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Enhanced activity of In and Ga-supported sol–gel alumina catalysts for NO reduction by hydrocarbons in lean conditions

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Abstract

Nitrogen monoxide was reduced efficiently by hydrocarbons in the presence of oxygen over sol–gel alumina supported indium, gallium, cobalt and tin catalysts. The support alumina prepared by a sol–gel method had high surface area and accordingly active alumina sites for the reaction. Particularly indium/alumina showed a high activity to reduce NO preferably by propene, propane and ethene but also by alcohols in the absence and the presence of water vapor. The activities of alumina supported cobalt, silver and tin catalysts were increased when calcinating the catalysts at 800°C instead of 600°C. In the case of gallium/alumina, NO₂ has higher reactivity than NO to nitrogen when propene was used as a reductant, proving the significance of the oxidation step of NO to NO₂. The step of NO oxidation was promoted by preparing a physical mixture of 5 wt% Mn₃O₄ with indium/alumina or gallium/alumina. The NO conversion to nitrogen was increased from 58 to 84% with the manganese oxide promotion over indium/alumina in the presence of water. The reaction mechanistic differences between the alumina supported catalysts and Cu/ZSM-5 were also discussed. © 1998 Elsevier Science B.V.

Keywords: Nitrogen oxide; Selective reduction; Hydrocarbon; Indium; Gallium; Alumina

1. Introduction

Significant amounts of nitrogen oxides (NO_x) are formed thermally from atmospheric nitrogen at high temperature or due to the oxidation of fuel-bound nitrogen when fuels are used in combustion. Tradi-

tionally NO_x has been reduced by combustion adjustments, with three-way catalysts (TWC) in stoichiometric air/fuel conditions or selective catalytic reduction (SCR) with NH₃ (ammonia, urea, etc.) in lean conditions. However, it is not practical and safe in mobile applications (automotive vehicles) to use nitrogen containing reductants, which need a storage tank and an accurate control system to avoid toxic slip. The NO decomposition over Cu/ZSM-5 and noble metal catalysts has been investigated in various studies, but the reaction inhibition and catalyst deactivation in the presence of oxygen and water have not been solved out [1]. The recent progress

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in the SCR of nitrogen monoxide by hydrocarbons in lean conditions has taken a great attention as a possible way to reach the future stricter emission standards [2]. During the last years, the NO reduction by hydrocarbons both on zeolite and oxide based catalysts has given promising results [3–6]. Cu/ZSM-5 and other zeolite based catalysts have been introduced as efficient NO reduction methods with the practical space velocities in the presence of water and sulfur oxides, although their hydrothermal durability has been reported to be a problem due to the dealumination of zeolites and the sintering of copper centers [7–9].

Pure alumina has been observed to have a fine surface for the high temperature (over 500°C) NO reduction by hydrocarbons, but it is relatively weak against moisture [10,11]. The activity of oxide based catalysts can be attributed to their acidity [12]. The addition of active metals on alumina enhances the lower temperature performance for NO reduction by catalyzing hydrocarbon and/or NO reactions. NO has been proposed to be oxidized on catalyst surface to adsorbed NO₂, which will be converted to molecular nitrogen through nitrogen containing intermediate species [3]. In this regard, the cooperation between alumina and the active metal center has been investigated in many recent studies. With noble metal catalysts, it is possible to reach low temperature reduction window under 300°C, but the N₂O formation is an undesirable side reaction particularly for platinum catalysts. Elements from the periodic table groups of 11 (Cu, Ag, Au), 13 (Ga, In) and 14 (Sn) have been shown to be active for nitrogen oxides reduction with hydrocarbons on various non-zeolite supports such as alumina [13–20]. For example, cobalt/alumina has been noticed to effectively catalyze NO reduction by propene and propane around at 400–450°C [21].

In this work, the reduction of NO by various light hydrocarbons on sol-gel alumina based indium, gallium, tin, silver and cobalt catalysts has been investigated. Various activity tests in lean conditions have been used to find out the reaction mechanistic features during the NO reduction by hydrocarbons. The promotive effect of manganese oxide additives on NO reduction activity was also investigated over several alumina based indium and gallium catalysts.

2. Experimental

2.1. Catalyst preparation

High surface area alumina denoted as Al-sg, which was prepared by sol-gel method (Toyo Gosei, synthesized from aluminium isopropoxide in 2-methyl-2,4-pentanediol) was used. The alumina consisted mainly of γ -Al₂O₃ after final calcination at 600°C. Commercial γ -Al₂O₃ (Sumitomo NK 324, coded as Al-ref) was also used as a reference to the sol-gel alumina. Cobalt, gallium, indium, manganese, silver and tin were impregnated by pore filling method using Co(NO₃)₂ · 6H₂O, Ga(NO₃)₃ · 9H₂O, In(NO₃)₃ · 3H₂O, Mn(NO₃)₂ · 6H₂O, AgNO₃ and SnCl₄ · 5H₂O as precursor salts in aqueous solutions. Because of the very different atomic weights, the comparable metal loading of the catalysts was based on the molar contents in the catalysts to have the same number of metal atoms in each catalyst. The molar ratio of Al/M (M = impregnated metal) was fixed to be between 20 and 650. After impregnation, the catalysts were dried at 110°C overnight, calcinated at 600°C for 3 h and screened to the particle size of < 250 micrometers to homogenize the samples and to decrease mass transfer limitations in the activity tests. New samples were then prepared by calcinating these samples at elevated temperatures (700–1000°C). Commercial TiO₂ (Degussa, P-25) and SiO₂ (Fuji Silysia Chemical, Cariat-10) were also used as carriers for indium.

In/ZSM5 was prepared by a conventional ion exchange method. Washed ZSM-5 zeolite powder (Tosoh, SiO₂/Al₂O₃ = 23.3) was ion exchanged in a 0.04 M solution of In(NO₃)₃ · 3H₂O for 24 h at 80–90°C, dried and calcinated at 500°C for 3 h. The ion exchange ratio of In³⁺ in zeolitic aluminum sites was calculated to be 147% by a quantitative XRF analysis, which was confirmed by plasma analysis.

