

NO reduction by C₃H₆ in excess oxygen over fresh and sulfated Pt- and Rh-based catalysts

A. Toubeli*, E.A. Efthimiadis and I.A. Vasalos

Chemical Process Engineering Research Institute, PO Box 1517, University City, 540 06 Thessaloniki, Greece
E-mail: toubeli@alexandros.cperi.certh.gr

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The selective catalytic reduction (SCR) of NO with C₃H₆ was studied over three noble-metal-based catalysts: 2% Pt/ γ -Al₂O₃, 2% Rh/ γ -Al₂O₃ and 1.5% Rh/TiO₂(4% WO₃). The SO₂ effect on the catalyst activity was examined using sulfated samples of the above catalysts and SO₂-containing feeds. Temperature-programmed desorption and oxidation studies were carried out to examine the adsorption characteristics of NO and C₃H₆, respectively, in the absence or the presence of SO₂. The adsorption data were linked to variations in the NO reduction rates over fresh and sulfated samples. Modification of the support surface as a result of the SO₂ presence affects the NO and propene sorption characteristics, the NO oxidation and the propene consumption rates.

Keywords: NO, reduction, propene, TPD, Pt, Rh, alumina, doped titania, SO₂

1. Introduction

The selective catalytic reduction (SCR) is an attractive method to convert nitrogen oxides (NO_x) to N₂. Despite the continuous efforts to remove sulfur from the fuels, the inlet gas stream in deNO_x units contains sulfur in the form of SO₂. The activity of a catalyst in the presence of SO₂ is decisive for its implementation in practical problems. Parvulescu et al. [1] reviewed the catalytic removal of NO from flue gases. They acknowledged that the SCR by hydrocarbons is the most promising method to reduce the NO. This is denoted by the large number of relevant patents [2] and publications (references in [1,3,4]). Parvulescu et al. [1] classified the catalysts for the SCR by hydrocarbons to metal-ion-exchanged zeolites, supported noble metals and base metal oxides. Noble metals impregnated on metal oxides are studied in this work.

Noble metals are tolerant to the SO₂ presence in the feed [5,6], while transition metals [5] and silver [7] are deactivated by SO₂ as a result of the sulfates formation. Ag/alumina, however, was tolerant to the SO₂ presence when methanol was used as reductant [8]. This was attributed to different reaction mechanisms that lead to N₂ formation over the same metal. Burch and coworkers [9,10] also examined the effect of the reaction mechanism on the activity and the SO₂ tolerance over Pt/alumina using C₃H₆ and C₃H₈ as reductants. Change of the reaction mechanism as a result of the catalyst sulfation was observed over Rh/alumina [11]. The deactivation of Pd/TiO₂ by SO₂ was attributed to the complete oxidation of the active Pd⁰,

while in the absence of SO₂ Pd was partially oxidized [12]. Finally, the activity of Cu impregnated on a commercial, sulfated zirconia did not change upon the addition of traces of SO₂ (20 ppmv) [13].

Verykios and coworkers studied the effect of W⁶⁺-doping of TiO₂ on the interaction of supported Rh with NO [14] and CO [15] and the adsorption of NO (CO) and displacement by CO (NO) [16,17]. Carrier doping was shown to induce a large increase in the extent of transient NO decomposition and the selectivity towards N₂ formation. The concentration of CO adsorbed on the Rh surface also increased upon carrier doping. These observations were attributed to electronic interactions between Rh crystallites and the doped carrier, which in turn results to modifications in the electronic configuration of Rh atoms as compared to the undoped titania-supported catalyst. Accordingly, the activity of Rh/TiO₂ for the selective catalytic reduction of NO with propene was considerably enhanced upon carrier doping.

In our previous studies [18] we presented kinetic expressions for the NO reduction over Pt/ γ -alumina and Rh/ γ -alumina and we discussed differences in the reaction mechanism that leads to the N₂ formation over these catalysts. The scope of this work was to investigate the sulfur effect on the NO reduction over the above catalysts using both fresh and presulfated samples. Moreover, experiments were carried out using SO₂-free or SO₂-containing feeds. In addition to the alumina-based catalysts, the performance of Rh impregnated on titania doped with WO₃ was investigated. The concept of the dopant-induced promotion for the NO reduction over Rh sites was, thus, examined.

* To whom correspondence should be addressed.

2. Experimental

2.1. Sample preparation

Pt and Rh catalysts supported on γ -alumina were prepared by the dry impregnation technique. The γ -alumina carrier (Engelhard, Al-3992 E 1/8") was in the particle form of 180–355 μm . The impregnation was performed with aqueous solutions of H₂PtCl₆ (Merck) and RhCl₃ (Merck) producing catalysts with nominal loadings of 2% Pt and 2% Rh, respectively. The catalysts were dried at 120 °C for 2 h and, then, calcined under air flow at 600 °C for 9 h (Rh) or 16 h (Pt).

Doped catalysts were prepared in the laboratory of Heterogeneous Catalysis, University of Patras. Doping of titania was carried out by the solid state diffusion technique. The catalyst had a nominal loading of 1.5% Rh. Details of the preparation procedure can be found elsewhere [19].

