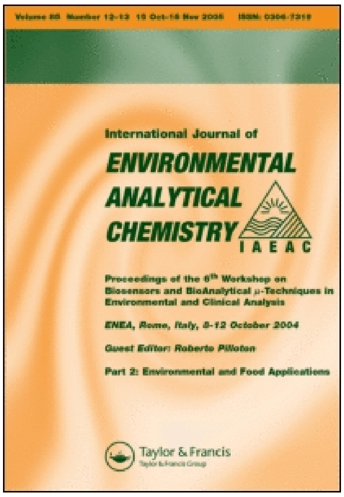

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A method for quantitative analysis of nitrogen oxides and N_2 by means of mass spectrometry with the assistance of a catalytic technique for the reduction of NO with CO or hydrocarbons

Fei Li[ab]; Dehai Xiao[a]; Jing Li[a]; Xiangguang Yang[a]
[a] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, P.R. China [b] Graduate University of the Chinese Academy of Sciences, Beijing, P.R. China

To cite this Article Li, Fei , Xiao, Dehai , Li, Jing and Yang, Xiangguang(2009) 'A method for quantitative analysis of nitrogen oxides and N_2 by means of mass spectrometry with the assistance of a catalytic technique for the reduction of NO with CO or hydrocarbons', International Journal of Environmental Analytical Chemistry, 89: 2, 119 — 128

To link to this Article: DOI: 10.1080/03067310802603941

URL: http://dx.doi.org/10.1080/03067310802603941

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 2, 15 February 2009, 119–128

A method for quantitative analysis of nitrogen oxides and N_2 by means of mass spectrometry with the assistance of a catalytic technique for the reduction of NO with CO or hydrocarbons

Fei Li[ab], Dehai Xiao[a], Jing Li[a] and Xiangguang Yang[a]*

[a]*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Laboratory of Green Chemistry and Process, Changchun, P.R. China;* [b]*Graduate University of the Chinese Academy of Sciences, Beijing, P.R. China*

(*Received 7 April 2008; final version received 3 November 2008*)

Mass spectrometry is not able to differentiate NO_x and N_2 from other interferences (e.g. CO and C_2H_4) in the deNO$_x$ reactions. In the present study, a quantitative method for analysis of NO_x and N_2 simultaneously in these reactions with an assisted converter operated at higher temperature under O_2-rich condition, which eliminates the interferences, is developed. The NO_x conversion from this method is comparable to the one from an Automotive Emission Analyser equipped with NO_x electrochemical sensor. Two types of deNO$_x$ reactions are tested in terms of selectivity of N_2 production. The application of this method is discussed.

Keywords: mass spectrometry quantification; nitrogen oxides; catalytic assisted method; DeNOx reactions

1. Introduction

Nitrogen oxides (NO_x: NO and NO_2) are major air pollutants causing acid rain and forming photochemical smog. The emission of various nitrogen oxides into the atmosphere occurs on a massive scale. Worldwide, over 30 million tons of NO_x are vented to earth's atmosphere each year [1]. There has been a worldwide effort to develop improved solutions for the removal of NO_x emission from stationary and mobile sources. NO reduction with CO and selective catalytic reduction (SCR) of NO with hydrocarbons (HCs) or other reductants are two sorts of typical deNO$_x$ techniques. NO reduction with CO can be applied in controlling automotive exhaust gas emission and SCR can be used for the removal of NO_x under oxygen-rich condition. In deNO$_x$ studies, gas chromatography (GC), NO_x gas electrochemistry sensors and NO_x/NO chemiluminescent analyser have been widely used for the quantitative analysis in these catalytic reactions by determining N_2 or NO_x in the exit gases. In the GC analysis of NO_x, thermal conductivity detector (TCD) has been found rather insensitive and unreliable [2,3], especially for very low NO concentration (~ppm) due to the detection limit of TCD. Low NO_x concentration has to be detected on-line by NO_x gas electrochemistry sensors or NO_x/NO chemiluminescent analyser, but N_2 cannot be analysed by the two methods. Therefore, the results of N_2 production in the outflow gases often need to be analysed by GC except

---

*Corresponding author. Email: xgyang@ciac.jl.cn

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802603941
http://www.informaworld.com

for NO_x conversion. Namely, GC and one of the chemical methods have to be used at the same time [4–7].

