

1 Performance analysis on a novel self-adaptive sorption system to 2 reduce nitrogen oxides emission of diesel engine

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6 **Abstract:** A novel self-adaptive sorption system is proposed and analyzed, which is considered as an
7 alternative solution to reduce nitrogen oxides emission. Compared with conventional selective catalytic
8 reduction technology, urea solution tank is replaced with sorption reactor for ammonia storage.
9 Composite sorbents are developed with expanded natural graphite treated with sulfuric acid as the
10 matrix. Different sorption working pairs are selected for evaluating working performance of novel
11 system based on the testing nitrogen oxides emission of a diesel engine. It is indicated that for
12 operation mode 8, the highest required mass of urea solution per hour could reach 1.9 kg, which is 2.32
13 times higher than that of composite ammonium chloride. For different composite sorbents, annual
14 required mass ranges from 143 kg to 246 kg and 81 kg to 140 kg in terms of mode 8 and 6 whereas
15 annual required volume is in the range from 358 L to 615 L and 204 L to 350 L, respectively. Cost of
16 novel sorption system by using composite sorbents is generally lower than that of conventional system
17 by using urea solution. It analyzes the feasibility of novel self-adaptive sorption system, which reveals
18 great potential for reducing nitrogen oxides emission.

19
20 **Keywords:** Selective catalytic reduction, Sorption, Composite sorbents, Expanded natural graphite

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21 Nomenclature

BSFC	Brake specific fuel consumption
DSG	Data system group
EGR	Exhaust gas recirculation
ENG-TSA	Expanded natural graphite treated with sulfuric acid
ESC	European stationary cycle
MTS	Middle temperatue salt
LCPD	Large combustion plant directive
LTS	Low temperatue salt
NO _x	Nitrogen oxides
Q	Heat (kW)
SCR	Selective catalytic reduction

22 Greek letters

ΔH	Reaction ethalpy ($\text{J}\cdot\text{mol}^{-1}$)
ΔS	Reaction entropy ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
Δx	Cycle sorption capacity ($\text{kg}^{-1}\cdot\text{kg}^{-1}$)

23 Subscripts

am	Ammonia
c	Cycle
de	Desorption
e	Experiment
eva	Evaporation
s	Sorption
sor	Sorbent
v	Variation

24

25 1. Introduction

26 It is widely acknowledged that vehicle emission is a main source of urban air pollution, which has become
27 a hot topic of environmental protection and energy saving[1]. To deal with this urgent issue, two main methods
28 have been investigated to reduce nitrogen oxides (NO_x) of diesel engine, which have drawn a burgeoning
29 number of attentions. One is to reduce NO_x by decreasing oxygen concentration and combustion temperature
30 through exhaust gas recirculation (EGR)[2, 3]. The disadvantage of this method is that combustion efficiency of
31 diesel engine will simultaneously be influenced. The other is selective catalytic reduction (SCR) technology by
32 using agent to react with NO_x , which is initially applied in thermal power plant[4]. Compared with EGR
33 technology, SCR has gradually become the mainstream in reducing NO_x due to its excellent selectivity with high
34 combustion efficiency remained[5].

35 32.5% aqueous urea solution (adblue) is often used as ammonia source for conventional SCR technology,
36 which will result in several interrelated disadvantages such as low ammonia storage density, low NO_x conversion
37 efficiency, urea crystallization and relatively high cost[6]. Low ammonia storage density implies frequent
38 replenishment of adblue. Low NO_x conversion efficiency usually occurs at low exhaust temperature and easily
39 leads to crystallization. Therefore, research status of urea SCR technology is that various novel catalysts are
40 attempted to further improve NO_x conversion efficiency. Nie et al. developed a novel dispersed $\text{Cu}_y\text{Ti}_1\text{O}_x$ catalyst
41 from Cu-Ti- CO_3 layered double hydroxides, which was able to reach a high NO_x conversion of 88.9% at
42 200°C [7]. A novel catalyst with a core-shell structure was prepared by a chemical deposition method for
43 low-temperature SCR. It was indicated that the catalyst exhibited a relatively high NO conversion rate in the
44 temperature range from 110°C to 220°C [8]. Zhao et al. investigated the performance of Cu-beta zeolite SCR
45 catalyst with Ce and Nb as additives for diesel particulate filter system. Results revealed that the additives
46 greatly improved NO_x conversion efficiency when compared with that without additives[9].

47 Nonetheless, improvement of NO_x conversion efficiency by using novel catalysts tends to be limited when

48 considering temperature application range[10]. This is mainly because urea SCR technology doesn't change in
49 terms of its working mechanism by injecting adblue into the converter directly. It is desirable to develop a novel
50 alternative SCR technology for further improving NO_x conversion efficiency[11]. Solid-gas sorption technology
51 driven by the heat has been recognized as a prospective energy conversion technology, which manifests various
52 functions of refrigeration[12], heat pump[13], energy storage[14] and electricity generation[15]. No relevant
53 research is reported to apply solid-gas sorption technology to NO_x reduction of diesel engine. As a typical
54 sorption type, chemisorption is characterized as monovariant reaction process and large sorption capacity, which
55 could be flexibly adjusted to external conditions by using different metal halides[16]. Interaction between
56 ammonia and metal halides provides a stable ammonia storage method, which is possible to be applied for NO_x
57 reduction technology of diesel vehicles. Different sorption working pairs have been investigated by various
58 researchers[17]. Among them, CaCl₂-NH₃ working pair has been widely investigated for sorption kinetics due to
59 its good thermal stability and large sorption capacity[18]. Similar with CaCl₂-NH₃, SrCl₂-NH₃ is another good
60 selection for sorption SCR technology due to proper equilibrium desorption and sorption temperature[19]. One
61 remarkable fact is that granular metal halides usually have low sorption and desorption capacity due to the fact
62 that heat and mass transfer performance will be attenuated by swelling and agglomeration in working processes.
63 Lower sorption and desorption capacity increase the required mass of sorption SCR system, which will
64 inevitably result in excessive load for the vehicle. Composite sorbent is a common solution to overcome
65 drawbacks of granular metal halides by improving thermal conductivity and permeability, which will be
66 conducive to its sorption and desorption capacity[20]. Recently, expanded natural graphite treated with sulfuric
67 acid (ENG-TSA) had proved to be a good matrix for metal halides, which enhanced heat and mass transfer
68 without performance attenuation[21, 22].