The catalysts' sulfation was carried out in a fixed-bed, quartz microreactor of 17 mm i.d. 1.5 g of the catalyst was heated to 540 °C under a flow of 2500 ppmv SO₂ and 5 vol% O₂ in He. The total flow rate was 500 cm³/min. The reaction was allowed to proceed for 5 and 7.5 h over 2% Pt/ γ -alumina and 2% Rh/ γ -alumina, respectively, and for 4.5 h over 0.5 g of 1.5% Rh/TiO₂(4% WO₃). The sulfation experiment was terminated when the SO₂ concentration at the reactor exit reached 90% of the inlet SO₂ concentration.

2.2. Sample characterization

The actual metal loading of the catalysts was determined by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Perkin–Elmer). Measurements of the surface area were based on N₂ adsorption data obtained from an Autosorb-1 (Quantachrome) apparatus. The sulfur content of the alumina-supported catalysts was determined with the ASTM D 5453 standard method using an ANTEK 7000B model 740 instrument.

2.3. Activity measurements

Kinetic experiments were performed in a quartz microreactor (7 mm i.d.) loaded with 0.15 g of the catalyst sample. The typical composition of the feed gas was 1000 ppmv NO, 1000 ppmv C₃H₆, 5 vol% O₂ and 0 or 300 ppmv SO₂ in He. The total flow rate of the reactants was equal to 500 cm³/min ($W/F = 0.018 \text{ g s/cm}^3$). The catalyst was purged with pure He at 600 °C for 1 h prior to the activity experiment. The reduction of NO was carried out at temperatures ranging from 550 down to 200 °C. At each temperature a pseudo-steady state was obtained before advancing to the next reaction temperature. The product gas stream was analyzed by a set of on-line analyzers placed in series and a gas chromatograph (HP 5890, Hewlett–Packard). The on-line analyzers were: an ultraviolet SO₂ analyzer (AR-3000, Anarad), a chemiluminescence NO–NO₂–NO_x analyzer (42C-HL, Thermo Environmental), non-dispersive infrared CO and CO₂ analyzers

(VIA-510, Horiba) and a magnetopneumatic O₂ analyzer (MPA-510, Horiba). The GC had two packed columns in series: a Porapak-N (Hewlett–Packard) for separating CO₂, N₂O and CO and a MS 5 Å (Hewlett–Packard) for separating O₂ and N₂, and, in parallel with these two, one capillary Rt-Qplot column (Restek) for the determination of the C₃H₆ concentration.

2.4. Temperature-programmed experiments

Temperature-programmed desorption (TPD) experiments were performed in the same reaction/analysis unit with a quartz reactor of 17 mm i.d. loaded with 0.5 g of the catalyst sample. The sample was pretreated with pure helium at 320 °C for 1 h. The flow rate was 500 cm³/min. At this temperature the feed (NO or NO + SO₂ or NO + O₂ in He) was sent to the reactor for 1 h and the catalyst was then cooled down to 100 °C. At 100 °C the feed was purged with pure helium (1000 cm³/min) for 1 h. Desorption was carried out under pure He flow from 100 to 600 °C with a heating rate of 20 °C/min. The exit of the reactor was connected to the gas analysis system described in section 2.3.

The first stage in the temperature-programmed oxidation studies was the adsorption of C₃H₆ or C₃H₆ + SO₂ on the sample surface using the same conditions as with the TPD experiments. The sample was flushed with helium at 100 °C for 1 h and oxidation started using 5 vol% O₂/He and the same temperature range and heating rate as with the TPD studies.

3. Results and discussion

3.1. Catalyst characterization

The catalyst characterization data are summarized in table 1. The noble metal content in the γ -alumina-based samples was similar, while less Rh was detected in the titania-based sample. The sulfation of fresh catalysts did not change their surface area, implying that the pore structure changes due to sulfation are negligible. The sulfur content was ca. 20% higher in sulfated Pt/alumina than in sulfated Rh/alumina. This implies that the extent of the sulfation was about the same over these two samples. The sulfur content of sulfated Rh/TiO₂(4% WO₃) was not determined.

3.2. TPD studies

The NO sorption of alumina using a feed of 3000 ppmv NO in He gave a NO_x desorption peak at 270 °C, while traces of NO_x were detected at 490 °C. These peaks correspond to desorption of nitrite and nitrate species, respectively, according to previous TPD studies [20,21]. A list of the TPD experiments of this study is given in table 2. The temperature where each peak exhibits its maximum intensity and the overall amount of the desorbed species

Table 1
Catalysts used in the activity and temperature-programmed experiments.

Catalyst	Actual metal loading (wt%)	Surface area (m ² /g catalyst)		Sulfur content (wt%)
		Fresh	Sulfated ^a	
2% Pt/ γ -Al ₂ O ₃	1.64 ± 0.04	183	182	1.61 ± 0.16
2% Rh/ γ -Al ₂ O ₃	1.73 ± 0.08	182	175	1.25 ± 0.30
1.5% Rh/TiO ₂ (4% WO ₃)	1.3 ± 0.03	20	18	ND ^b

^a Samples sulfated with 2500 ppmv SO₂ and 5 vol% O₂ in He at 540 °C.

