An investigation into catalysts to improve low temperature performance in the selective catalytic reduction of NO with NH$_3$

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Selective catalytic reduction with NH$_3$ is considered one of the most effective technologies controlling NOx emission. Metal Fe-based catalysts were used in the investigation to improve low temperature performance of NOx conversion. The temperature range studied was between 150°C and 350°C in increments of 50°C. The honeycomb catalysts were prepared by an impregnation method. The study also included characterisation of catalysts by BET, XRD, H$_2$-TPR and XPS methods.

It was found that an increase in metal Fe content from 2 to 6% wt offered an improvement in the catalytic performance. However, a further increase in Fe content resulted in a decrease in its performance. More than 90% NOx conversion rate could be achieved over the Fe-based honeycomb catalyst at a low temperature by doping with different weights of Ni and Zr metals. Amongst all the catalysts studied, the mixed metal catalyst of Fe-Ni-Zr was the one with most potential. This was because of its higher NOx conversion rate at a low temperature and also because of its wider operating temperature window. The effect of gas hourly space velocity (GHSV) was also investigated and the results showed that as GHSV increased, the reduction of NOx decreased.

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1984 and 1990 respectively. He has 24 years experience in the control of noise, vibrations and exhaust gas emissions of power equipment. Since 2006, he had been a vice-president at the University of Harbin Engineering University.

INTRODUCTION

Since the 1970s, diesel engines have dominated the marine market for the provision of propulsion and electrical power. However, international shipping is considered to be a significant source of air pollution. NOx emissions originating from shipping have been estimated to be about 10Mt per annum; approximately 14% of total global NOx emissions from fossil fuels.[1] They contribute to the formation of photochemical smog and acid rain, which produces eutrophication (ie, acidification) of lakes and rivers.

There is worldwide interest in developing efficient catalysts for the removal of NOx from diesel engine exhaust systems. Selective catalytic reduction (SCR) with ammonia is a well-proven technique for NOx removal in diesel engines. The principal engine manufacturers provide SCR catalysts based on the TiO_2/V_2O_5 and urea solution with efficiencies above 95%.[2]

SCR catalysts used in industrial practice are based on TiO_2, with vanadium oxide as the catalytic active phase. WO_3 and MoO_3 have been reported to be used as promoters.[2,3] The range of operating temperatures of these catalysts is 300°C to 400°C.

For large slow speed diesel engines, the exhaust gas temperatures are often below 300°C after the turbocharger especially at part load. Gas re-heating is often required to ensure high efficiency of the catalytic conversion.

Because of this, there has been a strong interest in developing SCR catalysts that activate at a temperature lower than 300°C. Some transition-metal-contained catalysts have been investigated to improve the low temperature performance of an SCR, such as chromic,[4] $NiSO_4/Al_2O_3$,[5] $MnOx/Al_2O_3$,[6] V_2O_5/carbon-coated monoliths,[7] iron–silica aerogels[8] and MnOx/NaY.[9] The use of these catalysts has shown some improvement in SCR activity at temperatures below 200°C.

Iron-based catalysts have been extensively used in several processes related to NOx elimination, mainly due to their low cost compared with that of noble metals and their good performance with different reducing agents. It has been reported that Fe_2O_3,[10-16] Fe containing oxides[17-19] and Fe-exchanged materials[20-24] have greater SCR activity than other types of catalyst. The process of selective catalytic reduction of NOx at low temperature with ammonia has been investigated with metal Ni[25-28] and the results show that Ni is efficient for the reduction of NOx. ZrO_2 has better thermal stability and sulphur resistance,[29] can be very effective for NOx reduction[30,31] ZrO_2 is seldom used as the catalyst for SCR, but reports[32,33] have shown that a Zr catalyst is durable and highly active for NOx reduction.

With fixed-bed catalysts, large volumes of pellets, or granules, may cause high flow resistance and plugging problem due to particulates being carried over in flue gas stream. In contrast, honeycomb catalysts produce low pressure drops, high surface areas, superior abrasive wear resistance and low tendency to fly ash plugging.[43-45] For these reasons, the honeycomb vanadia–titania catalyst has been used in industry to remove NOx from flue gas.[46] Based on their successful applications, the paper presents a study on the use of ceramic honeycomb structured catalysts. Fe, Fe-Ni, Fe-Ni-Zr catalysts are used to improve the low temperature conversion rate of NOx.