MS has been used increasingly as a means to investigate the deNO_x reactions [8,9], but it is usually considered as only a qualitative technique. It is well known that different substances may have the same molecular fragments in MS spectra, which can lead to an ambiguous signal. For example, the key information of N_2 in deNO_x reactions can be influenced by CO and some HCs with the fragment of $m/e = 28$. Therefore, the production of N_2 in deNO_x reactions cannot be determined by MS directly without any modification. In this work, we present a method for the quantitative analysis of mixture containing nitrogen oxides and N_2 from the reduction reaction of NO by MS with the assistance of catalytic technique. Two typical examples of deNO_x reactions, NO reduction with CO and SCR of NO with C_3H_8 were presented. It is shown that the results are satisfying for the quantitative analysis of nitrogen oxides and N_2 by means of MS with the assistance of catalytic technique.

2. Experimental

2.1 *Catalyst preparation*

2.1.1 *Preparation of deNO_x catalyst*

The deNO_x catalysts, composed of 1 wt.% Pt/γ-Al_2O_3 or 3 wt.% Co/γ-Al_2O_3, were prepared by impregnating γ-Al_2O_3 with required amounts of H_2PtCl_4 solution or $Co(NO_3)_2$ solution, respectively, followed by drying and calcination at 923 K for 3 h. These two catalysts were used in the investigation of NO reduction, besides 1 wt.% Pt/γ-Al_2O_3 was also used as an assisted catalyst, vide infra.

2.1.2 *Preparation of assisted catalyst*

Co_2CuAlO_x assisted catalyst for the SCR of NO with C_3H_8 was used in the assisted converter ahead of MS. After 0.8 mol $Co(NO_3)_2 \cdot 6H_2O$, 0.4 mol $Cu(NO_3)_2 \cdot 9H_2O$ and 0.4 mol $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 5 L distilled water, the solution was mixed dropwise with equal volume of 0.028 mol/L Na_2CO_3 and 0.0079 mol/L NaOH solutions, followed by stirring for 10 h. The precipitate was filtered and washed several times with deionised water. After drying, the precursor was calcined in air at 773 K for 2 h, then 973 K for another 2 h. Another assisted catalyst which was used for the analysis of the product in the reaction of NO reduction with CO, i.e. 1 wt.% Pt/γ-Al_2O_3, is the same as deNO_x catalyst described in Section 2.1.1.

2.2 *Catalytic runs*

The experiments of both reactions of NO reduction with CO or C_3H_8 were carried out in a temperature-programmed mode with a heating rate of 5 K/min. Outflow gases were analysed by an on-line QIC-20 quadrupole mass spectrometer, Hiden Analytical Ltd, (detection limit: 5 ppb) controlled by MASsoft software. The operation vacuum of the MS is about 3×10^{-6} torr. There are only small amounts of gases introduced into the MS for keeping the operation vacuum and most of gases are bypassed and vented to the atmosphere. For comparison a FGA-4100 Automotive Emission Analyser (AEA) equipped with NO_x electrochemical sensor (detection limit: 1 ppm), Foshan Analytical

Instrument Co. LTD, was also used to measure the concentration of NO_x. AEA was calibrated with five standard gases of NO, ranging from 200 to 1000 ppm of NO balanced with Ar. The MS or AEA was positioned immediately after the catalyst bed or the assisted converter, which was described in detail in Section 3.1. Before the experiment, the catalyst was flushed with feed gases to obtain a smooth baseline of every component in MS. MS data were collected after the temperature began rising. The total amount of NO_x (NO and NO_2) was determined with the m/e ratio of 30 (NO^+), while the partial pressure of NO_2 can be monitored separately with its molecular ion peak ($NO_2^+, m/e = 46$). Thus, the amount of NO can be determined indirectly in this article. The amount of C_3H_8 was monitored with the partial pressure of its base peak ion ($C_2H_5^+, m/e = 29$), overlapped by negligible quantity of $N^{14}N^{15}$ (< 5 ppm). The m/e ratios of 28 (CO^+, N_2^+ and $C_2H_4^+$) and 44 (CO_2^+, N_2O^+ and $C_3H_8^+$) were also monitored on line. The m/e ratios of 29, 30 and 46 was denoted as C_3H_8, NO_x (NO and NO_2) and NO_2, respectively, if not illustrated specifically. The total flow rate of gas was 70 ml/min. The feed gas compositions and the catalysts used in the experiments are summarised in Table 1.

