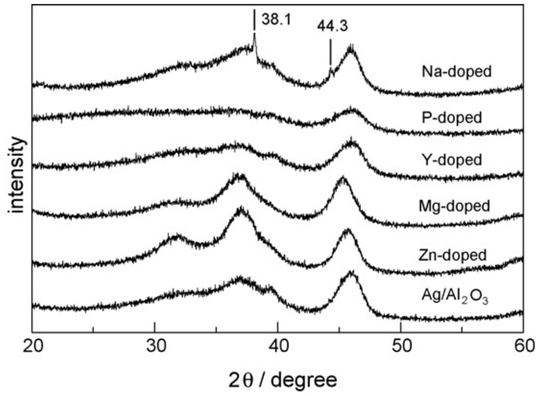

Fig. 3. XRD patterns of pure and modified Ag/alumina catalysts.

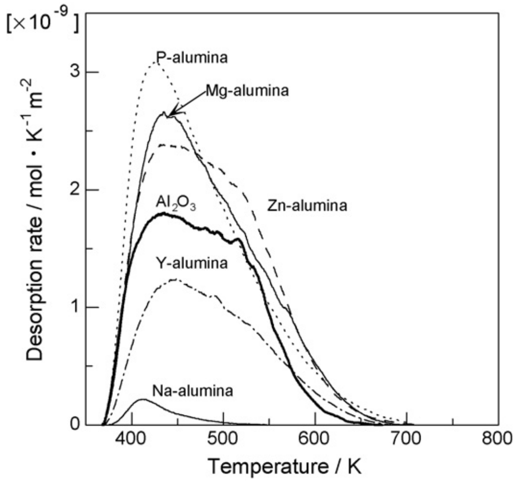

Fig. 4. NH_3-TPD profile of pure and doped alumina supports.

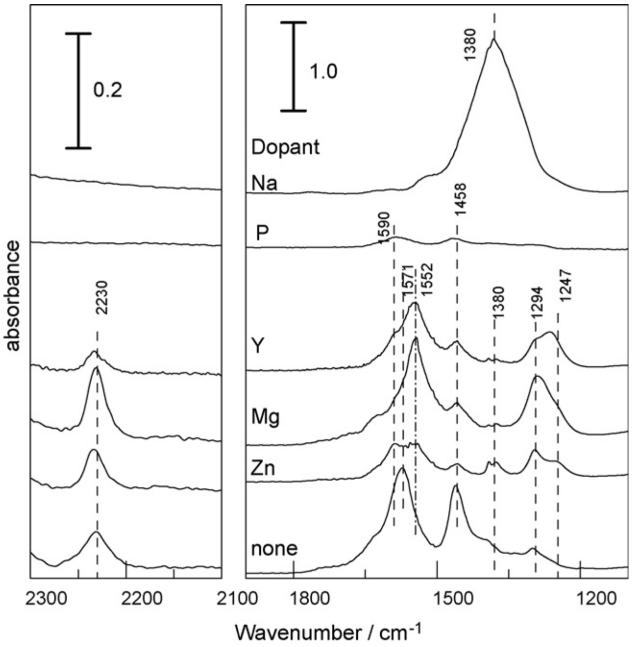

Fig. 5. IR spectra of adsorbed species on pure and modified Ag/alumina under C_3H_8–H_2-SCR at 573 K for 1 h.

is the major nitrate on pure and Zn- and Mg-doped Ag/alumina, while the monodentate and bidentate nitrates are comparable on Y-doped Ag/alumina. The Na-doped catalyst showed the strong band at 1380 cm^{-1}, which is assignable to nitrate adsorbed on Na [34]. In the case of P-doped catalyst, only very weak bands of acetate were observed.

