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Activity and stability of Ag–alumina for the selective catalytic reduction of NO_x with methane in high-content SO_2 gas streams

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Abstract

In this work, we investigated the activity and stability of Ag–alumina catalysts for the SCR of NO with methane in gas streams with a high concentration of SO_2, typical of coal-fired power plant flue gases. Ag–alumina catalysts were prepared by coprecipitation–gelation, and dilute nitric-acid solutions were used to remove weakly bound silver species from the surface of the as prepared catalysts after calcination. SO_2 has a severe inhibitory effect, essentially quenching the CH_4-SCR reaction on this type catalysts at temperatures <600 °C. SO_2 adsorbs strongly on the surface forming aluminum and silver sulfates that are not active for CH_4-SCR of NO_x. Above ~600 °C, however, the reaction takes place without catalyst deactivation even in the presence of 1000 ppm SO_2. The reaction light-off coincides with the onset of silver sulfate decomposition, indicating the critical role of silver in the reaction mechanism. SO_2 is reversibly adsorbed on silver above 600 °C. While alumina sites remain sulfated, this does not hinder the reaction. Sulfation of alumina only decreases the extent of adsoption of NO_x, but adsorption of NO_x is not the limiting step. Methane activation is the limiting step, hence the presence of sulfur-free Ag–O–Al species is a requirement for the reaction. Strong adsorption of SO_2 on Ag–alumina decreases the rates of the reaction, and increases the activation energies of both the reduction of NO to N_2 and the oxidation of CH_4, the latter more than the former. Our results indicate partial contribution of gas phase reactions to the formation of N_2 above 600 °C. H_2O does not inhibit the reaction at 625 °C, and the effect of co-addition of H_2O and SO_2 is totally reversible.

Keywords: Silver; Alumina; Nitrogen oxides; Methane; Sulfur dioxide; Catalyst; Selective catalytic reduction of NO_x; Sulfate

1. Introduction

Supported silver on alumina is one of the most promising catalysts for lean SCR of NO to nitrogen by hydrocarbons and oxygenates as described in recent literature reviews [1,2]. Ever since Miyadera et al. [3] identified Ag/alumina as an efficient catalyst for SCR of NO with propene or ethanol, extensive work has been carried out to investigate the active catalyst structure and mechanism [4–12], as well as to evaluate the practical application of this type catalyst in actual engine exhausts [13,14]. From various literature reports, a consensus has been reached on the SCR-active silver structure, namely; oxidized silver species in contact with alumina catalyze the reaction [4,8,12,15]. Adsorbed nitrates and partially oxidized hydrocarbons have been shown as important intermediates of the propene-SCR, while NCO has been suggested as a precursor to dinitrogen formation [9]. Investigations of methane as a reductant have also appeared in recent years [8,12]. The distinct catalytic roles of oxidized silver species, silver nanoparticles and alumina in the SCR of NO with methane were investigated by comparing as prepared Ag/alumina catalysts and their nitric-acid-leached derivatives [12].

Typically, SO_2 is present in exhaust gas effluents, such as diesel engine exhausts and coal-fired power plant flue gases, generally acting as a poison to metal catalysts. Hence, it is important to investigate the SO_2-tolerance of Ag–alumina catalysts for the HC-SCR of NO_x. This has been examined in various papers for reductants other than methane [15,16–22]. SO_2 has been reported to act both as a poison [15,19,20] and as a promoter [16–18] of the Ag–alumina catalysts for NO reduction, depending on the type of hydrocarbon and silver loading used. Sulfates were typically identified on the catalysts after interaction with SO_2, however, the debate in the literature continues as to the role of sulfates for HC-SCR of NO. Satokawa et al. [20] and Meunier et al. [19] have reported

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formation of sulfates on Ag–alumina and attributed the observed activity loss in SCR of NO with propane and propene, respectively, to the presence of sulfates. On the contrary, Angelidis and Kruse [16,18] reported a beneficial effect of SO_2 (0–100 ppm) on a 5 wt.% Ag/Al_2O_3 catalyst for the SCR of NO_x with a C_3H_6/C_3H_8 mixture at 480 °C. Surface sulfur accumulation and a change of mechanism were proposed to explain the promotion by SO_2. Park et al. [17] reported enhanced NO reduction to N_2 by C_3H_6 on a 8 wt.% Ag/Al_2O_3 with addition of 30 ppm SO_2 at 500 °C, which was attributed to silver sulfate formed on the catalyst. Silver sulfate has also been proposed to catalyze the ethanol-SCR of NO_x [23]. Ke et al. [24] reported enhanced SO_2 resistance of Ag–alumina catalysts in propene-SCR by increasing the Ag/Ag^+ ratio using $AgNO_3$ and Ag_2SO_4 as precursors for these two species, respectively.

Methane, as the main component of natural gas, is an attractive reductant of NO_x. Gas turbine-exhausts and natural gas vehicle exhausts may require treatment by an active CH_4-SCR catalyst. In a previous report [8], we identified Ag–alumina catalysts to be active for CH_4-SCR of NO at 450–700 °C, and we also observed that addition of 30 ppm SO_2 in the feed gas did not affect the NO reduction to N_2 at 600 °C over a 1.5 wt.% Ag–alumina catalyst. In a more detailed recent study [12], we found that [Ag–O–Al] sites are the active sites for CH_4-SCR, and that the limiting step is activation of methane on the silver sites. Activation takes place above 300 °C in the absence of SO_2 [12]. Other than the above data, to our knowledge, there has been no systematic investigation of the effect of SO_2 on the SCR of NO with CH_4 over Ag–alumina catalysts. Further, there are no reports on the role of sulfates in CH_4-SCR of NO. In the present work, Ag–alumina catalysts were examined for this reaction in a gas containing ~1000 ppm SO_2, which is typical of coal-fired power plant exhaust gas. The effect of SO_2 was investigated with respect to SO_2 adsorption, sulfate formation/decomposition, NO_x adsorption and CH_4 activation, and in kinetics measurements. The role of sulfates was examined in separate tests with pre-sulfated catalysts.

2. Experimental

2.1. Catalyst preparation

Ag–alumina catalysts were prepared by a coprecipitation–gelation (co–gel) method using aq. nitrate solutions and tetramethyl ammonium hydroxide as the precipitant as reported before [8]. Low-content silver samples were prepared by leaching the parent $Ag–Al_2O_3$ samples using a dilute nitric-acid solution [12]. The as-prepared co–gel catalysts were generally calcined at 650 °C for 5 h, and the leached samples were further calcined at 650 °C for 3 h. The as-prepared Ag–alumina catalysts are denoted as AlAg(x, CG), where x is the wt.% of Ag determined by ICP analysis, and CG means coprecipitation–gelation. The leached catalysts are denoted by AlAg(x, L), where x is the wt.% of Ag left after leaching, as determined by ICP analysis, and L indicates a leached sample. Only the leached samples were tested in this work. Silver-free alumina was also tested for comparison.

2.2. Catalytic activity tests

The activity tests reported in this work were typically steady-state, isothermal runs with SO_2 present in the gas stream. The reaction was performed at 625 °C at atmospheric pressure. A space velocity of 50,000 h^{-1} (0.15 g catalyst and flow rate of 200 ml/min (STP)) was used, and the gas composition was (mol %) 0.25NO–2CH_4–5O_2–0 or 0.1 SO_2–bal. He. The reaction was carried out in a quartz tube (1 cm i.d.) packed-bed flow reactor equipped with a K-thermocouple for temperature measurement and a temperature controller. A detailed description of the reactor set up is given in [8]. The product gas stream was analyzed by a gas chromatograph (HP 5890), which was equipped with a thermal conductivity detector (TCD) and a 10 ft long × 1/8-in. diameter 5A molecular sieve column capable of separating NO, CH_4, O_2, N_2 and CO species. The SO_2 concentration was followed by FTIR (Mattson, Research Series 1) equipped with a 0.75 L/5.6 m gas cell operating at 150 °C. The conversions of CH_4 to CO_x and NO to N_2 were calculated from the gas analysis by gas chromatography, and the selectivity of CH_4 for the SCR reaction was calculated as follows [12]: S_{CH_4} = 2[amount of N_2 produced]/[amount of reacted CH_4].

Reaction rates in the presence of SO_2 were measured at 615–650 °C in the above gas composition, and the activation energies were calculated from low (<15%) conversions of NO at essentially differential reactor conditions.

To evaluate the activity of sulfates, catalysts were pre-sulfated in the reactor in the full reaction gas stream, 0.25% NO–2% CH_4–5% O_2–0.1% SO_2–He, at 625 °C for 24 h. A few samples were sulfated under different conditions or purchased in sulfated form and used as blanks.

2.3. Catalyst characterization

The BET specific surface areas of catalysts were measured by single-point N_2 adsorption/desorption on a Micromeritics Pulse Chemisorb 2705 instrument.

X-ray powder diffraction (XRD) analysis to identify crystalline phases in the fresh and used samples was performed on a Rigaku 300 X-ray diffractometer. Copper Kα radiation was used. The tube voltage was 60 kV, and the current was 300 mA.