3. Results and discussion

3.1 *Experimental principle*

In $deNO_x$ reactions, it is very easy to determine the NO_x concentration by MS and NO_x conversion can also be obtained. The signal of $m/e = 30$ will not be interfered by other species in our system, and the contribution of $^{15}N_2^+$ at $m/e = 30$ is negligible. Though some of HCs have fragment of $m/e = 30$, it will be diminished after completed oxidation by the assisted catalyst, as all of HCs are converted to CO_2. It is difficult to evaluate the efficiency of catalysts by MS because the effective conversion of NO_x must be calculated with the amount of N_2 produced in $deNO_x$ reactions. The main compositions such as CO and N_2 with the same m/e ratio cannot be differentiated unambiguously by MS from the reaction mixture, unless isotopically labelled ^{15}NO was used [10]. However, the interference to N_2 in MS generally comes from some substances such as carbon monoxide and HCs. But these ingredients can be oxidised completely to CO_2 under specific condition, therefore, all the interferences to N_2 with the molecular fragments of $m/e = 28$ can be eliminated. As shown in Figure 1, a single-pass flow micro-reactor (assisted converter operated at high temperature) filled with oxidation catalyst was added downstream and a bypassed O_2 was introduced into the assisted converter if necessary. With the assisted converter all of the interference to N_2 from CO and HCs will be from the signal of CO^+ (fragment from CO_2).

Table 1. Catalysts and assisted catalysts in the reactions of NO reduction with CO and SCR with C_3H_8 and gases composition in both reactions.

Reactions	Catalyst (mass)	Assisted catalyst (mass)	Gases composition
NO reduction with CO	1 wt% Pt/Al_2O_3 (50 mg)	1 wt% Pt/Al_2O_3 (0.2 g)	1000 ppm CO, 1000 ppm NO and Ar balanced (bypassed 5% O_2 in total)
NO-SCR with C_3H_8	3 wt% Co/Al_2O_3 (0.2 g)	Co_2CuAlO_x (0.2 g)	1000 ppm C_3H_8, 1000 ppm NO, 5% O_2 and Ar balanced

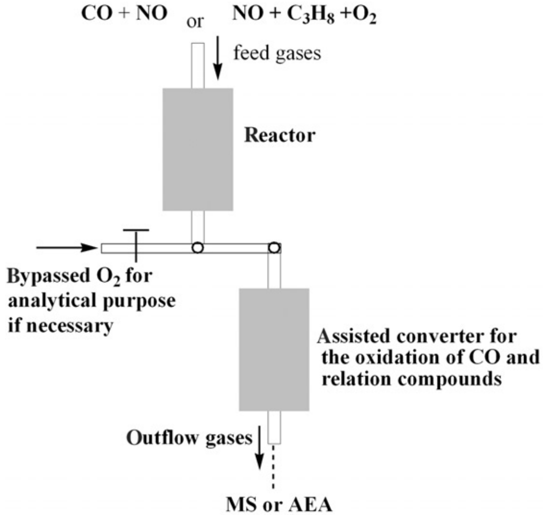

Figure 1. Schematic diagram of the assisted catalytic converter for the completely catalytic oxidising the residual CO or HC to CO_2.