InO_x sample was prepared by precipitation from a 0.06 M indium nitrate solution with Na₂CO₃ solution (0.8 g dm⁻³). Dried sample was calcinated at 600°C. After the preparation of the sample, In₂O₃ can be assumed to be the main stable form of indium. Commercial pure Mn₃O₄ was tried as a promoter by softly mixing it physically with alumina based catalyst samples in the weight ratio of 1 : 19 (5 wt%).

Table 1
The composition of the catalysts used in this study

Catalyst (Al/M)	Loading wt%	Surface area $\text{m}^2 \text{g}^{-1}$	
		calculated at	
		600°C	800°C
In/Al-sg(20)	10.1	180	140
In/Al-sg(45)	4.8	206	166
In/Al-sg(65)	3.3	216	161
In/Al-sg(130)	1.7	214	174
In/Al-sg(300)	0.74	223	166
In/Al-sg(650)	0.34	223	162
In/Al-ref(65)	3.3	145	126
In/Ti	3.3	45	na
In/Si	3.3	335	na
InO _x	pure	27	na
Mn ₃ O ₄	pure	1	na
Mn/Al-sg(65)	1.63	181	181
Co/Al-sg(65)	1.75	215	152
Ag/Al-sg(65)	3.14	205	153
Sn/Al-sg(65)	3.52	195	167
Ga/Al-sg(65)	2.07	231	171
Cu/ZSM5	3.7	237	200
In/ZSM5	7.2	269	na
Al-sg	—	301	181
Al-ref	—	162	na
Ti	—	50	na
Si	—	260	na
ZSM5	untreated	219	139

2.2. Catalyst characterization

The composition and the physical properties of the catalysts are summarized in Table 1. The surface area (BET) was determined by the standard nitrogen adsorption at -196°C (Micromeritics Flow Sorb II) after the pretreatment in N_2/He flow at 300°C for 30 min. X-ray diffraction (XRD) was used to detect separate metal and oxide phases after treatments (Shimadzu XD-D1). Powder samples were analyzed using a $\text{CuK}\alpha$ target and a 0.6 mm received slit by the rotation speed of $2^\circ/\text{min}$. The chemical composition of the catalysts were confirmed by XRF analysis (Seiko Instruments SEA2010), which was quantitative by the reference samples and was matched to plasma analysis.

2.3. Catalytic activity test

The steady-state activities of the catalysts were evaluated using simulated lean exhaust gas containing

about 1000 ppm NO or NO_2 , 1000 ppm propene, 10% oxygen and 0 or 8% water in helium in the temperature range of $200\text{--}600^\circ\text{C}$. In addition to propene, propane (1000 ppm), ethene (1000 ppm), methane (1000 ppm), methanol (1000 ppm), ethanol (400 ppm) and 2-propanol (400 ppm) were also tested as the reducing agents in the same mixture. The total gas flow rate was 66 ml min^{-1} and the standard amount of a sample was 0.2 g ($W/F = 0.05 \text{ g h dm}^{-3}$). A quartz flow reactor, heated by an IR gold image furnace, was equipped with a thermocouple installed in a pocket just touching the outlet of the catalyst bed. Water was vaporized into the reactor and removed in two condensers before the gas composition analysis. The composition of the product gas was analyzed by using two parallel gas chromatographs (Shimadzu GC 8A equipped with Porapak Q and Molecular sieve 5A columns) and a chemiluminescence NO_x/NO analyzer (Shimadzu NOA-305A). The quantitation of GC peak areas was made by the calibration gas mixture containing about 250–300 ppm nitrogen, nitrous oxide, CO and CO_2 in He. According to these analysis it was possible to calculate the total mass balance for nitrogen (N_2 , N_2O , NO, NO_2) and carbon (CO_2 , CO, C_3H_6 , C_2H_4 , CH_4) compounds, if no other undetected compounds were formed.

3. Results and discussion

3.1. Activity of various metal supported alumina catalysts

The activity of sol-gel alumina supported indium, gallium, silver, tin and cobalt catalysts were investigated after the calcination at 600 and 800°C (Fig. 1). The metal loading as the molar ratio of Al/M was 65 in this evaluation. In/Al-sg showed the highest activity for NO reduction over the broad operation window. Ga/Al-sg had a sharp high activity peak (maximum conversion 99% when calcinated at 600°C) at 500°C having the same shape of the operation window as the sol-gel alumina-only catalyst. The calcination at 800°C instead of 600°C lowered the activity of In/Al-sg and Al-sg catalysts but increased the activity of Co/Al-sg, Sn/Al-sg and particularly Ag/Al-sg. The maximum nitrogen formation coincided to the conversions of 80–90% from propene

