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Hydrogen applications in selective catalytic reduction of NO_x emissions from diesel engines

Ibrahim Aslan Resitoglu [a,*], *Ali Keskin* [b]

[a] *Department of Automotive Technology, Mersin University, Technical Sciences Vocational School, TR-33343 Mersin, Turkey*

[b] *Department of Automotive Engineering, Cukurova University, Engineering and Architecture Faculty, TR-01330 Adana, Turkey*

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ABSTRACT

Diesel engines have been considered as a major source in nitrogen oxide (NO_x) formation worldwide. The widespread use of diesel engines in consequence of their low fuel consumption, high durability and efficiency increases NO_x emissions day by day. NO_x emissions from diesel engines cause unavoidable damage on environment and people health. Although so many technologies such as exhaust gas recirculation (EGR), lean burn combustion, electronic controlling fuel injection systems, etc. have been developed to control NO_x emissions from diesel engines, they couldn't meet the desired reduction in NO_x emissions. In any case, Selective Catalytic Reduction (SCR) as one of the most promising aftertreatment-emission control technologies is an effective solution in restriction of NO_x emissions. The use of SCR systems especially in heavy-duty diesel powered vehicles has been increasing nowadays. In these systems, to use of hydrogen (H_2) as a reductant or promoter have been improved the conversion efficiency especially at low exhaust temperatures. Many researchers have been focused on the use of H_2 in SCR systems for controlling NO_x emissions.

In this study, the applications of H_2 in SCR of NO_x have been discussed. The studies on use of H_2 in SCR of NO_x emissions were examined and the effects on NO_x conversions were determined. Consequently, it is confirmed that H_2 is a promising and alternative reductant in SCR of NO_x and it has been kept as an attracting subject for many researchers.

Introduction

NO_x emissions (NO and NO_2) make major contribution to air pollution. They cause many adverse effects on environment and people health [1,2]. Acidification of rain, photochemical smog, greenhouse effect and ozone depletion are the main damages of NO_x on environment while respiratory tract diseases are the most harmful effect of NO_x on people health [3–5]. Although many sources such as agriculture, thermal plants, industry etc. have been considered as contributor to NO_x emissions, transport sector especially diesel powered vehicles is the main contributor of NO_x emissions [6,7].

Road transport is responsible for around 40% of total NO_x emissions and 85% of NO_x emissions from transport sector are

* *Corresponding author*. Fax: +9 (0)324 361 0043.
E-mail address: aslanresitoglu@gmail.com (I.A. Resitoglu).

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emitted by diesel-powered vehicles [8,9]. To eliminate NO_x emissions from diesel engines without causing to any decrease in engine performance have been a major barrier for vehicle manufacturers and researchers. To provide this aim, researches have been adopted to SCR technology for diesel vehicles since 2000s and SCR of NO_x emissions from diesel vehicles by urea solution have become one of the most effective methods for vehicles [1,10].

SCR system is currently best choice to eliminate NO_x emissions from diesel engines [7]. NO_x emissions in exhaust gas can be eliminated with a reductant in SCR system [4]. Although different reductants such as alcohols, hydrocarbons, hydrogen, etc. have been sampled, Ammonia (NH_3) is the most commonly used reductant and has high conversion efficiency in SCR of NO_x [6,11]. To prevent the burning of NH_3 in high exhaust temperatures before the reaction, NH_3 is obtained from urea solution [12]. Urea-SCR is the current emission control technology to reduce NO_x emissions from vehicles and other power generating systems. However, many problems such as low activity at low temperatures, ammonia slip, high running cost, NH_3 storage, ash odour, deterioration of catalysts and complex of systems have been direct the researches to alternative SCR technologies [13–16].

Low exhaust temperature is a major problem for urea-SCR applications [17]. At low exhaust temperatures below 200 °C, the reactions of urea solution (thermolysis and hydrolysis) cannot occur properly. Biurea, cyanide acid, ameline, melamine and amelide are constituted due to faulty of reactions [18]. Light off temperature of urea-SCR catalyst is generally around or above 200 °C and NO_x conversion efficiency of urea-SCR is limited at low temperatures [12].

Another SCR technology, the use of HC as reductant in SCR of NO_x, has been worked by many researches currently [19]. Ag/Al_2O_3 is the most promising catalyst type in HC-SCR system [20,21] while V_2O_5-WO_3/TiO_2 catalyst is conventional for urea-SCR system [12]. Compared to urea-SCR, HC-SCR systems provide advantages such as existence of HC in exhaust gas and eliminated the urea tank [19]. However, H_2O vapour leads to significantly decrease in activity of HC-SCR [17].