69 This paper aims to propose and evaluate novel self-adaptive sorption SCR system to reduce NO_x of diesel

70 engine. The operating principle and conceptual design of sorption SCR based on chemisorption processes are
 71 firstly introduced, and various sorption working pairs are adopted to verify the feasibility of this technology
 72 based on emission results of a diesel engine. Composite sorbents are developed with ENG-TSA as the matrix for
 73 better sorption and desorption capacity. Performance of novel self-adaptive sorption SCR system is analyzed and
 74 compared in terms of working modes, cost, required mass and volume.

75

76 **2. Diesel engine testing**

77 Fig.1 indicates the diagram of diesel engine bench for NO_x measurement, in which Fig.1a shows the
 78 schematic whereas Fig.1b displays the photo of experimental set-up. The testing rig is mainly composed of a
 79 diesel engine, a fuel system, a dynamometer, an intercooler, a turbo-charger and exhaust gas analysers. A
 80 heavy-duty diesel engine ISBe 5 is investigated, which is coupled with an eddy current dynamometer, and
 81 detailed information is indicated as in Table 1. A data acquisition system provided by data system group (DSG)
 82 is used to control and analyse engine performance, i.e. power, torque, brake specific fuel consumption (BSFC). A
 83 common rail with four solenoid injectors are adopted to control pressure and mass of oil injection, and
 84 temperature of air intake is controlled by intercooler. After combustion process, all exhausts are measured by
 85 HORIBA MEXA 1600D gas analyser and solid particles are counted by HORIBA MEXA 1000 SPCS.

86 To increase the reliability of the measurements, all performance parameters are recorded under steady state
 87 working conditions, which indicates that diesel engine has run for more than 30 minutes under warming-up
 88 mode in advance. Also worth noting that all the experiments are operated under the condition of 990 mbar
 89 ambient pressure and 40% relative humidity. Different operation modes are investigated and compared according
 90 to European stationary cycle (ESC) as shown in Table 2. The rotation speed is classified into three levels, which
 91 are 1680 rpm, 1810 rpm and 1940 rpm. The load is selected in the range from 25% to 100%.

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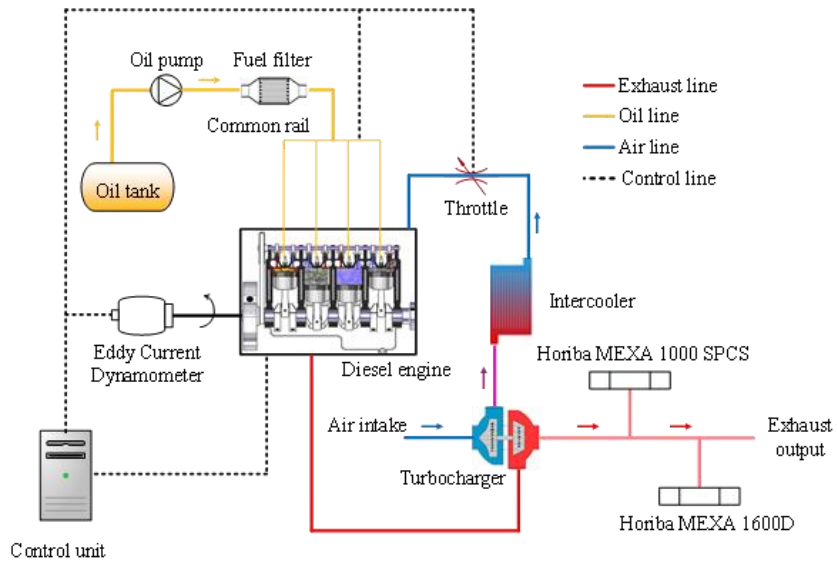
93 Table 1. Specification of diesel engine ISBe 5.

Specification	Explanations
Type	Vertical-inline, turbo-charged, water cooling, 4-stroke
Cylinder	4
Chamber	ω type
Displacement	4.5 L

Bore × Stroke	107 mm × 124 mm
Max. power	152 kW@2300 rpm
Max. torque	760 Nm@1400 rpm
Compression ratio	17.3
Emission standard	Euro V

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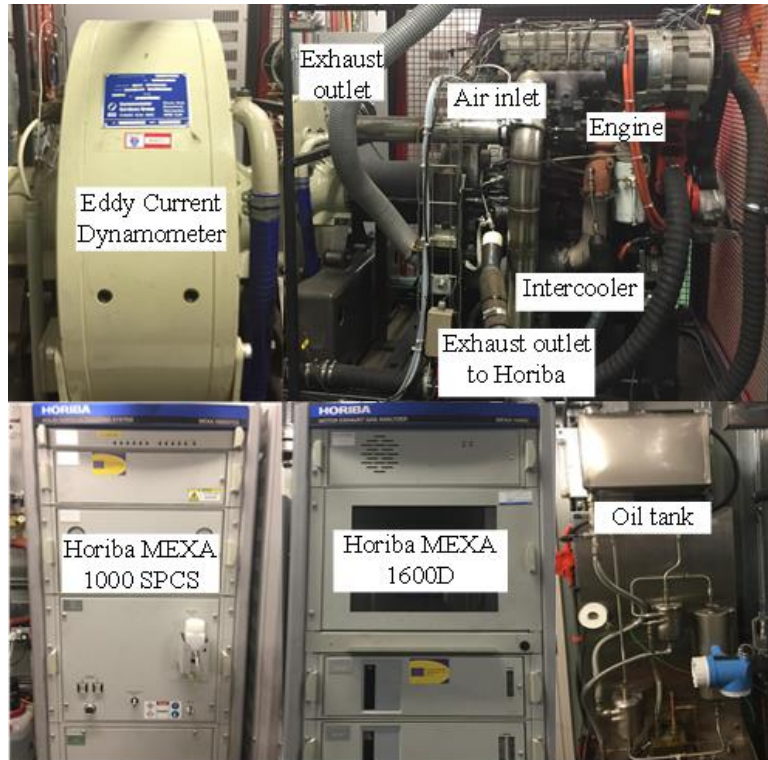


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(a)



(b)