^b ND = not determined.

Table 2
Peak temperatures (°C) and quantities of species desorbed (μ mol/g) after adsorption of NO or NO + O₂ or NO + SO₂ on γ -Al₂O₃, Pt/ γ -Al₂O₃ and Rh-based catalysts at 320 °C.

Catalyst	Sorption mixture	NO		NO ₂		NO _x	
		T_{peak}	Quantity	T_{peak}	Quantity	T_{peak}	Quantity
γ -Al ₂ O ₃	NO	270	16.5	270	9.5	270	26
	NO + O ₂	490	Traces			490	Traces
		192	15	192	4	192	19
2% Pt/ γ -Al ₂ O ₃	NO	506	65.5	476	28.5	493	94
		190	17	228	8	215	25
	NO + O ₂	418	4	418	1	418	5
S-2% Pt/ γ -Al ₂ O ₃ ^a	NO	234	22				
		483	30	434	136	434	188
	NO + O ₂	170	8	170	4	170	12
2% Rh/ γ -Al ₂ O ₃	NO	291	76	242	62	256	138
						–	Traces
	NO + SO ₂	240	22	220	5	240	27
S-2% Rh/ γ -Al ₂ O ₃ ^a	NO	388	12			388	12
		215	17				
	NO + O ₂	413	54.5	362	94	362	165.5
TiO ₂ (4% WO ₃)	NO	169	5	–	1.5	169	6.5
				253	35	253	35
	NO + O ₂	506	74	506	18.5	506	92.5
1.5% Rh/TiO ₂ (4% WO ₃)	NO		3		1		4
						–	Traces
	NO + O ₂	455	26		1	455	27
S-1.5% Rh/TiO ₂ (4% WO ₃) ^a	NO	385	22		1	385	23
		386	43.5		4	386	47.5
	NO + O ₂	–	4.5	–	1	–	5.5
		–	17	–	2	–	19

^a Samples sulfated with 2500 ppmv SO₂ and 5 vol% O₂ in He at 540 °C.

are given in this table. The NO desorption curves of unpromoted alumina, fresh and sulfated 2% Rh/alumina are compared in figure 1. The impregnated metal causes a shift of the nitrite peak toward lower temperatures, while a second peak was observed at 388 °C implying that the NO–Rh bond is stronger than the NO–alumina one. The sulfated sample desorbed significantly lower amounts of NO_x and at lower temperatures as compared to the fresh samples. Moreover, when 250 ppmv SO₂ coexisted in the feed with NO, almost no NO was desorbed from the sample (table 2). The selective sorption of SO₂ on Rh sites inhibited the NO sorption almost completely. Qualitatively similar results were noticed using Pt/alumina. These data are in a good agreement with previous TPD studies [10,11]. Comparison of the integrated, desorbed NO_x during the TPD experiments showed that about the same amount of NO_x is desorbed from unpromoted γ -alumina and Pt/alumina while this amount is higher by 30% over Rh/alumina. Upon sul-

fation of Pt/alumina and Rh/alumina the amounts of NO_x measured during desorption were 40 and 17% of those detected over the fresh samples, respectively.

In the presence of 5 vol% O₂ in the feed more NO_x was desorbed as compared to the O₂-free experiments. The nitrate peak was the dominant one over unpromoted alumina and Rh/alumina (figure 2). The oxidation of NO on the metal sites and the spillover to the support gives rise to the accumulation of nitrates on the catalyst surface. Upon the sulfation of the Rh/alumina less nitrates and more nitrites (peak at 253 °C) were measured. Therefore, sulfates formed during the pretreatment of the sample block the oxidation of NO. Similar results were obtained over Pt/alumina. However, SO₂ was detected at the reactor exit during the NO sorption over sulfated Pt/alumina using an NO/O₂ feed. Integration of the SO₂ vs. time curve of this experiment resulted in 146 μ mol/g catalyst. This value is close to the amount of NO_x desorbed from sulfated Pt/alumina. There-

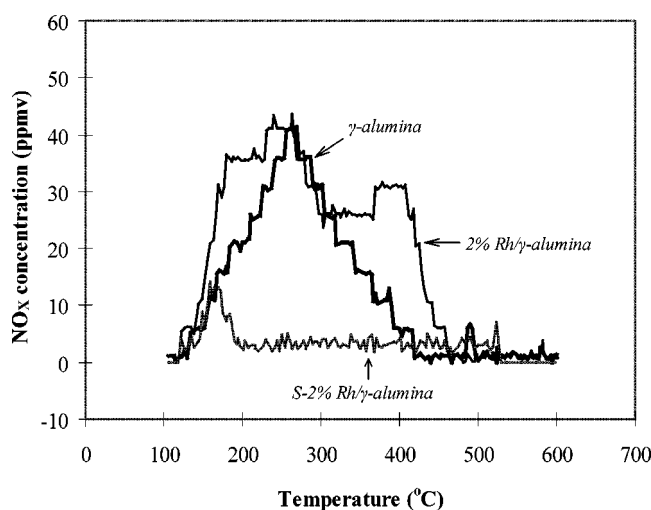


Figure 1. NO_x evolution during temperature-programmed desorption (TPD) experiments over γ -alumina, 2% Rh/ γ -alumina and sulfated 2% Rh/ γ -alumina after sorption of NO at 320 °C. Sorption mixture: 3000 ppmv NO in He.