In urea-SCR and HC-SCR systems, to reduce NO_x emissions at low temperature with high O_2 presentation in exhaust gas is a major problem [22]. The low activities of catalysts at low temperatures have been focused on intensively by many researches for decades. To increase activity at low temperature can be possible to use different reductants or additives.

H_2 has been used in many studies as an alternative fuel for internal combustion engines to eliminate pollutant emissions and improve engine performance [23,24]. The combustion of hydrogen in combustion chamber has improved activity of SCR systems enhancing NO_2/NO_x ratios [25].

Hydrogen also has been considered as a reductant or promoter in SCR systems for mobile applications [26]. Use of hydrogen in SCR of NO_x emissions has been considered as a green environmental technique because of only H_2O formation following the H_2 combustion. Also high NO_x conversion efficiencies of H_2-SCR at low temperatures have increased the attention of H_2-SCR systems [27]. In this study, the H_2-SCR was explained and the studies on the effects of H_2-SCR on NO_x emissions were discussed.

Use of hydrogen in selective catalytic reduction of NO_x

H_2-SCR system

Generally, H_2 is not used as a reductant in SCR of NO_x. Urea and hydrocarbons are the mainly reductants for SCR reactions. However, hydrogen offers high NO_x conversion efficiency for SCR applications at low temperatures. This advantage makes it to use a promoter [22,28,29] or reductant [13,30,31] in SCR applications. Compared to conventional urea-SCR, H_2-SCR reduces NO_x emissions without forming another pollutants such as biurea, cyanide acid, etc. [1,32]. Fig. 1 presents a typical H_2-SCR system.

H_2-SCR is selective catalytic reduction of NO_x by hydrogen. In H_2-SCR system, H_2 has been choice as reductant agent. It has been used for increasing of NO_x reduction especially at low exhaust temperatures of engine [16]. H_2 is an alternative low temperature (e.g. below 200–300 °C) reductant for SCR systems. Compared NH_3, H_2 is non-corrosive, nontoxic and less processed reductant for SCR applications [33,34]. The reactions occurred in H_2-SCR systems are given in Eqs. (1)–(3) [35,36].

$$2NO + 4H_2 + O_2 \rightarrow N_2 + 4H_2O \quad (1)$$

$$2NO + 3H_2 + O_2 \rightarrow N_2O + 3H_2O \quad (2)$$

$$O_2 + 2H_2 \rightarrow 2H_2O \quad (3)$$

Eq. (1) is the desired reaction which converts NO to N_2. However, Eq. (2) presents an undesired reaction which leads N_2O formation. N_2O is quite harmful and has adverse effects on environment and climate change. It contributes to greenhouse effect more than CO_2. To prevent the formation of NO_2, N_2 selective catalyst must be used. Eq. (3) is the reaction in the oxidation of H_2.

H_2 has an improving effect on catalyst activity and removes the poisonings which restrict the reaction. H_2 supports the formation of NO_2, which is forceful in eliminating of carbon poisoning [37].

The lack of H_2-SCR systems is to supply of H_2 used in SCR of NO_x. The presence of hydrogen in real engine exhaust gas has been in a small amount [38]. So hydrogen has been provided from reliable sources such as tanks and onboard reforming. This option causes increase in costs and safety problems [39].

The use of H_2 in SCR of NO_x has been studied extensively by researchers for a long time. The studies on H_2-SCR systems have been generally based on a small scale with simulated engine emissions in laboratory conditions [10,40,41]. However, a few of researches have been based on a large scale with real diesel engine exhaust gas [26,42,43].

Catalysts and conversion efficiencies of H_2-SCR systems

Supported noble metals are primary choice catalysts in SCR of NO by hydrogen [11]. Noble metals can degrade H_2

actively and degraded H_2 provides NO conversion effectively [36]. Pt is the most common noble metal catalyst for H_2-SCR [41]. The reactions initiate with a low light-off temperature about 90 °C over Pt/Al_2O_3 catalyst by the presence of H_2 as reductant [44].

Although Pt based catalysts have high activity at low temperatures, it has high selectivity for N_2O formation and lower selectivity for N_2 [22,31]. However, many studies have been carried out on new catalysts and to improve the N_2 selectivity of Pt based catalyst with reductant of hydrogen under excess oxygen [35].