EXPERIMENT

Catalyst preparation

In the laboratory test, a ceramic honeycomb substrate with a chemical composition of $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ was cut into small columns 40mm in length and 8mm in diameter. After pre-treatment with a 40% nitric acid solution, the chosen nitrates were coated to the ceramic honeycomb substrates by an impregnation method. It has been reported that the acid treatment of the substrate exhibits an increased surface area and improved dispersion of active components.[34] The catalysts, eg, substrates coated with metal oxides were tested and analysed, including characterisation examination of the mixed oxides catalysts using X-Ray Diffraction (XRD), Temperature Programme Reduction-H_2 (TPR-H_2) and X- laboratory ray Photoelectron Spectroscopy (XPS) methods. The objective of these analyses was to establish the influence of meso-porosity on the performance of the catalysts prepared.

In this study, three types of catalyst – Fe, mixtures of Fe-Ni, and Fe-Ni-Zr were studied. The catalysts Fe, Ni and Zr were obtained from the mixture of the compounds of $Fe(NO_3)_3$, $Ni(NO_3)_2$ and $Zr(NO_3)_4$ solutions. Firstly, the ceramic honeycomb substrate was immersed in a nitric acid solution at a mass concentration of 40% for about 8 hours to clean its surface. Then the substrate was washed to pH = 7 with distilled water. The treated honeycomb substrate was then dried at 150°C for 8 hours before it was immersed into the aqueous solution of nitrates for a day. Finally, the substrate – saturated by catalyst – was dried at 250°C for 8 hours and calcined in the air at 600°C for 8 hours.

Catalytic activity tests

In the laboratory scale experiment, the honeycomb substrates – coated with different metallic oxides (shown in Table 1) – were tested in a selective reduction reactor under

Catalyst	BET (m²/g)
Fe(4)Ni(0)Zr(0)	131.0
Fe(6)Ni(0)Zr(0)	134.6
Fe(8)Ni(0)Zr(0)	114.1
Fe(6)Ni(1)Zr(0)	185.3
Fe(6)Ni(2)Zr(0)	192.2
Fe(6)Ni(2)Zr(1)	256.2
Fe(6)Ni(2)Zr(2)	252.4

Table 1: BET Surface of catalysts

conditions close to an isothermal axial profile and at various reaction temperatures. The support catalysts are presented by Fe(a)Ni(b)Zr(c), where (a), (b) and (c) represent the weight percentages of Fe, Ni and Zr in the catalysts including the weight of the substrate. The catalyst substrate was weighed to measure the amount of catalyst coated on it. If the quantity of the coated catalysts was not satisfactory, the impregnating process was repeated.

Description of test rig

As shown in Fig 1, urea solution is used to provide gas phase ammonia that is employed by most SCR systems as the reducing agent. The ammonia generated from urea is either anhydrous or aqueous and is vaporised before being supplied to the reactor (SCR).
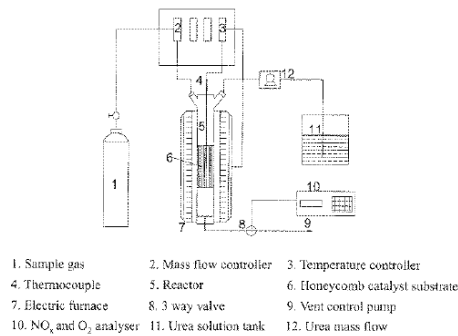

1. Sample gas   2. Mass flow controller   3. Temperature controller
4. Thermocouple   5. Reactor   6. Honeycomb catalyst substrate
7. Electric furnace   8. 3 way valve   9. Vent control pump
10. NO$_x$ and O$_2$ analyser   11. Urea solution tank   12. Urea mass flow

Fig 1: Schematic diagram of testing rig

In the presence of a suitable catalyst, the following processes will take place inside the reactor:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad (1)$$

$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O \qquad (2)$$
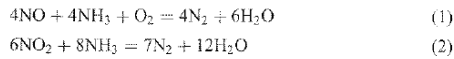
NOx in diesel exhaust gases is typically over 95% of NO and less than 5% of NO$_2$. Therefore, the main reaction of an SCR with ammonia is represented by equation (1), which indicates that one mole of NH$_3$ is required to remove one mole of NO. The presence of a catalyst lowers the required activation energy for the reduction and increases the NO conversion rate.

A laboratory-scale stainless steel fixed-bed reactor (with inner diameter of 10mm and a length of 200mm) was used in the experiment to investigate the activity of each chosen synthetic catalyst in reaction with NH$_3$ at atmospheric pressure. A catalyst substrate of 8mm diameter and 40mm in length was installed inside the reactor for the catalytic testing, as shown in Fig 1. The reaction temperature was maintained by a programmed temperature controller at 150°C to 350°C with increments of 50°C. Every measurement temperature was maintained for 30min before sampling was taken.

Sample gas was prepared to simulate an engine exhaust gas. This comprised 1200 ppm NO, 2% by vol. of O$_2$ balanced by N$_2$, and was fed into the reactor at a flow rate of 180 ml/min controlled by a flowmeter. 10% by mass of urea solution was used to provide the required NH$_3$. The urea solution was injected into the reactor at a flow rate of 0.015 ml/min. It vaporised inside the reactor due to heating and released NH$_3$ to perform the chemical reactions presented in equation 1 and 2.