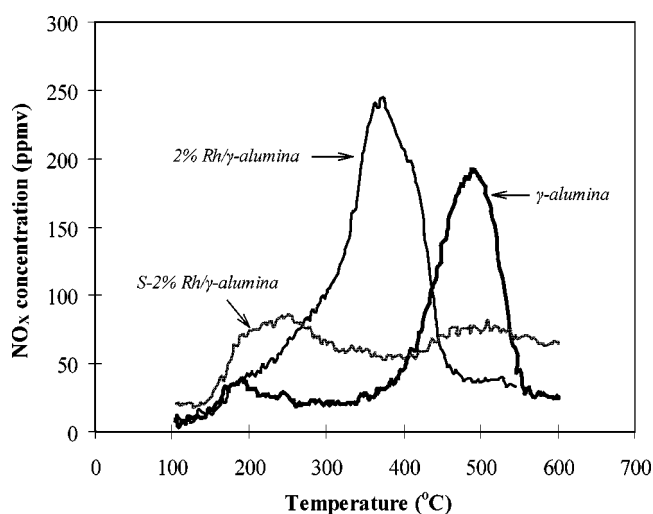


Figure 2. NO_x evolution during temperature-programmed desorption (TPD) experiments over γ -alumina, 2% Rh/ γ -alumina and sulfated 2% Rh/ γ -alumina after sorption of NO + O₂ at 320 °C. Sorption mixture: 3000 ppmv NO and 5 vol% O₂ in He.

fore, we postulate that during the NO sorption stage, nitrites and nitrates substituted SO_x initially sorbed on this sample. This phenomenon was not noticed over the sulfated Rh/alumina. Moreover, NO_x were desorbed at lower temperatures from the sulfated Pt/alumina than from the sulfated Rh/alumina.

The NO sorption capacity of titania doped with W⁶⁺ (TiO₂(4% WO₃)) and Rh/TiO₂(4% WO₃) was studied, as well. Only the latter sample exhibited significant NO sorption capacity (table 2). The addition of 5 vol% O₂ in the feed gave rise to relatively small NO desorption peaks at 455 and 386 °C for TiO₂(4% WO₃) and Rh/TiO₂(4% WO₃), respectively. Upon sulfation lower amounts of NO were desorbed from the Rh-based catalyst.

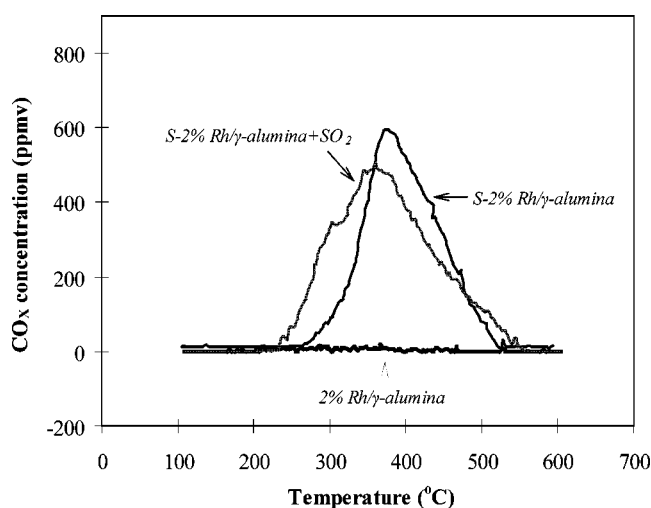


Figure 3. CO_x evolution during oxidation experiments over γ -alumina, 2% Rh/ γ -alumina and sulfated 2% Rh/ γ -alumina after sorption of C₃H₆ or C₃H₆ + SO₂ at 320 °C. Sorption mixture: 3000 ppmv C₃H₆, 0 or 250 ppmv SO₂ in He.

3.3. Oxidation studies

The oxidation studies included two stages. In the first one, C₃H₆ was sorbed on the catalyst in the presence or absence of SO₂ in the feed. In the second one, adsorbed species were removed using temperature-programmed oxidation. CO was measured when fresh Rh/alumina was exposed to C₃H₆ implying the reduction of Rh₂O₃ by the hydrocarbon. Integration of the CO concentration vs. time curve during the adsorption stage of the experiment showed that 23 μ mol/g CO were produced, while 168 μ mol/g Rh exist on this sample. The oxidation data of figure 3 show that practically no CO_x were detected during the oxidation stage of the experiment. Similarly to the propene adsorption over fresh Rh/alumina, 165 μ mol/g CO_x were measured during the propene adsorption over the sulfated Rh/alumina. Following that, 345 μ mol/g CO_x were released during the oxidation experiment. About the same amount of CO_x was also measured when the feed in the adsorption stage was 3000 ppmv C₃H₆ and 250 ppmv SO₂ in He. Moreover, SO₂ was desorbed during the oxidation stage when the adsorption mixture contained SO₂ (table 3).