And then the steady background signal of $m/e = 28$ can be obtained and seen as a blank. Based on this principle, measurement of N_2 production can be achieved. An important feature of this approach is the combination of appropriate control of O_2 concentration and a suitable assisted catalyst in the assisted converter. In other words, CO and HCs in the sample are oxidised to CO_2 over the assisted catalyst in the presence of a large excess of O_2 under selected temperature, but the reduction of NO_x to N_2 can be almost ruled out in the assisted converter. Therefore, in order to obtain N_2 information correctly, an assisted converter is necessary as described above. An expected catalytic converter should possess high oxidisability but no activity to NO_x. Taking the reaction of NO-SCR with C_3H_8 for an example, a calcined hydrotalcite catalyst, Co_2CuAlO_x, was selected as assisted catalyst in the converter, due to its strong oxidisability [11] and very low catalytic activity for SCR of NO at high temperature under lean-burn condition. In order to determine the optimal temperature for the assisted catalyst, a temperature-programmed reaction experiment was carried out at a ramp rate of 5 K/min. The composition of the feed gas was 1000 ppm NO, 1000 ppm C_3H_8, 5% O_2 and Ar balanced and operated with a flow rate of 70 ml/min. Figure 2 shows the partial pressure changes with respect to time (also to temperature). C_3H_8 ($m/e = 29$) was completely oxidised at about 600 K. A certain amount of NO_2 ($m/e = 46$) is appeared at the temperature higher than 600 K, which is the reason why the partial pressure of NO_x ($m/e = 30$) does not completely return to the initial value in the temperature range from 723 to 973 K. There is little interference from the CO or C_3H_8 since they are oxidised at 723 K. The $m/e = 44$ is presumably CO_2 as N_2O cannot be formed between 773 and 1123 K as reported by Teraoka *et al.* [12]. The fragment of $C_3H_8^+$ ($m/e = 44$) was eliminated due to the complete oxidation of C_3H_8. In addition, there was a clear NO desorption peak at ~360 K. With the temperature rising, the partial pressure of NO fluctuated between 473 and 773 K owing to the reaction among C_3H_8, NO and O_2, which is common for NO-SCR reaction under lean-burn condition. However, the partial pressure of NO_x was scarcely changed and maintained to a constant level above ~823 K,

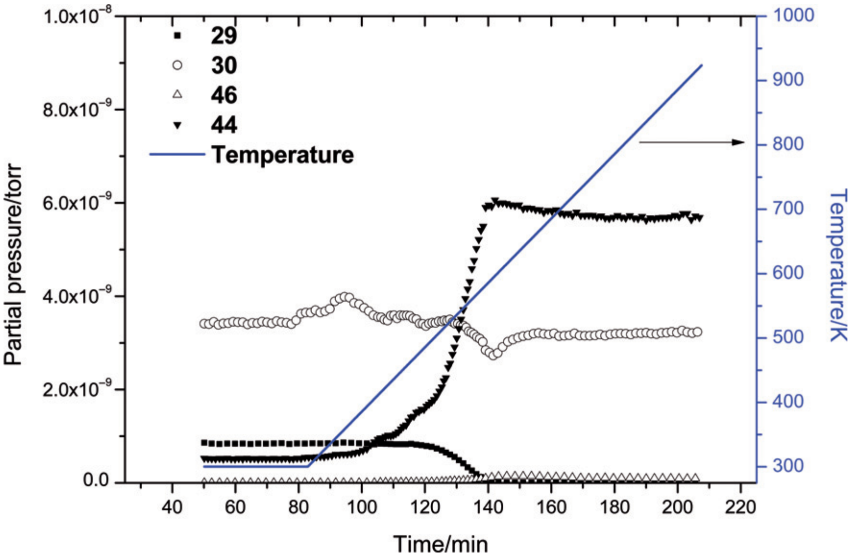

Figure 2. Partial pressures of 29, 30, 44, and 46 (m/e) in MS over the Co_2CuAlO_x catalyst (0.2 g) in the temperature-programmed reaction; gas composition: 1000 ppm NO, 1000 ppm C_3H_8, 5%O_2 and the balance of Ar.

which is nearly equal to initial value at the starting period. The base-line of partial pressure of the m/e ratio of 28 is mainly composed of $C_2H_4^+$ (MS fragment of C_3H_8) and N_2^+ (as an impurity in Ar). With the increase of reaction temperature, C_3H_8 was oxidised to CO_2 continuously. Both the ionisations of C_3H_8 and CO_2 in MS can bring fragments with the m/e ratio of 28, i.e. $C_2H_4^+$ and CO^+, respectively. Thus, the variation of the partial pressure of the m/e ratio of 28 included the decrease of $C_2H_4^+$ and formation of CO^+. C_3H_8 was completely oxidised at ~600 K, which made the resulting partial pressure of 28 (m/e) lower than base-line value above 723 K. And then the partial pressure of 28 (m/e) completely came from CO^+ (fragment of CO_2) and background N_2^+. In a word, the partial pressures of the m/e ratios of 30, 46, 29, 28 and 44 were getting towards a constant level, especially above 823 K. Different concentrations of HC will be chosen in our future deNO$_x$ studies, thus higher temperature is beneficial to the oxidation of higher concentrations. Therefore, we chose 923 K as the optimal temperature for the assisted converter. Similarly, in the study of NO reduction with CO, 0.2 g Pt/Al_2O_3 was selected for the assisted converter to oxidise residual CO. Owing to the lack of O_2 in this reaction, O_2 was introduced from bypass and made up the concentration to 5% in total, as shown in Figure 1. A smooth background line of the m/e ratio of 28 was obtained (not shown) when temperature was set at 823 K for the assisted converter.