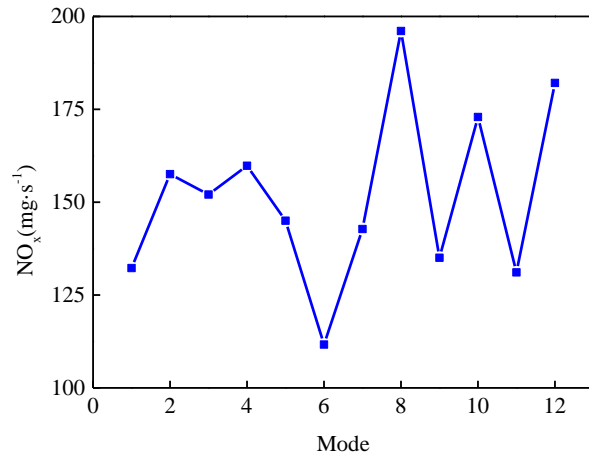
Fig.1. Diagram of engine test bench (a) schematic; (b) photo.

Table 2. European stationary cycle (ESC) test modes.

Mode	Engine Speed	Load %	Weight %	Duration
1	1680	100	8	2 minutes
2	1810	50	10	2 minutes
3	1810	75	10	2 minutes
4	1680	50	5	2 minutes
5	1680	75	5	2 minutes
6	1680	25	5	2 minutes
7	1810	100	9	2 minutes
8	1810	25	10	2 minutes
9	1940	100	8	2 minutes
10	1940	25	5	2 minutes
11	1940	75	5	2 minutes
12	1940	50	5	2 minutes

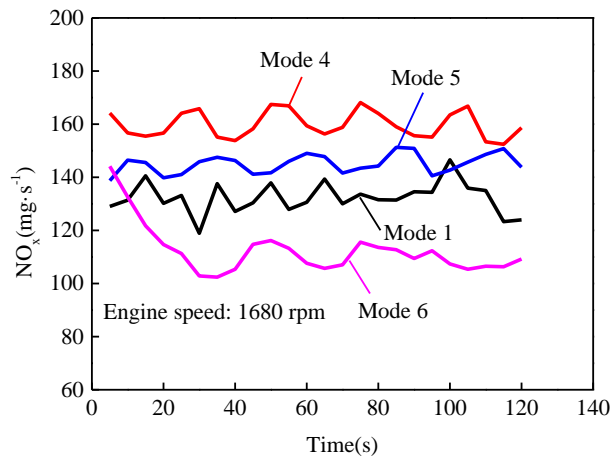
106 Fig.2 indicates overall NO_x emission under the condition of 12 different operation modes. According to
107 large combustion plant directive (LCPD, 2001/80/EC)[23], unit of NO_x emission is usually defined as mg·m⁻³,
108 while unit of exhaust flow rate of engine is used as L·h⁻¹. Thereby unit of NO_x emission could be transferred to
109 mg·s⁻¹ in this study. It is indicated that the highest NO_x emission is able to reach 196 mg·s⁻¹ in mode 8 whereas
110 the lowest NO_x emission is 112 mg·s⁻¹ in mode 6. These two modes are operated in the same load (25%), NO_x
111 emission increases with the increase of speed. This is mainly because fuel consumption increases with engine
112 speed in the same brake mean effective pressure. In the whole ESC cycle, NO_x emission is proportional to fuel
113 consumption and exhaust flow rate, respectively. Fuel consumption in mode 6 is the lowest due to the lowest
114 load and speed have been defined in this mode, thus NO_x emission also reaches the lowest value. Comparably,
115 the maximum NO_x emission is observed in mode 8 due to the fact that it works with the highest exhaust flow rate
116 in all modes.

117 Fig.3 demonstrates instantaneous NO_x emission, which is classified into Fig.3a, Fig.3b and Fig.3c in terms
118 of different engine speeds. It is worth noting that instantaneous NO_x emission is almost within a certain range
119 which displays a small fluctuation in the same working mode. Fig.3a presents results obtained from constant
120 speed of 1680 rpm in four engine loads. NO_x emission in mode 4, mode 5 and mode 1 indicates similar trends,
121 while result in mode 6 is a little different from the other three, which decreases sharply at the initial stage due to
122 the fact that fuel consumption is relative high in previous operation mode. Also worth noting that the lower
123 engine load (25%) works at a higher air-fuel ratio, and stoichiometric burning decreases with the increase of
124 air-fuel ratio, which reduces combustion temperature[24]. If combustion temperature is below 2000 K, NO_x
125 emission will be relatively low in mode 6[25]. Comparably, NO_x emission (mg·s⁻¹) in mode 8 reach the highest
126 instantaneous value with constant speed of 1810 rpm as shown in Fig.3b. Although the same of 25% load is
127 conducted with a lower NO_x emission (ppm), exhaust flow rate is quite high which results in the highest NO_x
128 emission (mg·s⁻¹). Results in mode 2, 3 and 7 are mutually close. Fig.3c shows similar trends of four different
129 operation modes with a speed of 1940 rpm, NO_x emissions in mode 10 and 12 are relatively high throughout the
130 working period since exhaust flow rate in these two modes increases with the decrease of load. In contrast,
131 results in mode 9 and 11 are relatively low, which fluctuate from 120 mg·s⁻¹ to 140 mg·s⁻¹ in high speed and
132 load.



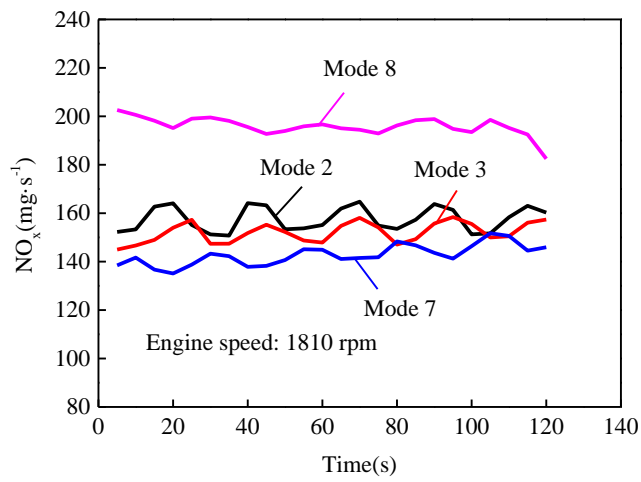
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Fig.2. Overall NO_x emission vs. different operation modes.



