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THE BEHAVIOR OF IRIDIUM BASED CATALYSTS IN THE SELECTIVE CATALYTIC REDUCTION OF NOX IN LEAN AUTOMOTIVE EXHAUST GAS CONDITIONS: A REVIEW

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ABSTRACT

The selective reduction of NO with hydrocarbons (HC-SCR), hydrogen (H_2-SCR) and CO (CO-SCR) over iridium based catalysts in the O_2-rich conditions is reviewed. The different factors that can affect catalytic activity are addressed for the three reactions (promoting and poisoning elements, operating conditions, etc.). For HC-SCR reaction, the important findings emerging from the studies revealed the effect of iridium particle size, role of support, effect of promoters, effect of reducing agent, and sulfur and water tolerance. The mechanism involved for HC-SCR reaction consists of NO oxidation to NO_2 on basic sites of alumina and reaction with C_3H_6 to form acetate species which reduce NO into N_2. In the case of H_2-SCR, the activity of Ir is low and coexisting SO_2 in the reaction gas considerably promotes NO reduction. The best support for Ir is SiO_2. For CO-SCR, coexisting SO_2 is also essential for CO-SCR on Ir/SiO_2. The role of SO_2 for both H_2-SCR and CO-SCR on Ir/SiO_2 is to keep Ir in the form of the catalytically active Ir metal state. WO_3 and Nb_2O_5 considerably promote the activity of Ir/SiO_2 for CO-SCR and catalyze CO-SCR even in the absence of SO_2. Ir metal is the active species on WO_3-promoted Ir/SiO_2.

KEYWORDS: nitric oxide, hydrocarbons, hydrogen, carbon monoxide, selective catalytic reduction, Ir.

INTRODUCTION

In the past years, several technologies have been developed in order to catalytic removal of NO_x under rich-oxygen environment including the catalytic decomposition, selective catalytic reduction, storage and selective catalytic reduction combined with Diesel Particulate Filter system of a 2-way (SCR/DPF) [1−8]. Among these catalytic systems, supported noble metal catalysts have been for many years at the center of focus in the field of SCR of NO_x under lean-burn conditions, in the view of their application in lean-burn gasoline or diesel engines processes [3, 9–12]. Consequently, significant research efforts have been devoted to the development of novel catalytic systems, capable for the efficient lean NOx reduction using in principle the gases which already exist in the effluents as reducing agents, e.g., unburned hydrocarbons, H_2 or CO [13–25]. Among the supported Platinum Group Metals (PGM), the most studies investigated on Pt-based catalysts have shown good de-NO_x activity at low temperatures, due to their typically high thermal/chemical stability and to their strong resistance to poisoning by SO_2 and H_2O [26-29]. Ir-based catalysts have shown high catalytic activity and N_2 selectivity when NO reduced with hydrocarbon in rich-oxygen environment, and then they have been proposed as active and durable solids. Ir on various supports [30] and specially Ir on $BaSO_4$ [31] as well as Ir-H-ZSM5 [19] have been studied. Compared to other noble metals, iridium supported on γ-Al_2O_3 has been found to be active at higher temperatures than platinum based catalysts, typically between 400 and 600°C and N_2O formation has been low [13−16].

A variety of reducing agents has been tested over iridium based solids for their activity and selectivity in the NO reduction under lean burn conditions. It has been long believed that H_2 and CO cannot reduce NO selectively in oxygen-rich conditions because they are used as reductants in the stoichiometric three-way catalyst system as well as hydrocarbons. However, it has been proved recently that H_2 and CO can also act as effective reductants for SCR [32-37]. Since the selective catalytic reduction of NO with H_2 (H_2-SCR) proceeds at relatively low temperatures, H_2-SCR is an attractive approach to the efficient removal of NO_x in the exhaust of lean-burn and diesel engines, the temperature of which has become lower due to the improvement of engine thermal efficiency. H_2 can be formed by reforming of hydrocarbon fuels. H_2-SCR is also a promising measure for NO_x treatment

emitted from hydrogen fueled vehicles. Wang et all [28, 38] reported that among Pt, Pd, Rh and Ir catalysts, Ir/ZSM-5 catalyst exhibits the highest activity for the NO reduction by CO in the presence of excess O_2 and H_2O. Haneda et all [29, 39, 40] discovered that Ir/SiO_2 shows marked catalytic activity for the NO reduction with CO in the presence of O_2, H_2O and SO_2. Tauster and Murrell [41] were the first who studied NO reduction by CO with Ir catalysts. They showed that Ir is the only noble metal favoring the NO–CO over the CO–O_2 reaction in the presence of O_2. Absorbed oxygen on Ir was the predominant surface species and its reaction with gaseous CO generated free surface sites. These sites were available for the chemisorption of NO and O_2. Taylor and Schlatter [42], who studied NO reduction by CO in the presence of O_2 over alumina-supported Ir, Rh, Pt and Pd catalysts, confirmed these results. The high effectiveness of Ir compared to the other metals was attributed to its ability to adsorb NO dissociatively in the presence of excess O_2. The selective catalytic reduction of NO with CO (CO-SCR), on the other hand, is more attractive from a practical point of view, since CO is generally contained in vehicle exhausts and can be relatively more easily produced by engine operation compared with H_2.