A gas analyser, model-FGA-4100, was used to measure the concentration of NO and O$_2$ before and after the reactor. The reaction results were evaluated in terms of NOx conversion rate, ie, the ratio of NOx converted via the reactor to the total NOx level before the reactor.

RESULTS AND DISCUSSION

SCR performance with different catalysts

Effect of Fe catalyst
Fig 2 shows the results of NOx conversion rate with Fe as the catalyst. The reaction temperature was from 150 to 350°C. Other test conditions were GHSV= 12000 h^{-1}, NOx = NH$_3$ =1200 ppm, 2.0 vol. % O$_2$, N$_2$ balance.

The balance between dispersion and loading of metal catalysts is a vital factor and affects the catalytic activity directly. Increasing the catalyst loading will result in an aggregation of the catalyst and a decrease in the dispersion. Although low loading is beneficial for a good dispersion, it results in a low number of the active sites over the support and consequently the catalytic performance will be reduced. NOx conversion rates with different Fe loadings are shown in Fig 2.
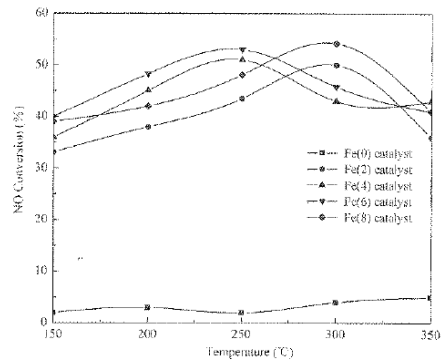

Fig 2: Catalytic performance with Fe catalyst

It was found that at 250°C, the NOx conversion rate increased as the Fe loading increased and reached its maximum at 53% when loading was 6%wt. When the Fe content was 8%wt, the NOx conversion rate was reduced to 43%.

A possible reason for the drop of NOx conversion rate

at a high loading is there might be a clustering of Fe species when its loading is high. This is consistent with the results shown in Table 1, where the BET surface at 8 %wt. of Fe catalyst was significantly small compared with that at 6%wt.

Therefore, the catalysts with 6%wt Fe content were selected for the subsequent experimental work. Fig 2 also shows that the low temperature performance of the catalytic reduction was improved significantly.

Effect of Fe doped with Ni and Zr

Fig 3 represents NO conversion rates with different mixtures of catalysts as a function of reaction temperatures that varied from 150 to 350°C. Other test conditions were GHSV = 12000 per hour, NOx = NH$_3$ =1200 ppm, 2.0vol% O$_2$, N$_2$ balance.

Based on the catalytic results of different Fe loading catalysts, different loadings of metal Ni and Zr were doped into the 6%wt Fe catalyst. As shown in Fig 3, the combination of iron-nickel- zirconium (Fe-Ni-Zr) offered the highest reaction activity amongst the catalysts studied at the full temperature measurement range, with the maximum NOx conversion rate of 95.1% at a temperature of approximately 250°C. The activity of Fe itself was the lowest, reaching its maximum NOx conversion rate of 52% at 250°C. It was observed that the order of activeness of the catalysts for NOx conversion was Fe(6)Ni(2)Zr(2) > Fe(6)Ni(2)Zr(1) > Fe(6)Ni(2) > Fe(6)Ni(1) > Fe(6).
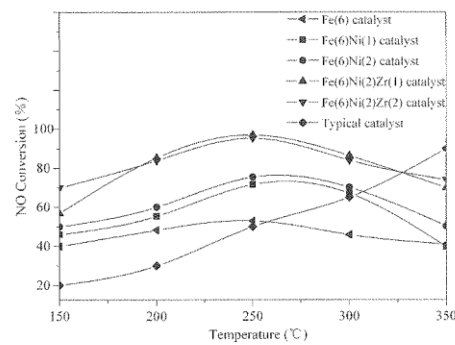

Fig 3: NOx reduction rate with different mixtures of catalysts

The activity of Fe catalyst was substantially lower than that of other Fe based oxides catalysts. Thus, iron alone was unsuitable due to its low activity. The catalysts iron-nickel (Fe-Ni) have an improved activity compared with Fe and the NO conversion increased more rapidly when the temperature was over 200°C, but it then dropped again when the temperature was over 300°C. However, the activity of Fe-Ni catalyst was lower than 50% when the temperature was higher than 300°C. The Fe-Ni catalyst with 2%wt Ni had an increased catalytic performance compared with the

Fe-Ni catalyst with 1%wt Ni. The effect of increasing Ni on the NOx conversion was not obvious. Based on this, the metal Zr was introduced to promote the NOx conversion rate.