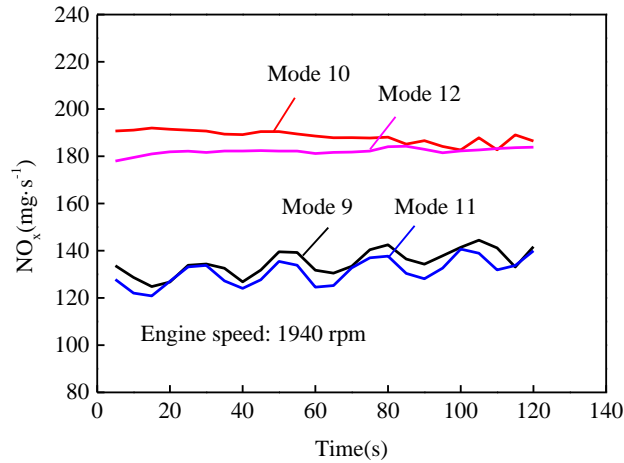
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(a)



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(b)



(c)

Fig.3. Overall NO_x emission vs. different operation modes (a) 1680 rpm; (b) 1810 rpm; (c) 1940 rpm.

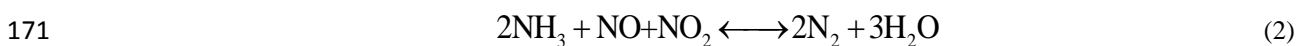
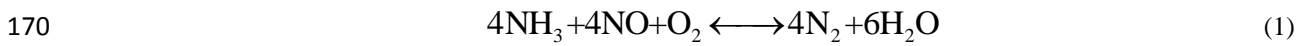
3. Sorption SCR system

3.1. Concept design and operating principle

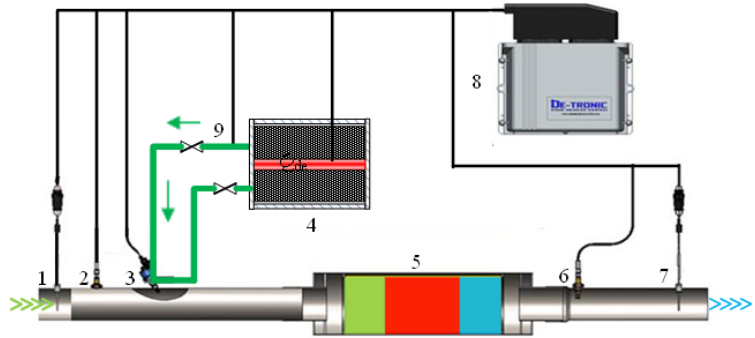
Fig.4 indicates schematic diagram of novel self-adaptive sorption SCR system, which is mainly composed of two temperature and NO_x sensors at the inlet and outlet of SCR catalytic converter, an ammonia nozzle, a SCR catalytic converter, a pressure sensor, an electric control unit and an ammonia storage reactor. The same position of adblue tank in conventional urea SCR system could be used for ammonia storage reactor. Structure of ammonia storage reactor is indicated in Fig.5. Composite sorbent will be compressed into the reactor with middle heater remained and mass transfer channel surrounded. Compared with adblue tank, it is worth noting that the biggest advantage of novel sorption SCR system is that adblue pump won't be required for ammonia storage reactor due to the fact that chemical sorption is characterized as monovariant process, which is flexible to adjust the outlet pressure of ammonia. Working processes of sorption SCR system for reducing NO_x are partially similar with sorption refrigeration which are as follows:

- (1) Desorption process for reducing NO_x (as shown in Fig.4a): When the outlet NO_x concentration of SCR catalytic converter is higher than a standard value, electric control unit will operate the heater to heat ammonia storage reactor with heat input of Q_{de} . Thus pressure of the reactor will be increased to eject ammonia through nozzle. Ammonia will be first mixed and then react with NO_x in the converter. The main reaction processes between NO_x and ammonia could be referred to equations 1-2. Electric control unit adjusts the injection capacity in this working process until NO_x emission concentration is in the standard range. The remained ammonia will be recovered to the reactor.

163 (2) Sorption process for ammonia storage (as shown in Fig.4b): When ammonia in the storage reactor is
 164 almost depleted, the reactor will be taken out and replenished through the sorption process. Ammonia
 165 storage reactor and liquid ammonia tank will be mutually connected. In this process, ammonia reactor
 166 will be immersed and cooled in cooling medium for releasing sorption heat of Q_s . Liquid ammonia tank
 167 is kept at environmental temperature by consuming evaporation heat of Q_{eva} . When composite sorbent
 168 reaches saturated state, sorption storage process will be finished. Ammonia will be stored in form of
 169 chemical potential inside chemical working pair.



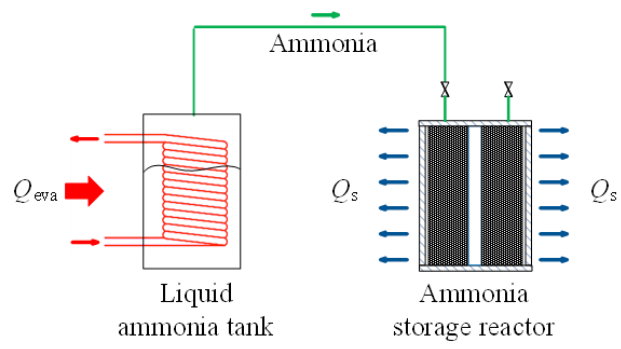
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173 1-Temperature measurement 1; 2-NO_x measurement 1; 3-Nozzle;
 4-Ammonia storage reactor; 5-SCR catalytic converter; 6-NO_x measurement 2;
 7-Temperature measurement 2; 8-Electric control unit; 9-Pressure measurement

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(a)



(b)

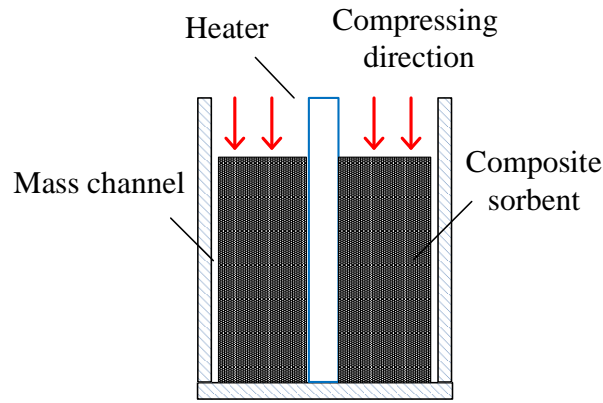
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177 Fig.4. System schematic diagram and working processes of sorption SCR system (a) desorption process; (b)

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sorption process.