In our previous surface characterization studies [11], we noticed that the temperature rise from 250 to 350 °C caused a significant decrease in the concentration of the surface species on Rh/alumina, while sulfates on Rh/alumina were reduced by propene in the same temperature range. Based on these data we postulate that propene reduced Rh³⁺ on the fresh sample and it was converted to species that were easily desorbed at 320 °C over this fresh sample. On the other hand, propene formed species over the sulfated sample that are not desorbed at 320 °C.

The experimental data over fresh and sulfated Rh/TiO₂ (4% WO₃) were consistent with the corresponding data over fresh and sulfated Rh/alumina. Namely, CO_x were observed during the propene sorption stage and no CO_x were measured during the oxidation of the fresh sample.

Table 3
Peak temperatures (°C) and quantities of species desorbed (μmol/g) during temperature-programmed oxidation experiments after adsorption of C₃H₆ or C₃H₆ + SO₂ on γ-Al₂O₃, Pt/γ-Al₂O₃ and Rh-based catalysts at 320 °C.

Catalyst	Sorption mixture	SO ₂		CO		CO ₂		CO _x	
		<i>T</i> _{peak}	Quantity	<i>T</i> _{peak}	Quantity	<i>T</i> _{peak}	Quantity	<i>T</i> _{peak}	Quantity
γ-Al ₂ O ₃	C ₃ H ₆			558	3	568	159	568	162
2% Pt/γ-Al ₂ O ₃	C ₃ H ₆					243	236	251	236
S-2% Pt/γ-Al ₂ O ₃ ^a	C ₃ H ₆					555	4	555	4
2% Rh/γ-Al ₂ O ₃	C ₃ H ₆							–	Traces
S-2% Rh/γ-Al ₂ O ₃ ^a	C ₃ H ₆			–	13	374	332	374	345
	C ₃ H ₆ + SO ₂	274	26	243	1	364	330	364	331
TiO ₂ (4% WO ₃)	C ₃ H ₆							–	Traces
1.5% Rh/TiO ₂ (4% WO ₃)	C ₃ H ₆					258	7	258	7
S-1.5% Rh/TiO ₂ (4% WO ₃) ^a	C ₃ H ₆			–	2	357	134	357	136
	C ₃ H ₆ + SO ₂	270	35	–	2	396	98	396	100

^a Samples sulfated with 2500 ppmv SO₂, 5 vol% O₂ in He at 540 °C.

The CO_x formed during the oxidation of the sulfated sample were lower than those from sulfated Rh/alumina in the absence and presence of SO₂ in the feed (table 3). This difference was attributed to the type of support of the two samples.

The oxidation experiment over alumina showed that sorbed C₃H₆ is burned only at elevated temperatures (568 °C). Higher amounts of C₃H₆ are sorbed on Pt/alumina and oxidized at 243 °C due to the O₂ activation on the Pt sites. On the other hand, the formation of sulfates on Pt/alumina inhibited the C₃H₆ sorption since only traces of CO₂ are detected at 555 °C. This is in disagreement with the experimental data over sulfated Rh/alumina. Burch and Watling [9] reported that C₃H₆ does not reduce sulfates on a Pt/alumina catalyst. The presence of sulfates on the catalyst surface has a different effect on Rh/alumina, since propene sorbed on Rh is converted to carbonaceous species that can reduce the sulfates.

3.4. NO reduction studies

The activities of the three noble-metal-based catalysts, 2% Pt/alumina, 2% Rh/alumina and 1.5% Rh/TiO₂(4% WO₃), are shown in figures 4, 5 and 6, respectively. In the same figures the NO reduction performance of the three sulfated samples is depicted in the presence and absence of SO₂ in the reactor feed, in comparison to the SO₂-free behavior of the corresponding fresh catalyst samples. Pre-sulfation of the samples affected the NO reduction activity of the noble-metal-based catalysts as follows: inhibition was noticed over Rh/alumina at temperatures lower than the activation temperature *T*_{peak} (figure 5(a)), while over Rh/TiO₂(4% WO₃) an activity enhancement was observed at temperatures higher than *T*_{peak} (e.g., ≥330 °C) (figure 6(a)). An activity enhancement was also observed over Pt/alumina at temperatures lower than *T*_{peak}, (e.g., between 200 and 280 °C) (figure 4(a)). Burch and Watling [9] reported that sulfation had no significant effect on the NO reduction performance of the catalyst. We attribute this difference to the sulfation procedure followed in each study. In this work higher sulfation temperature and SO₂ concen-