It should be pointed out that Pt/Al_2O_3 is not suitable for an assisted catalyst in the reaction of NO-SCR with C_3H_8 due to its reactivity in NO-SCR. Therefore, in order to eliminate the interference to N_2, an appropriate assisted catalyst should be selected for the specified reaction and an optimal temperature in the converter should also be chosen. Thus, Co_2CuAlO_x with stronger oxidative catalytic ability is chosen as the assisted catalyst for the analysis of N_2 production in the reaction of NO-SCR with C_3H_8 but Pt/Al_2O_3 is selected as an assisted catalyst in the study of NO reduction with CO.

3.2 *NO reduction with CO*

As shown in Figure 3, the partial pressures were monitored by MS without the assisted converter. The following *m*/*e* ratios were detected as a function of temperature: 30 (NO_x), 28 (CO, N_2 and part of CO_2), 44 (CO_2 and N_2O), 46 (NO_2) over 1 wt.% Pt/Al_2O_3 catalyst. The decrease of NO_x and the formation of CO_2 are shown in Figure 3. Also, the NO conversion can be calculated easily according to the formula: NO_x conversion $(\%) = 100 \times (NO_{x\,\mathrm{in}} - NO_{x\,\mathrm{out}})/NO_{x\,\mathrm{in}}$. The conversions of NO in this experiment are also displayed in Figure 3. The information of NO_x can be utilised to evaluate the reaction in part, but the signal of N_2 or CO cannot be detected unambiguously by MS because of fragments overlapping with the same *m*/*e* ratio of 28. Besides, CO_2 formed in the NO reduction with CO would produce CO^+ ($m/e = 28$) in MS. Therefore, the selectivity of N_2 production, defined as $100 \times 2[P_{N_2}$ (outlet) $- P_{N_2}$ (inlet)]/[P_{NO_x}(inlet) $- P_{NO_x}$(outlet)], cannot be obtained without the assisted converter.

With the assistance of the converter filled with 1 wt.% Pt/Al_2O_3 (0.2 g) and operated at 873 K, the partial pressures of 30 (NO_x), 28 (N_2), 44 (CO_2 and N_2O), 46 (NO_2) were monitored as a function of temperature, as shown in Figure 4(a). As can be seen, CO_2 ($m/e = 44$) partial pressure scarcely changed and the signal of N_2 ($m/e = 28$) can be detected with confidence. There was almost no N_2O production in the O_2-rich system at the higher temperature. Though NO reduction with CO over platinum group metal catalyst will usually produce a certain amount of N_2O, however, N_2O cannot be converted to NO by the assisted converter at high temperature under O_2-rich condition, which would enable the total NO_x amount to be the real value. Here the selectivity of N_2 production and NO conversion can be obtained clearly as shown in Figure 4(b). There are some oscillations of N_2 selectivity in Figure 4(b), which is caused by the signal fluctuation of MS.