Surface analysis of the sulfated catalysts was conducted on a Perkin-Elmer Model 5200C X-ray photoelectron spectrometer (XPS). The instrument operates at 2-mm spatial resolution with an Al Kα anode used as the X-ray source. C 2p (284 eV) was used as the internal reference to correct the XP spectra. S 2p signal was compared to reference compounds Ag_2SO_4 (Aldrich, 99%) and Al_2O_3 (Condea, 220 m^2/g) impregnated with sulfuric acid (Alpha, 95–98%). The atomic percent of accumulated sulfur was based on the core level spectra of Ag (3d), Al (2p), O (2s) and S (2p). Time-resolved XPS was performed on a SSX-100 ESCA spectrometer (Al source, 18 mA, 10 kV; spot size: 1000; analyzer resolution: 4.0).

2.3.1. SO_2 uptake tests in a TGA apparatus

Uptake of SO_2 was performed on a Cahn 121 thermogravimetric analyzer (TGA), with a resolution of 0.1 microgram.

The uptake experiment was run isothermally at selected temperatures. Generally, ~10 mg sample was weighed and placed in the TGA quartz pan. A high gas flow rate (400 ml/min) was used in all the tests. The catalyst was first pretreated in flowing helium at 500 °C for 0.5 h, then the temperature was increased to 625 °C in helium. After the TG signal was stabilized, the gas was switched to 0.1% SO_2–5% O_2–He at 625 °C, and the weight change was monitored and recorded for the desired time (generally till saturation).

2.3.2. *Sulfate decomposition*

Temperature programmed heating of the sulfated catalysts was used to examine the stability of surface sulfates, and the evolution of SO_2 with temperature was monitored by an on-line UV-analyzer (Western research series 900 Analyzer, AMETEK). The sulfate decomposition tests were carried out in a Micrometrics Pulse Chemisorb 2705. The sample, typically 0.1 g, was placed in a U-shape quartz sample holder inside a furnace connected to a temperature controller. The temperature was monitored by a K-thermocouple embedded in the furnace. Helium purge was used first at 50 ml/min at ambient temperature followed by temperature ramping conducted from RT to 1000 °C at 5 °C/min. The effluent gas composition was monitored by a UV–vis analyzer. Similar tests were performed with two reference samples, $Al_2(SO_4)_3 \cdot xH_2O$ (99.999%) (Alfa) and silver sulfate (99%) (Aldrich). For bulk silver sulfate, the decomposition starts at 800 °C with a sharp peak seen at 960–990 °C.

2.4. *Surface adsorption and reaction*

The experiments conducted in this section were generally repeated at least once to ensure that reproducible results were obtained. A quadrupole mass spectrometer (MKS-PPT-200EM) was used to continuously monitor the gas composition. The mass spectrometer (MS) was calibrated for the desired gas components. The following corrections were made to the MS signals: (1) for *m/e* signal 28, which could be due to N_2 or CO, 0.12 of the CO_2 (44) signal was subtracted to account for CO produced by CO_2 cracking in the chamber; (2) for the *m/e* signal of NO (30), 2.7 times the signal of NO_2 (46) was subtracted to account for the NO produced from NO_2, whenever these two components showed up simultaneously.

2.4.1. *Reaction light-off in CH_4–O_2–NO or CH_4–O_2–NO–SO_2*

Transient reaction data in gas mixtures containing NO were collected to evaluate the effect of SO_2 on NO reduction with temperature. The tests were carried out in the microreactor coupled to the MS and FTIR instruments. The main purpose of using IR was to check for CO formation, since mass spectrometry cannot discriminate between CO and N_2, both of *m/e* ratio of 28. Generally, 0.3 g samples were used in these tests. After pretreatment at 500 °C in He for 1.5 h, the catalyst was cooled down to RT. Then, the reaction gas mixture, comprising 0.25% NO–2% CH_4–5% O_2–balance He or 0.25% NO–2% CH_4–5% O_2–0.08% SO_2–balance He, was switched in at a flow rate of 100 ml/min. The heating rate was 10 °C/min, from RT to 700 °C. The following reactant and product gas species were monitored by MS: CH_4 (15), O_2 (32), SO_2 (64, 48), NO (30), CO_2 (44), CO/N_2 (28), NO_2 (46) and H_2O (18), together with some sulfur-containing components – H_2S (34), COS (60), CS_2 (76), CHS (45) and SO_3 (80). Duplicate or triplicate tests were run to ensure reproducibility.

2.4.2. *NO–O_2-TPD*

To examine the effect of sulfate formation on NO adsorption, temperature-programmed desorption of NO in O_2/He carrier gas, NO–O_2-TPD, was performed over fresh and corresponding sulfated samples.

The TPD experiments were carried out in the fixed-bed microreactor. Generally, ~0.15 g sample was placed into the quartz reactor between two layers of quartz wool. The catalyst temperature was measured by a thermocouple which was in contact with the catalyst bed. The reactor outlet was connected to a mass spectrometer for gas analysis. Typically, the sample was pretreated under two conditions: (a) 625 °C, He, 200 ml/min, 3 h, denoted as "fresh"; (b) 625 °C, 0.25% NO–2% CH_4–5% O_2–1000 ppm SO_2, 200 ml/min, 24 h, denoted as "sulfated". After either pretreatment, the catalyst was cooled down to RT, where adsorption was performed by flowing 1.5% NO, 5% O_2/He at 50 ml/min over the catalyst till saturation (~2.5 h). Then, pure He at 50 ml/min was used to purge the catalyst overnight to remove weakly adsorbed species as monitored by the mass spectrometer. Desorption was performed in 5% O_2/He at 50 ml/min by ramping the temperature from RT to 700 °C at 10 °C/min. This O_2-containing carrier gas was used to mimic the oxidative environment of the SCR reaction. The following species were monitored by mass spectrometry: NO(30), O_2(32), NO_2(46), N_2O(44) and N_2(28).

2.4.3. *TPSR in CH_4/O_2/SO_2*

Temperature-programmed surface reaction (TPSR) tests in a CH_4–O_2–SO_2–He gas mixture were performed with presulfated Ag–alumina catalysts. Generally, 0.15 g catalyst was weighed and placed in the fixed-bed reactor. First, the catalyst was pretreated in the SO_2-containing full gas stream (0.25% NO–2% CH_4–5% O_2–0.1% SO_2–He) at 625 °C for 24 h. After cooling down to RT, a gas mixture of 1.5% NO/5% O_2/He at 50 ml/min flowed over the catalyst, and adsorption was monitored with the mass spectrometer till saturation. Helium purge was used to remove the physically adsorbed species, which were monitored by the mass spectrometer till stabilization. At RT, a gas mixture of 2% CH_4–5% O_2–0.16% SO_2 at 50 ml/min was switched into the reactor, and the catalyst was heated up to 700 °C at 10 °C/min. The effluent gas composition was monitored by IR and mass spectrometry simultaneously. The following reactant and product species were monitored by MS: CH_4 (15), O_2 (32), SO_2 (48, 64), NO(30), CO_2/N_2O(44), CO/N_2(28), NO_2(46) and H_2O(18), together with some sulfur-containing components – H_2S(34), COS(60), CS_2(76), CHS(45) and SO_3(80), which were found to be negligible. TPSR experiments were repeated twice and reproducible results were obtained.

3. Results and discussion

3.1. CH_4-SCR activity of catalysts in the presence of SO_2

In this section, we report the effect of SO_2 on the activity and stability of alumina and Ag–alumina catalysts in CH_4-SCR of NO. Typically ~1000 ppm SO_2 was added to the reaction gas mixture.

3.1.1. Temperature effect

The effect of SO_2 on catalyst activity depends strongly on the reaction temperature, as shown in Fig. 1 over the leached catalyst AlAg(7, L) at 550, 575, 600 and 625 °C. Addition of SO_2 causes a fast drop in both the conversion of NO to N_2 and CH_4 to CO_x at all the temperatures. However, a much more severe decrease in NO and CH_4 conversions took place upon addition of SO_2 at 550 and 575 °C. Essentially, the reaction was quenched at these two temperatures. When the temperature was increased to 600 °C, the NO conversion dropped by ~2/3, but could still be maintained at 32% in the presence of SO_2, while CH_4 conversion was only 9%. At 625 °C, a much milder effect of SO_2 was observed, specifically, the NO conversion dropped from 86 to 69%, while the CH_4 conversion decreased from 62 to ~29%. Moreover, at 625 °C, the catalyst stability was very good, since these conversions were maintained during 10 h-on-stream with SO_2 present. The selectivity of CH_4 for NO reduction was calculated both in the presence and absence of SO_2 at these four temperatures, and is shown in Fig. 1(c). Clearly, SO_2 enhances the selectivity of CH_4 for SCR of NO over Ag–alumina catalysts by suppressing the combustion of CH_4 with O_2.

The strong SO_2 inhibition at temperatures below 600 °C may be due to almost complete coverage of the active catalytic sites by adsorbed SO_2, thus hindering adsorption of NO_x or activation of CH_4. This point will be further addressed below. Satokawa et al. have also reported that the effect of SO_2 depends strongly on temperature in SCR of NO_x with C_3H_8 over a 2 wt.% Ag–alumina catalyst [20]. Only 4 ppm SO_2 was enough to suppress the reaction below 550 °C in that work.