The type of catalyst substrate (Al_2O_3, SiO_2, ZSM5, etc.) affects strongly the activity of Pt catalyst. Especially the alkalinity and acidity of catalyst has an impact on the dispersion of Pt on catalyst and thus on the activity of catalyst [17]. Expect of Al_2O_3 substrate, different substrate such as; Pt/SiO_2 [45], $NiFe_{1.95}Pt_{0.05}O_4$ [15], Pt/TiO_2 [46], Pt/MnO_x [34], Pt/$Ce_{1-x}Zr_xO_{2-\delta}$ [47] worked in researches. Burch and Coleman [44] compared Al_2O_3 and SiO_2 as Pt catalyst support considering their activity in H_2-SCR. Pt/SiO_2 showed best performance in terms of activity at low temperatures.

The effects of H_2 on selective catalytic reduction of NO over Pt/γ-Al_2O_3, Pd/γ-Al_2O_3 and Ir/γ-Al_2O_3 were studied by Goula et al. [10]. In this research, Pt based catalyst showed higher activity compared to other noble metal based catalysts.

The supplement of WO_3 to Pt/TiO_2 catalysts for H_2-SCR of NO_x investigated by Liu et al. [46]. They found that the supplement of WO_3 led to increase in conversion efficiency at low temperatures. The NO_x conversion efficiency at low temperatures reached up to 90% with the addition WO_3.

Park et al. [45] used zirconia as a main substrate expect conventional alumina and silica in H_2-SCR systems. Pt was used as based noble metal in this study. The results showed that zirconia had better performance as a catalytic support compared alumina and silica in the term of conversion efficiency and hydrothermal stability.

Li et al. [17] tested four different catalysts as, Pt/γ-Al_2O_3, Pt/MgO, Pt/HZSM-5 and Pt/ZrO_2 in H_2-SCR system. They found that conversion efficiency of catalysts were greatly depended on Pt content in catalyst and NO_x adsorption capacity of substrates.

Table 1 shows the activity of different catalyst type in H_2-SCR. In this table, $T_{con.}$ is the minimum temperature at which maximum conversion efficiency is obtained. Considering the studies carried out on H_2-SCR catalyst, it is shown that Pt based catalyst is best choice for H_2-SCR applications. NO_x conversions were obtained in high rates at low temperatures almost for all Pt based catalyst.

Clearly, Pd is the most promising catalyst which comes after Pt based catalysts with high conversion efficiencies near the Pt based catalysts. Compared Pt, Pd is remarkable with the specifications of cheaper, high thermal stability, easily available and higher N_2 selectivity [13,52]. Especially the activity of Pd based catalyst in SCR of NO is so high compared to Pt and other noble metal catalysts [53]. Different supports for Pd based catalysts such as Pd–Ir/TiO_2 [33], Pd/K_2O-6TiO_2 [50], Pd/TiO_2-Al_2O_3 [51] performed in H_2-SCR of NO_x by researchers. Qi et al. [5] used H_2 as a reductant to catalytic reduction of NO_x with Pd catalysts. They found that H_2 gave high NO conversion at low temperatures with Pd catalysts.