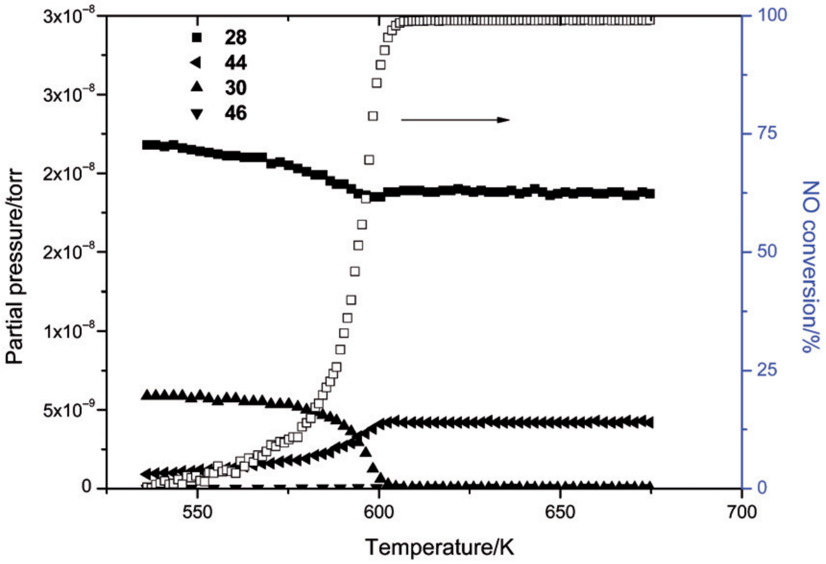

Figure 3. Partial pressures of 28, 44, 30 and 46 (*m*/*e*) and NO_x conversion as a function of temperature over the 1% Pt/Al_2O_3 catalyst (50 mg); gas composition: 1000 ppm NO, 1000 ppm CO and the balance of Ar.

Therefore, in order to make sure of the proportional relationship between NO_x depletion and N_2 production by the analytical results from MS with the assisted converter, the relative correction factor (RCF) of N_2 is defined as: $RCF = \Delta P_{NO_x}/2^*\Delta P_{N_2}$, in which $\Delta P_{NO_x} = P_{NO_x}$ (inlet) − P_{NO_x} (outlet) and $\Delta P_{N_2} = P_{N_2}$ (outlet) − P_{N_2} (inlet). After five parallel experiments were carried out, a RCF of 0.988 NO to N_2 was obtained. The results show that RCF value is near **1** (stoichiometrical value) and the standard deviation was not more than 5%, which means two parts decrement of NO for one part of N_2 increment. This result is reasonable. Therefore, no serious error would be introduced when RCF is taken as **1**.

3.3 *NO SCR with C_3H_8*

SCR of NO_x under lean-burn condition, NO_x reduced to N_2 with HC in the presence of an excess of oxygen, has recently received extensive attention because of its potential for commercial applications. Co/Al_2O_3 catalyst was chosen as an active and stable catalyst in the study of NO-SCR with propane under lean-burn condition [13].

In Figure 5, the partial pressures with the following *m*/*e* ratios were monitored without the assisted converter as a function of temperature: 30 (NO_x), 28 (CO or N_2), 29 (C_3H_8). As can be seen, NO_x partial pressure decreased gradually with the increase of temperature until near 723 K before C_3H_8 was oxidised completely. When the temperature exceeded 723 K, the conversion of NO_x began to decrease because a part of C_3H_8 was oxidised completely to CO_2 and then the reduction of NO was restrained due to the competitive

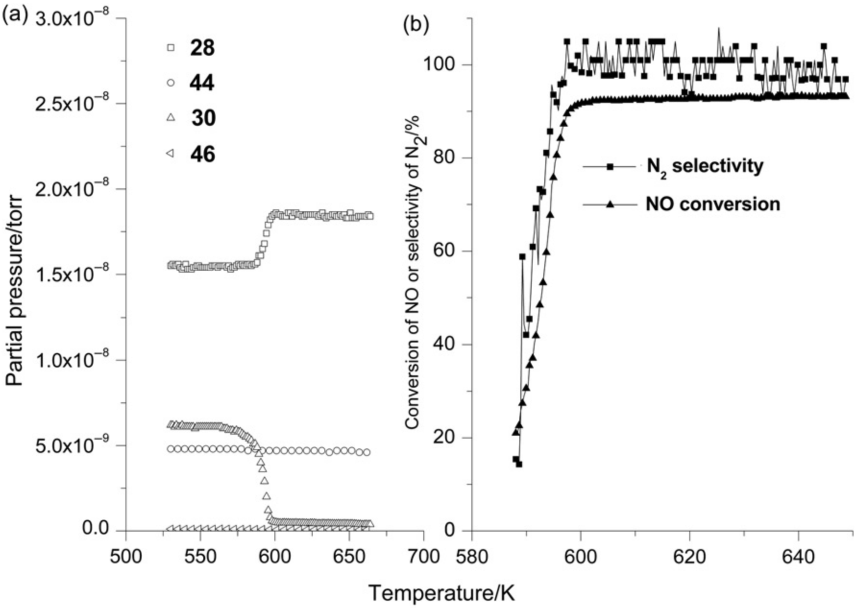

Figure 4. (a) The partial pressures of 28, 44, 30 and 46 (*m*/*e*) as a function of temperature over the 1% Pt/Al_2O_3 catalyst (50 mg) and the 1% Pt/Al_2O_3 (0.2 g) assisted catalyst at 873 K; (b) NO conversion and N_2 selectivity; gas composition: 1000 ppm NO, 1000 ppm CO, bypassed 5% O_2 in total (introduced into the assisted converter) and the balance of Ar.