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Fig.5. Schematic of ammonia storage reactor.

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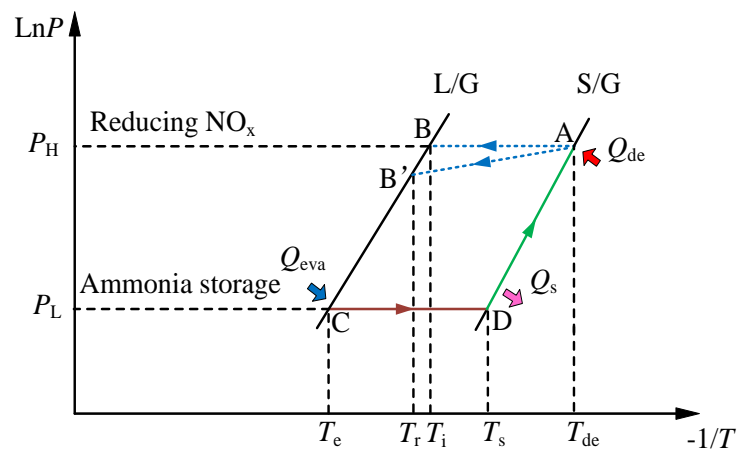
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Fig.6 indicates P - T schematic diagram of working processes of novel sorption SCR system, which are in accord with that shown in Fig.4. In desorption process for reducing NO_x , ammonia storage reactor will be heated with heat input of Q_{de} at temperature T_{de} , which happens at point A. Ammonia will be desorbed and injected into the exhaust pipe through ammonia nozzle, reacting with NO_x in catalytic converter. It is acknowledged that theoretical equilibrium desorption process proceeds from point A to point B. However, real desorption process is non-equilibrium process, which probably happens from point A to point B'. Real desorption processes are displayed with dotted line. In sorption process for ammonia storage, the reactor is cooled by cooling medium to release sorption heat Q_s at temperature of T_s whereas evaporation heat Q_{eva} produced by liquid ammonia tank will be consumed by environmental medium at temperature of T_e . The process happens from point C to point D.



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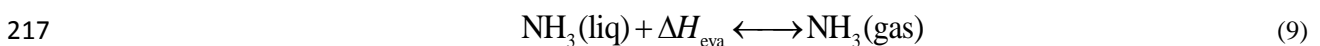
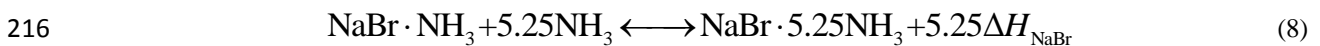
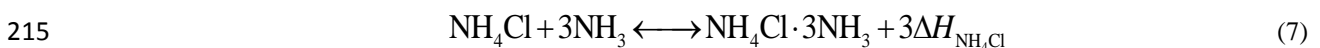
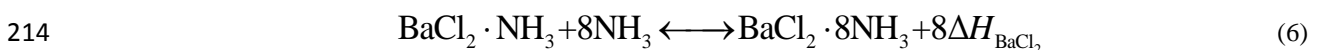
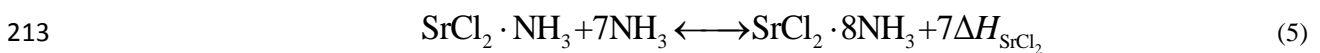
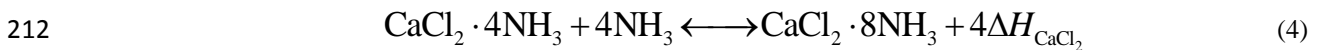
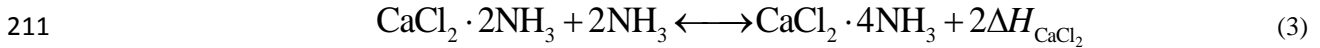
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Fig.6. P - T schematic diagram of working processes of novel sorption SCR system.

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196 *3.2. Material selection*

197 Decomposition temperature of adblue in conventional urea SCR system is about 150-160°C. One
 198 remarkable fact is that crystallization and coking will happen if temperature is not in a suitable range.
 199 Considering working temperature limit of conventional system lower than 150°C, middle temperature salt (MTS)
 200 and low temperature salt (LTS) will be suitable for ammonia storage reactor in novel sorption SCR system. MTS
 201 such as CaCl₂, SrCl₂ and LTS i.e. NH₄Cl, BaCl₂, NaBr will be selected for analyzing system performance due to
 202 their reasonable thermal and chemical characteristics. Chemical reaction processes of these salts with ammonia
 203 could be according to equations 3-9 without considering sorption hysteresis. Table 3 demonstrates main
 204 parameters of selected granular salts in terms of molar mass, equilibrium desorption temperature, reaction
 205 enthalpy, reaction entropy and maximum cycle sorption capacity. To simplify the description of chemisorption
 206 process of different sorbents, descriptions of CaCl₂ 4/2, CaCl₂ 8/4, SrCl₂ 8/1, BaCl₂ 8/0, NH₄Cl 3/0 and NaBr
 207 5.25/0 are used in this paper. For example, CaCl₂ 4/2 represents the process in which CaCl₂ ammoniate reacts
 208 with ammonia from 2 moles to 4 moles. Among these metal halides, CaCl₂ proceeds two reaction processes of
 209 CaCl₂ 8/4 and CaCl₂ 4/2 in selected temperature limit i.e.150°C. Also for chemical working pair, working
 210 pressure is determined by working temperature, which could be according to Clapeyron equation 10.



$$218 \quad \ln(P_{\text{eq}}) = -\frac{\Delta H_{\text{R}}}{RT_{\text{eq}}} + \frac{\Delta S}{R} \quad (10)$$

219

220

Table 3. The main parameters of selected granular salts.