After the introduction of Zr, it was found that the Fe-Ni-Zr catalyst had superior activity during the whole temperature window, especially in the lower temperature range. But the NOx conversion of the catalysts dropped slightly when the temperature was over 300°C.

For the purposes of comparison, a widely commercial catalyst (V$_2$O$_5$/WO$_3$)[37] in an SCR system was also presented in Fig 3, where it exhibited a high conversion rate at temperatures above 300°C, However, its low NOx conversion rate was poor.

According to the catalytic results of Fe(6)Ni(2)Zr(2), the catalyst can enhance the NO conversion dramatically at a low temperature.

Effect of gas hourly space velocity (GHSV) on NO conversion

Fig 4 shows catalytic performance of 6%wt Fe catalyst doped with Ni and Zr as a function of GHSV at a temperature of 250°C. Other test conditions were NOx = NH$_3$ = 1200 ppm, 2.0 vol % O$_2$, N$_2$ balance.

Space velocity is defined as the volume ratio of gas flow rate relative to the catalyst volume flow rate, expressed 'per-hour'.

At a constant gas flow rate, space velocity is inversely proportional to catalyst volume such that decreasing catalyst volume corresponds to increasing space velocity.

Typically, an increase in the space velocity decreases the NOx conversion for most catalysts since the net residence time of the gas species over the surface of the catalyst decreases. To some extent, temperature plays a role in determining the degree to which space velocity affects the NOx conversion.[37]

According to the above results, the temperature of best catalytic performance of the investigated catalysts was at 250°C. Thus this temperature was selected to investigate the effort of GHSV on NOx conversion.
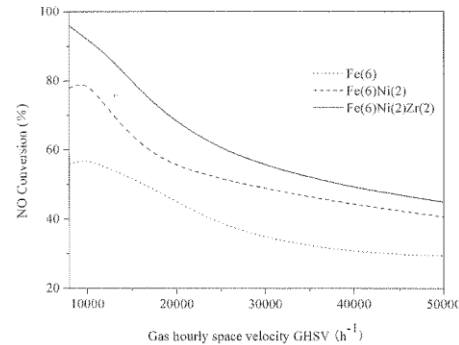

Fig 4: NO reduction rate change with GHSV

Fig 4 shows the effect of space velocity on the conversion rate of NOx. The NOx conversion rate is high when the space velocity is low. This is because a low space velocity property is beneficial for the diffusion, adsorption and reaction of the reactants. It also promotes the desorption and diffusion of reaction products. When the space velocity is high, the contacting time of reactants and catalysts becomes less. This will result in the contacting time of the reactants and the catalyst being insufficient for the catalytic reaction.

Consequently, the NOx conversion rate drops quickly. Therefore it is beneficial to decrease the space velocity for the NOx conversion. However, to achieve a low space velocity for a given engine exhaust system, the size (cross section area and/or length) of the catalyst converter will have to be increased accordingly.

X-ray diffraction

Fig 5 shows the XRD patterns of the pure honeycomb ceramic and that supported with Fe$_2$O$_3$, NiO, ZrO or a mixture of different oxides. All the samples exhibited the typical peaks of the ceramic honeycomb, indicating that the structure of the ceramic honeycomb remained intact after the treatment. Compared with the intensity of the XRD peaks of the bare ceramic honeycomb, the intensity of the peaks of the catalysts under investigation decreased. The reason for this is that the addition of metals caused the dispersion of the elements on the ceramic honeycomb.

As shown in Fig 5, typical lines of Fe catalyst were detected at 23.8°, 33.3°, 35.2°, 49.5° and 64.2°(2θ). These lines were due to the strongest lines of Fe$_2$O$_3$.

The additional lines appear in the XRD pattern of Fe-Ni catalyst at 43.3, 43.5, and 62.7° (2θ). These lines detected to be NiO. In the catalysts of Fe-Ni catalysts, the diffraction peaks of Fe$_2$O$_3$ were observed the same phrase as Fe catalyst,
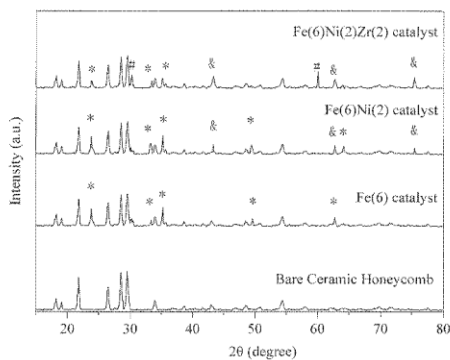
The diffractions at 30.2° and 60° (2θ) due to zirconia

Fig 5: XRD patterns of bare ceramic honeycomb, Fe(6) catalyst, Fe(6)Ni(2) catalyst and Fe(6)Ni(2)Zr(2) catalyst. (*: Fe$_2$O$_3$; &: NiO; #:ZrO$_2$)

phase[31,32] were clearly observed on the Fe-Ni-Zr catalyst sample. It was found that some of the lines of Fe disappeared and the intensity of some Fe$_2$O$_3$ decreased. This suggested that the Zr doping caused the dispersion of Fe and they interacted strongly.