The present paper provides a critical review which presents the state of art about the findings of the research carried out by the researchers on various iridium loaded catalysts as materials used in the selective catalytic reduction of NO by hydrocarbons, H_2 and CO as reducing agents in the rich-oxygen environment. The recent progresses in de-NO_x process have shown that for H_2-SCR, the Ir activity is low and can be promoted by the presence of SO_2. For CO-SCR reaction, Ir is a great catalytically active metal which is affected by the supports and additives.

SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES BY HYDROCARBONS (HC-SCR)
Early research on selective catalytic reduction of NO performed with Iridium based catalysts
In the last four decades, supported platinum group metals (PGM) have attracted much attention as active catalysts for the selective catalytic reduction of NO with hydrocarbons (HC-SCR) under lean-burn conditions. The majority of studies have been focused on Pt as the active metal component, whereas comparatively little attention has been paid to iridium although few reports concerning HC-SCR have been published on iridium based catalysts that have been already used for the exhaust after-treatment of diesel engines. It has been shown that Ir oxidizes when heated in air in the temperature range 600°C-1000°C and it is a very corrosion resistant component [43]. At higher temperatures, it loses in weight and this metal loss due to the oxidation was studied by several researchers [44−46]. In order to verify whether Ir could be a promising metal in any prospective commercial application for mobile diesel engines due to its very high price, it has been mentioned that the oxidation of a polycrystalline disc of Ir leads to the formation of volatile oxides and that the evaporation process is considerably increased when partial pressure of oxygen increases [44, 45]. Other investigations have been performed on the kinetics of the evaporation and oxidation of where it has been taken into consideration the evaporation of IrO_2, IrO_3 and Ir [47, 48].

The first experimental tests performed to study the selectivity of Ir/Al_2O_3 in the NO reduction with CO under lean conditions have been realized by Tauster and Murell in 1976 [41]. The potential of Ir was demonstrated by Lester et al. [49] and Taylor and Schlatter [42] during the synthetic exhaust gas mixtures instead of CO. It has been shown that several crucial factors as problems with Ir loss due to the formation of volatile iridium chlorides and oxychlorides and the unknown catalytic potential of Ir towards NO_x reduction into N_2 have limited the interest of Ir application in deNO_x catalysis application for the mobile diesel engines. Li et al [50] has found that the iridium in Ir/ZSM-5/cordierite might be stabilized and loss of active component iridium in the catalyst could be avoided to a great extent. It has been found that no iridium loss was observed after 30 hours' catalytic reaction (400°C, GHSV = 30,000 h^{-1}) and the iridium loading in catalyst was kept at the initial level (0.02% wt). The results of experimental tests of iridium loss for different Ir-based catalysts (Table 1) showed that iridium loss after long time aging on Ir/Al_2O_3 was 43.90 %, while iridium loss was only 2.31 % on Ir/ZSM-5 with the similar initial iridium loading.

Table 1: Testing of Iridium loss for Ir-based catalysts [50].

Sample	Iridium loading (wt %)[a]		Ir loss (%)
	After calcination[b]	After aging[c]	
Ir/ZSM-5	0,1601	0,1564	2,31
Ir/Al$_2$O$_3$	0,1417	0,0795	43,90

[a] Determined by ICP, average of multiple metering.
[b] 550°C, 6h, in the air.
[c] 500°C, 240h, in the air.

In several investigations [51-57], Ir was reported to possess less good catalytic properties than other platinum group metals (Pt and Rh) (figure 1 tired from [58]). Part of the reason for this contention is that iridium requires special pretreatment conditions to develop its catalytic efficiency [14−16, 59−61]. One of the earliest accounts of