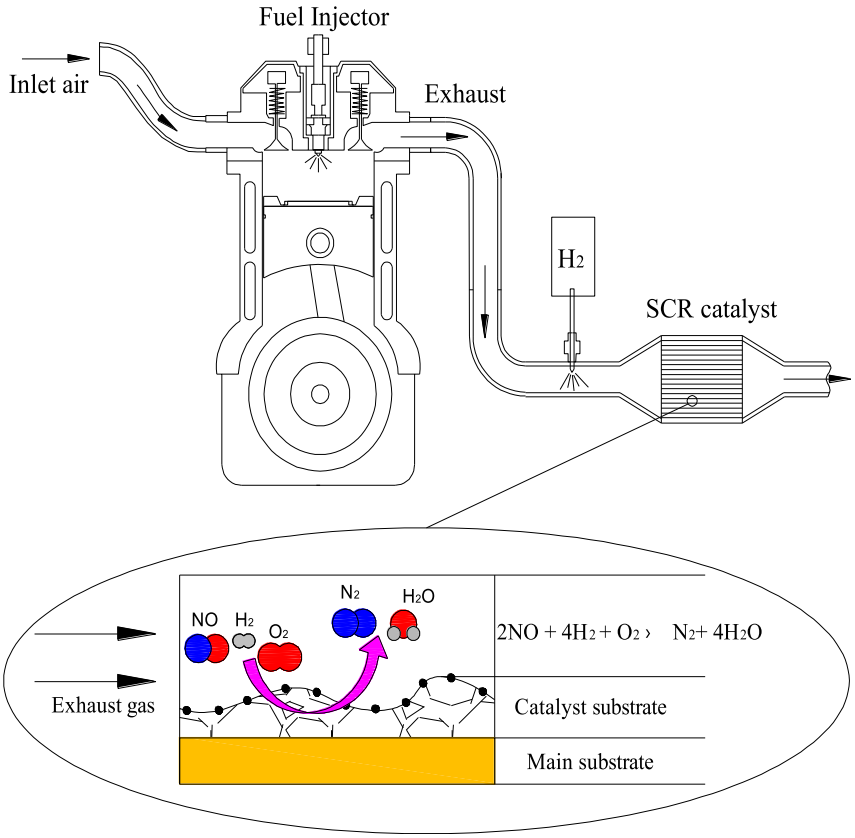

Fig. 1 – Selective catalytic reduction of NO by hydrogen.

Table 1 – Different catalyst type used in H_2-SCR applications.

Catalyst	Gas concentrations				~$T_{con.}$ (°C)	~ Max. NO conversion (%)	Ref.
	H_2	O_2 (%)	NO	GHSV (h^{-1})			
%1 Pt/Al_2O_3	0.8%	5	480 ppm	–	50	100	[45]
0.5% Pt/Al_2O_3	2000 ppm	6	500 ppm	22,000	80	82	[41]
0.5% Pt/y-Al_2O_3	0.5%	2	1000 ppm	40,000	120	93	[10]
%1 Pt/SiO_2	0.8%	5	480 ppm	–	100	98	[45]
%0.5 Pt/TiO_2	1%	5	0.25%	53,000	200	82	[46]
%0.5 Pt/2% WO_3/TiO_2	1%	5	0.25%	53,000	125	88	[46]
Pt/ZSM5	1000 ppm	–	1000 ppm	60,000	100	100	[48]
1% Pt/ZSM35	0.5%	6.7	1%	80,000	120	80	[40]
1% Pt/Beta	0.5%	6.7	1%	80,000	115	55	[40]
0.3 Pt/ZrO_2	2000 ppm	6	500 ppm	22,000	150	95	[41]
Pt/Si-MCM	5000 ppm	6.7	1000 ppm	80,000	100	60	[49]
0.95% Pd/Al_2O_3	5000 ppm	5	1000 ppm	60,000	125	55	[50]
0.94% Pd/TiO_2	5000 ppm	5	1000 ppm	60,000	100	60	[50]
1.9% Pd/TiO_2	3000 ppm	5	1000 ppm	60,000	375	40	[33]
%1 Pd/TiO_2-Al_2O_3	4000 ppm	5	500 ppm	–	150	98	[51]
1.8% Rh/TiO_2	3000 ppm	5	1000 ppm	60,000	550	35	[33]
Rh/ZSM5	1000 ppm	–	1000 ppm	60,000	300	100	[48]
1.7% Ir/TiO_2	3000 ppm	5	1000 ppm	60,000	475	65	[33]
0.5% Ir/y-Al_2O_3	0.5%	2	1000 ppm	40,000	340	16	[10]
$NiFe_2O_4$	10,700 ppm	2	1070 ppm	23,400	220	42	[32]
$NiFe_{1.95}Pd_{0.05}O_4$	10,700 ppm	2	1070 ppm	23,400	190	100	[32]
$NiCo_2O_4$	10,700 ppm	2	1070 ppm	48,000	350	40	[1]
$NiCo_{1.95}Pd_{0.05}O_4$	10,700 ppm	2	1070 ppm	48,000	200	92	[1]
Co/ZSM5	1000 ppm	–	1000 ppm	60,000	500	100	[48]
Cu/ZSM5	1000 ppm	–	1000 ppm	60,000	600	90	[48]
$CoFe_2O_4$	10,000 ppm	2	1000 ppm	23,400	250	84	[32]
$CoFe_{1.95}Pd_{0.05}O_4$	10,000 ppm	2	1000 ppm	23,400	170	95	[32]

Except Pt and Pd, different catalysts such as Rh, Ni, Ir, TiO_2, Co, etc. have been developed by researchers as alternative catalysts for H_2-SCR applications. Xu et al. [13] developed $NiFe_{2-x}Pd_xO_4$ catalysts for the SCR of NO by hydrogen. They obtained nearly 100% NO conversion at 190 °C. In their other study [27], they searched the effect of aluminate spinel oxides ($CuAl_2O_4$, $CoAl_2O_4$, $ZnAl_2O_4$) and palladium-substituted aluminates ($CuAl_{1.95}Pd_{0.05}O_4$, $CoAl_{1.95}Pd_{0.05}O_4$, $ZnAl_{1.95}Pd_{0.05}O_4$) on H_2-SCR of NO. Palladium-substituted aluminates showed better activity compared to aluminate spinel oxides under the same reaction conditions. Approximately maximum conversion efficiency was obtained as 95% with $CoAl_{1.95}Pd_{0.05}O_4$.