Temperature programme reduction

Temperature programmed reduction (TPR) was used to characterise the ceramic honeycomb supported catalysts as shown in Fig 6. During the TPR process, the reduction sequence of iron oxide is as following Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO →Fe.
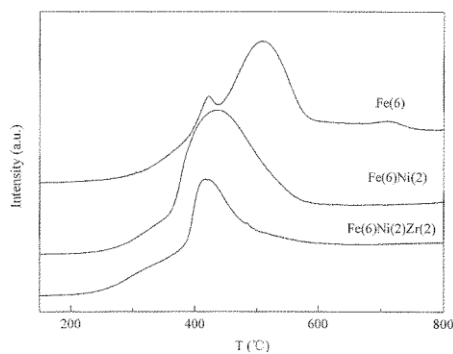

Fig 6: TPR profiles of Fe(6), Fe(6)Ni(2) and Fe(6)Ni(2)Zr(2) catalyst

From various H$_2$-TPR studies of Fe catalyst,[38-40] there is general agreement that the peak for hydrogen consumption – centred at around 410°C – can be attributed to the reduction of the Fe$_2$O$_3$ to Fe$_3$O$_4$ in Fe species. The second reduction peak was assigned to the reduction of Fe$_3$O$_4$ to Fe^0. But according to,[30] there have two reduction peaks attributed to the reduction of Fe$_3$O$_4$ small nanoclusters to FeO, and then of FeO to Fe^0. Some theories suggest that the two processes of the reduction from Fe$_3$O$_4$ into Fe and from FeO into Fe^0 are completed by one step. So the two reduction peaks should be one. Therefore there is only one reduction peak of hydrogen consumption.

A high temperature reduction peak and a weak temperature peak were observed in the Fe-Ni and Fe-Ni-Zr catalysts. The high peak should be the reduction peak of the Fe$_2$O$_3$ to Fe$_3$O$_4$ and the low peak could be the reduction of NiO species centred at about 350°C. It was found that Zr reduction peak was not observed in Fe-Ni-Zr catalyst and Ni reduction peak was weak in the catalysts Fe-Ni and Fe-Ni-Zr catalysts. The reason is that the doping of Ni and Zr changed the structure of pure iron catalyst, and the Ni, Zr interact with Fe and substrate strongly. Meanwhile the high peak moved to the lower temperature, and this lead to the decreasing of reduction reaction energy and made the re-

duction reaction much easier than with the iron catalyst and improved the effectiveness of the catalytic reaction.

X-ray photoelectron spectroscopy

Fig 7 shows the XPS spectrum of Fe $2p_{3/2}$ on the Fe, Fe-Ni and Fe-Ni-Zr catalyst.

A broad XPS band centred at 711.7 eV was observed on the sample of Fe and Fe-Ni catalyst. This value is close to the binding energy of $2p_{3/2}$ of iron in Fe_2O_3,[3] indicating that iron in Fe and Fe-Ni catalysts was mainly present as a valence of +3. As a general rule, if the formation of an interfacial oxide takes place, some modifications of the X-ray photoemission spectrum are expected to have an energy shift and/or the presence of satellite peaks.[1] This can be seen in Fig 7. With the addition of Zr, the binding energy value was increased from 711.3 eV to 712 eV and the intensity of the peak values for this oxidation state was decreased dramatically.
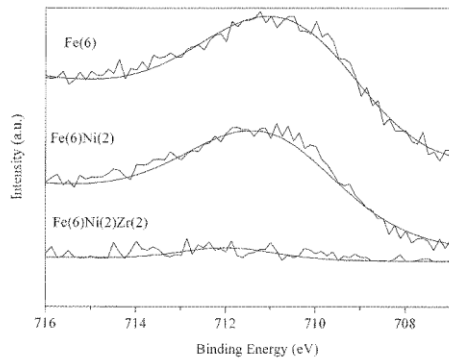

Fig 7: XPS spectra of Fe $2p_{3/2}$ on Fe(6), Fe(6)Ni(2) and Fe(6)Ni(2)Zr(2) catalyst

Fig 8 illustrates Ni 2p XPS spectrum on both Fe-Ni and Fe-Ni-Zr catalyst. The presence of peak values at 856.0 and 862.5 eV of Fe-Ni catalyst is due to the binding energy of Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively, since the nickel is in oxidation state +2. For catalyst of Fe-Ni-Zr, the peaks at 856.8 and 863.8 eV are attributed to the binding energies of Ni^{2+} $2p_{3/2}$ and Ni^{2+} $2p_{1/2}$, respectively. However, with the addition of Zr, the maximum intensity decreased. Furthermore, there were two peaks; each appeared on the higher binding energy side of Ni^{2+} $2p_{3/2}$ and Ni^{2+} $2p_{1/2}$, respectively. Although the exact phase of these peaks was unknown, it is possible to consider that they were the mixture of iron oxides and nickel or zirconium oxides.