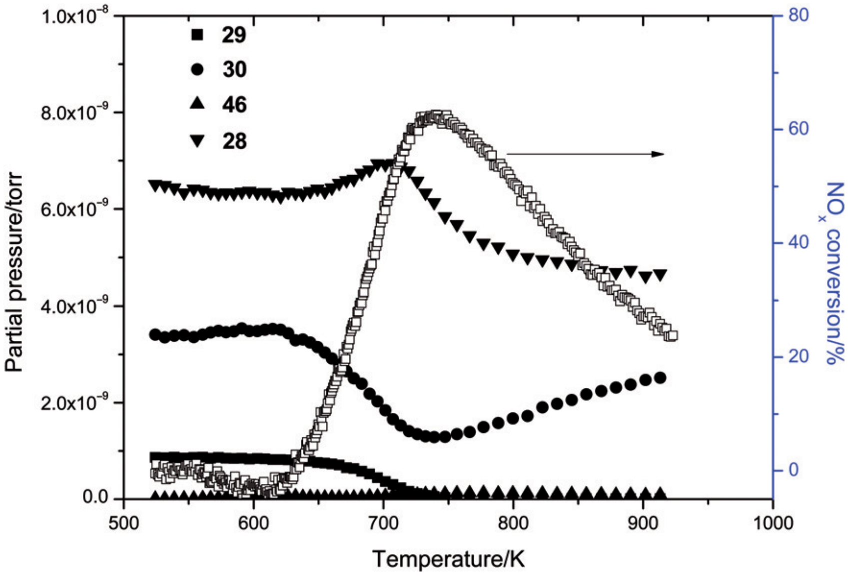

Figure 5. Partial pressures of 29, 30, 46 and 28 (m/e) and NO_x conversion as a function of temperature over the 3 wt.% Co/Al_2O_3 catalyst (0.2 g) as a function of temperature; gas composition: 1000 ppm NO, 1000 ppm C_3H_8, 5% O_2 and the balance of Ar.

reactions between NO and O_2 for the reductant (C_3H_8), especially at higher temperature. It is not difficult to imagine that a typical volcano-shape plot [13,14] of NO_x conversion can be obtained. A small amount of NO desorbs from the surface of catalyst at about 623K, which results in so-called minus NO_x conversion. On the other hand, the production of N_2 forming a peak at ~723 K is shown in Figure 5, which is interfered from other substances with the m/e ratio of 28 such as CO^+ and $C_2H_4^+$. Therefore, the data of N_2 obtained from MS without the assisted converter cannot be utilised to evaluate the SCR of NO_x with C_3H_8.

As described in Figure 2, the assisted converter enables to eliminate the interferences from the MS fragmentation possessing the same m/e value as N_2^+. Figure 6(a) shows the partial pressures of the m/e ratios: 30 (NO_x), 28 (N_2 only), 29 (C_3H_8) over 3 wt.% Co/Al_2O_3 with the assisted converter. Figure 6(a), similar to Figure 4, shows the relation between m/e of N_2 (or NO_x) and temperature, which is denoting the N_2 production and NO_x conversions. In addition, residue C_3H_8 was oxidised completely in the assisted converter at 923 K. Figure 6(b) also exhibits the selectivity of N_2 calculated from the N_2 production and NO_x conversion according to RCF of MS. The result of NO conversion from AEA is also shown in Figure 6(b) as a reference. The slight difference between MS and AEA in the monitoring NO_x can be neglected. The agreement on the conversion from both the results by MS and AEA illustrates the reliability of the results by mentioned method for the analysis of reaction productions of $deNO_x$.