H_2 assisted HC-SCR system

H_2 has been also used as promoter in HC-SCR systems. H_2 improves conversion efficiency of HC-SCR affecting catalyst and other reactants [39]. Especially at low temperature, the supplement of H_2 into exhaust gas increase catalyst activity [54]. Many researches have been carried out on H_2 assisted HC-SCR systems. Ag/Al_2O_3 has been most common catalyst in these researches due to its high activity and efficiency in SCR of NO by hydrocarbons [55]. Except Al_2O_3, different supports like MFI zeolite [29,56] have been used in Ag based catalyst for H_2 assisted HC-SCR.

Abu-Jrai and Tsolakis [42] studied the effect of H_2 and CO addition on HC-SCR activity over 1% Pt/Al_2O_3. Unlike other studies they performed their study using real diesel engine exhaust gas. H_2 addition improved the HC-SCR activity at low temperatures between 100 °C and 300 °C. Another study on the effect of hydrogen on the efficiency of NO_x reduction with HC-SCR was carried out by Gu et al. [43] using both laboratory and engine test-bench. They preferred Ag/Al_2O_3 catalyst in their research because of its high performance for HC-SCR applications. Results showed that H_2 had an improving effect on NO_x conversion at both laboratory condition and real working situation. NO_x conversion rates increased up to three times with the use of H_2 in the tests carried out on engine test-bench. Shimizu et al. [29] investigated the hydrogen effect on HC-SCR. Ag-MFI was used as catalyst in this experimental study. The use of hydrogen led to increase the coverage of surface intermediates, NO_2 concentration and N_2 formation.

The hydrogen effect on SCR of NO by propane over Ag/Al_2O_3 catalyst was investigated by Richter et al. [57]. They found that the propounding of H_2 avoid to NO conversion to NO_2 form substantially. The presence of H_2 raised the NO_x conversion up to 60% from marginal conversion rates.

Theinnoi et al. [58] searched the effect of H_2 promotion on passive HC-SCR activity. They performed their study over Ag/Al_2O_3 catalyst promoting H_2 (500–3000 ppm) with real diesel exhaust gas. Consequently, they reached two results for H_2 effects on silver catalysis. These results were the increase in initial activity and the decrease in deactivation rate of catalyst.

Sadokhina et al. [2] searched the catalytic activity of Ag/Al_2O_3 catalyst in SCR of NO_x in the presence of small amount of H_2. In this experimental study, the addition of ~1000 ppm hydrogen improved activity and selectivity of catalyst.

Zhang et al. [59] searched the effect of hydrogen on reaction intermediates in the selective catalytic reduction of NO_x

by C_3H_6. Ag/Al_2O_3 was preferred as catalyst in their study since its high NO_x conversion efficiency by alcohols. They found that the addition of H_2 was significantly increased NO_x conversion at low temperature range of 200–350 °C.

Stakheev et al. [60] investigated the effects of H_2 addition amount on HC-SCR of NO_x over Ag/Al_2O_3. They used different H_2 amounts from 0 to 1600 ppm in their researches. Consequently, NO_x conversion showed increase in direct proportionally with H_2 addition amount.

Conclusions

This review focused on H_2 applications in SCR technology. The H_2-SCR technology was expressed and the researches on H_2-SCR was scrutinised in this study. The researches carried out on H_2-SCR showed that the addition of hydrogen resulted in conversion of the oxidized nitrogen to N_2 on the catalyst surface. H_2 has an improving effect on SCR activity especially at low temperature. Pt and Pd based catalysts are the most feasible and current for H_2-SCR applications while Ag based catalysts have high efficiency in H_2 assisted HC-SCR applications. The most of researches on H_2-SCR have been carried out in laboratory conditions. The studies carried out in real working conditions of engine are substantially restricted. Investigations in real working situations must be increased with future studies. In conclusion, H_2 is a promising reductant for SCR applications of NO_x without caused any formation of pollutants and the researches on improving of H_2-SCR will continue for a longer time.

REFERENCES

[1] Cai X, Sun W, Xu C, Cao L, Yang J. Highly selective catalytic reduction of NO via SO_2/H_2O-tolerant spinel catalysts at low temperature. Environ Sci Pollut Res 2016;23:18609–20.