3.1.2. Cyclic and long-term effect of SO_2 on SCR over Ag–alumina catalysts

The long-term effect of SO_2 was investigated with another leached sample, AlAg(7.2, L), pre-sulfated at a more severe condition with 2000 ppm SO_2 in the gas mixture for 24 h, as shown in Fig. 2(a). The test was carried out at 625 °C, the added SO_2 concentration was 1000 ppm, and a space velocity of 72,000 h^{-1}, higher than in Fig. 1, was used. The experiment began without SO_2, and it was observed that both the NO and CH_4 conversions rose with time from 42 to 60%, and from 34 to

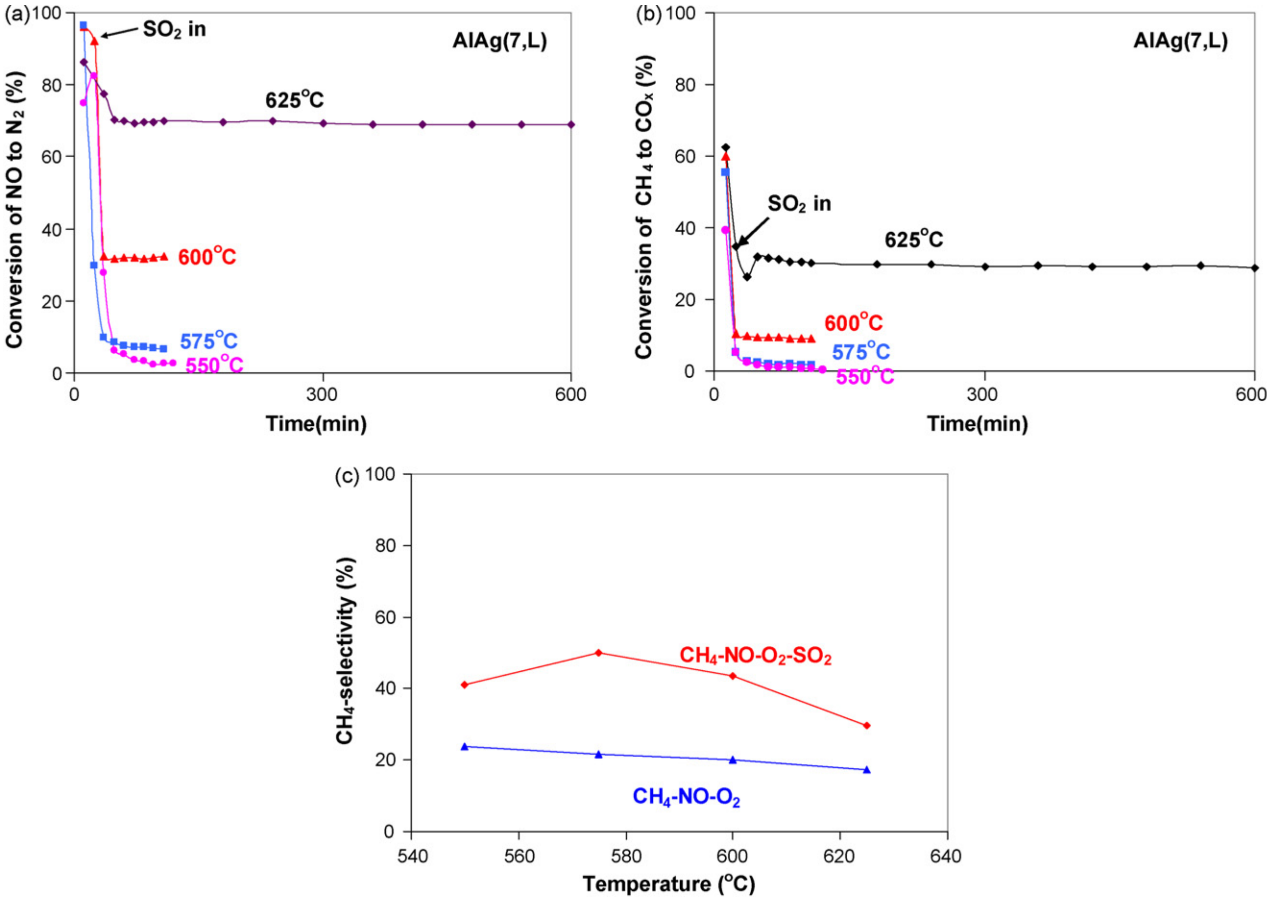

Fig. 1. CH_4-SCR of NO over AlAg(7, L) in the presence of SO_2 as a function of reaction time at different temperatures. (a) Conversion of NO to N_2; (b) conversion of CH_4 to CO_x; (c) selectivity of CH_4 for NO reduction. Catalyst: 0.15 g; feed gas: 0.25% NO–2% CH_4–5% O_2–0/1200 ppm SO_2, 200 ml/min; SV = 50,000 h^{-1}.

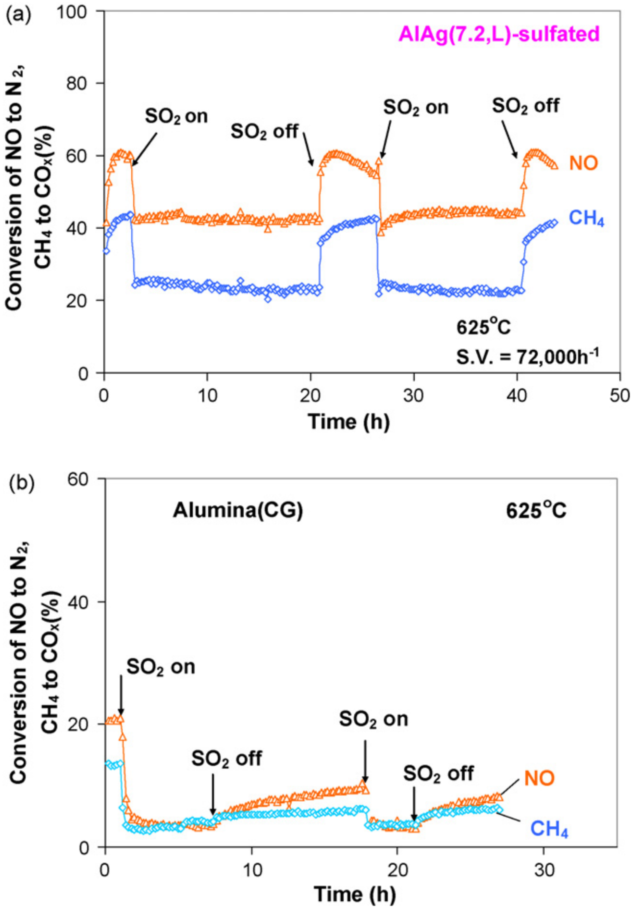

Fig. 2. (a) CH_4-SCR of NO over sulfated AlAg(7.2, L). Sulfation: 0.25% NO–2% CH_4–5% O_2–2000 ppm SO_2–He, 625 °C, 24 h. Catalyst load: 0.10 g. Feed gas: 0.25% NO–2% CH_4–5% O_2–0/1000 ppm SO_2–He, 200 ml/min. $T = 625$ °C; SV = 72,000 h^{-1}. (b) Effect of SO_2 on the CH_4-SCR of NO over alumina(CG). Catalyst load: 0.15 g. Feed gas: 0.25% NO–2% CH_4–5% O_2–0/1200 ppm SO_2–He, 200 ml/min. $T = 625$ °C. SV = 50,000 h^{-1}.

43%, respectively, in ~3 h. This is attributed to the gradual decomposition of the sulfated surface at the reaction temperature. When SO_2 was added, both the NO and CH_4 conversions decreased instantaneously to 42 and 23%, respectively, and remained stable for 18 h. The catalytic activity can be totally recovered in ~1 h after removal of SO_2. However, in the absence of SO_2, NO reduction cannot be maintained and conversion decreases to 54% in 5.8 h. The second cycle of addition and removal of SO_2 exhibits the same behavior as the first cycle. Similar to the findings of Fig. 1(c), the selectivity of CH_4 for NO increases from 17.6 to 22.7% in the presence of SO_2 over this pre-sulfated Ag–alumina catalyst.

The fast conversion drop with addition of SO_2 followed by instantaneous recovery upon its removal indicates that the interaction of SO_2 with the catalyst at 625 °C is governed by a fast adsorption equilibrium. The activity loss may then be due to loss of active sites occupied by SO_2, possibly via formation of surface sulfates, a point verified below by XPS and sulfate-decomposition analysis of the used catalysts. The immediate activity recovery with removal of SO_2 indicates that the catalyst was not permanently deactivated, and that adsorption of SO_2 was reversible. Interestingly, although addition of SO_2 causes loss of activity, the catalyst stability was enhanced by SO_2, compared to a drop in NO conversion with time-on-stream observed in the SO_2-free gas mixture, especially for parent catalysts [25]. The stabilization of Ag–alumina catalysts under reaction conditions in the presence of SO_2 appears to derive from suppression of growth of silver particles [25] and is the topic of a future report.