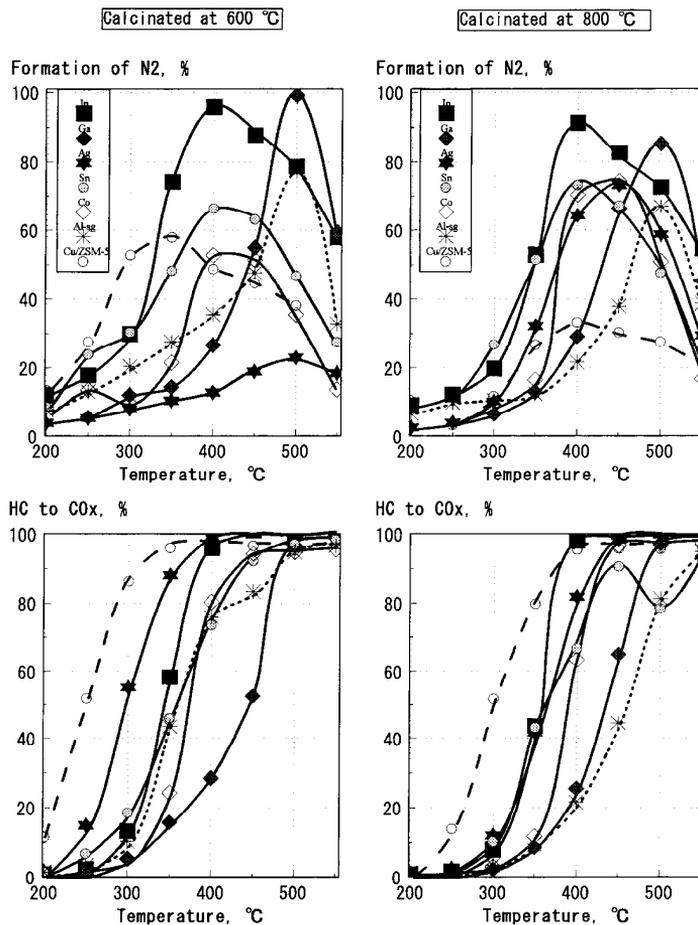


Fig. 1. The NO reduction by propene over Al-sg supported In, Ga, Ag, Sn and Co catalysts in the absence of water (W/F 0.05 g h dm⁻³, 1000 ppm NO and C₃H₆, 10% O₂).

to CO_x. According to these results it can be assumed that in the range of 600–800°C, the main state of In, Sn and Ga did not change largely, but it is evident for Co and Ag catalysts. In fact the rate of propene oxidation over In/Al-sg was not influenced by the higher calcination temperature, the propene light-off temperature (T_{50}) being in both cases (calcination at 600 and 800°C) about 450°C. The NO reduction activity was slightly lower when calcinated at 800°C. The loss of the reduction capability can be proposed to be caused by the degradation of alumina

surface and its acidic sites, which have an essential role in the adsorption and the reduction of nitrogen species [22].

The propene oxidation initiated at too low temperatures preventing NO reduction on Ag/Al-sg(65 600). It is assumed that the silver concentration was too high and finely dispersed silver oxide particles still exist on the sol-gel alumina calcinated at 600°C, but larger silver and silver aluminate particles were formed in higher temperature calcination (800°C) suppressing the total hydrocarbon oxidation,

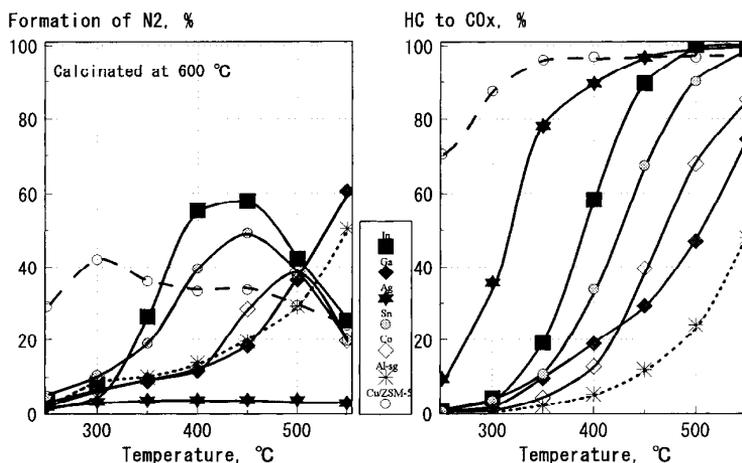


Fig. 2. The NO reduction by propene in the presence of water over Al-sg supported In, Ga, Ag, Sn and Co catalysts calcinated at 600°C (W/F 0.05 g h dm⁻³, 1000 ppm NO and C₃H₆, 10% O₂, 8% H₂O).

which thus enhanced the reduction of NO to nitrogen [15].

The comparison between the conventional and the sol-gel γ -alumina proved clearly the high activity of sol-gel alumina as a support for indium (Fig. 2). The initial surface area of sol-gel alumina (301 m² g⁻¹) is much higher than that of commercial alumina (162 m² g⁻¹) typically used as a raw material for the catalyst preparation. After the indium addition (3.3 wt%), the difference between the surface areas was still significant (Table 1): In/Al-sg (216 m² g⁻¹) and In/Al-ref (145 m² g⁻¹). The higher surface area is a reason for the activity of sol-gel alumina based catalysts. It is presumed that the cooperation between activated alumina and indium oxide during the preparation of the In/Al-sg and/or the reduction reaction is another reason for the higher activities.

In the presence of water all the catalysts except for silver/alumina calcinated at 600°C had relatively high activity when W/F was 0.05 g h dm⁻³ (Fig. 2). In/Al-sg (58% to nitrogen at 400–450°C), Sn/Al-sg (50% to nitrogen at 450°C) and Co/Al-sg (40% to nitrogen at 500°C), Ga/Al-sg (60% to nitrogen at 550°C) and Al-sg-only (50% to nitrogen at 550°C) were competitive catalysts compared to the reference catalyst, Cu/ZSM-5, over the broad temperature win-

dow above 370°C. In contrast to Cu/ZSM-5, alumina based catalysts showed a strong mutual interaction between the hydrocarbon oxidation and the NO reduction rates both in dry and wet conditions. When the hydrocarbon oxidation initiated at temperatures under 300°C, the NO reduction was always almost totally prevented because of the lack of the actual reductant on the surface. The NO reduction over Cu/ZSM-5 has been reported to proceed by a different reaction mechanism, in which partially oxidized hydrocarbons attached on the zeolite catalyst, reduce NO or NO₂ to nitrogen [9]. It can be proposed that on alumina based catalysts the coverage of hydrocarbon oxidation intermediates except carbonates stayed at a very low level when the oxidation rate was high causing this lack of the actual reductant. The ZSM-5 zeolite has higher adsorption capacity for hydrocarbon species, stronger acidity and higher hydrophobicity [23] compared to alumina based samples. These differences may give a reason for the noticed NO reduction properties. Probably the slow reaction rates of surface species result a broad NO reduction window and are also the reason for the fact that no conversions over 50–60% were accomplished with the Cu/ZSM-5 catalyst in any circumstances. Cu/ZSM-5 and other alumina silicate based zeolites have been known to be sensitive for hydrothermal deactivation. Alumina supported silver

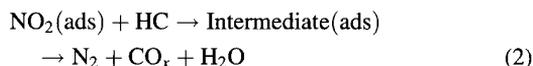
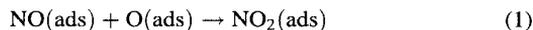
has found to be more durable than indium and tin against the deactivation caused by SO₂ [14]. The hydrothermal durability of the alumina structure is known to be good, but the deactivation and the poisoning caused by SO₂ over this kind of sol-gel alumina supported catalysts, would have to be investigated in the future.