[2] Sadokhina NA, Prokhorova AF, Kvon RI, Mashkovskii IS. Dependence of the catalytic activity of Ag/Al_2O_3 on the silver concentration in the selective reduction of NO_x with n-hexane in the presence of H_2. Kinet Catal 2012;53:107–16.

[3] Wang X, Zheng Y, Xu Z, Liu X, Zhang Y. Low-temperature selective catalytic reduction of NO over MnO_x/CNTs catalysts effect of thermal treatment condition. Catal Commun 2014;50:34–7.

[4] Zhang Q, Qiu C, Xu H. Low-temperature selective catalytic reduction of NO with NH_3 over monolith catalyst of $MnO_x/CeO_2–ZrO_2–Al_2O_3$. Catal Today 2011;175:171–6.

[5] Qi G, Yang RT, Thompson LT. Catalytic reduction of nitric oxide with hydrogen and carbon monoxide in the presence of excess oxygen by Pd supported on pillared clays. Appl Catal A: General 2004;259:261–7.

[6] Clark PD, Nielsen AD, Dowling NI. Catalytic reduction of nitric oxide by hydrogen sulfide over γ-alumina. Catal Lett 2005;104:73–8.

[7] Qi G, Wang Y, Yang RT. Selective catalytic reduction of nitric oxide with ammonia over ZSM-5 based catalysts for diesel engine applications. Catal Lett 2008;121:111–7.

[8] Roy S, Hegde MS, Madras G. Catalysis for NO_x abatement. Appl Energy 2009;86:2283–97.

[9] Lee T, Park J, Kwon S, Lee J, Kim J. Variability in operation based NO_x emission factors with different test routes, and its effects on the real-driving emissions of light diesel vehicles. Sci Total Environ 2013;461–462:377–85.

[10] Goula MA, Charisiou ND, Papageridis KN, Delimitis A. A comparative study of the H_2-assisted selective catalytic reduction of nitric oxide by propene over noble metal (Pt, Pd, Ir)/g-Al_2O_3 catalysts. J Environ Chem Eng 2016;4:1629–41.

[11] Valiheikki A, Petallidou KC, Kalamaras CM, Kolli T. Selective catalytic reduction of NO_x by hydrogen (H_2-SCR) on WO_x-promoted $Ce_zZr_{1-z}O_2$ solids. Appl Catal B: Environ 2014;156–157:72–83.

[12] Resitoglu IA, Altinisik K, Keskin A. The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. Clean Technol Environ Policy 2015;17:15–27.

[13] Xu C, Sun W, Cao L, Yang J. Selective catalytic reduction of nitric oxide by hydrogen over $NiFe_{2-x}Pd_xO_4$ catalysts at low temperature. Chem Eng J 2016;283:1137–44.

[14] Alkemade UG, Schumann B. Engines and exhaust after treatment systems for future automotive applications. Solid State Ion 2006;177:2291–6.

[15] Sun W, Qiao K, Liu J, Cao L, Gong C, Yang J. Pt-doped $NiFe_2O_4$ spinel as a highly efficient catalyst for H_2 selective catalytic reduction of NO at room temperature. ACS Comb Sci 2016;18:195–202.

[16] Wang X, Wen W, Mi J, Li X, Wang R. The ordered mesoporous transition metal oxides for selective catalytic reduction of NO_x at low temperature. Appl Catal B Environ 2015;176–177:454–63.

[17] Li X, Zhang X, Xu Y, Liu Y, Wang X. Influence of support properties on H_2 selective catalytic reduction activities and N_2 selectivities of Pt catalysts. Chin J Catal 2015;36:197–203.

[18] Schaber P, Colson J, Higgins S, Thielen D, Anspach B, Brauer J. Thermal decomposition (pyrolysis) of urea in an open reaction vessel. Thermochim Acta 2004;424:131–42.

[19] Azis MM, Harelind H, Creaser D. Kinetic modeling of H_2-assisted C_3H_6 selective catalytic reduction of NO over silver alumina catalyst. Chem Eng J 2015;278:394–406.

[20] Shimizu K, Satsuma A. Selective catalytic reduction of NO over supported silver catalysts-practical and mechanistic aspects. Phys Chem Chem Phys 2006;8:2677–95.

[21] Arve E, Eranen K, Snare M, Klingstedt F, Murzin D. Selective catalytic reduction of NO_x over Ag/Al_2O_3 using various biodiesels as reducing agents. Top Catal 2007;42:399–403.