the usefulness of the Iridium-Zeolite system in the development of a Pt/Ir/Rh on MFI-zeolite catalyst by Mazda researchers [56] which met the Japanese emission standards and Hori et al presented a new Ir-Based catalyst for gasoline lean burn engines [62]. Testing of various precious metal combinations gave the order Pt-Rh-Ir > Pt-Ir > Pt > Ir for NO_x reduction activity at 300°C (using propene as the reductant). The formation of N_2O over the Pt/Rh/Ir catalyst has been reported to be negligible and although some deactivation has been observed upon aging at 700°C. Durability of the related catalyst system has been found to be adequate for the application but the obtained data relating to the state of the metals in the catalyst have not been well provided, so it was not clear if Pt/Rh/Ir alloy particles are indeed the active sites (as opposed to mono- or bi-metallic particles) [58]. However, these reports have provided a useful starting point for the study of Ir-containing catalysts. Iridium based catalysts have been used by Mitsubishi for lean burn vehicles sold in Europe [63].
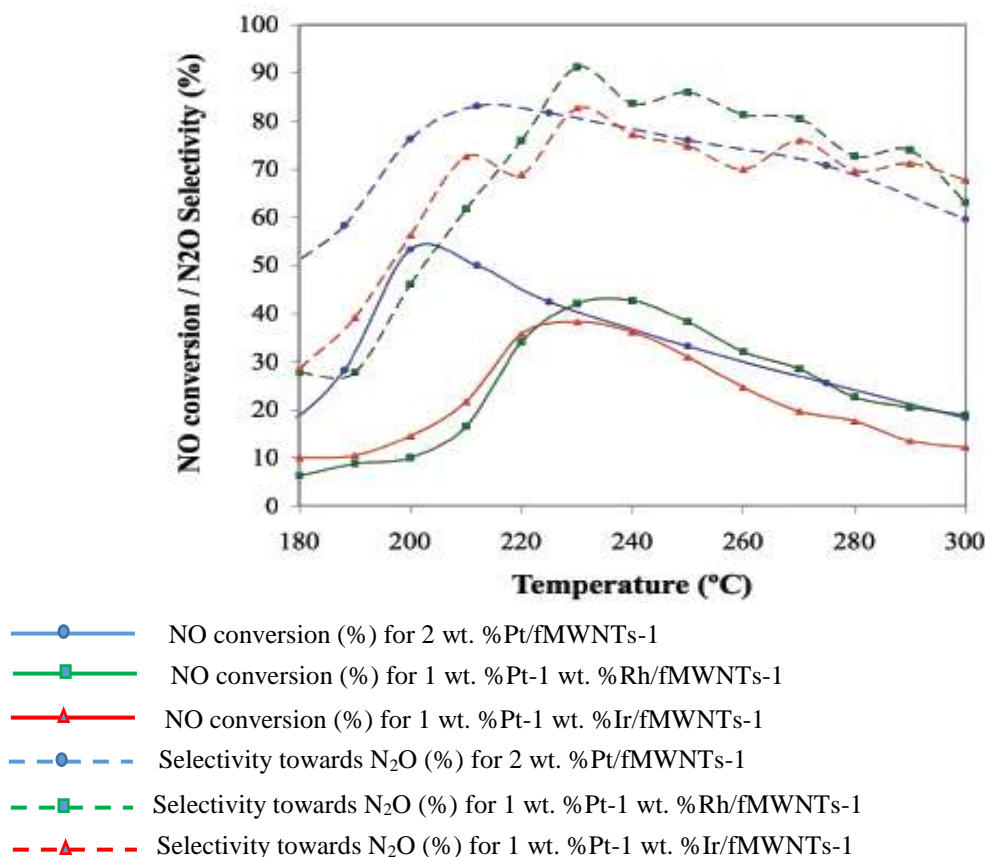

Figure 1. Combined plot comparing the performance of 2 wt.% Pt/fMWNTs-I, 1 wt. %Pt-1 wt. %Rh/fMWNTs-I and 1 wt. %Ir/fMWNTs-I in NO reduction with C3H6. Feed composition: 500 ppm NO, 500 ppm C3H6, 10% O2 and 10% H2O, balance nitrogen. Gas flow: ca. 50,000 Lgas. L cat−1. h−1 [58].

Catalytic activity under HC-SCR process

Supported [16, 20, 30] as well as unsupported iridium [64] catalysts were shown to exhibit high activity and N_2 yields in the reduction of NO in excess oxygen. The important findings emerging from these studies included the effect of iridium particle size, role of support, effect of promoters, effect of reducing agent, and sulfur and water tolerance. It should be pointed out that research on iridium catalysts can be distinguished in investigations performed using supported Ir catalysts [16, 21, 30, 56, 57] and unsupported Ir powders [18, 56, 57, 64]. Various studies showed that the catalytic performance of iridium catalysts strongly depends on the pretreatment (activation, conditioning) [15, 16, 65, 66]. Supported iridium catalysts neither after calcinations in air nor after prereduction, exhibit a-priori good activity for the selective reduction of NO_x [56]. Thus special attention has to be given to proper pretreatment or conditioning. Catalyst activation can be achieved by high temperature hydrothermal pretreatment [15, 65, 66] or by in situ activation (conditioning), i.e. exposure to feed gas at reaction temperature [15, 16]. In our previous studies [14–16], we have demonstrated that Ir/Al_2O_3 catalysts did activate under ($NO–C_3H_6–CO–O_2$) mixture at 600°C and NO was selectively converted into N_2 above 300°C. The activation process was accompanied by iridium sintering [15, 16]. However, our experiments proved also unambiguously that Ir sintering was not considered as the unique factor to the activation process for $deNO_x$ activity of Ir/Al_2O_3. It has been shown that Ir/Al_2O_3 treated under ($NO–C_3H_6–O_2$) did not lead to the reduction of NO to