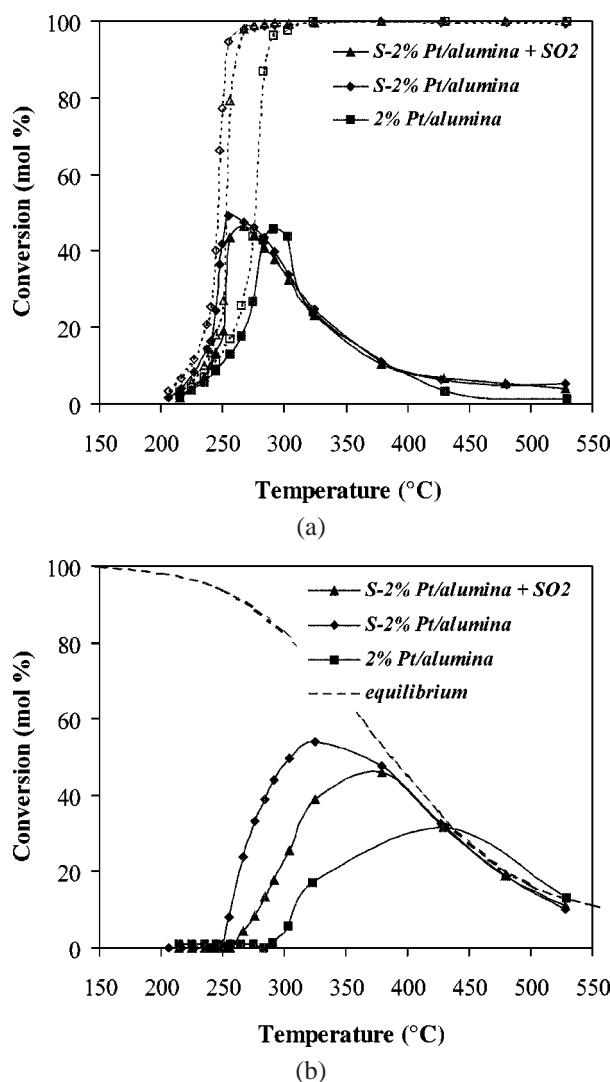


Figure 4. Effect of SO₂ on the selective catalytic reduction of NO with C₃H₆ over 2% Pt/γ-alumina. (a) NO reduction (—) and propene oxidation (---) and (b) NO oxidation. Reactor feed composition: 1000 ppmv NO, 1000 ppmv C₃H₆, 5 vol% O₂, 0 or 300 ppmv SO₂.

tration are expected to result in complete sulfation of the surface alumina.

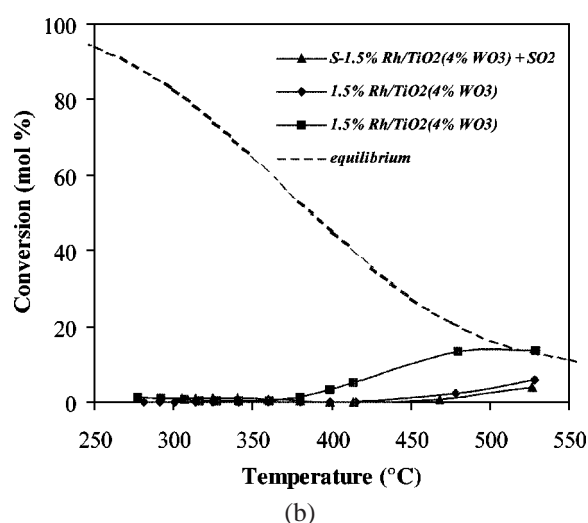
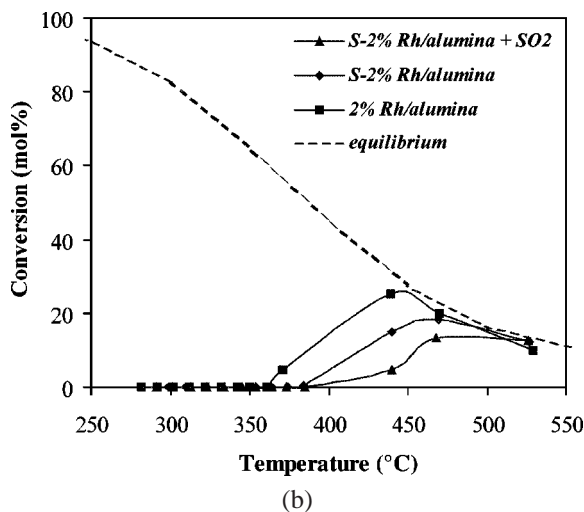
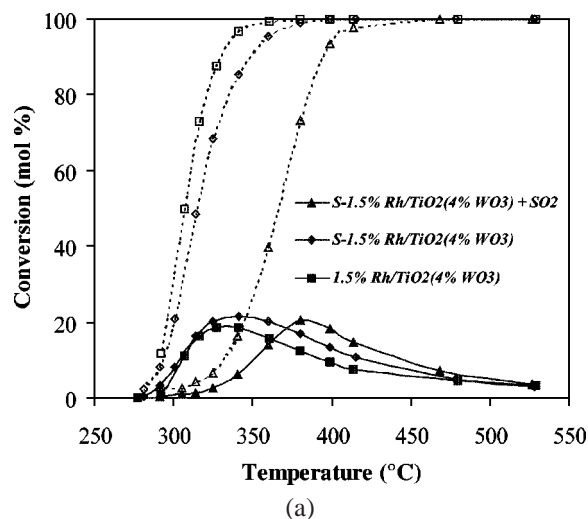
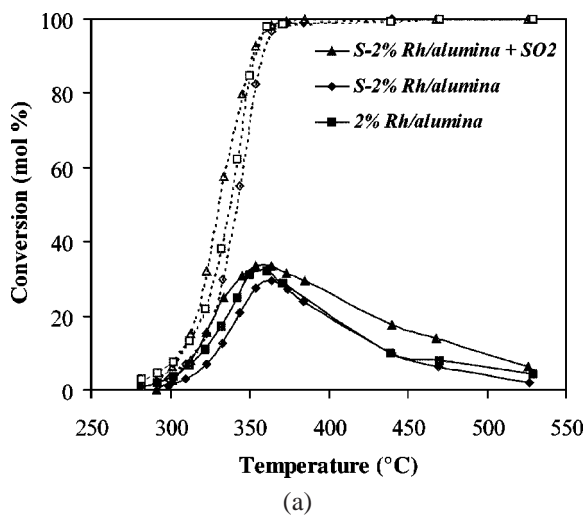