The Ag/Al-sg preserved as high hydrocarbon oxidation activity as noticed in dry conditions. Silver metal particles were highly dispersed as AgO or Ag but not as silver aluminate or Ag₂O when the catalyst was calcinated at 600°C. Ag/Al-sg calcinated at 800°C in the presence of water had a high activity (42% to nitrogen at 450–500°C) predicted by earlier studies [15]. The observations in the earlier studies that water stabilizes partially oxidized hydrocarbons and active hydroxyl groups on oxygenated silver surfaces, can give an explanation for the higher activity of silver/alumina in the presence of water [24,25]. It is proposed that there exists an equilibrium between silver hydroxyl and tightly bound silver oxygen species. The shift from hydroxyls to surface oxygen occurs around at 330°C in the presence of water. Ammonia and other nitrogen containing species (amine, nitroso, HNO_x compounds), which were not detectable in this study, have been detected in small concentrations over silver/alumina by Miyadera et al. 1994 [26], especially when ethanol was used as a reductant.

Tin and gallium catalysts had the highest tendency for the CO formation as an intermediate from partial oxidation of propene: alumina supported Sn (C₃H₆ → CO : 36%) > Ga(31%) > In(15%) > Al-sg only (5%) > Co(4%) > Ag(0%). The silver catalyst had high activity for CO oxidation, which seems to be negatively correlated to the NO reduction activity. A very small amount of ethene was formed in the temperature range of 300–550°C, preferably over the catalysts (Sn, Ga, Al-sg-only).

Silver (6%) and cobalt (3%) catalysts had clearly the highest activity for the nitrous oxide formation. All the other catalysts showed an excellent tendency for the low N₂O formation (≤ 1% of NO) with high selectivity to nitrogen. The concentration of NO₂ in the reactor outlet is an indicator to know if the NO oxidation rate to NO₂ is a limiting factor in the overall reaction. If the NO₂ formation is low (< 1–2%) and the total NO conversions is less than about 80–90%,

this step can be a limiting step for the formation of nitrogen, which is assumed to proceed in the critical step by the reactions between NO₂ and the hydrocarbon [9]:



where ads denotes adsorption on the active sites.

The limitation caused by the low NO₂ formation was evident for Sn/Al-sg at the temperatures below 350°C. The NO₂ concentrations were also almost as low for In/Al-sg, but in this case the total NO conversion to nitrogen were over 80%. The NO₂ formation can be a limiting factor over the metal oxide catalysts like Sn and In supported on alumina especially in the low temperature range of the NO reduction. The conversions to nitrogen with the mixture of NO₂ + HC + O₂ have been noticed in many earlier studies to be higher than with the mixture of NO + HC + O₂ over various metal oxide catalysts (Fig. 3).

3.2. Different support materials for indium

In the screening tests indium was shown to be a promising catalyst for the NO reduction when supported on alumina. Therefore, its activity and performance over other support materials were also investigated (Fig. 4). Indium oxide alone was not active for the NO reduction, but it was seen that the propene oxidation was controlled by indium oxide over various supports. In/silica was very inactive both in the NO reduction and the propene oxidation. Silica alone is also the most inactive of these supports. Titania alone is active for oxidation reactions, but it has a minor activity for the NO reduction by hydrocarbons unlike alumina and ZSM-5 zeolite. In/titania showed the activity at the low temperature but its activity was decreased at higher temperatures probably because titania has not the same capacity as alumina to adsorb NO_x and partially oxidized hydrocarbons. In/ZSM-5 had a broad operation window but no tendency for the higher NO conversions matching to the same reaction mechanism presented earlier for Cu/ZSM-5.

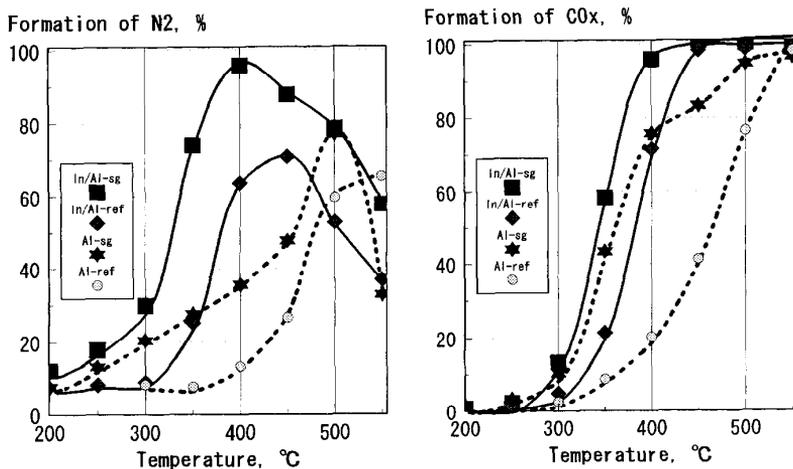


Fig. 3. The enhancement of sol-gel alumina and indium for NO reduction by propene (W/F 0.05 g h dm⁻³, 1000 ppm NO and C₃H₆, 10% O₂). A commercial γ -alumina used as a reference.