[22] Caraviggo G, Nossova L, Burich R. Influence of supports on Pd catalysts for the selective catalytic reduction of NO_x with H_2 and CO. Emiss Control Sci Technol 2016;2:10–9.

[23] Zhou JH, Cheung CS, Leung CW. Combustion, performance and emissions of a diesel engine with H_2, CH_4 and $H_2–CH_4$ addition. Int J Hydrogen Energy 2014;39:4611–21.

[24] Saravanan N, Nagarajan G. An insight on hydrogen fuel injection techniques with SCR system for NO_x reduction in a hydrogen–diesel dual fuel engine. Int J Hydrogen Energy 2009;34:9019–32.

[25] Chong JJ, Tsolakis A, Gill SS, Theinnoi K, Golunski SE. Enhancing the NO_2/NO_x ratio in compression ignition engines by hydrogen and reformate combustion, for improved aftertreatment performance. Int J Hydrogen Energy 2010;35:8723–32.

[26] Abu-Jrai A, Tsolakis A, Megaritis A. The influence of H_2 and CO on diesel engine combustion characteristics, exhaust gas emissions, and after treatment selective catalytic NO_x reduction. Int J Hydrogen Energy 2007;32:3565–71.

[27] Xu C, Sun W, Cao L, Li T, Cai X, Yang J. Highly efficient Pd-doped aluminate spinel catalysts with different divalent cations for the selective catalytic reduction of NO with H_2 at low temperature. Chem Eng J 2017;308:980–7.

[28] Arve K, Backman H, Klingstedt F, Eranen K, Murzin D. Kinetic considerations of H_2 assisted hydrocarbon selective catalytic