4. Conclusions

Two typical $deNO_x$ reactions have been exemplified for MS quantitative research with the assistance of catalytic technique. Reliable results of both NO_x conversion and selectivity of

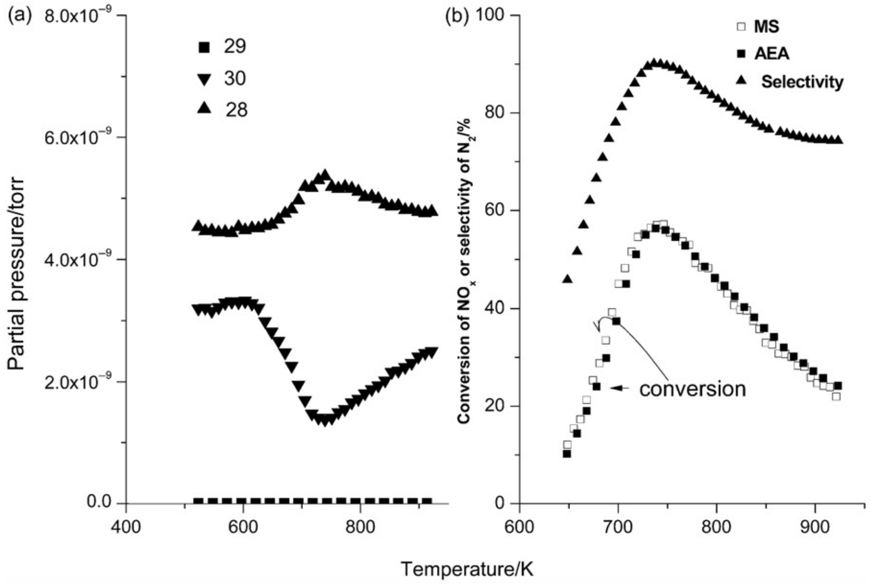

Figure 6. (a) Partial pressures of 29, 30 and 28 (m/e) in MS over the 3wt.% Co/Al_2O_3 catalyst (0.2 g) and the Co_2CuAlO_x assisted catalyst (0.2 g) in assisted converter; (b) Comparison of NO_x conversion from AEA and MS; N_2 selectivity; gas composition: 1000 ppm NO, 1000 ppm C_3H_8, 5%O_2 and the balance of Ar.

N_2 production were obtained. It is demonstrated that MS assisted by catalytic technique is a route for a quantitative analytical method of nitrogen oxides and N_2 in NO reduction with CO over 1 wt.% Pt/Al_2O_3. In addition, NO-SCR with C_3H_8 over 3 wt.% Co/Al_2O_3 catalyst was also investigated with this method and a consistent result was obtained in comparison with the AEA for the analysis of NO_x. Therefore, both critical values of NO_x and N_2 can be obtained from a mass spectrometer solely.

Acknowledgements

We thank the Ministry of Science and Technology of China (973 program 2004 CB719502) and the National Natural Science Foundation (20177022) for the support of this research.

References

[1] J.N. Armor, Appl. Catal. B: Environ. **1**, 221 (1992).
[2] S.A. Greene and H. Pust, Anal. Chem. **20**, 1039 (1958).
[3] G.D. Mitra and S.K. Ghosh, J. High. Resolut. Chrom. Chrom. Comm. **8**, 150 (1985).
[4] R. Zhang, H. Alamdari, and S. Kaliaguine, Catal. Lett. **119**, 108 (2007).
[5] F. Dorado, R. Romero, J. Cruz, P.B. García, A. Romero, and J.L. Valverde, Catal. Comm. **8**, 736 (2007).
[6] R. Marques, K.E. Kabouss, P.D. Costa, S.D. Costa, F. Delacroix, and G.D. Mariadassou, Catal. Today. **119**, 152 (2007).
[7] A. Tomita, T. Yoshii, S. Teranishi, M. Nagao, and T. Hibino, J. Catal. **247**, 137 (2007).

[8] J.P. Breen, R. Burch, C. Hardacre, C.J. Hill, and C. Rioche, J. Catal. **246**, 1 (2007).

[9] J.P. Breen, C. Rioche, R. Burch, C. Hardacre, and F.C. Meunier, Appl. Catal. B: Environ. **72**, 178 (2007).

[10] P. Granger, J.J. Lecomte, L. Leclercq, and G. Leclercq, Top. Catal. **16**, 349 (2001).

[11] Y. Liu, Ph.D. thesis, Changchun Institute of Applied Chemistry, Chinese Academy of Science, 1999.

[12] Y. Teraoka, H. Fukuda, and S. Kagawa, Chem. Lett. **19**, 1 (1990).

[13] R. Burch, J.P. Breen, and F.C. Meunier, Appl. Catal. B: Environ. **39**, 283 (2002).

[14] Z. Liu and S.I. Woo, Catal. Rev. Sci. Eng. **48**, 43 (2006).