N_2 in spite of dispersion similar to that obtained in other mixtures producing the activation of the catalyst. We have demonstrated that the composition of the gas mixture reacted with the catalyst at 600◦C prior to catalytic testing in SCR is a key factor for the SCR performance of Ir/Al_2O_3 catalysts [15, 16]. The presence of both CO and O_2 in the activation mixture appears essential to the process. For the pre-reduced catalyst, the large excess of O_2 in the ($NO–C_3H_6–CO–O_2$) mixture is likely to oxidize iridium particles. Then, the temperatures at which CO and propene are totally converted into CO_2 are considerably higher in the cooling down step than in the heating up step (Table 2).

Table 2: Catalytic activities with the standard ($NO-CO-C_3H_6-O_2$) mixture[a] [16].

Catalyst	Cycles		N_2 temperature window (°C)	Max NO-N_2 conversion (%)	Max NO-NO_2 conversion (%)	CO-CO_2 T_{100} (°C)	C_3H_6-CO_2 T_{100} (°C)
Reduced	1st cycle	Heating	No N_2	No N_2	60 (348)	186	288
		Cooling	392-514	24 (452)	40 (392)	364	364
	2nd cycle	Heating	402-552	27 (464)	20 (495)	376	382
		Cooling	370-552	29 (430)	20 (495)	376	382
Oxidised		Heating	420-482	6 (435)	36 (375)	326	347
		Cooling	400-495	24 (450)	30 (360)	360	380
Stabilised[b]		Heating and cooling	408-600[c]	36 (504)	35 (408)	394	400

[a]Activity–temperature window (temperature range in which N_2 is detected). Maximum NO conversion into N_2 or NO_2. T_{100}, temperatures at which CO and C_3H_6 conversions reach 100%. The values in parenthesis are in ◦C.
[b]Stabilised calcined or in situ reduced and then treated under the ($NO-CO-C_3H_6-O_2$) mixture with a plateau at 600°C for 8h.
[c]0% at 408◦C and 18% at 600°C.

Some other specific features of the catalytic behavior of Ir/Al_2O_3 catalysts in the SCR of NO_x by propene have been pointed out. The NO–N_2 conversion over Ir/Al_2O_3 starts at a temperature close to that at which the NO_2 formation is maximum and that N_2 forms under conditions where reductants are fully converted into CO_2 (figure 2). This catalytic behavior is surprising and contrasts with that of Pt-based catalysts for which $deNO_x$ activity proceeds under conditions where reductants are not fully converted [9]. For Pt catalysts, the conversion of NO into N_2 and N_2O reaches its maximum at the temperature when C_3H_6 conversion reaches 100%. At higher temperatures the NO–N_2 activity of Pt catalysts decreases, which is attributed to the consumption of reductants by O_2. We checked that, although being totally consumed, propene is necessary to the $deNO_x$ activity of Ir catalysts since these catalysts are inactive for NO decomposition in the presence or in the absence of oxygen.
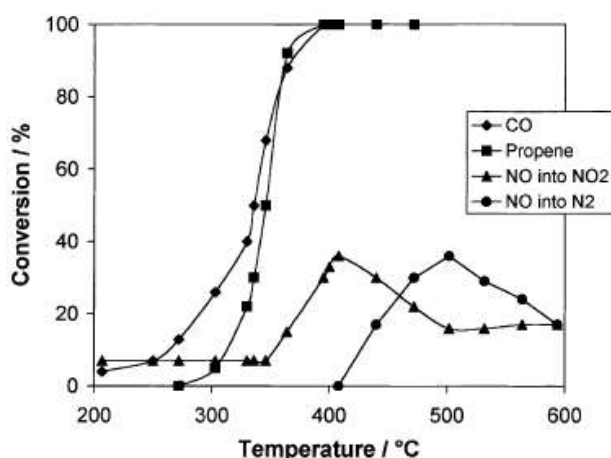

Figure 2. Conversions of NO into N_2 and NO_2 and conversions of CO and C_3H_6 as a function of temperature under ($NO–CO–C_3H_6–O_2$) mixture over Ir/Al_2O_3 treated at 600•C for 8 h under the same gas mixture. Feed composition: 1000 vpm NO, 2000 vpm C_3H_6, 500 vpm CO, 10 vol.% O_2 and balance He; total flow rate: 10 L.h^{-1} [16].