A poisoning effect of SO_2 on bare alumina is shown in Fig. 2(b). When 1200 ppm SO_2 was added to the reaction gas mixture, the conversions of NO to N_2 and CH_4 to CO_x dropped very fast to 5 and 3%, respectively, from 20 and 14%, and were both stabilized at 4% in 5 h. When SO_2 was removed from the gas stream, recovery was only partial. Therefore, SO_2 inhibition of both the NO reduction and CH_4 oxidation reaction was only partially reversible over alumina at 625 °C. A second cycle gave similar results. Further, compared to the instantaneous activity recovery of AlAg(7.2, L) in Fig. 2(a), alumina(CG) is only gradually regenerated at 625 °C after removal of SO_2. This also indicates that once alumina sites are sulfated, heating to 625 °C is not adequate to free up but only a few of these sites, which is due to the high decomposition temperature (>800 °C) of aluminum sulfate, as shown below in Fig. 5. Burch et al. [26] compared the SCR activity of fresh and sulfated alumina using methanol and propane as reductants of NO, and found that pre-sulfation did not affect the CH_3OH-SCR activity, while the C_3H_8-SCR activity was suppressed significantly. Apparently, sulfated alumina sites can catalyze the former, but not the latter reaction. Propane-SCR is very different from propene-SCR, the latter being promoted by sulfates, as mentioned above [16,17]. Thus, sulfated alumina and Ag–alumina catalyze the SCR reaction when the reductant is C_3H_6 or CH_3OH, but not when alkanes, such as C_3H_8 or CH_4, are used. How this activation takes place is interesting to investigate.

3.2. SO_2 uptake on Ag–alumina

Alumina is an important catalyst for the Claus reaction and its interaction with SO_2 has been extensively investigated [27,28]. SO_2 is reported to adsorb on surface hydroxyls, surface O^{2-} anions, or aluminum ions to form surface sulfites. In oxidative adsorption, surface sulfates were also identified by FTIR [29–31], with the surface aluminum sulfate thermally decomposing at >800 °C [30]. To our knowledge, there are very few detailed studies of the adsorption of SO_2/O_2 on Ag–alumina catalysts [32]. Sulfates on both Al sites and Ag sites were identified by DRIFTS in SO_2/O_2 gas mixture at 200–500 °C, and DFT calculations also corroborate the formation of these two types of sulfates on Ag–alumina [32].

In this work, we examined the uptake of SO_2/O_2 by Ag–alumina by thermogravimetric analysis (TGA), and the results are shown in Fig. 3. The experiment was performed at 625 °C, same as the reaction temperature used in Fig. 2. At this temperature, the weight change of the sample in the flowing 0.1% SO_2–5% O_2–He gas mixture was monitored with time over alumina and leached AlAg(5.4, L), as well as over a high silver-content catalyst, AlAg(11, CG). For each sample, the experiment was done twice and the results are reproducible.

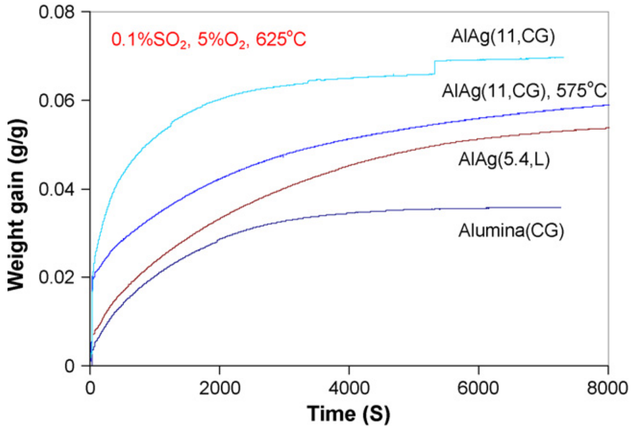

Fig. 3. SO_2 uptake over alumina and Ag–alumina catalysts at 625 °C in 0.1% SO_2–5% O_2–bal. He.

SO_2 uptake at the above conditions reached saturation in ~2 h over these catalysts. Based on the weight change, catalyst surface area, and SO_2 molecular area [31], the saturated surface sulfur coverage was calculated for these catalysts, as shown in Table 1. As in Ref. [31], we took sulfite (SO_3) as the adsorbed state, and used the value of molecular area of 0.1 $m^2/\mu mol$ for adsorbed SO_2. For alumina, leached AlAg(5.4, L) and AlAg(11, CG), the surface sulfur coverage was thus calculated to be 20, 29 and 40% of a monolayer, respectively. These values indicate the presence of a partially sulfated Ag–alumina surface in flowing SO_2 at 625 °C.

For AlAg(11, CG), the SO_2 uptake was measured also at 575 °C, as shown in Fig. 3, and the sulfur coverage was calculated to be 35% (Table 1), less than that at 625 °C, which indicates that adsorption of SO_2 is activated over the AlAg(11, CG) catalyst. We attribute this to the alumina part of the catalyst. Nam et al. [31] measured the SO_2 uptake on γ-alumina at two different temperatures, 500 and 700 °C, and found it to be lower at 500 °C than at 700 °C, indicative of activated SO_2 adsorption on alumina. They reported a sulfur coverage of 25% at 700 °C by flowing 1% SO_2–14% O_2 over γ-alumina. There exist many other literature reports which agree that the interaction of SO_2 or SO_2/O_2 with alumina is limited to the surface (less than a monolayer) [33,34]. The results in Fig. 3 and the calculated surface sulfur coverage (Table 1) also indicate that silver enhances the SO_2 uptake on alumina. There are two possible explanations for this: (1) SO_2 adsorbs onto silver sites and forms sulfite/sulfate, as is well known by the work of Madix and co-workers [35,36]; or (2) silver catalyzes the formation of SO_3 from SO_2 and O_2, and SO_3 can strongly bind to the Ag surface as identified by Vayenas and Saltsburg's work on silver films [37]. The adsorbed SO_2 or SO_3 on silver sites can diffuse to aluminum sites to form sulfates, as suggested by Abe et al. [23].

Table 1
SO_2 uptake by alumina and Ag–alumina catalysts at 625 °C calculated from the data of Fig. 3

Sample	Weight gain (g/g)[a]	SA (m^2/g)	$\mu mol/m^2$	Surface sulfur coverage (%)[c]
Alumina(CG)	0.035	217.5	2.0	20
AlAg(5.4, L)	0.053	225.1	2.9	29
AlAg(11, CG)	0.065	202.8	4.0	40
AlAg(11, CG)[b]	0.057	202.8	3.5	35

[a] As shown in Fig. 3, SO_2 uptake on alumina and AlAg(11, CG) at 625 °C reaches saturation within 2.2 h, even though the uptake on AlAg(5.4, L) at 625 °C and AlAg(11, CG) at 575 °C is still below saturation after 2.2 h. Hence, for the former two samples, saturated SO_2 uptake values were used to calculate the weight gain, while for the latter, SO_2 uptake values at the time point of 2.2 h were used.

[b] SO_2 uptake measured at 575 °C.

[c] Adsorbed SO_2 was assumed in the form of surface sulfite, and surface coverage was calculated based on the molecular area of SO_2: 0.1 $m^2/\mu mol$ [30].

3.3. Chemical states of sulfur on sulfated Ag–alumina catalysts

Silver sulfate has been identified on Ag–alumina catalysts aged in SO_2-containing reaction gas streams [23,17]. Abe et al. [23] found extensive agglomeration in SO_2-aged 4.6 wt.% Ag/alumina catalysts ($SO_2/O_2/NO/H_2O$, at 450 °C, without addition of ethanol (used in that work as the NO_x reductant), and identified the presence of $Ag_2(SO_4)$ by XRD. Park et al. [17] also identified $Ag_2(SO_4)$ by XRD in a 8 wt.% Ag/Al_2O_3 catalyst after 33 h-on-stream in C_3H_6-SCR with 30 ppm SO_2 at 500 °C. In the latter work, silver sulfate was even proposed to be active for C_3H_6-SCR of NO. To check this point with our catalysts, we conducted XRD analysis (results not shown) of both fresh and sulfated catalysts, including Al_2O_3, leached AlAg(7.2, L), and AlAg(11, CG). Sulfation took place in SO_2-containing full gas at 625 °C for 24 h. We found only peaks due to γ-alumina present in all samples, both fresh and sulfated. No phases due to metallic silver, silver sulfate or aluminum sulfate were observed, in contrast to the detection of Ag_2SO_4 reported at lower temperatures [17,23]. The high dispersion of silver in the fresh material prepared by co–gelation may explain the lack of silver phases. Moreover, the temperature of 625 °C used here is probably high enough for silver sulfate decomposition. Of course, surface sulfates of silver and aluminum could be present, but these are hard to detect by XRD.