reduction of NO over Ag/Al_2O_3 I. Kinetic behaviour. Appl Catal A General 2006;303:96–102.
[29] Shimizu K, Sugino K, Kato K. Reaction mechanism of H_2-promoted selective catalytic reduction of NO with C_3H_8 over Ag-MFI zeolite. J Phys Chem C 2007;111:6481–7.
[30] Furfori S, Russo N, Fino D, Saracco G, Specchia V. NO SCR reduction by hydrogen generated in line on perovskite-type catalysts for automotive diesel exhaust gas treatment. Chem Eng Sci 2010;65:120–7.
[31] Huai L, Wang H, He C, Wen H. Effect of subsurface oxygen on selective catalytic reduction of NO by H_2 on Pt(100): a first-principles. Study J Phys Chem C 2015;119:24819–26.
[32] Xu C, Sun W, Cao L, Yang J. Highly efficient Pd-doped ferrite spinel catalysts for the selective catalytic reduction of NO with H_2 at low temperature. Chem Eng J 2016;289:231–8.
[33] Li J, Wu G, Guan N, Li L. NO selective reduction by hydrogen over bimetallic Pd–Ir/TiO_2 catalyst. Catal Commun 2012;24:38–43.
[34] Park SM, Kim MY, Kim ES, Han HS, Seo G. H_2-SCR of NO on Pt–MnO_x catalysts: reaction path via NH_3 formation. Appl Catal A General 2011;395:120–8.
[35] Rodriguez GC, Kelm K, Saruhan B. H_2-selective catalytic reduction of NOx activity and microstructural analysis of new $BaTi_{0.95}Pd_{0.05}O_3$ catalyst. Appl Catal A General 2010;387:173–84.
[36] Wang L, Yin C, Yang RT. Selective catalytic reduction of nitric oxide with hydrogen on supported Pd: enhancement by hydrogen spillover. Appl Catal A General 2016;514:35–42.
[37] Breen JP, Burch R, Hill CJ. NO_x storage during H_2 assisted selective catalytic reduction of NO_x reaction over a Ag/Al_2O_3 catalyst. Catal Today 2009;145:34–7.
[38] More PM. Effect of active component addition and support modification on catalytic activity of Ag/Al_2O_3 for the selective catalytic reduction of NO_x by hydrocarbon–a review. J Environ Manag 2017;188:43–8.
[39] Lee DH, Lee J, Kim K, Song Y, Kim E, Han H. Hydrogen in plasma-assisted hydrocarbon selective catalytic reduction. Int J Hydrogen Energy 2012;37:3225–33.
[40] Yu Q, Richter M, Kong F, Li L. Selective catalytic reduction of NO by hydrogen over Pt/ZSM-35. Catal Today 2010;158:452–8.
[41] Schott FJP, Balle P, Adler J. Reduction of NO_x by H_2 on Pt/WO_3/ZrO_2 catalysts in oxygen-rich exhaust. Appl Catal B Environ 2009;87:18–29.
[42] Abu-Jrai A, Tsolakis A. The effect of H_2 and CO on the selective catalytic reduction of NO_x under real diesel engine exhaust conditions over Pt/Al_2O_3. Int J Hydrogen Energy 2007;32:2073–80.
[43] Gu H, Chun KM, Song S. The effects of hydrogen on the efficiency of NO_x reduction via hydrocarbon-selective catalytic reduction (HC-SCR) at low temperature using various reductants. Int J hydrogen energy 2015;40:9602–10.
[44] Burch R, Coleman MD. An investigation of the NO/H_2/O_2 reaction on noble-metal catalysts at low temperatures under lean-burn conditions. Appl Catal B Environ 1999;23:115–21.
[45] Park SM, Jang H, Kim ES, Han HS, Seo G. Incorporation of zirconia onto silica for improved Pt/SiO_2 catalysts for the selective reduction of NO by H_2. Appl Catal A: General 2012;427–428:155–64.
[46] Liu Z, Lu Y, Yuan L, Ma L. Selective catalytic reduction of NO_x with H_2 over WO_3 promoted Pt/TiO_2 catalyst. Appl Catal B Environ 2016;188:189–97.
[47] Kalamaras CM, Olympiou GG, Parvulescu VI, Cojocaru B, Efstathiou AM. Selective catalytic reduction of NO by H_2/C_3H_6 over $Pt/Ce_{1-x}ZrxO_{2-\delta}$: the synergy effect studied by transient techniques. Appl Catal B Environ 2017;206:308–18.
[48] Burch S, Scire S. An investigation of the mechanism of the selective catalytic reduction of NO on various metal/ZSM-5 catalysts: reactions of H_2/NO mixtures. Catal Lett 1994;27:177–86.
[49] Wu P, Li L, Yu Q, Wu G, Guan N. Study on Pt/Al-MCM-41 for NO selective reduction by hydrogen. Catal Today 2010;158:228–34.
[50] Li L, Zhang F, Guan N, Schreier E, Richter M. NO selective reduction by hydrogen on potassium titanate supported palladium catalyst. Catal Commun 2008;9:1827–32.
[51] Qi G, Yang RT, Rinaldi FC. Selective catalytic reduction of nitric oxide with hydrogen over Pd-based catalysts. J Catal 2006;237:381–92.
[52] Huai L, He C, Wang H, Wen H. NO dissociation and reduction by H_2 on Pd (111): a first-principles study. J Catal 2015;322:73–83.
[53] Martin JC, Suarez S, Yates M, Avila P. Pd/c–Al_2O_3 monolithic catalysts for NO_x reduction with CH_4 in excess of O_2: effect of precursor salt. Chem Eng J 2009;150:8–14.
[54] Sitshebo S, Tsolakis A, Theinnoi K. Promoting hydrocarbon-SCR of NOx in diesel engine exhaust by hydrogen and fuel reforming. Int J Hydrogen Energy 2009;34:7842–50.
[55] Klingstedt F, Arve K, Eranen K, Murzin D. Toward improved catalytic low-temperature NO_x removal in diesel-powered vehicles. Acc Chem Res 2006;39:273–82.
[56] Sawabe K, Hiro T, Shizimu K, Satsuma A. Density functional theory calculation on the promotion effect of H_2 in the selective catalytic reduction of NO_x over Ag–MFI zeolite. Catal Today 2010;153:90–4.
[57] Richter M, Bentrup U, Eckelt R, Schneider M, Pohl M, Fricke R. The effect of hydrogen on the selective catalytic reduction of NO in excess oxygen over Ag/Al_2O_3. Appl Catal B: Environ 2004;51:261–74.
[58] Theinnoi K, Sitshebo S, Houel V, Rajaram RR, Tsolakis A. Hydrogen promotion of low-temperature passive hydrocarbon-selective catalytic reduction (SCR) over a silver catalyst. Energy Fuels 2008;22:4109–14.
[59] Zhang X, Yu Y, He H. Effect of hydrogen on reaction intermediates in the selective catalytic reduction of NO_x by C_3H_6. Appl Catal B Environ 2007;76:241–7.
[60] Stakheev AY, Pributkov PV, Dahl S, Gekas I. Two reaction pathways in the selective catalytic reduction of NO_x by C_6H_{14} over Ag–Al_2O_3 with H_2 co-feeding. Top Catal 2009;52:1821–5.