Both activation processes cited in the literature lead to growth of Ir crystallites and the establishment of a certain Ir^0/IrO_2 ratio. The effect of on-stream conditioning of Ir-H-ZSM-5 catalysts [56] leads to an increase of the

crystallite size of iridium. Under HC-SCR reaction conditions, iridium is generally present as a mixture of Ir^0 and IrO_2. The presence of metallic Ir is essential for high $deNO_x$ activity [57]. The ratio of Ir^0/IrO_2 depends mainly on the exhaust gas composition and the iridium particle size [18, 57]. The contribution of metallic Ir generally increases with larger crystallite size and lower air to fuel ratio. Large iridium crystallites can only be fully oxidized in air at very high temperatures, whereas small crystallites are easily oxidized and favor NO oxidation to NO_2 as well as oxidation of reductants. This has been consistently observed for unsupported [18] as well as supported iridium catalysts [30, 57]. Wögerbauer et coll [64], have studied propene, propane, CO, and H_2 as reducing agent on the selective reduction of NOx over Ir black in the presence and absence of oxygen and with either NO or NO_2 as NO_x component. It has been found that all reducing compounds applied were able to reduce IrO_2 in a similar way and that propane is no suitable reductant for the reduction of NO under lean conditions over Ir black. In comparison, propene gives high yields of N_2 even under large excess of oxygen. Under oxygen deficient experiments propene produced a considerable amount of HCN and the main product with H_2 was NH_3. Propene and propane produced CO as partial oxidation product. The concentration of propene has a strong effect on the production of NO_2, N_2O and, hence, on the yield of N_2. With increasing propene concentration the production of N_2O and N_2 increases whereas NO_2 formation is suppressed. The authors have proved that propene produced the highest amounts of carbonaceous cracking deposits among the applied reducing agents (propene, propane, butene, 2-methyl-propene) and that these deposits are highly active in the reduction of NO suggesting the possibility of an adsorbate-assisted reduction of NO [64].

The SCR process of NO_x has been widely studied on noble metals loaded honeycomb monoliths (Pt, Pd, Rh and Ir) [38, 50, 65−67]. Wang et coll [38] has investigated the reduction of NO by C_3H_8 under lean-burn conditions over binderless Ir/ZSM-5 monoliths, which were prepared by a vapor phase transport (VPT) technique. The catalytic activity has been found to be dependent on the Ir content and on the ZSM-5 loading of the monolith. NO conversion increased when Ir content is decreased or the ZSM-5 loading of the monolith is increased. The authors have reported that the NO conversion reached maximum value of 73% at 533 K and space velocity of 20000 $h^{−1}$ when the ZSM-5 loading on the cordierite monolith was raised up to ca. 11% and the metal Ir content was about 5 g/L [38]. It has been shown that the presence of 10% water vapor in the feed gas and the variation of the space velocity of the reaction gas have little effect on the NO conversion. The comparison of the Ir/ZSM-5 and Cu/ZSM-5 catalysts, as well as the variation of the feed gas compositions has revealed that Ir/ZSM-5 is very active for the reduction of NO by CO under lean conditions, although it is a poor catalyst for the C_3H_8-SCR process. Recently [13], we have performed the C_3H_6-SCR experiments on Ir/TiO_2 supported on a cordierite monolith and doped with K, Fe and trace amounts of Zr. The commercial automotive converter exhibited high $deNO_x$ activity and then, NO reduction into N_2 reached its maximum of 80% at very good selectivity during a thermal treatment cycle (heating from 25 to 620°C and cooling from 620 to 25°C with a plateau at 620°C for 20 min (figure 3). The NO-N_2 and the NO-NO_2 conversions start at a temperature close to that at which the oxidation of CO and C_3H_6 by oxygen has been already complete (figure 2). It can be pointed out that N_2 forms under conditions where reductants are fully converted into CO_2.
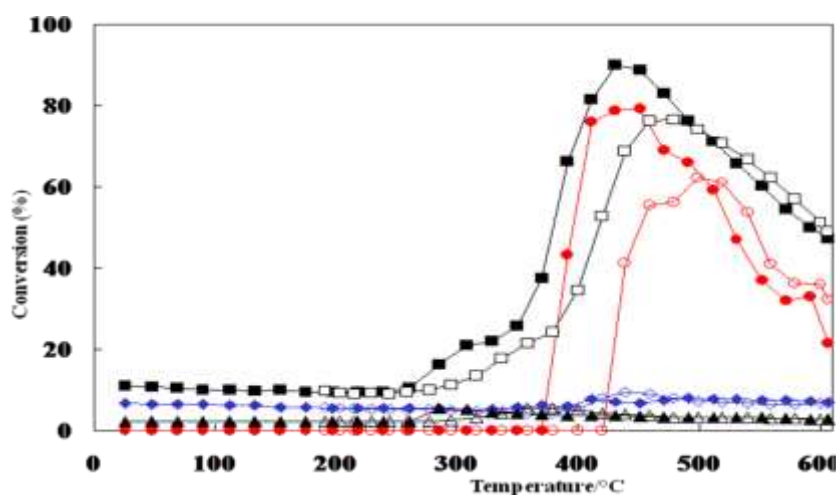