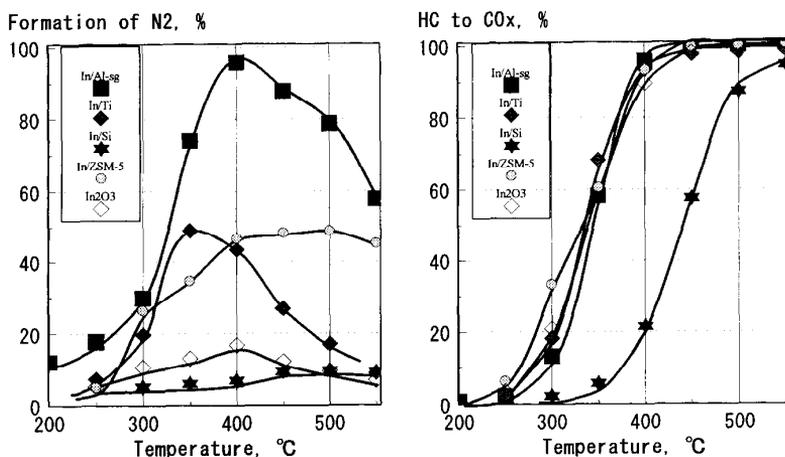


Fig. 4. The effect of support material on the activity of indium catalysts in NO reduction by propene (W/F 0.05 g h dm⁻³, 1000 ppm NO and C₃H₆, 10% O₂).

3.3. Efficiency of various hydrocarbons for NO reduction

3.3.1. Indium/alumina

The promising activity of various sol-gel alumina supported catalysts was further investigated using instead of propene other hydrocarbons like ethene,

propane, methane, methanol, ethanol and 2-propanol as a reductant. All these hydrocarbons are very likely present in real exhaust gases from gasoline and diesel engines or they can be injected as reductants into a reaction mixture. In/Al-sg was shown to be an active catalyst in the presence of propene, propane and ethene, which gave more than 85% NO conversions

Table 2

The efficiency of different hydrocarbons for the NO_x reduction over In and Sn loaded and unloaded sol–gel alumina in a dry mixture (1000 ppm NO; 10% O₂; C₃H₆=C₃H₈=C₂H₄=CH₄=MeOH=1000 ppm and EtOH=2-PrOH=400 ppm; balance He, no water)

Reductant	Max. formation of N ₂ % (at T, °C)			Oxidation of reductant T ₅₀ , °C		
	In/Al-sg	Sn/Al-sg	Al-sg	In/Al-sg	Sn/Al-sg	Al-sg
C ₃ H ₆	96(400)	66(400)	77(500)	330	360	360
C ₃ H ₈	89(500)	na	99(500)	460	na	470
C ₂ H ₄	96(450)	na	62(500)	380	na	465
CH ₄	8(550)	na	14(500)	530	na	470
MeOH	31(300)	34(300)	44(250)	270	270	315
EtOH	28(350)	27(350)	20(350)	295	315	345
2-PrOH	36(350)	na	40(450)	320	na	400

na: Not available.

Catalysts calcinated at 600°C.

Table 3

The efficiency of different hydrocarbons for the NO_x reduction over In and Sn loaded and unloaded sol–gel alumina in a wet mixture (1000 ppm NO; 10% O₂; C₃H₆=MeOH=1000 ppm and EtOH=2-PrOH=400 ppm; 8% H₂O; balance He)

Reductant	Max. formation of N ₂ % (at T, °C)			Oxidation of reductant T ₅₀ , °C		
	In/Al-sg	Sn/Al-sg	Al-sg	In/Al-sg	Sn/Al-sg	Al-sg
C ₃ H ₆	58(450)	49(450)	50(550)	385	420	555
MeOH	26(300)	21(300)	29(350)	265	285	330
EtOH	30(300)	na	22(350)	280	na	390
<i>i</i> -PrOH	33(400)	na	na	375	na	na

na: Not available.

Catalysts calcinated at 600°C.

to nitrogen when HC/NO molar ratio was fixed at unity in the lean dry conditions (Table 2). Alcohols did not show so high activity for the NO reduction with the NO conversion of less than 40%. Their oxidation took place at lower temperatures and methanol was totally oxidized over 330°C. It was again clearly confirmed that the maximum NO reduction coincided to the total hydrocarbon conversion of about 80–95%.

In the presence of 8% water, the reduction efficiency of saturated and unsaturated hydrocarbons was decreased but alcohols as reductants were seen to be insensitive to the reaction inhibition caused by water (Table 3). The oxidation reactions with hydrocarbons were diminished but the oxidation of oxygen containing alcohols was not altered in the presence of water. Water maintains surface concentrations of hydroxyls on alumina [27]. In the absence of water the hydroxyl groups are lost at elevated temperatures leading to the

activation of hydrocarbons by weakly bonded hydroxyl groups or surface oxygen. This explains the different performance of the reductants noticed in the dry and wet conditions on various alumina supported catalysts.

3.3.2. Tin/alumina

The activity of Sn/Al-sg was studied in addition to propene with methanol and ethanol, which have been reported to be efficient NO reductants on tin catalysts. The results indicated in Tables 2 and 3 proved that the inhibition effect of water was low for the tin catalyst compared to alumina itself but the final conversion to nitrogen was not as high as expected. The main reason for the lower activity was probably too high tin concentration (3.5 wt%), which enhanced the hydrocarbon oxidation and covered necessary free alumina sites. In earlier studies, the optimal tin concentration on alumina was found to be about 0.5–1.0 wt% when

methanol was used as a reductant [20]. Another reason can be the unusual properties of sol–gel prepared alumina support compared to commercial alumina supports. The preparation of the tin catalyst from chloride precursor may not be optimal to have an active catalyst.

3.3.3. Alumina only

As a base line for previous catalysts, an unimpregnated sol–gel alumina calcinated at 600°C, was investigated by the same way. The results are also shown in Tables 2 and 3. Propane gave surprisingly high NO conversions to nitrogen (over 95%) at 500°C in the dry conditions. The temperature window (with nitrogen formation more than 50%) was at higher temperatures compared to metal oxide/alumina catalysts, for which the window was in the range of 450–600°C. However with methanol as a reductant the low temperature (nitrogen 45% at 250°C) activity was achieved. 2-propanol showed a broad operation window but the maximum conversion to nitrogen was as low as 39% and with ethanol about 20%.