Figure 5. Effect of SO_2 on the selective catalytic reduction of NO with C_3H_6 over 2% Rh/ γ -alumina. (a) NO reduction (—) and propene oxidation (---) and (b) NO oxidation. Reactor feed composition: 1000 ppmv NO, 1000 ppmv C_3H_6 , 5 vol% O_2 , 0 or 300 ppmv SO_2 .

NO_2 formation was suppressed over the sulfated Rh-based catalysts while it was favored over Pt/alumina as compared to the fresh catalyst samples (figures 4(a), 5(a) and 6(a)). In our earlier work [11] we postulated that over Rh/alumina and Pt/alumina the NO oxidation sites are the Rh- Al_2O_3 interface and the Pt particles, respectively. Consequently, sulfation of these catalysts inhibits the NO oxidation over the former sample, in accordance with the experimental evidence. In contrast, sulfates enhance the NO oxidation over Pt/alumina.

The presence of SO_2 in the feed over the sulfated Pt- and Rh-based catalysts caused a modification of their catalytic performance. Thus, over sulfated Rh/alumina we observed an enhancement of the NO reduction activity upon the addition of SO_2 in the feed (figure 5(a)). This is in agreement with our previous works [5,11] where we noticed a reversible enhancement in the catalyst activity when SO_2 was added to the feed. This enhancement was attributed to the inhibition of the NO_2 formation. We believe that there is balance among the beneficial (inhibition of NO_2

Figure 6. Effect of SO_2 on the selective catalytic reduction of NO with C_3H_6 over 1.5% Rh/TiO₂(4% WO₃). (a) NO reduction (—) and propene oxidation (---) and (b) NO oxidation. Reactor feed composition: 1000 ppmv NO, 1000 ppmv C_3H_6 , 5 vol% O_2 , 0 or 300 ppmv SO_2 .

formation) and the detrimental (competitive adsorption between NO and SO_2) effects of the SO_2 presence in the feed over Rh/alumina. Depending on the reaction conditions one of the above two effects may dominate. Over sulfated Rh/TiO₂(4% WO₃) the NO conversion was maintained at the same levels but was shifted to higher temperatures by about 40 °C in the presence of SO_2 (figure 6(a)). On the other hand, the addition of SO_2 over sulfated Pt/alumina resulted in a loss of its NO reduction performance at low temperatures, while, at higher temperatures, the NO reduction fell on the same curve both in the presence and absence of SO_2 (figure 4(a)). These results agree with those of Burch and Watling over sulfated Pt/alumina [9]. The formation of NO_2 was inhibited over all the sulfated catalysts examined when SO_2 was present in the feed (figures 4(a), 5(a) and 6(a)).

The overall SO_2 effect on the NO reduction performance of the noble-metal-based catalysts for the SCR of NO was beneficial in the case of Rh and Pt supported on γ -alumina,

since their activity was enhanced, and unfavorable over Rh supported on doped TiO₂, given that the catalyst became active at higher temperatures as compared to its SO₂-free behavior. At T_{peak} the selectivity of the catalysts towards N₂ did not change and was equal to 40, 85 and 80 mol% over Pt/alumina, Rh/alumina and Rh/TiO₂(4% WO₃), respectively. CO was measured over all the catalyst samples examined at temperatures close to the propene light-off temperature. The presence of SO₂ had no effect on the amount of CO formed over Pt/alumina (3 mol%) while CO formation was favored over Rh/alumina (6 mol%) as compared to the fresh catalyst (3.5 mol%). The apparent activation energies for NO reduction estimated in the SO₂-containing experiments were higher as compared to experiments performed on fresh Pt/alumina and Rh/alumina. In the following part of this work we will attempt to correlate the TPD, oxidation and NO reduction experiments.

Our NO desorption studies showed that NO forms a stronger bond with Rh or Pt than with the support, alumina or doped titania. It was also noticed that the overall amounts of NO_x desorbed from the doped titania-supported catalyst are significantly lower in comparison to those from catalysts supported on γ -alumina. This observation may explain the higher NO reduction activity of fresh Pt/alumina and Rh/alumina as compared to fresh Rh/TiO₂(4% WO₃). The sulfation of the catalysts inhibits the NO adsorption in the presence or absence of O₂ in the feed. The NO desorption for the three noble-metal-based catalysts are consistent; however, this was not the case for the oxidation experiments and for the SO₂ effect on the NO reduction.