Figure 3. Conversions of NO and of NO into NO_2, N_2 and N_2O (%) vs temperature (K) with NO-CO-C_3H_6-O_2 during a first temperature cycle with plateau at 873 K for 20 min. (■, □) Conversion of NO, (♦, ◊) NO-NO_2, (●, ○) NO-N_2 and (▲, ∆) NO-N_2O. The full symbols indicate the heating-up steps and the empty symbols the cooling-down steps [13].
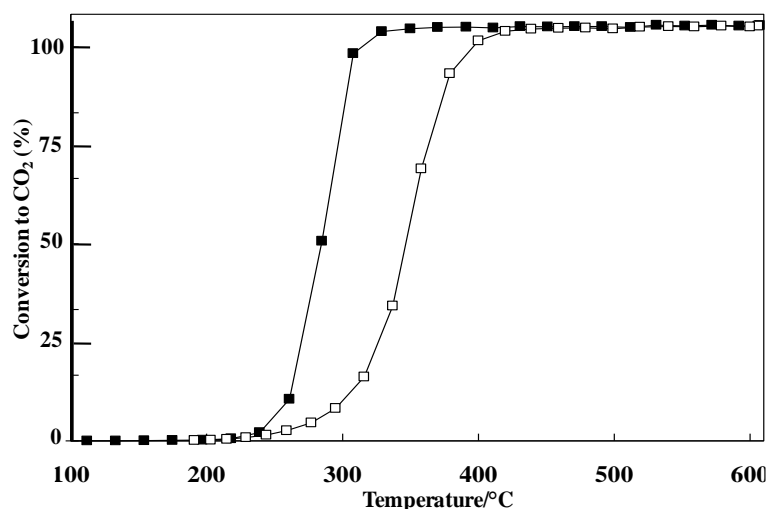
Figure 4. Conversions of CO and C₃H₆ into CO₂ vs temperature (K) with (NO-CO-C₃H₆-O₂) mixture during a first temperature cycle with plateau at 873 K for 20 min. (■: the heating-up steps and □: the cooling-down steps) [13].

For the aged catalyst in $10\% H_2O/N_2$ mixture at 720°C for 20 hours, high activity has been shown only during the heating-up step under the standard mixture ($NO-CO-C_3H_6-O_2$) and the maximum $NO-N_2$ conversion reached 60% at 380°C with N_2 selectivity of 68 % in the temperature window range 320 – 620°C. However, during cooling down-up step, no activity of reduction of NO into N_2 has been observed on the aged catalyst (results not shown). This deactivation process seemed to depend on the time on stream since a second heating-cooling cycling of temperature on the wet aged sample did not lead to reduction of NO into N_2 by hydrocarbons in the widening of the temperature range at which the catalyst converted NO into N_2. Simultaneously, the activity for NO oxidation into NO_2 is almost the same on the wet aged catalyst after one or two heating-cooling cycles (see Table 2, ref. [13]). Whenever the activity for total NO conversion is very decreased after the second cycling of temperature on the sample (89 % at 380°C and 40 % at 470°C during heating-up temperature respectively after 1 and 2 cycling temperature). The activity for N_2O formation remained low and the $NO-N_2O$ conversion has been less than 10% compared to the 33–40% total conversion of NO at maximum activity. These results proved unambiguously that the commercial automotive catalyst deactivated completely under standard reaction mixture and did not exhibit any $deNO_x$ activity between 320 and 620°C without any good selectivity toward nitrogen. It can be noted that the $NO-NO_2$ maximum conversion was detected at temperatures (see table 2, ref. [13]). above T_{100} temperatures at which CO and C_3H_6 conversions into CO_2 reached 100 %. In this work, it seems that the surface area do not play a crucial role since the catalyst could perform well despite a poor initial surface area ($\sim$ 5 m^2/g) indicating that the stability performance may be affected by chemical deactivation of the SCR catalysts rather than a sintering of its active surface particles.

Mechanisms for HC-SCR reaction on iridium-based catalysts and comparison with noble and transition metals based catalysts

On Pt-based catalysts, two mechanisms of dissociation and reduction of NO have been proposed [9, 68]. Burch et al. showed that the reduction of NO begins with a dissociative adsorption leading to the formation of ″N″ and ″O″ species [69, 70]. The molecules of propene or fragments of hydrocarbons from its adsorption react with the O species to give CO_x and H_2O, while the N species can recombine into N_2 or react with NO molecules to give N_2O. It has been shown that a more complex mechanism of reduction on the support and metal has been mentioned involving an oxidation step of NO to NO_2 which migrate into the support to react with the C_3H_7 fragments from the C_3H_6 adsorption [71]. This leads to the formation of N_2, N_2O, CO_2 and H_2O. It can be anticipated that, in the absence of sites other than those of metal, the mechanism of dissociation is only valid for noble metals based catalysts. Similar reactions have been proposed for the SCR process of NO by hydrocarbons on catalysts Pt/SiO_2 [72]. It has been reported that with the metal not fully reduced, an "associative" mechanism can occur. NO can adsorb as dimer, dinitrosyl or hyponitrite on Pt^{n+} ionic species. These adsorbed species decompose further to N_2O or to N- and O-atoms [73]. Within the second type of mechanism, NO_x reduction starts with a reaction between NO or NO_2 and the hydrocarbon to give a series of organic intermediates before ending to N_2 or N_2O. Four main classes of organic intermediates have been detected [73]:

• Isocynates (R−NCO)
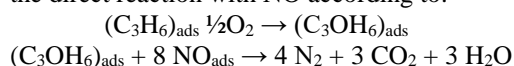• Nitriles (R−CN) or isonitriles (R−NC)

• Nitro (R−NO$_2$), nitrito (R−ONO) or nitrato (R−ONO$_2$) compounds.
• Oximes (R−CH=NOH), amines (R−NH$_2$) or ammonia.

Detailed investigations centered on the identification and reactivity of isocyanate species were carried out over Cu/Al$_2$O$_3$ [74, 75], Rh/Al$_2$O$_3$ [55], Ag/Al$_2$O$_3$ [76], PtO$_x$ [69], Pt/Al$_2$O$_3$ and Pt–Ba–Al$_2$O$_3$ [77]. The transformation of isocyanate intermediates into N$_2$ + N$_2$O was ascertained by injecting isocyanate compounds as reducers into the NO + O$_2$ mixture [78, 79]. The reactions probably leading to isocyanates species as intermediates during HC-SCR are the reduction of nitro compounds, the oxidation of isonitriles, and the Hofmann rearrangement of alkylamides [80]. The chemical species that can be involved in the reduction of R−NO$_2$ to R−N=C=O are CO, CH$_x$ species issued from the decomposition of propylene. Small amounts of H$_2$O are sufficient for the hydrolysis of isocyanates into amines. Nitrile or isonitriles have been detected over Cu/MFI [81], Rh/Al$_2$O$_3$ [82], and Pt/SiO$_2$ [83], sometimes together with isocyanates [70]. In the presence of H$_2$O, nitriles are hydrolyzed into amides. Nitro, nitrito, or nitrato surface species are formed on Pt/SiO$_2$ [84], Pt/Al$_2$O$_3$ [85], Cu/ZSM5 [86], Ce/ZSM5 [87], and Ag catalysts [88]. Nitro, nitrito, and nitrato species can be formed by reaction of NO$_2$ (or adsorbed nitrates) on an alkane. With olefins, nitrosoalkenes can be formed and can isomerize into oximes or oxidize into nitro, nitrito, and nitrato species. Nitro. The reactivity of nitro compounds as NO reducers over Pd/Al$_2$O$_3$ was investigated by several researchers [89] who elucidated the role of the R−NO$_x$ nitrogen organic species as intermediates. According to these authors, R−NO$_x$ intermediates may be transformed into oxygenates, especially on CeZrO$_x$ catalysts. Adsorbed amines or −NH species were sometimes detected together with nitriles or isocyanates [90]. Isocyanates and other organic species are suspected to be the precursors of carbonaceous deposits, which could be the reducer species, especially at high temperatures (typically above 300°C) [91].

Nitrate and acetate species were detected by Shimizu et al. [92, 93] on Al$_2$O$_3$ under mixture [C$_3$H$_6$-O$_2$] during the SCR of NO by C$_3$H$_6$. For these authors, the activation process for NO reduction by propene has as a first step the formation of nitrate species (oxidation of NO to NO$_2$ adsorbed on basic sites) and then reaction with C$_3$H$_6$ to form acetate species which reduce NO into N$_2$. The same species (nitrates, acetates and formates) have been observed on Ir/Al$_2$O$_3$ catalysts. These species are stable up to 673 K, temperature at which C$_3$H$_6$ begins to reduce NO into N$_2$ on the solids [17]. The nitrate species are formed during the reaction by adsorption of NO$_2$ on the basic sites of alumina surface while the acetates and formates are formed by the incomplete oxidation of propene. On a Ag/Al$_2$O$_3$ catalyst [94, 95], the mechanism for this activation is not fully established, but N$_2$ is assumed to form via a series of reactions involving many intermediates adsorbed on Ag and on the alumina. It is assumed that the inorganic nitrates at the surface react with nitro-organic compounds to produce N$_2$ [94]. The reaction intermediates are similar to those of the selective reduction by ammonia or urea. The proposed mechanisms have been classified into two types. The first has as a first step the formation of NO$_2$ and reaction of NO$_2$ with C$_3$H$_6$:

$$NO + \tfrac{1}{2}\,O_2 \rightarrow NO_2$$
$$9\,NO_2 + 2\,C_3H_6 \rightarrow N_2 + 6\,CO_2 + 6\,H_2O$$
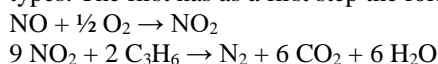
The second involves an intermediary form by the partial oxidation of the hydrocarbon adsorbed at the surface and the direct reaction with NO according to:

$$(C_3H_6)_{ads}\,\tfrac{1}{2}O_2 \rightarrow (C_3OH_6)_{ads}$$
$$(C_3OH_6)_{ads} + 8\,NO_{ads} \rightarrow 4\,N_2 + 3\,CO_2 + 3\,H_2O$$