Fig. 6a shows UV–vis spectra after treatment in a flow of 0.1%H_2/10%O_2/He at 573 K, which is similar condition to the C_3H_8–H_2-SCR reaction. In the case of pure Ag/Al_2O_3, a very broad band was observed below 400 nm, indicating very wide distribution of the types of surface Ag species. This wide band is composed of the band at 210–235 nm assignable to the $4d^{10}$ to $4d^9\ s^1$ transition of Ag^+ ion [20,30,31,37], the bands at 250–310 nm assignable to ionic $Ag_n^{\delta+}$ clusters such as Ag_3^{2+} [38] and Ag_4^{2+} [39], the band at 350–380 nm due to metallic Ag clusters [18,37,40,41]. The Zn-, Mg-, and Y-doped Ag/alumina catalysts showed slightly different spectra from Ag/Al_2O_3. To emphasize the difference in these spectra, the relative intensities of these modified Ag/alumina compared to pure Ag/Al_2O_3 are shown in Fig. 6b. The Zn-doping enhanced the formation of $Ag_n^{\delta+}$ clusters at 280 nm and the decrease in metallic Ag clusters above 350 nm. The Mg-doping also decreased the Ag metal particles above 350 nm, while the maximum relative intensity at 310 nm indicates the formation of larger Ag clusters than Ag/Al_2O_3. The Y-doping enhanced the formation of Ag metal particles above 400 nm in a flow of H_2/O_2. On the other hand, the absorption bands of the Na- and P-doped catalysts are more intense above 400 nm, indicating the formation of metallic Ag species. The formation of Ag metal particles on Na-doped catalysts was also confirmed by the XRD pattern. The absorption band around 500 nm, which can be attributed to plasma resonance absorption band of crystallites of Ag [37], also indicates the formation of Ag metal particles on Na-alumina. Although, there were no diffraction lines due to Ag metal in the XRD pattern of Ag/P-alumina, indicating the Ag species are too small to detect by XRD, very strong absorption bands was observed in UV–vis spectrum around 400 nm. There are two possibilities of the strong UV–vis band of P-doped catalyst around 400 nm; the plasma resonance absorption of metallic Ag clusters (~1 nm) [37] and contribution of any phosphate phases such as *ortho*-Ag_3PO_4 [42]. Since this band was not observed in a flow of O_2/He at 573 K, the contribution of phosphate phases can be excluded. The strong UV–vis band of Ag/P-alumina can be attributed to the abundance of metallic Ag clusters (~1 nm).

4. Discussions

The good agreement of the promotion effect of additives on the NO conversion (Fig. 1) and the amount of acid sites (Fig. 4) suggests that the acid amount of alumina support is one of the controlling factors for the SCR activity. In Fig. 7, the reaction rates of NO at 573 K were plotted as a function of the surface concentrations of acid sites to confirm this hypothesis. A good correlation was observed between these parameters, except Ag/P-alumina. This figure clearly shows that the acid amount of alumina support is one of the controlling factors for the SCR activity. One may expect that the strength of the acid sites is also the possible controlling factor for the SCR activity.

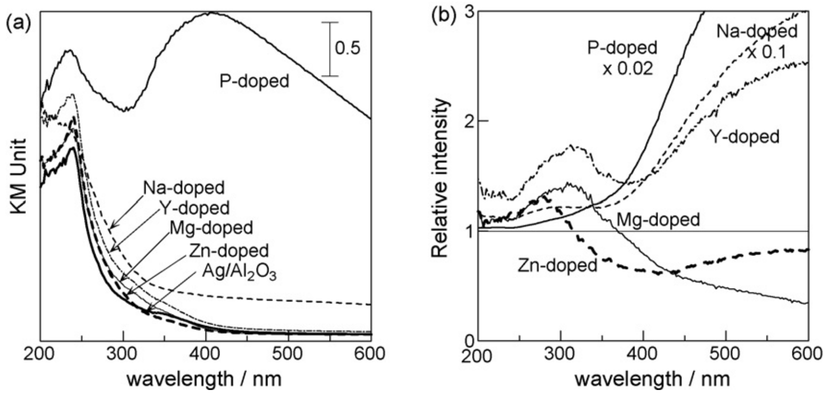

Fig. 6. UV–vis spectra of pure and modified Ag/alumina after treatment in a flow of 0.1%H_2/10%O_2/He at 573 K for 1 h (a) and relative intensity of modified Ag/alumina to that of pure Ag/alumina (b).

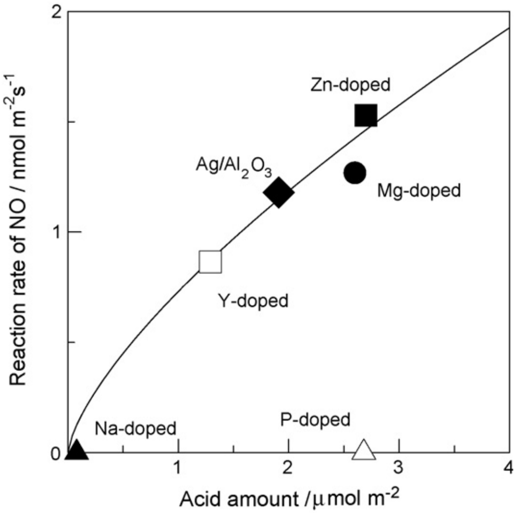

Fig. 7. Correlation between acid concentrations of alumina supports and NO conversion at 573 K over pure and modified Ag/alumina.