The efficiency of propene, ethanol and methanol was also tested in the presence of water. As expected, alumina only catalysts lost their activity when hydrocarbons were used as reductants. Oxygenated reductants kept relatively better NO reduction capability in wet conditions. Alcohols did not show a high drop in their oxidation rate because of water. In the presence of water, hydroxyls of alcohols can be expected to keep the alumina hydroxyl concentrations in balance. About 30% nitrogen formation at 350°C was reached with methanol and about 50% nitrogen formation at 550°C with propene.

In the case of alcohols and methane as reductants it should be noted that C_1/NO was lower than with other hydrocarbons in these tests. This fact strengthens the value of the conversions with them. C_1/NO in these tests was as follows: Propene and propene 3; ethene 2; methane 1; 2-propanol 1.2, ethanol 0.8; methanol 1.

3.3.4. The formation of N_2O , CO, C_2H_4 and C_3H_6 as by-products

The formation of these by-products depended on the catalyst and the hydrocarbon used as a reductant. Propene was formed in a high degree (maximum over 50%) over these catalysts by the dehydration of 2-propanol especially in the presence of water at lower

temperatures (200–300°C). Likewise, ethene was formed by the dehydration of ethanol at lower temperatures.

The order of the maximum ethene formation from ethanol was found to be:

$In/Al-sg(4\%) < Sn/Al-sg(8\%) < Al-sg(10\%)$ dry

$In/Al-sg(13\%) < Al-sg(40\%)$ wet

This kind of reductant decomposition gave an excellent possibility for NO to be reduced both by oxygenates and efficient olefins like ethene and propylene. Unfortunately these oxygenates are decomposed even in the lower temperature range where olefins are not so reactive.

Nitrous oxide formation was the highest when methanol was used as a reductant and followed the next orders by the maximum formations:

$Al-sg(3\%) < In/Al-sg(5\%) < Sn/Al-sg(9\%)$ dry

$Al-sg(2\%) < In/Al-sg(13\%) < Sn/Al-sg(29\%)$ wet

The N_2O formation with light alcohols took place at lower temperatures when the oxidation of the alcohols initiated. When propene was used, the N_2O formation rates were lower in the wet than in the dry mixtures.

The maximum hydrocarbon conversion to CO depended on the catalyst and the hydrocarbon used as shown in Table 4. The CO formation peaks coincided with the intermediate hydrocarbon conversions, which depend mostly on the basic tendency of a hydrocarbon to be activated on the current catalyst. If the catalyst has in some degree an oxidation capacity for a hydrocarbon but the poor ability to oxidize CO to CO_2 and the adsorption strength of CO is strong enough, reducing conditions can be assumed to be prevailing on the catalyst surface. The steady state

Table 4

The maximum HC conversion to CO in wet and dry mixtures by the catalyst and the hydrocarbon when $W/F = 0.05 \text{ g h dm}^{-3}$ (dry CO%/wet CO%)

Catalyst	C_3H_6	C_3H_8	C_2H_4	MeOH	EtOH	2-PrOH
In/Al-sg	15/15	2/-	7/-	23/24	10/15	12/10
Sn/Al-sg	35/21	—	—	43/10	15/6	—
Al-sg	5/28	25/-	10/-	23/24	15/6	—

— = Not measured.

Catalysts calcinated at 600°C.

formation of CO during the reaction proved that new adsorbing hydrocarbon molecules sweep continuously formed CO molecules from the surface and the reaction can proceed. Methanol and propene among the investigated hydrocarbons had the highest possibility to the CO formation over these catalysts. Before the hydrocarbon light-off, the NO reduction cannot be expected to initiate but the surface is steadily covered with CO, carbonates, hydrocarbons or nitrates.

3.4. Effect of the loading and the calcination temperature on the activity of In/alumina

The performance of In/Al-sg catalysts was investigated more carefully in respect of the calcination temperature and the indium loading. When the calcination temperature was increased from 600 to 900°C, a drop in the activity happened at the temperatures over 700°C, where alumina itself is losing drastically its surface area and the active sites controlling the adsorption ability towards reactants (Fig. 5). The activity was first lost at low temperatures (300–400°C) due to the kinetic requirement for the higher surface area and the small active metal oxide particles on the surface where the reactions initiate. The calcination of In/Al-sg(65) even at 900°C made no dif-

ference in the activity in the reaction temperature range of 450–550°C.

When the indium loading was varied between 65–20 (0.43–10.4 wt% In) by Al/In, an optimal loading was found both in the dry and the wet conditions (Fig. 6). The calcination temperature was fixed in this case at 600°C. Indium on sol-gel alumina was very durable against water. NO conversions to nitrogen as high as 78% were reached in the presence of 8% water with W/F of 0.05 g h dm⁻³. The differences of the activity in the range of these loading were relatively small, especially in dry mixtures, because our alumina has a good baseline activity alone. Relatively high In concentrations (Al/In 65..45) advanced the operation window at the low temperature side (350–400°C) but low In concentrations (Al/In 130..300) are preferable to keep the activity level at higher temperatures (450–500°C). In the presence of water the operation window covering the broadest range was achieved with 1.7 wt% In on Al-sg (Al/In 130). Even the indium loading of 0.34 wt% enhanced clearly the activity of sol-gel alumina. The propene oxidation to CO_x was accelerated as a function of the increasing indium concentration up to 3.3 wt% In. Over that concentration the addition of indium had no clear effect on the HC oxidation activity.

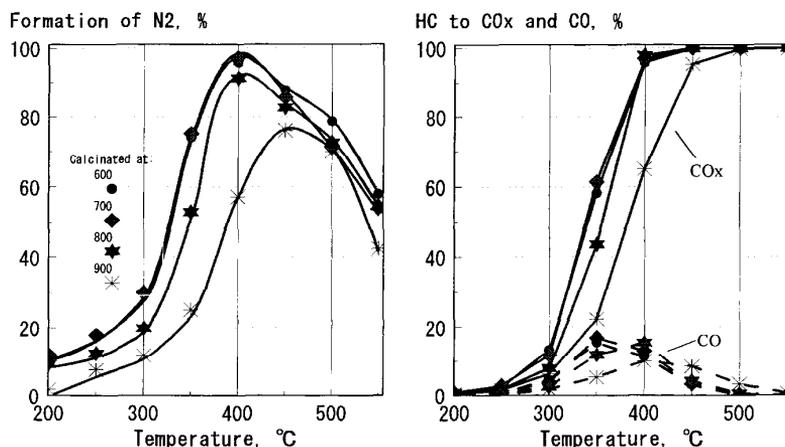


Fig. 5. The effect of calcination temperature on the performance of an In/Al-sg(65) catalyst (3.3 wt% In) in dry conditions (W/F 0.05 g h dm⁻³, 1000 ppm NO and C₃H₆, 10% O₂).