Granular salt	Equilibrium desorption temperature (°C)	Molar mass (kg)	Reaction enthalpy ΔH (J·mol ⁻¹)	Reaction entropy ΔS (J·mol ⁻¹ ·K ⁻¹)	Maximum cycle sorption capacity Δx_{\max} (kg·kg ⁻¹)
CaCl ₂ 4/2	99	110.8	42269	229.7	0.31
CaCl ₂ 8/4	87	110.8	41013	230.1	0.62
SrCl ₂ 8/1	96	158.4	41432	228.6	0.75
BaCl ₂ 8/0	56	208.2	38250	232.4	0.65
NH ₄ Cl 3/0	48	53.4	29433	207.9	0.96
NaBr 5.25/0	51	102.9	35363	225.2	0.87

221

222 Since granular metal halide suffers from swelling andglomeration, composite sorbent is developed to

223 evaluate the performance of novel self-adaptive sorption SCR system for reducing NO_x due to the relatively

224 larger experimental sorption capacity. The developing processes of composite sorbent can be referred to the

225 reference[26]. ENG-TSA is first dried in an oven with a controlled temperature of 120°C. Then ENG-TSA will

226 be mixed with metal halide water solution. After that, mixture of composite sorbent is dried in an oven with a

227 controlled temperature of 120°C to remove the water. Then temperature of oven will be further increased to

228 240°C to remove crystal water of some metal halides. Finally composite sorbent will be compressed into block

229 by pressing machine for testing. Fig.7 indicates theoretical and experimental cycle sorption capacity of different

230 composite sorbents. Experimental results could be referred to our previous work[27, 28] and reference[29] which

231 are all investigated at a working pressure of 4 bar. Although experimental sorption capacity of composite

232 sorbents comes from different tests, it is convinced that these results can be used for analyzing the performance

233 of novel sorption SCR system due to their similar operation conditions and measurement accuracies. It is

234 indicated that composite NH₄Cl has the largest experimental cycle sorption capacity of 0.65 kg·kg⁻¹ whereas

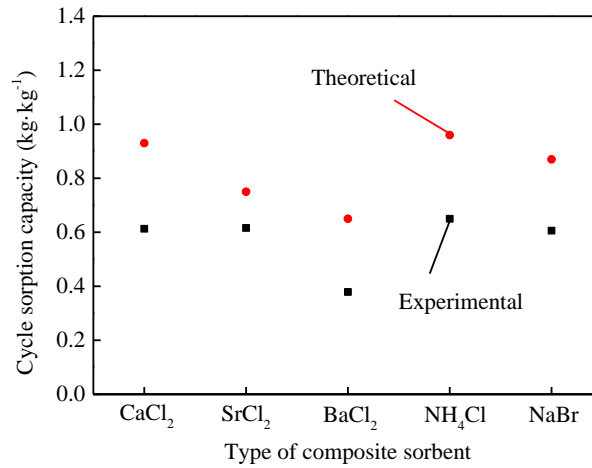
235 composite BaCl₂ shows lowest experimental value of 0.381 kg·kg⁻¹. Also worth noting that composite SrCl₂ has

236 the smallest difference between theoretical and experimental cycle sorption capacity whereas composite BaCl₂

237 has the largest difference, which is decreased by 41.6%. This is mainly because theoretical sorption capacity

238 could be obtained under equilibrium condition i.e. sufficient reaction duration and temperature difference
 239 whereas non-equilibrium reaction process proceeds in the experiment with limited reaction duration and
 240 temperature difference.

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243 Fig.7. Theoretical and experimental cycle sorption capacity of different composite sorbents.

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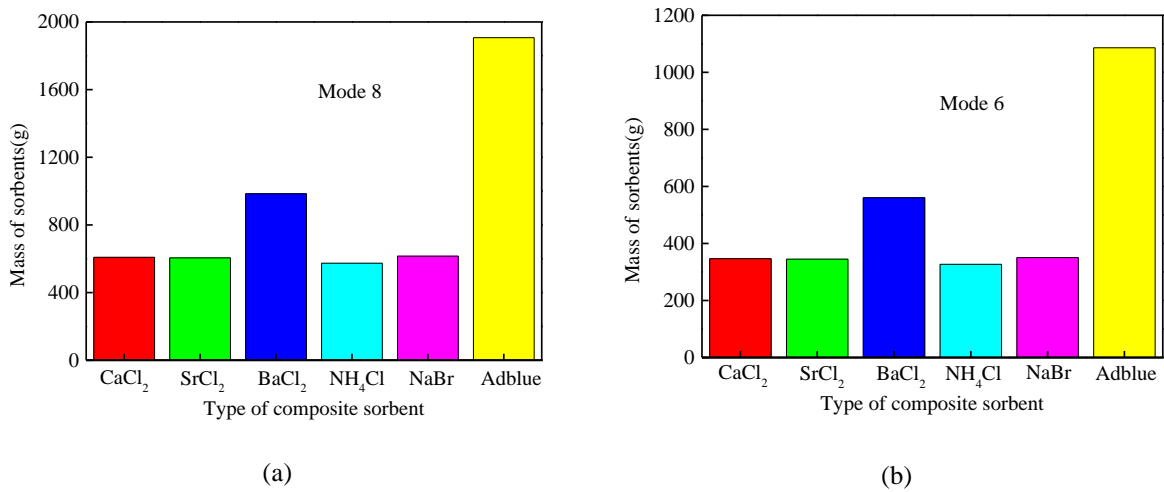
245 *3.3. Performance analysis*

246 Since operation mode 8 and 6 of experimental diesel engine indicate the highest and lowest value of NO_x
 247 emission, these two working conditions are exemplified for further illustrations based on experimental cycle
 248 sorption capacity of composite metal halides. Fig.8 shows the required mass per hour of different composite
 249 sorbents and adblue when diesel engine operates in mode 8 and 6 for an hour, which is evaluated by equation 11.
 250 It is worth noting that the required mass per hour of adblue is much higher than that of different composite
 251 sorbents. Results show that in mode 8 the lowest required mass per hour is 0.57 kg by using composite NH₄Cl. It
 252 is also observed that the highest required mass of adblue per hour is able to reach 1.9 kg, which is 2.32 times
 253 higher than that of composite NH₄Cl. Composite BaCl₂ shows the highest required mass per hour of 0.98 kg due
 254 to the fact that it has the lowest experimental cycle sorption capacity, which still accounts for only half of the
 255 required mass of adblue. For different composite sorbents, the required mass per hour ranges from 0.57 kg to
 256 0.98 kg and 0.33 kg to 0.56 kg in terms of mode 8 and 6, respectively.