Fig 9 shows the binding energy of the Zr 3d photoelectron reach its peaks at 182.3 and 184.5eV for Zr $3d_{5/2}$ and Zr $3d_{3/2}$ elements, respectively, due to existence of Zr^{+4} in the catalyst. The result agrees with the results of XRD.

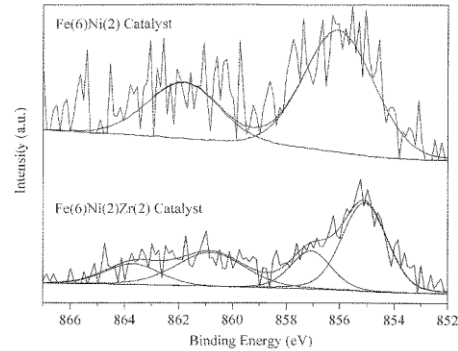According to the results of XRD, TPD and XPS, it was

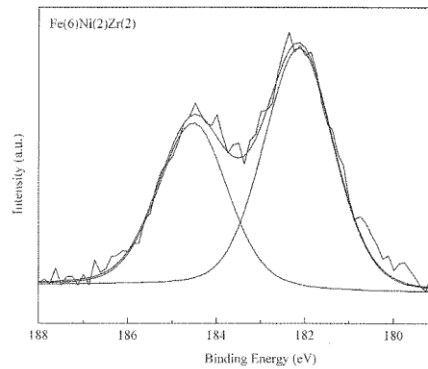Fig 8: XPS spectra of Ni 2p on Fe(6)Ni(2) and Fe(6)Ni(2)Zr(2) catalyst

Fig 9: XPS spectrum of Zr 3d on Fe(6)Ni(2)Zr(2) catalyst

reasonable to conclude that the doping Ni can improve the activity of Fe catalyst and NiO played a preponderant role in the SCR reaction. The addition of Zr helped to stabilise and disperse NiO clusters, preventing the known affinity of nickel to form philosilicates in silica-based surfaces, and enhance the activity of the Fe-Ni catalyst.

CONCLUSIONS

The paper has presented the results of an investigation into the NOx conversion rate of Fe-based catalysts at a low temperature range, using ceramic honeycomb as the substrate. The study has revealed properties and their association with the NOx reduction rate of the catalysts.

Conclusions have been reached that compared with the current commonly used catalysts; Fe-based catalysts have a much higher conversion rate of NOx in an SCR under the

temperature range of 150°C to 350°C. Results have shown that amongst the catalysts studied, the catalyst of combined Fe-Ni-Zr is the most active one for the SCR of NOx by NH$_3$. Fe$_2$O$_3$ is the main active specie in the catalyst, while the addition of NiO and ZrO$_2$ is important to improve activities of the catalysts. Tests have found that the catalysts offer the highest NOx reduction rate when the loading ratio of the catalysts is 6% wt. of Fe, 2% wt. of Ni and 2% wt. of Zr.

REFERENCES

1. Goldsworthy L. 2002. *Design of ship engines for reduced oxides of nitrogen emissions.* In: Engineering a Sustainable Future Conference Proceedings. Australia.

2. Cho SM. 1994. *Properly apply selective catalytic reduction for NOx removal.* Chemical Engineering Progress, pp39–45.

3. Tol MFHV, Quinlan MA, Luck F, Somorjai GA and Nieuwenhuys BE. 1991. *The catalytic reduction of nitric oxide by ammonia over a clean and vanadium oxide-coated platinum foil.* Journal of Catalysis **129**: 186–194.

4. Schneider H, Scharf U, Wokaun A and Baiker A 1994. *Conjugated polymer-supported catalysts -polyaniline protonated with 12-tungstophosphoric acid.* Journal of Catalysis **147**: 545–551.

5. Chen JP, Yang RT, Buzanowski MA and Cichanowicz JE. 1990. *Cold selective catalytic reduction of nitric oxide for flue gas applications.* Industrial and Engineering Chemistry Research **29**: 1431–1435.

6. Singoredjo L, Korver R, Kapteijn F and Moulijn J.1992. *Alumina supported manganese oxides for the low-temperature selective catalytic reduction of nitric oxide with ammonia.* Applied Catalysis B: Environmental **1**: 297–316.