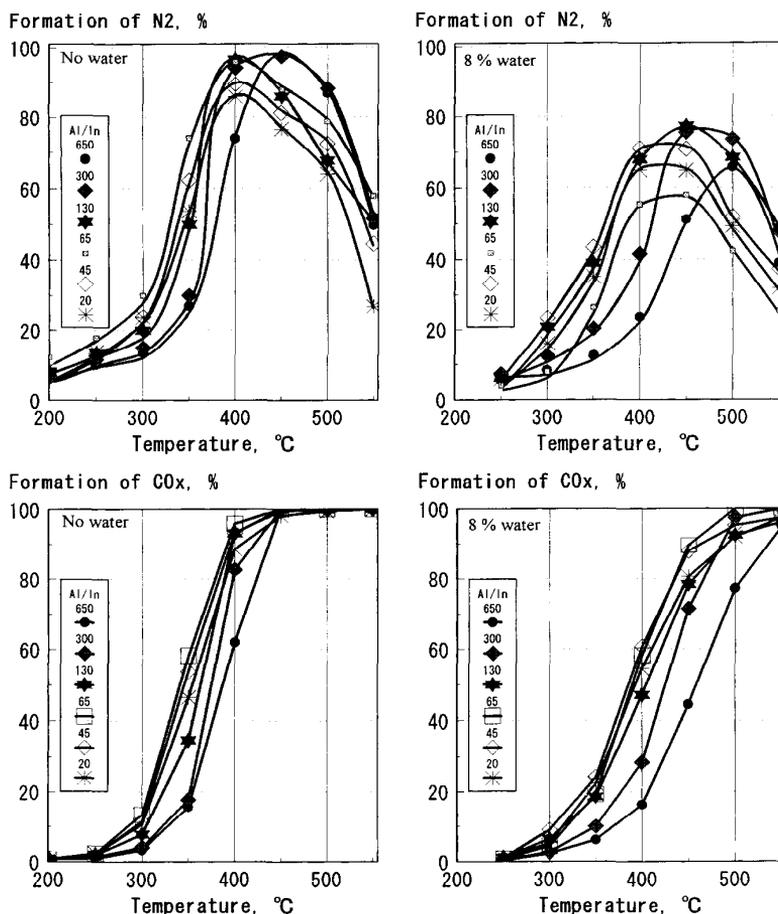


Fig. 6. The effect of the indium loading on the performance of the In/Al-sg calcinated at 600°C in dry and wet conditions (W/F 0.05 g h dm⁻³, 1000 ppm NO and C₃H₆, 10% O₂).

3.5. Activity enhancement by the addition of manganese oxide

Mn₂O₃ mixed physically with an active deNO_x catalyst has been reported to increase NO reduction rates to nitrogen [4]. In real lean exhaust gas conditions MnO₂ is not expected to be stable but manganese with lower valence is more permanent (MnO, Mn₃O₄, Mn₂O₃) [28]. The manganese oxide used was primary chosen by the stability evaluation. In our study 5 wt% of fine-grained Mn₃O₄ was softly mixed without grinding into In/Al-sg(65 600) and Ga/Al-

sg(65 600). Manganese oxides themselves were proven to be too active for hydrocarbon oxidation to have NO reduction ability [29].

As a comparison NO was replaced with NO₂ in the reaction gas to elucidate the role of NO oxidation in the overall reaction chain. Ga/Al-sg showed a very high activity in the presence of NO₂, which proved that NO oxidation rate was the limiting factor with this gallium catalyst (Fig. 7). The addition of Mn₃O₄ increased clearly the formation of nitrogen but still the activity was lower than in the case of NO₂ without manganese oxide. NO₂ promoted markedly the hydro-

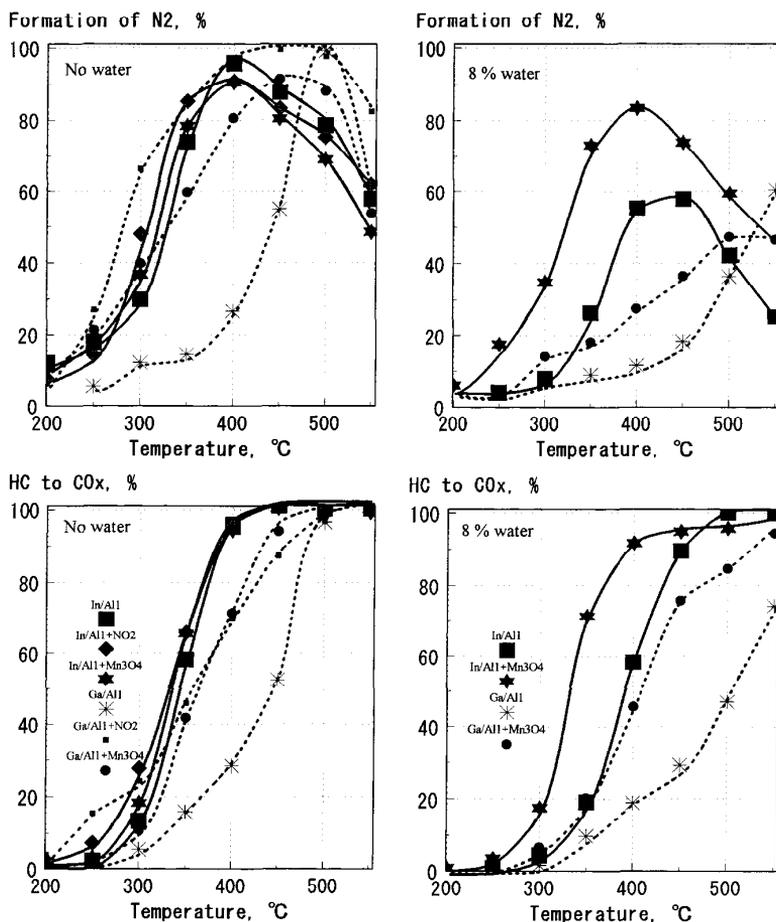


Fig. 7. The effect of the addition of 5 wt% Mn_3O_4 on the performance of the In/Al-sg(65 600) and Ga/Al-sg(65 600) calcinated at 600°C to reduce NO and NO_2 (W/F 0.05 g h dm^{-3} , 1000 ppm NO_x and C_3H_6 , 10% O_2).