When fresh Rh/alumina or Rh/TiO₂(4% WO₃) is flushed with C₃H₆ at 320 °C the olefin is preferentially adsorbed on Rh and subsequently oxidized forming species (CO and CO₂) that do not deposit on the support. Solymosi and Sarkany [22] reported that the active sites of Rh-based catalysts are reduced rhodium atoms. Therefore, the role of propene in the NO reduction is to reduce the oxidation state of the rhodium atoms. Over these sites NO is dissociatively sorbed in an SO₂-free atmosphere [11,16,17]. The addition of sulfur-containing species on the catalyst surface by applying the pre-sulfation procedure inhibits the NO sorption in an oxidizing atmosphere. However, propene reduces the sulfates forming carbonaceous compounds that are sorbed on sulfated Rh-based samples. The oxidation of such species formed over sulfated Rh/alumina results in the CO_x formation in figure 3. The addition of SO₂ in the sorption mixture had almost no effect on the amount of CO_x formed during the oxidation experiment (table 3) and the peak temperature of the CO_x desorption curve (figure 3) over Rh/alumina, due to the preferential sorption of SO₂ on the noble metal particles. In the case of sulfated Rh/TiO₂(4% WO₃), however, the presence of SO₂ resulted in the sorption of lower amounts of propene over the catalyst and the up-shift of the evolution of CO_x by 40 °C (table 3). This behavior implies that SO₂ adsorbs not only over Rh sites but is also competitively sorbed over active sites on the support. The peak temperatures of CO_x forma-

tion noticed during the oxidation experiments over the sulfated Rh-based catalysts, both with and without SO₂ in the feed, appear to be in fairly good agreement with the T_{peak} of the corresponding NO reduction activity curves (table 3, figures 4 and 5). This coincidence of peak temperatures for NO reduction (kinetic experiments) and propene oxidation (temperature-programmed experiments) implies that the partially oxidized species of propene formed on sulfated Rh-based catalysts play an active role in the reaction rate-determining step which is in agreement with the mechanism we proposed earlier for NO reduction over Rh/alumina in the presence of SO₂ [11].

The presence of Pt on alumina facilitates the C₃H₆ sorption that migrates to the support during the sorption stage. The formation of sulfates around the Pt particles inhibits the spillover process, but does not affect the cleanup of the Pt surface from O₂ during the NO reduction (NO decomposition mechanism) [23]. In contrast, the reduction of the Pt surface becomes easier since more propene is available and NO reduction rates increase at temperatures lower than T_{peak} over the sulfated Pt/alumina as compared to its fresh sample. On the other hand, the presence of SO₂ in the gas phase gives rise to the competition of NO and SO₂ for the Pt sites resulting to lower NO conversions.

A complex reaction scheme was recently proposed for the NO_x reduction by C₃H₆ over acid sites [24,25]. This mechanism involves the formation of acrylonitrile and ammonia from nitrosonium ions and the hydrolysis of acrylonitrile is the controlling step. We employed the NO decomposition mechanism in the interpretation of our experimental results, though there is no experimental evidence from the data of this study to support this choice that was based on previous works [5,11,18,23].

4. Conclusions

Experimental data from TPD studies showed that similar amounts of NO were desorbed from Pt/Al₂O₃ and Rh/Al₂O₃ and lower from Rh/TiO₂(4% WO₃). Sulfation caused a significant reduction of the desorbed NO from all catalysts, the largest decrease being observed over the Rh-based samples. When the sorption mixture was NO and SO₂ in helium, SO₂ was selectively sorbed on the catalysts. In temperature-programmed oxidation experiments CO_x was detected over fresh Pt/Al₂O₃ and sulfated Rh-based catalysts.

Sulfation of the catalysts modified the NO reduction as follows: the activation temperature of Pt/Al₂O₃ was shifted to lower temperatures, the reaction rate slightly decreased at low temperatures over Rh/Al₂O₃ and the reaction rate increased at high temperatures over Rh/TiO₂(4% WO₃). The addition of SO₂ in the feed did not affect the activity of sulfated Pt/Al₂O₃, enhanced the activity of Rh/Al₂O₃ and shifted the activation temperature of Rh/TiO₂(4% WO₃) to higher temperatures. Sulfation of Pt/Al₂O₃ and Rh-based catalysts enhanced and inhibited, respectively, the NO oxidation.

In the absence of SO₂ in the sorption mixture, NO was desorbed on the catalysts at temperatures close to those where the maximum NO reduction is measured. SO₂ was preferentially sorbed on the samples as compared to NO. Noble-metal-based catalysts maintained their NO reduction activity when SO_x existed on the catalyst surface or in the gas feed for the following reasons: C₃H₆ was not sorbed on sulfated Pt/Al₂O₃, thus, more reductant was available for the cleanup of the Pt sites, and the NO oxidation over the Rh-based catalysts was inhibited, thus, leading to more NO available for reduction. The competitive adsorption of NO and SO₂ for the metal sites inhibited the NO reduction over all samples. As a result, the observed NO reduction rate over sulfated catalysts increased or decreased as compared to the fresh ones depending on the reaction conditions.

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