7. Zhu ZP, Liu ZY, Niu HX and Liu SJ. 1999. *Promoting effect of SO2 on activated carbon-supported vanadia catalyst for NO reduction by NH3 at low temperatures.* Journal of Catalysis **187**: 245–248.

8. Fabrizioli P, Burgi T, Baiker A. 2002. *Environmental catalysis on iron oxide–silica aerogels: selective oxidation of NH$_3$ and reduction of NO by NH$_3$.* Journal of Catalysis **206**: 143–154.

9. Richter M, Trunschke A, Bentrup U, Brzezinka KW, Schreier E, Schneider M, Pohl MM and Fricke R. 2002. *Selective catalytic reduction of nitric oxide by ammonia over egg-shell MnOx/NaY composite catalysts.* Journal of Catalysis **206**: 98–113.

10. Weisweiler W, Retzlaff B and Hochstein B. 1988. *Selective catalytic reduction of nitrogen oxides. Activity studies of transition metal oxides.* Staub-Reinhalt der Luft **3**: 119–126.

11. Ramis G, Yi L, Busca G, Turco M, Kotur E and Willey RJ. 1995. *Adsorption, activation, and oxidation of ammonia over SCR catalysts.* Journal of Catalysis **157**: 523–535.

12. Weisweiler W, Mallonn E and Görke O. 2003. *Removal of nitrogen oxides by the NH$_3$-SCR process: Catalysts based on industrial residues containing iron (III) oxide.* Chemie-Ingenieur Technik **75**: 72–76.

13. Chmielarz L, Kustrowski P, Zbroja M, Lasocha W and Dziembaj R. 2004. *Selective reduction of NO with NH3 over pillared clays modified with transition metals.* Catalysis Today **90**: 43–49.

14. Weisweiler W and Maurer B. In: Essers W, Editor, Dieselmotorentechnik 1998, Expert-Verlag, Renningen, p92.

15. Bosch H and Janssen F.1988. *Formation and control of nitrogen oxides.* Catalysis Today 2:369–379.

16. Kato A, Matsuda S, Nakajima F, Imanari M and Watanabe Y. 1981. *Reduction of nitric oxide with ammonia on iron oxide-titanium oxide catalyst.* Journal of Physical Chemistry 85: 1710–1713.

17. Palmqvist A, Jobson E, Andersson L, Granbro R, Wendin M, Megas L, Nisius P, Wiartalla A, Lepperhoff G, Blakeman P, Ilkenhans T, Webster D, Haeffler G, Voorde P, Schmidt-Zhang, Guth PU and Wallin M. 2004. *Lotus: A co-operation for low temperature urea-based selective catalytic reduction of NOx.* SAE Paper 2004-01-1294.

18. Wu S and Nobe K. 1977. *Reduction of nitric oxide with ammonia on vanadium pentoxide.* Industrial & Engineering Chemistry Product Research and Development. **16**: 136–141.

19. Willey RJ, Lai H and Peri JB. 1991. *Investigation of iron oxide-chromia-alumina aerogels for the selective catalytic reduction of nitric oxide by ammonia.* Journal of Catalysis **130**: 319–331.

20. Long RQ and Yang RT. 1999. *Selective catalytic reduction of nitrogen oxides by ammonia over Fe^{3+}-exchanged TiO$_2$-pillared clay catalysts.* Journal of Catalysis **186**: 254–268.

21. Long RQ and Yang RT. 2000. *The promoting role of rare earth oxides on Fe-exchanged TiO$_2$-pillared clay for selective catalytic reduction of nitric oxide by ammonia.* Applied Catalysis B: Environmental **27**: 87–95.

22. Long RQ and Yang RT. 2001. *Enhancement of activities by sulfation on Fe-exchanged TiO$_2$-pillared clay for selective catalytic reduction of NO by ammonia.* Applied Catalysis B: Environmental 33: 97–107.

23. Long RQ and Yang RT. 2002. *Selective catalytic reduction of NO with ammonia over Fe^{3+}-exchanged mordenite (Fe–MOR): catalytic performance, characterization, and mechanistic study.* Journal of Catalysis **207**: 274–285.

24. Qi G, Yang RT and Chang R. 2003. *Low-temperature SCR of NO with NH$_3$ over USY-supported manganese oxide-based catalysts.* Catalysis Letters **87**: 67–71.

25. Mosqueda-Jiménez BI, Jentys A, Seshan K, Lercher JA. 2003. *Structure-activity relations for Ni-containing zeolites during NO reduction I. Influence of acid sites.* Journal of Catalysis 218:348–353.

26. Shimizu KI, Maeshima H, Satsuma A and Hattori T. 1998. *Transition metal-aluminate catalysts for NO reduction by C$_3$H$_6$.* Applied Catalysis B: Environmental **18**: 163–170.