carbon oxidation (T_{50} , 450°C \rightarrow 350°C), so did the addition of 5 wt% Mn_3O_4 over the gallium catalyst. Ga/Al-sg showed alone a poor oxidation tendency for propene and NO. This fact limited the operation window to higher temperatures.

In the case of In/Al-sg no remarkable difference was detected when NO_2 or NO was in the feed. In dry conditions Mn_3O_4 showed a slight promotion against nitrogen formation over the indium catalyst. The basic oxidation activity of the indium catalysts seemed to be clearly higher than that of the gallium catalysts. Mn/Al-sg(65) calcinated at 600 or 800°C had a very

high activity for the propene oxidation (T_{50} about 270–280°C) and therefore the conversions to nitrogen were as low as 18–23% in the absence of water.

When 8 wt% water was added into the reaction gas mixture, the high activity was still reached with the indium catalysts. Even if manganese oxide had a low promotion in the dry condition, in the wet mixture Mn_3O_4 was shown to promote the oxidation reactions resulting in the highest activity among all of the investigated catalysts in this study. The maximum NO conversion to nitrogen exceeded 82% at 400°C. The catalyst containing manganese oxide kept the

same hydrocarbon oxidation activity both in the dry and the wet conditions, but alumina based indium and gallium catalysts without Mn_3O_4 promotion lost that with 50°C higher T_{50} of hydrocarbon in the presence of water.

Manganese oxide gave an appropriate aid for the overall NO reduction by enhancing the NO oxidation to NO_2 in the presence of water. The addition of manganese oxide had no effect on the maximum level of the CO appearance in the reactor outlet. In the wet conditions the maximum CO formation peak about 15% of propene rose up around at 400–450°C over In/Al-sg but around at 350°C over In/Al-sg + Mn_3O_4 . In the dry conditions manganese oxide addition had no effect on these reactions. Water can be expected to have inhibiting effects on the active sites for NO oxidation in alumina based catalysts but no effect on the reduction sites (In or Ga sites). The catalyst composition with the highest activity was created by mixing physically the promoter for NO oxidation and the effective deNO_x catalyst. Manganese oxide is an ideal promoter, because it has a higher activity for NO oxidation but not too high activity for hydrocarbon oxidation in the presence of water. Probably In/Al-sg is responsible for NO_2 reduction to N_2 in the mixture of In/Al-sg and Mn_3O_4 . If manganese was impregnated on alumina it will appear as highly dispersed species having an intimate interaction with alumina and too high activity for the total hydrocarbon oxidation.

The addition of 5 wt% Mn_3O_4 into Ga/Al-sg had a positive promotion, but in the presence of water NO reduction ability was relatively low compared to the similar mixture of indium/alumina. The increase in the hydrocarbon oxidation capacity was promising but probably Ga/Al-sg itself was deactivated by water in respect to the NO reduction as presented in earlier studies [14]. Profound studies on the effects of the preparation method of these catalysts are under consideration.

4. Conclusions

Indium, gallium, cobalt and tin supported on sol-gel alumina were shown to be very active catalysts for the NO reduction with hydrocarbons in the presence of oxygen. The highest activity was obtained when pro-

pane, propane and ethene were used as reductants. A remarkable enhancement was achieved by using sol-gel alumina instead of conventional γ -alumina as a support or a catalyst. Sol-gel alumina based catalysts showed a promising resistance against the deactivation caused by water. Higher activities than for Cu/ZSM-5 as a reference catalyst were accomplished in the presence of water with sol-gel alumina supported indium (> 370°C), tin (> 390°C), cobalt (> 470°C), gallium (> 500°C) and even sol-gel alumina-only (> 510°C) catalysts. Cu/ZSM-5 had a broad NO reduction window, even if the catalyst had a high activity for the hydrocarbon oxidation ($T_{50} < 250^\circ\text{C}$). With respect to alumina based catalysts, the hydrocarbon oxidation and the NO reduction activity have a strong mutual correlation. When the hydrocarbon oxidation initiated at the temperatures under 300°C, the NO reduction was drastically prevented because of the lack of reductants at higher temperatures. This is assumed to depend on the differences of adsorption capacities and the reaction rate of the surface species between alumina and zeolite based catalysts.

A moderate NO conversion of over 30% was also obtained when light alcohols (C_1 – C_3) with a low reductant/NO molar ratio of unity were used with sol-gel alumina supported indium and tin catalysts as well as with the alumina-only catalyst. TiO_2 and ZSM-5 were also appropriate supports for indium. The indium and tin catalysts had an operation window (> 300°C) matching partly to the medium-temperature operation window requirement (300–450°C), which is missing with many other candidate catalysts for deNO_x . Noble metal catalysts have a property of the low-temperature reduction operation (150–250°C) and many other alumina based catalysts (cobalt, gallium, alumina-only) have a high temperature operation window (> 400°C), too. The investigated catalysts showed a very small formation of nitrous oxide except when methanol was used as a reductant.

The addition of manganese oxide had a high promotion effect on the activity of alumina based indium and gallium catalysts. In this study Mn_3O_4 mixed physically with a good deNO_x catalyst was proven to be an efficient ingredient to enhance the NO oxidation, which is the limiting reaction steps in the overall NO reduction to nitrogen.

Acknowledgements

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