To further explore the chemical states of sulfur on the surface of sulfated Ag–alumina catalysts, XPS analysis of the above sulfated catalysts was done, the data shown in Fig. 4. A strong S 2p band is seen for sulfated AlAg(11, CG) and AlAg(7.2, L). From the XPS survey analysis, the surface sulfur amount was estimated to be ~7.5 wt.% on both catalysts. The peaks of S 2p over the above two catalysts were positioned at 169.3 eV (referenced to C at 284.0 ev), which corresponds very well to the S 2p peak of the two reference samples, Ag_2SO_4 and Al_2O_3 doped with $SO_4{}^{2-}$ ions (via H_2SO_4 impregnation). Hence, sulfate species exist on the two sulfated catalysts. However, it is not possible to distinguish between sulfates associated with silver or Al_2O_3 by XPS, as discussed in the literature [20]. On the other hand, surface aluminum sulfate and silver sulfate exhibit different thermal stability and decompose at different temperature ranges, as reported in literature [23,20,32,38]. To further differentiate the two types of surface sulfates, we studied the thermal decomposition of sulfated

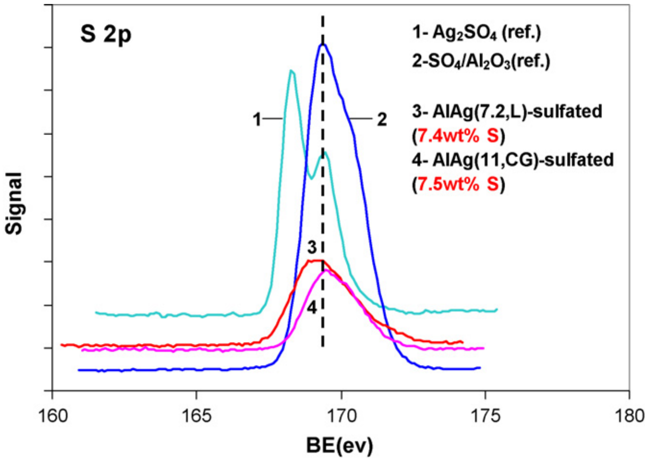

Fig. 4. XP spectra of S 2p of sulfated Ag–alumina catalysts.

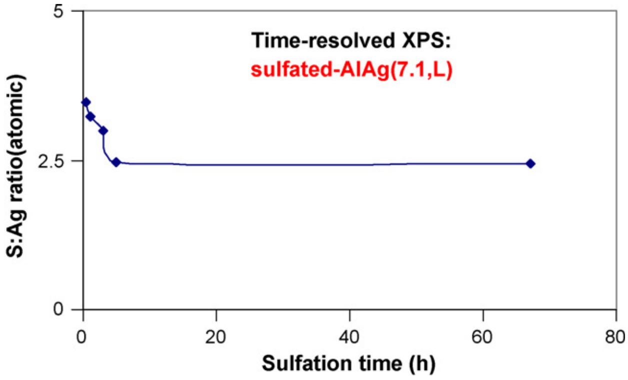

Fig. 6. Surface S:Ag ratio in sulfated AlAg(7.1, L) after different sulfation times. Sulfation: 625 °C, 0.25% NO–2% CH_4–5% O_2–0.1% SO_2, 0.15 g, 200 ml/min.

Ag–alumina catalysts in He, monitoring the SO_2 produced with temperature ramping.

Fig. 5 presents results obtained from AlAg(5.6, L) sulfated for 0.5, 1 and 3 h. Very similar SO_2 profiles were found over the three sulfated catalysts, indicating that sulfation is a facile process and limited to the surface, since no further sulfur accumulation was found on the longer time-sulfated samples. A small broad peak is present in the range 500–700 °C, with a maximum at ~625 °C. A strong second peak starts from 700 °C, and continues up to ~1000 °C. The above observed temperature range is very close to other reports [23,20,32]. Abe et al. [23] found two SO_2 peaks at 427 and 727 °C by similar experiments, and assigned these peaks to decomposition of sulfate from silver sites and alumina sites, respectively. Satokawa et al. [20] also reported two SO_2 peaks at 427–877 °C and at 877–1027 °C, assigning them to silver sulfate and aluminum sulfate, respectively. On the basis of the above, we may also assign the first peak in Fig. 5 to decomposition of silver sulfate and the second peak to aluminum sulfate. The weak signal of the first peak could be due to the high sulfation temperature we used here, 625 °C, at which temperature most silver sulfate has decomposed according to the above-cited literature. It is worth noting that although Sumiya et al. [38] reported decomposition of silver sulfate at a temperature as low as 227 °C, we observed SO_2 elution only from 500 °C, which is close to the temperature reported by other groups [23,20,32].

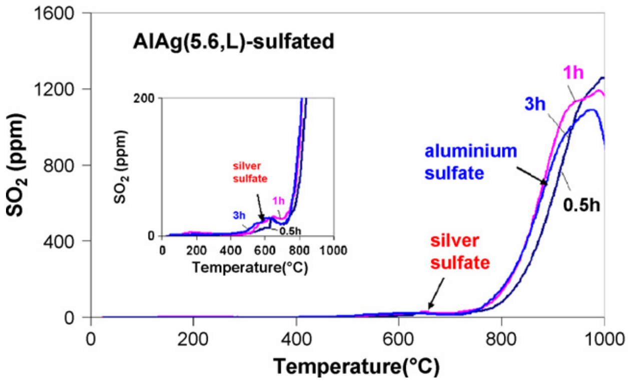

Fig. 5. Sulfate decomposition from sulfated AlAg(5.6, L). Catalyst load: 0.15 g. Sulfation: 0.25% NO–2% CH_4–5% O_2–1000 ppm SO_2–He, 200 ml/min, 625 °C. TPD: 5 °C/min, RT-1000 °C, 50 ml He/min.

Fig. 6 shows the time-resolved S:Ag atomic ratio on the surface of AlAg(7.1, L) measured by XPS. After sulfation for 0.5 h, the value of surface S:Ag ratio is 3.4. A slight decrease was observed after further sulfation to 5 h, and then the value was stabilized at 2.5 up to 67 h-sulfation, which again implies that sulfation reaches equilibrium fast. The S/Ag atomic ratio is much higher than one, showing that aluminum sulfate as well as silver sulfate is present on the surface.

Surface aluminum sulfates are the dominant feature on Ag–alumina catalysts sulfated at 625 °C, as identified by XPS and sulfate decomposition, while most of the silver sites are free of sulfur due to the decomposition of silver sulfate at this temperature (Fig. 5). This surface structure is active for the SCR of NO_x with methane as shown in Fig. 1. Thus, the critical feature for activity is to have free silver/silver oxide sites. When all silver is sulfated as is the case at temperatures below 550 °C, reaction is quenched (Fig. 1). While alumina is more extensively sulfated in the Ag–O–Al samples, the activity of the latter is much higher, as seen by comparing Fig. 2(a) and (b). This is because in the absence of silver, Al–O sites alone cannot activate one of the key reaction species, methane [12].

3.4. *Effect of SO_2 on NO_x adsorption and reaction light-off*

On the basis of the above findings, sulfur accumulation on Ag–alumina catalysts in the form of silver and aluminum sulfates seems to reversibly occupy some of the active sites. It is interesting to examine how the presence of sulfates affects the NO_x adsorption and the lightoff of the reaction of CH_4-SCR reaction over Ag–alumina surfaces.

3.4.1. *Reaction light-off in CH_4–O_2–NO and CH_4–O_2–NO–SO_2*

The effect of SO_2 on NO reduction was investigated by comparing the reaction products during heating (10 °C/min) in CH_4–O_2–NO and CH_4–O_2–NO–SO_2 gas mixtures. The results are shown in Fig. 7.