257

$$m_{\text{sor}} = \frac{m_{\text{am}}}{\Delta x_c} \quad (11)$$

258 where m_{am} is mass of ammonia (kg), Δx_c is the difference between sorption and desorption capacity ($\text{kg}^{-1}\cdot\text{kg}^{-1}$).
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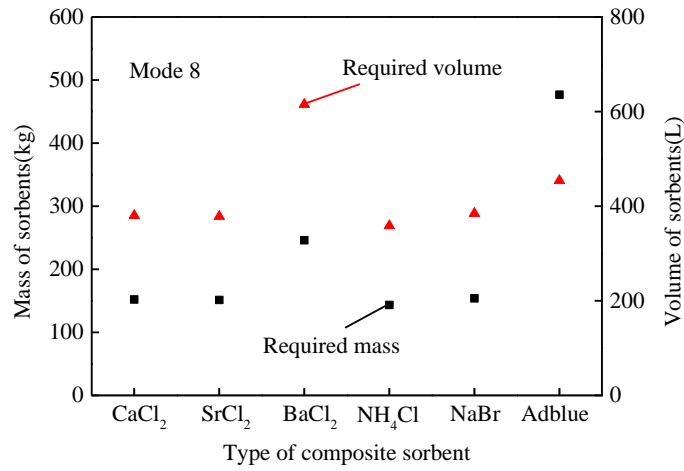
260 Fig.8. The required mass per hour vs. different composite sorbents (a) mode 8; (a) mode 6.

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262 Assuming that ammonia storage reactor is replaced and filled annually, total annual required mass and
 263 volume of composite sorbents and adblue will be important parameters which determine the size of storage
 264 reactor for vehicles. Annual required mass and volume rather than total mass and volume in different operation
 265 modes are used for further elaboration due to the fact that the reactor maybe replenished for every few years i.e.
 266 more than one year, which are demonstrated in Fig.9. It is indicated that annual required mass of composite
 267 sorbents is much less than that of adblue which is similar with that of required mass per hour. One remarkable
 268 fact is that annual required volume of composite BaCl₂ is higher than that of adblue. This is mainly because
 269 composite BaCl₂ has the lowest experimental sorption capacity. Another reason is because density of adblue is
 270 relatively higher than that of composite sorbents. Results also demonstrate that in mode 8 the highest annual
 271 required volume of adblue could reach 454 L, which is 26.6% higher than that of composite NH₄Cl. For different
 272 composite sorbents, annual required mass ranges from 143 kg to 246 kg and 81 kg to 140 kg in terms of mode 8
 273 and 6 whereas annual required volume is in the range from 358 L to 615 L and 204 L to 350 L, respectively. The
 274 maximum annual required mass and volume should be considered for real design due to the limited size of diesel

275 vehicle.

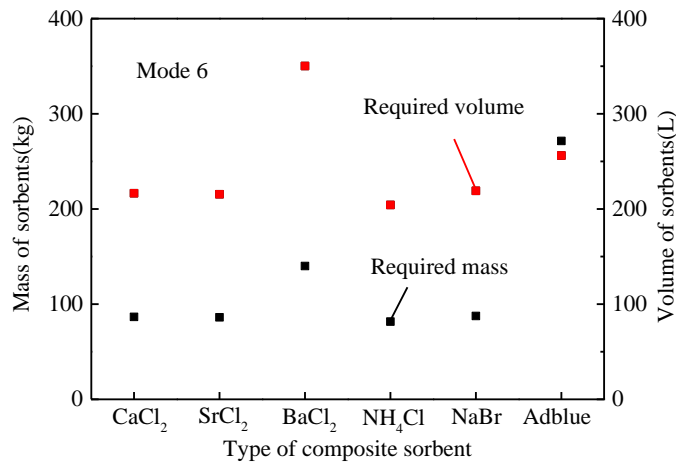
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277

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(a)



279

280

(b)

281 Fig.9. Annual required mass and volume of sorption SCR system (a) mode 8; (a) mode 6.

282

283 Table 4 demonstrates a comprehensive comparison between novel self-adaptive sorption SCR system and

284 conventional urea SCR system in terms of system compactness, energy input, mechanical stability, thermal

285 stability, NO_x conversion efficiency and total cost. Since less annual required mass and volume could be

286 obtained by novel sorption SCR system, system compactness will be further improved. Less mass of sorption

287 SCR system will also reduce fuel consumption while the reduced system volume provides more flexibility of

288 apparatus arrangement.

289 Also worth noting that electricity is mainly used for the pump of urea SCR system whereas novel sorption
290 SCR system could use electric heater separately or use both electric heater and exhaust gas to heat ammonia
291 storage reactor. If combined electric and exhaust heating is adopted, electric heater will be used for heating the
292 reactor at the initial stage of starting diesel engine for reducing NO_x emissions since exhaust temperature is not
293 reach desorption temperature of composite sorbent. For stable operating condition of diesel engine, sorption
294 reactor will be heated by exhaust gas for desorption. Although layout of novel system is required to be
295 rearranged, a combined mode will not only reduce NO_x emission but also improve energy efficiency. As for
296 mechanical and thermal stability, solid-gas sorption reaction by using composite sorbent is flexible to adjust the
297 constant working pressure of ammonia, which also has a higher ammonia content than adblue (Theoretical
298 ammonia content is about 18.42% in terms of 32.5% standard adblue). Problems such as crystallization or
299 coking will be solved by supplying ammonia into the converter directly rather than adblue, which could
300 remarkably improve NO_x conversion efficiency of the system. Also pump will be removed from novel sorption
301 SCR system, which reduces system complexity.