Comparing the SCR activity and the distribution of the NH_3 desorption in TPD profiles, the strength of acid sites is fairly correlated to the SCR activity. The Zn- and Mg-doped alumina, which showed higher SCR activity than Ag/Al_2O_3, showed the NH_3-TPD profiles more weighted at higher temperatures. On the other hand, the NH_3 desorption terminated at lower temperatures on the less active Na-doped alumina. Actually, the similar correlation to Fig. 7 is observed between the reaction rate of NO and the concentration of acid sites. The exceptional low SCR activity of Ag/P-alumina shown in Fig. 7 suggests a contribution of another controlling factor for the SCR activity of Ag/alumina.

It is well investigated that nitrates and acetate play very important role in the selective reduction of NO [8,21,33]. The selective reduction of NO on alumina-based catalysts involves the surface reaction between these species adsorbed on Al–O or metal–O sites [35,36]. Especially, in the HC-SCR with the presence of H_2, the acceleration of formation rate of nitrates and acetate results in the higher reaction rate of NO to N_2 [21]. In the case of Ag/P-alumina, however, only weak bands were observed in in situ IR spectrum. Thus, the low activity of Ag/P-alumina can be rationalized by the suppression of the formation rate of these species. Morterra et al. [43] reported that the P-doping to γ-alumina leads to suppression of alumina basic sites, on which acidic CO_2 molecule preferentially adsorbs as carbonate species. Taking the acidic property of nitrates and acetate into account, the suppression of these species by the P-doping is reasonable. The significant modification of alumina surface by the P-doping may be correlated to the deformation of spinel structure to amorphous phase. The low SCR activity of the Na-doped catalyst can also be explained by not good balance of surface adsorbed species, i.e., absence of acetate species on the catalyst surface under the reaction conditions.

UV–vis spectroscopy is a useful tool for the characterization of Ag/alumina catalysts because they give the information of dispersion and valence of surface Ag species. Our research group previously indicated the contribution of the $Ag_n^{\delta+}$ clusters to the high SCR activity of Ag/alumina catalyst in the co-feeding of H_2 [22]. In the present study, the positive promotion effect on the HC-SCR and the increase in the band of $Ag_n^{\delta+}$ clusters in a flow of H_2/O_2 was observed by the Zn- and Mg-doping. On the other hand, the Na and P-doped alumina enhanced the formation of metallic Ag species and the less SCR activity. These trends agree well with the previous conclusion obtained from pure Ag/alumina and Ag-zeolites [19,20,22]: The formation of $Ag_n^{\delta+}$ clusters is favorable for the SCR reaction, while non-selective oxidation of hydrocarbons proceeds over metallic Ag species.

Furthermore, the promotion effects of these additives on the SCR activity and the formation of $Ag_n^{\delta+}$ clusters were also in harmony with the amount of acid sites of alumina. The role of acid sites of alumina can be speculated by the analogy of the role of acid sites on Ag-zeolites [19,28]. The strong dependence of zeolite supports was also found on the formation of $Ag_n^{\delta+}$ clusters under the H_2 containing atmospheres and the HC-SCR activity. The major Ag species are Ag^+ ions for MOR, $Ag_n^{\delta+}$ clusters for MFI and BEA, and metallic Agclusters for Y. The increase in the Ag/Al ratio in Ag/MFI also affected the SCR activity. The sequence of Ag agglomeration was in accordance with the strength and amount of the acid sites of zeolites. It was suggested that the interaction between the positive charge of $Ag_n^{\delta+}$ clusters and acid sites, i.e., the anionic site of zeolites, stabilizes $Ag_n^{\delta+}$ clusters. In the case of alumina supports, the surface acid sites would play a similar role of zeolite acid sites, i.e., an acceptor of Ag^+ ions or $Ag_n^{\delta+}$ ionic clusters for the fixation of these species under the reaction conditions. The positive effect of Zn- and Mg-doping on the amount and strength of acid sites may be correlated to the formation of spinel phase. Although, further characterization of alumina surface should be necessary, the dispersion of Ag species on alumina, which controls the HC-SCR activity, can be rationalized by acid sites of alumina as the first approximation.

5. Conclusions

Through the investigation of the effect of modified alumina supports on the C_3H_8–H_2-SCR over Ag/alumina catalyst, it was indicated that the acid amount of alumina support is one of the controlling factors for the SCR activity. The control of the surface concentration of nitrates and acetates under the reaction conditions is another important role of the promoters. The acid sites of alumina may stabilize the $Ag_n^{\delta+}$ clusters, which are favorable for the selective reduction of NO, under the reaction conditions.

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