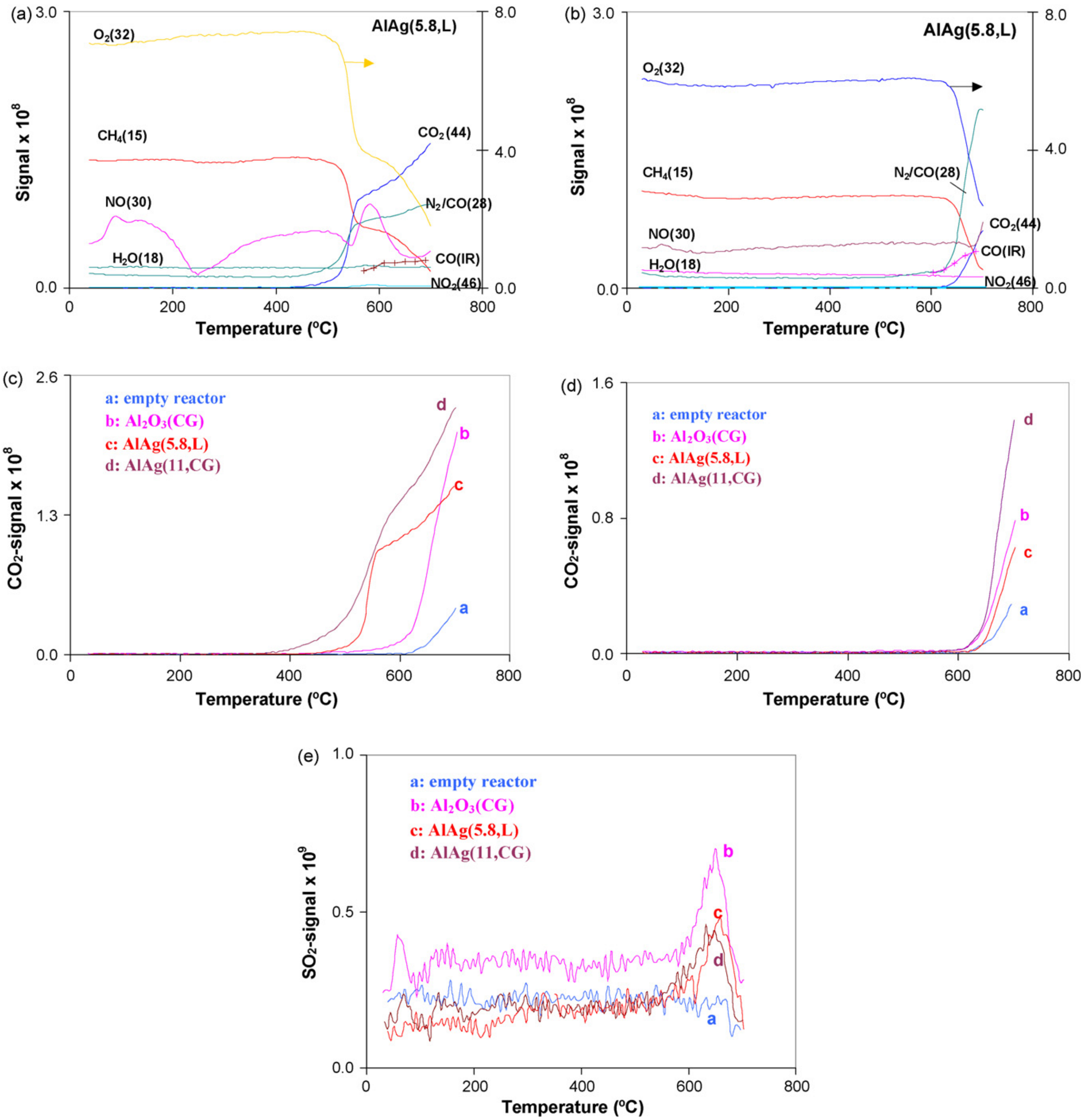

Fig. 7. (a) Reaction light-off in NO/CH_4/O_2 over AlAg(5.8, L). Catalyst load: 0.3 g; pretreatment: 500 °C, in He, 1 h. Feed gas: 0.25% NO–2% CH_4–5% O_2, 100 ml/min. Temperature ramping: 10 °C/min, RT-700 °C. (b) Light-off in NO/CH_4/O_2/SO_2 over AlAg(5.8, L). Catalyst: 0.3 g; pretreatment: 500 °C, in He, 1 h. Feed gas: 0.25% NO–2% CH_4–5% O_2–0.08% SO_2, 100 ml/min. Temperature ramping: 10 °C/min, RT-700 °C. (c–e) Comparison of CO_2 and SO_2 produced during light-off in CH_4/NO/O_2 (c) or CH_4/NO/O_2/SO_2 (d and e).

Fig. 7(a) and (b) shows the reaction profiles over the leached AlAg(5.8, L) sample in CH_4–O_2–NO and in CH_4–O_2–NO–SO_2 gas mixtures, respectively. Without SO_2 in the reaction gas stream, adsorption of NO_x on the catalyst is shown by a consumption peak of NO at 230–300 °C in Fig. 7(a). Strong consumption of CH_4 and O_2 was observed accompanied by production of CO_2 (44) and N_2/CO (28), beginning at ~450 °C. To differentiate between the CO produced from N_2, CO was also monitored by FTIR and the thus obtained CO signal is shown as CO (IR). The above value is higher than the light-off temperature of 300 °C observed in TPSR of the same sample by flowing the CH_4–O_2 gas mixture over its surface, saturated by pre-adsorbed NO_x [12]. This difference is not easy to explain, unless the pretreatment with NO_x as in [12] totally changes the catalyst surface. More dramatic is the effect of SO_2 on the consumption/production of the various gases, as shown in Fig. 7(b). Firstly, the NO adsorption peak at 230–300 °C disappears, which indicates that SO_2 inhibits NO_x adsorption in this temperature range. Secondly, the consumption of CH_4/O_2 and production of CO_2/N_2/CO begins at a much higher temperature, ~600 °C, for the reaction in CH_4–NO–O_2–SO_2, compared to ~450 °C for the reaction in CH_4–NO–O_2 (Fig. 7(a)). The SO_2 elution profiles are shown in Fig. 7(e). The SO_2 signal is flat up to 600 °C, and then begins to increase and peaks at 650 °C. The SO_2 peak is attributed to decomposition of surface sulfates, especially silver sulfates, as the data in Figs. 3–6 indicate. Clearly, the light-off temperature for CO_2 production coincides with the sulfate decomposition temperature, which takes place at ~600 °C. The results in Fig. 7 are consistent with the strong inhibition of the NO reduction by SO_2 below 600 °C, depicted in Fig. 1.

Similar light-off experiments were carried out under the above two conditions over other catalysts, including alumina and AlAg(11, CG), as well as in an empty reactor (to check for gas-phase reactions). Fig. 7(c) and (d) shows the CO_2 profiles in CH_4–O_2–NO and CH_4–O_2–NO–SO_2, respectively, and the profiles of eluted SO_2 are shown in Fig. 7(e). The presence of SO_2 suppresses NO adsorption and increases the light-off temperature to 600 °C over these catalysts, similar to the AlAg(5.8, L) sample. Gas-phase reactions also contribute to the reaction products above 600 °C.

In another test, Fig. 9, a pre-sulfated AlAg(5.8, L) was further fully sulfated with SO_2 in the gas stream at $T < 600$ °C, and no activation of CH_4 took place. At $T \sim 600$ °C, sulfates began to decompose, as indicated by the elution of SO_2. At this temperature, active (Ag–O–Al) sites were recovered and CH_4 activation took place on the free sites. Therefore, a pre-sulfated surface or the presence of SO_2 in the reaction gas stream shifts the CH_4 activation to the much higher temperature of 600 °C compared to the 300 °C-light-off temperature observed in the absence of SO_2 [12].

To our knowledge, previous reports of the effect of SO_2 on NO_x-SCR activity of Ag–alumina catalysts have mainly investigated pre-sulfated catalysts by TPD or DRIFTS [39,38,11]. No such transient study with co-existence of SO_2 in the reaction gas mixture has been reported for Ag–alumina catalysts. The present findings elucidate the interaction between SO_2 and NO_x, and have identified that CH_4 activation requires sulfur-free silver sites (Ag–O–Al). Silver sulfate is not a catalyst. Neither is aluminum sulfate.

3.4.2. NO–O_2-TPD

NO_x adsorption was compared between fresh and sulfated Ag–alumina catalysts by NO–O_2-TPD. Fig. 8(a) and (b) presents the results over alumina(CG) and leached AlAg(6, L), respectively. The catalysts were partially sulfated at 625 °C in the SO_2-containing full reaction gas for 24 h. For both samples, a main NO desorption peak appears at ~460 °C, and the signal intensity is clearly lower on the sulfated catalyst than on the fresh one. The amounts of desorbed NO over fresh and sulfated catalysts are listed in Table 2. Sulfation causes nearly 50% decrease of the adsorbed NO_x amount on these catalysts. However, as discussed above, sulfation of some of the surface sites does not modify the NO_x adsorption mechanism. NO_x and SO_2 compete for the same sites.

Similar sulfate inhibition effects have been reported in the literature for other HC-SCR systems [11,19,39,26]. For example, Burch et al. [26] reported a 45% decrease in strongly adsorbed NO (437 °C peak), but a 26% increase in weakly adsorbed NO species (132 °C peak) over sulfated alumina, compared to fresh alumina. The activity for C_3H_8-SCR of NO was severely suppressed on sulfated alumina, while methanol-SCR of NO_x was hardly affected by the sulfation. Meunier et al. [19] reported that a 1.2 wt.% Ag/alumina was severely deactivated by SO_2 in C_3H_6-SCR of NO, and further in situ DRIFTS [11] over Ag/alumina and sulfated Ag/alumina showed that sulfates formed on the catalyst decrease the concentration of adsorbed NO_x species under reaction

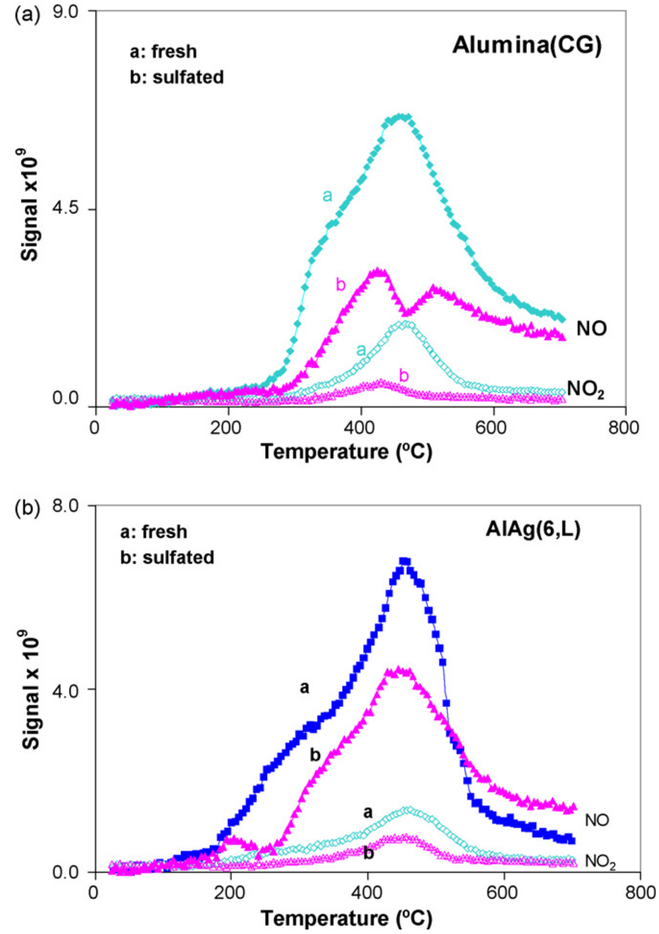

Fig. 8. NO–O_2-TPD over (a) fresh and sulfated alumina(CG); (b) fresh and sulfated AlAg(6, L). Catalyst: 0.15 g. Pretreatment: (a) 625 °C, He, 200 ml/min, 3 h; (b) 625 °C, 0.25% NO–2% CH_4–5% O_2–1000 ppm SO_2, 24 h. Adsorption: RT, 1.5% NO, 5% O_2, 50 ml/min, 2.5 h; purge: He, 50 ml/min, 12 h; desorption: 5% O_2/He, 50 ml/min, 10 °C/min, RT-700 °C.