302 With regard to system cost, novel self-adaptive sorption SCR system will be compared with that of urea
303 SCR system, which is calculated based on Chinese currency (RMB) as shown in Fig.10. $\text{NO}_{x,v}$ represents the
304 variant i.e. variable NO_x emission of different diesel engines whereas $\text{NO}_{x,e}$ refers to NO_x emission in the
305 experiment of this paper. Ratio between $\text{NO}_{x,v}$ and $\text{NO}_{x,e}$ is defined to illustrate the cost for different NO_x
306 emissions, which possibly implies different types of diesel vehicles. E.g. when the ratio between $\text{NO}_{x,v}$ and $\text{NO}_{x,e}$
307 is 0.9, it is indicated that NO_x emission is 0.9 times as high as that in this paper, which may represent a smaller
308 diesel vehicle under the same operation condition.

309 As Fig.10 shows, cost of novel sorption SCR system by using composite NH_4Cl is much higher than that by

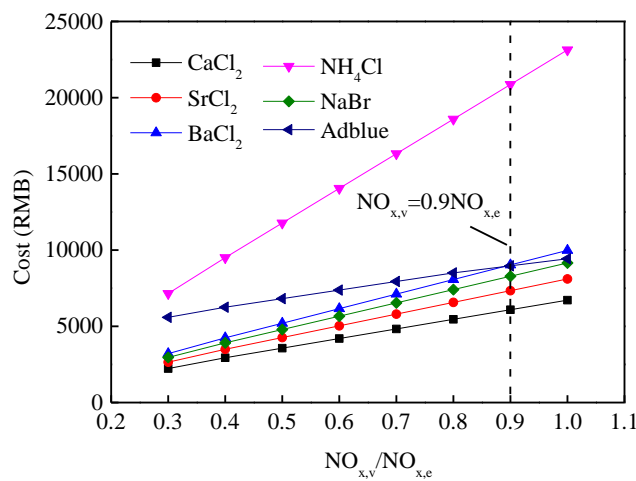
310 using other composite sorbents and adblue due to the higher price of granular NH_4Cl . Therefore, composite
 311 NH_4Cl is not suitable to be selected for novel sorption SCR system in spite of its high cycle sorption capacity.
 312 Also worth noting that cost of sorption SCR system by using other four composite sorbents will be lower than
 313 that by using adblue when the ratio is lower than 0.8. When the ratio is higher than 0.8, cost of the system by
 314 using composite BaCl_2 will be a little higher than that using adblue due to its relatively low cycle sorption
 315 capacity. Ratio between $\text{NO}_{x,v}$ and $\text{NO}_{x,e}$ is selected in the range from 30% to 100%, which almost includes
 316 diesel engines from small type to heavy duty type with regard to different kinds of vehicles. Considering cost
 317 and system compactness, composite CaCl_2 and SrCl_2 will be desirable sorbents for novel sorption SCR system to
 318 reduce NO_x emission of diesel engine.

319

320 Table 4. Comparison between sorption SCR and urea SCR system for reducing NO_x .

Type	System compactness	Energy input	Mechanical Stability	Thermal Stability	NO_x conversion efficiency	Cost
Sorption	High	Electricity /Exhaust heat	High	High	High	Low
Adblue	Moderate	Electricity	Moderate	Moderate	Moderate	Moderate

321



322

323 Fig.10. Cost comparison between sorption SCR system of different composite sorbents and adblue.

324

325 4. Conclusions

326 A novel self-adaptive sorption SCR system is proposed to reduce NO_x of diesel engine. Various
327 chemisorption working pairs are selected to investigate this technology base on emission results of a diesel
328 engine, which is operated in 12 different working modes. Performance of novel system is analyzed and
329 compared by using different composite sorbents and adblue. Conclusions are yielded as follows:

330 [1] NO_x emissions are investigated and compared under the condition of different engine speeds and
331 loads. It is indicated that the highest NO_x emission is able to reach $196 \text{ mg}\cdot\text{s}^{-1}$ in mode 8 whereas the
332 lowest NO_x emission is $112 \text{ mg}\cdot\text{s}^{-1}$ in mode 6. For instantaneous NO_x emission, results in mode 6 and
333 8 are different from the other three modes in their respective speed of engine i.e. 1680 rpm and 1810
334 rpm. When the speed is 1940 rpm, NO_x emissions in mode 10 and 12 are relatively high throughout
335 the working period whereas results in mode 9 and 11 are relatively low, which fluctuate from 120
336 $\text{mg}\cdot\text{s}^{-1}$ to $140 \text{ mg}\cdot\text{s}^{-1}$.

337 [2] It is worth noting that the required mass of adblue is higher than that of composite metal halides.
338 Results show that in mode 8 the highest required mass of adblue per hour could reach 1.9 kg, which is
339 2.32 times higher than that of composite NH_4Cl . For different sorbents, composite BaCl_2 shows the
340 highest required mass per hour. The required mass per hour range from 0.57 kg to 0.98 kg and 0.33 kg
341 to 0.56 kg in terms of mode 8 and 6, respectively.

342 [3] For mode 8 the highest annual required volume of adblue could reach 454 L, which is 26.6% higher
343 than that by using composite NH_4Cl . For different composite sorbents, annual required mass ranges
344 from 143 kg to 246 kg and 81 kg to 140 kg in terms of mode 8 and 6 whereas annual required volume
345 is in the range from 358 L to 615 L and 204 L to 350 L.

346 [4] Cost of sorption system by using composite NH_4Cl is much higher than that using other composite

347 sorbents and adblue, which is not suitable to be selected for novel sorption SCR system. Cost of
348 sorption SCR system by using other four composite sorbents will be lower than that using adblue
349 when ratio between $\text{NO}_{x,v}$ and $\text{NO}_{x,e}$ is lower than 0.8. When the ratio is higher than 0.8, cost of the
350 system by using composite BaCl_2 will be a little higher than that using adblue due to its relatively low
351 sorption capacity.

352 With the deterioration of air quality, haze weather becomes frequent, which has drawn a burgeoning number
353 of attentions. One representative example is north part of China, which suffers from heavy haze in winter.
354 Researches have reported that $\text{PM}_{2.5}$ is a main pollution composition of severe haze weather and reduction of
355 NO_x emissions is a key to control $\text{PM}_{2.5}$. The proposed sorption SCR system will be an alternative method to
356 reduce NO_x emission from vehicles with a high ammonia conversion efficiency by using composite sorbents.
357 With the potentially wide use of this novel technology in the near future, air pollution may gradually improve.

358

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