27. Efthimiadis EA, Lionta GD, Christoforou SC and Vasalos IA. 1998. *The effect of CH$_4$, H$_2$O and SO$_2$ on the NO reduction with C$_3$H$_6$.* Catalysis Today 40: 15–26.

28. Zhang S, Li L, Xue B, Chen J, Guan N and Zhang F.React. Kinet. Catal. Lett. Vol. 89, No. 1, 81–87 (2006).

29. Hickey N, Fornasiero P, Kašpar J, Grazian M, Martra G, Coluccia S, Biella S, Prati L and Rossi M. 2002. *Improvement of SOx-resistance of silver lean-deNOx catalysts*

by supporting on a CeO2-containing zirconia. Journal of Catalysis **209:** 271–274.

30. Monte RD, Fornasiero P, Kašpar J, Rumori P, Gubitosa G and Graziani M. 2000. *Pd/Ce0:6Zr0:4O2/Al2O3 as advanced materials for three-way catalysts Part 1. Catalyst characterisation, thermal stability and catalytic activity in the reduction of NO by CO.* Applied Catalysis B: Environmental **24:** 157–167.

31. Amin NAS and Chong CM. 2005. *SCR of NO with C3H6 in the presence of excess O2 over Cu/Ag/CeO₂-ZrO₂ catalyst.* Chemical Engineering Journal **113:** 13–25.

32. Wang C, Wang X, Xing N, Yu Q and WangY. 2008. *Zr/HZSM-5 catalyst for NO reduction by C2H2 in lean-burn conditions.* Applied, Catalysis A: General **334:** 137–146.

33. Zhu Z, Liu Z, Liu S and Niu H. 2001. *Catalytic NO reduction with ammonia at low temperatures on V₂O₅/AC catalysts: effect of metal oxides addition and SO₂.* Applied Catalysis B: Environmental **30:** 267–276.

34. Liu Q, Liu Z, Huang Z and Xie G. 2004. *A honeycomb catalyst for simultaneous NO and SO₂ removal from flue gas: preparation and evaluation.* Catalytic Today **93-95:** 833–837.

35. Brunauer S, Emmett PH and Teller E. 1938. *Adsorption of gases in multimolecular layers.* Journal of the American Chemical Society. 60: 309–319.

36. Rosenberg HS and Oxley JH. 1993. *Selective catalytic reduction for NOx control at coalfired power plants.* ICAC Forum' 93 Controlling Air Toxics and NOx Emissions. Baltimore, MD.

37. Schwidder M, Heinrich F, Kumar MS, Brückner A and Grünert W. 2004. Fe-*zsm-5 catalysts for the selective reduction of no: Influence of preparation route on structure and catalytic activity.* Studies in Surface Science and Catalysis 154: 2484–2492.

38. Lobree LJ, Hwang I, Reimer JA and Bell AT. 1999. *Investigations of the state of Fe in H–ZSM-5.* Journal of Catalysis **186:** 242–253.

39. Delahay G, Valade D, Guzma'n-Vargas1 A and Coq B. 2005. *Selective catalytic reduction of nitric oxide with ammonia on Fe-ZSM-5 catalysts prepared by different methods.* Applied Catalysis B: Environmental **55:** 149–155.

40. Chen HY, Sachtler WMH. 1998. *Activity and durability of Fe/ZSM-5 catalysts for lean burn NOx reduction in the presence of water vapour.* Catalysis Today **42:** 73–83.

41. Noel CM, Giulieri F, Combarieu R, Bossis G and Chaze AM. 2007. *Control of the orientation of nematic liquid crystal on iron surfaces: Application to the self-alignment of iron particles in anisotropic matrices.* Colloids and Surfaces A: Physicochemical Engineering Aspects **295:** 246–257.

42. Corbett JJ, Fischbeck PS and Pandis SN. 1999. *Global nitrogen and sulfur inventories for oceangoing ships.* Journal of Geophysical Research **104:** 3457–3470.

43. Choi H, Ham SW, Nam IS and Kim YG. 1996. *Honeycomb reactor washcoated with mordenite type zeolite catalysts for the reduction of NOx by NH₃.* Industrial and Engineering Chemistry Research 35: 106-112.

44. Forzatti P. 2001. *Present status and perspectives in de-NOx SCR catalysis.* Applied Catalysis A: General **222:** 221–236.

45. Williams JL. 2001. *Monolith structures, materials, properties and uses.* Catalysis Today **69:** 3–9.

46. Koebel M, Elsener M. 1998. *Selective catalytic reduction of NO over commercial DeNOx catalysts: comparison of the measured and calculated performance.* Industrial and Engineering Chemistry Research 37: 327–335.