Table 2
Comparison of amount of desorbed NO during NO–O_2-TPD from fresh and sulfated Ag–alumina catalysts[a]

Sample	Condition	Desorbed NO(μmol/m^2)
Alumina(CG)	Fresh	2.08
	Sulfated	1.2
AlAg(6, L)	Fresh	2.13
	Sulfated	1.66

[a] Calculated on the basis of the results presented in Fig. 8, integrated from RT to 700 °C.

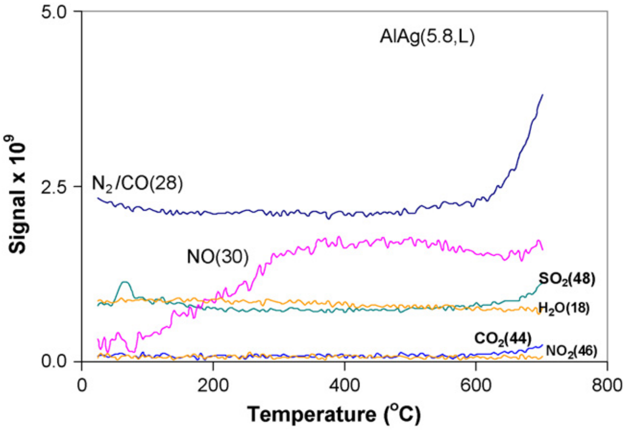

Fig. 9. TPSR in $CH_4/O_2/SO_2$ over AlAg(5.8, L). Catalyst: 0.15 g. Pretreatment: 625 °C, 0.25% NO–2% CH_4–5% O_2–0.1% SO_2, 200 ml/min, 24 h. Adsorption: RT, 1.5% NO, 5% O_2, 50 ml/min, 2.5 h; purge: He, 50 ml/min, 12 h; TPSR: 2% CH_4–5% O_2–0.16% SO_2–He, 50 ml/min, 10 °C/min, RT-700 °C.

conditions. Hence, they assigned the deactivation to loss of adsorbed sites for NO_x (possibly due to sulfated alumina sites) and to the lower oxidation activity of sulfated silver to form NO_2 from NO. Li et al. [40] investigated sulfation effect on NO uptake by Ce–Ag–ZSM-5 catalysts, and found that sulfation at 400 °C caused a 66% loss in NO uptake, while sulfation at 600 °C decreased the NO uptake by 26%, which correlated to the activity loss at the above two temperatures. However, in this case, the contribution of Ce to sulfation must be included.

3.4.3. Temperature programmed surface reaction (TPSR) in $CH_4/O_2/SO_2$

We further examined the reactivity of adsorbed NO_x on pre-sulfated Ag–alumina catalysts toward CH_4/O_2 for dinitrogen formation, even with SO_2 in the reaction gas. Fig. 9 presents the results of TPSR of pre-adsorbed NO_x on sulfated AlAg(5.8, L) in $CH_4/O_2/SO_2$. Similar to NO–O_2-TPD, firstly, a mixture of NO and O_2 was passed over the sulfated catalysts, and then TPSR was conducted in gas stream of 2% CH_4–5% O_2-0.16% SO_2, while heating the catalyst to 700 °C at 10 °C/min. As shown in Fig. 9, a small and broad NO desorption peak is seen at 200–600 °C. Interestingly, a common light-off temperature was observed at 600 °C for elution of CO_2 (*m*/*e* = 44), N_2/CO (*m*/*e* = 28) and SO_2 (*m*/*e* = 48). This also indicates that it is necessary to decompose the surface sulfates for CH_4-SCR to take place, which is consistent with the findings of Fig. 7.

Table 3 lists the amount of CO_2 produced in the reaction light-off tests with or without SO_2 present (Fig. 7) and in TPSR in $CH_4/O_2/SO_2$ (Fig. 9) over the pre-sulfated catalysts. Clearly, the presence of SO_2 suppresses 4–8 times the CO_2 product. The amount of CO_2 is much lower in the TPSR experiments than in the light-off tests of Fig. 7d, which could be due to higher SO_2 concentration (0.16%) in the former tests than the latter ones (0.08%).

The above findings differ from what has been reported for the activation of C_3H_6-SCR or C_2H_5OH-SCR on sulfated Ag–alumina [23,26]. Hence, it is essential to preserve free Ag–O–Al sites to conduct CH_4-SCR of NO in the presence of SO_2 which clearly depends on the stability of sulfates formed on the Ag–alumina catalyst. Figs. 5 and 7 together show the stability of sulfates in He, and in the full reaction gas ($CH_4/NO/O_2/SO_2$). The catalyst surface is partially sulfated, which is supported by both the calculated sulfur coverage from SO_2-uptake (Fig. 3) and the NO-TPD (Fig. 8) results. SO_x is adsorbed on alumina, and also on silver sites reaching equilibrium. Silver sulfate species decompose first at ~600 °C (Fig. 5), while alumina sites remain sulfated. Thus, it is the presence of free Ag–O–Al sites that is critical for reaction light-off. Activation of CH_4 coincides with the decomposition of surface silver sulfate at ~600 °C.

Table 3
Comparison of CO_2 produced during light-off tests in various gas compositions

Sample	Amount of CO_2 (μmol/m^2)		
	in $CH_4/NO/O_2$[a]	in $CH_4/NO/O_2/SO_2$[a]	in TRSR[b]
Alumina(CG)	899	227	17.3
AlAg(5.8, L)	1730	181	20.2
AlAg(11, CG)	2480	366	73.9

[a] CO_2 amount was calculated from Fig. 7c–d, RT-700 °C.
[b] CO_2 amount was calculated from Fig. 9, RT-700 °C.

3.5. Gas phase reactions

Above 600 °C, gas phase reactions can be involved in the CH_4-SCR reaction scheme. The data in Figs. 7–9 show participation of gas phase reactions. To explore this further, we conducted both steady-state activity measurements and reaction light-off experiments in an empty reactor. For comparison, silica beads were also loaded on the quartz frit, the experiment was repeated, and the results were similar to the empty reactor.

Homogeneous reduction of NO with CH_4 in excess O_2 and in the presence or absence of SO_2 takes place at ~600 °C, as can be seen in Fig. 10(a). The conversion of NO to N_2 was 9.7% and CH_4 conversion was 50.5% at 650 °C. Transient reaction rate results corroborate the above point, as shown in Fig. 10(b), the production of CO_2/N_2/CO beginning at 600 °C. Therefore, contribution of gas-phase reaction should be considered for the NO reduction activity observed at 625 °C for Ag–alumina catalysts. The selectivity of CH_4 for the SCR of NO over AlAg(7, L) is ~30% at 625 °C as shown in Fig. 1(c); from the empty reactor data in Fig. 10(a), the selectivity of CH_4 is ~3.4%. Thus, methane still participates in the reaction at this temperature.

While the data in Fig. 10(a) show clearly the importance of homogeneous reactions above 600 °C, heterogeneous surface reactions can not be excluded, since the NO reduction activity was different for different catalysts, e.g. Al_2O_3 versus AlAg(7.2, L)) in Fig. 2(a) and (b). Alternatively, activated species, e.g. CH_3 radicals, can be produced in the gas phase, and then react with the surface adsorbed NO_x species. Additional studies of a cooperative homogeneous/heterogeneous mechanism are warranted on the basis of these findings.

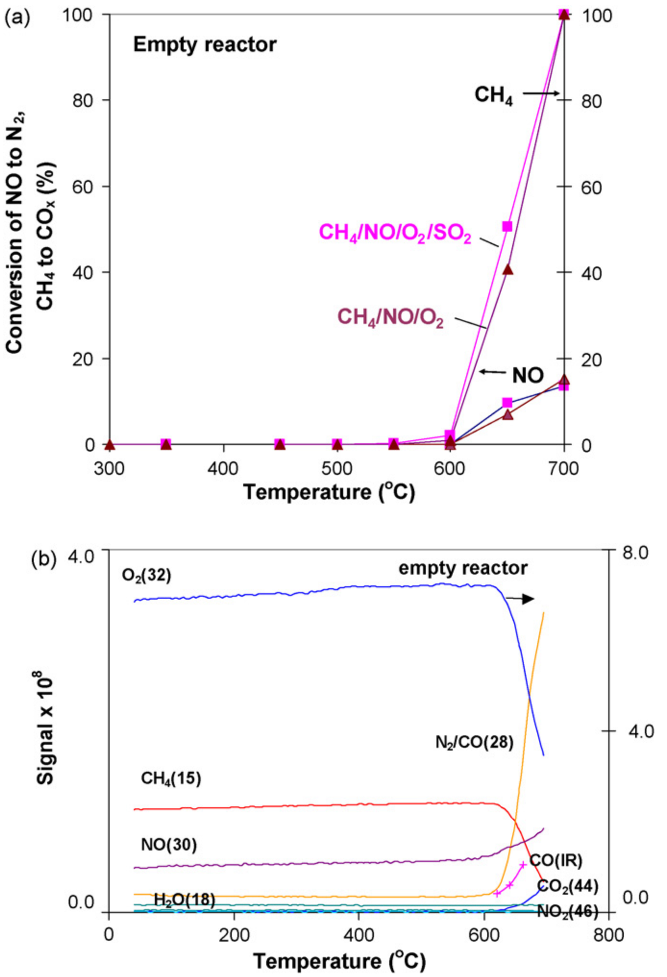

Fig. 10. (a) Gas phase reaction in empty reactor for CH_4–NO–O_2–SO_2. Feed gas: 200 ml/min, 0.25% NO–2% CH_4–5% O_2–0/1000 ppm SO_2–He. (b) Reaction light-off in empty reactor for CH_4–NO–O_2–SO_2. Feed gas: 0.25% NO–2% CH_4–5% O_2–0.08% SO_2, 100 ml/min. Temperature ramping: 10 °C/min, RT-700 °C.

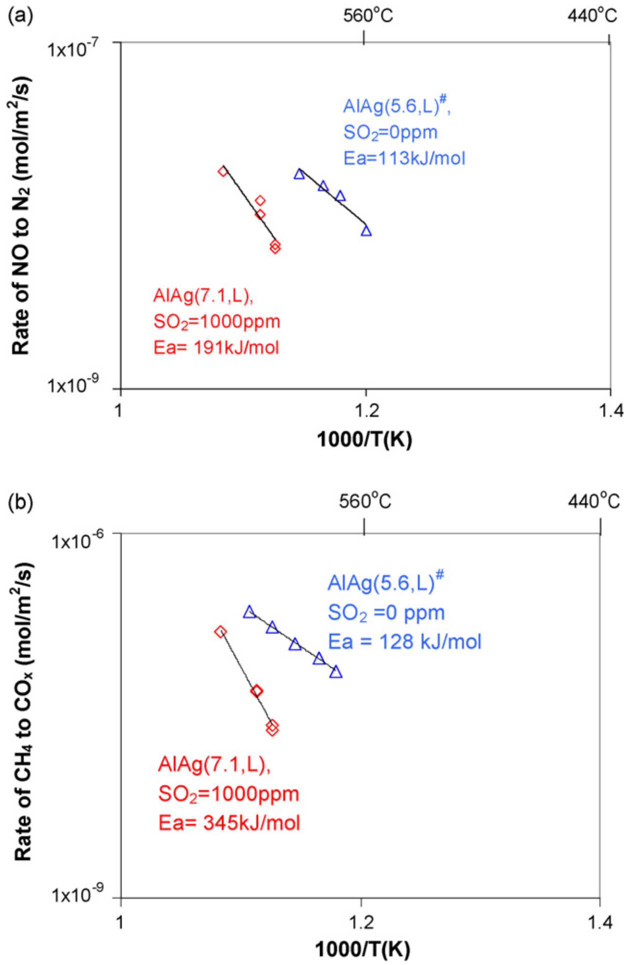

Fig. 11. Kinetics of CH_4-SCR of NO in the presence of SO_2 over AlAg(7.1, L). (a) Rates of NO reduction to N_2; (b) rates of CH_4 oxidation to CO_x. Feed gas: 200 ml/min, 0.25% NO–2% CH_4–5% O_2–0.1% SO_2–He. (#) The rates over AlAg(5.6, L) are from Ref. [12] in the absence of SO_2.

3.6. Kinetics of CH_4-SCR in the presence of SO_2

The SO_2 effect on the CH_4-SCR of NO over Ag–alumina catalysts was also examined in the kinetics regime, and rates of NO reduction to N_2 and overall CH_4 oxidation were measured with 1000 ppm SO_2 added in the gas mixture. Arrhenius-type plots are shown in Fig. 11 for the rates measured in the 615–650 °C temperature range. Also shown are the rates measured in the absence of SO_2 over Ag–alumina [12]. Clearly, the reaction rates are suppressed by SO_2. The apparent activation energies of the reduction of NO to N_2 and CH_4 oxidation to CO_x in the presence of SO_2 are 191 and 345 kJ/mol, respectively, compared to 113 and 128 kJ/mol in the SO_2-free gas. Hence, SO_2 increases the activation energies of both reactions, and the effect is stronger on the methane oxidation reaction. As discussed above, SO_2 competes with NO for adsorption sites on Ag–alumina. A heat of adsorption of SO_2 on alumina of 13.4 kcal/mol has been reported by Nam and Gavalas [31]. This or a higher value may apply to the heat of adsorption of SO_2 on the Ag-modified alumina. A strong adsorption of SO_2 on Ag–alumina may be invoked to rationalize the observed lower reaction rates and higher activation energies through Langmuir–Hinshelwood kinetics. This point warrants further investigation.

3.7. H_2O effect

Water vapor is a ubiquitous component of exhaust gas streams, and its effect on the catalyst performance must be considered for practical catalyst development. Of course H_2O is produced in situ from the CH_4–NO–O_2 reaction and this effect is included in the kinetic measurements reported before [12]. In the present work, we examined the coexistence of SO_2 (1000 ppm) and H_2O (6.2%) on SCR of NO with CH_4 over a leached AlAg(5.4, L) at 625 °C, as shown in Fig. 12. First, in SO_2-free gas, but with 6.2% H_2O, the NO conversion decreases with time, similarly to what was reported in Fig. 2a without addition of H_2O. This gradual activity loss is due to sintering of silver at this temperature [25]. Thus, the extra amount of H_2O in the gas neither suppresses nor does it enhance the sintering process. When H_2O and SO_2 were added together to the gas stream, NO and CH_4 conversions dropped instantly to 32 and

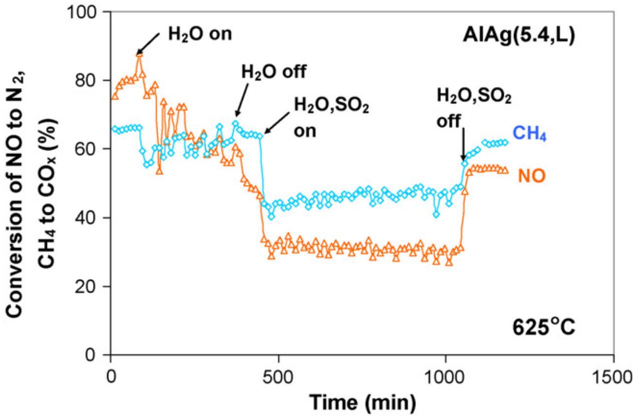

Fig. 12. Effect of H_2O and SO_2 on the activity of SCR of NO with CH_4 over AlAg(5.4, L). Catalyst load: 0.15 g; feed gas: 0.25% NO–2% CH_4–5% O_2–0/6.2% H_2O–0/1000 ppm SO_2, 200 ml/min. $T = 625$ °C.

45%, respectively, and were stabilized at the above values for ~10 h. The catalyst activities were totally recovered after switching off H_2O and SO_2. Hence, also in the presence of SO_2, water vapor addition does not have any deleterious effect on the catalyst activity or stability. For application of Ag–alumina to practical exhaust gas streams, therefore, SO_2 is an inhibitor of the CH_4-SCR reaction, while H_2O is a mere diluent, without any kinetic or structural effect on this type catalyst.

4. Conclusions

This work has demonstrated the feasibility of using Ag–alumina catalysts for CH_4-SCR of NO in exhaust gases containing a relatively high concentration of SO_2 (~1000 ppm). Sulfates formed on Ag–alumina catalysts are not active for CH_4-SCR of NO, and the reaction initiates only when free silver sites (Ag–O–Al) are released by decomposition of surface silver sulfate at ~600 °C. Kinetic results show that SO_2 suppresses the rates of both the NO reduction and CH_4 oxidation reactions, while it increases the apparent activation energies of both reactions, the latter more than the former. However, no permanent poisoning effect of SO_2 was present, and SO_2 adsorption on the partially sulfated catalyst was fully reversible at 625 °C. Moreover, we found that while SO_2 has an inhibitory effect on the reaction, it stabilizes the catalyst activity at 625 °C. Thus, Ag–alumina catalysts may be developed as active and stable catalysts for the high-temperature CH_4-SCR of NO_x from flue gases laden with relatively high SO_2 concentrations.

Acknowledgements

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