Selective catalytic reduction with carbon monoxide (CO-SCR)

CO is one of the most practical reductants for the removal of NO because it is present in exhaust emissions from vehicles. However, CO has not been considered as an effective reductant for the selective catalytic reduction of NO in the oxygen-rich conditions. Supported noble metal solids catalyze the CO/O$_2$ reaction. In 1976, Tauster and Murrell [41] have published the first paper about NO reduction with CO on iridium based catalysts where they have measured the catalytic activity of 0.1% Ir/Al$_2$O$_3$ using a reaction gas mixture composed of 0.2% NO, 1.0% CO and 0.75% O$_2$ diluted in He at a flow rate of 100 L. h^{-1}. It has been shown that the maximum NO-N$_2$ conversion reached 90% at 400 °C, indicating that NO reacts preferentially with CO rather than with O$_2$. The authors have explained the high catalytic performance of Ir/Al$_2$O$_3$ catalyst by using the fact that the NO molecules were preferentially adsorbed onto surface free sites compared with O$_2$ molecules. The 0.001% Ir/Al$_2$O$_3$ solid has been found also highly active for the CO-SCR with shifting of the temperature window to a region about 100 °C higher.

Various materials have been investigated in order to develop effective catalysts for CO-SCR [27, 28, 37]. The activities of various catalysts reported during CO-SCR reaction are summarized in Table 3.

Table 3: Activities of various catalysts for CO-SCR [33].

Catalysts	NO (ppm)	CO (%)	O_2 (%)	SO_2 (ppm)	H_2O (%)	$NO-N_2$ conversion (%)	T_{max} (°C)	Ref.
0,1%Ir/Al$_2$O$_3$	2,000	1,0	0,75	0	0	90	400	[41]
0,02%Ir/silicate	1,000	0,75	1,0	0	0	95	370	[27]
0,02%Ir/silicate	1,000	0,75	1,0	150	0	55	400	[27]
0,5%Ir/SiO$_2$	1,000	0,3	0,65	20	10	49	400	[97, 98]
5%Ir/SiO$_2$	1,000	0,6	5,0	20	6	62	350	[29]
0,1%Ir/ZSM5[a]	1,000	1,5	2,0	0	0	92	310	[28]
5%Ir/WO$_3$	1,000	0,3	5,0	2	1	25	300	[37]
5%Ir/Nb$_2$O$_5$	1,000	0,3	5,0	2	1	14	320	[37]
5%Ir/Ta$_2$O$_5$	1,000	0,3	5,0	2	1	25	325	[37]

[a] The activity was evaluated in the presence of 0,1% C_3H_8, 0,5% H_2 and 12% CO.

Ogura et al [27] have reported that NO can be reduced to N_2 with CO over supported iridium catalysts such as 0,02% Ir/silicalite under the reaction conditions of 1000 ppm NO, 7500 ppm CO and 1% O_2. The catalytic activity has not been seemed to be influenced by coexisting SO_2. Ir/SiO_2 and Ir/Al_2O_3 catalysts have exhibited also high activities for CO-SCR reaction which indicates that Ir is a promising component for CO-SCR process. Ir/SiO_2, Ir/Al_2O_3 and Ir/silicalite have been employed by Ogura et al in order to study the effect of SO_2 on the activity of both catalysts during the CO-SCR reaction [27]. The authors have found that Ir/SiO_2 has been the highest active catalyst for $NO-N_2$ conversion at 400°C than Ir/silicalite in the absence of SO_2. When 150 ppm of SO_2 were added to gas mixture feed, NO conversion of Ir/SiO_2 has dropped even its activity has been recovered by elimination of SO_2 from reaction gas. On the other hand, it can be remarked that the catalytic activity of Ir/silicalite has not been interestingly influenced by coexisting 150 ppm SO_2. It has been revealed that the activity of Ir/SiO_2 for CO-SCR strongly depends on pretreatment conditions (figure 5). The catalyst pretreated with O_2 has showed little activity for NO reduction, whereas high activity has been achieved for Ir/SiO_2 reduced with H_2, suggesting that Ir metal rather than Ir oxide is the catalytically active species [29]. Therefore, it can be concluded that the low catalytic activity of highly dispersed Ir on SiO_2 is due to catalyst deactivation by oxidation of active Ir metal to IrO_2.
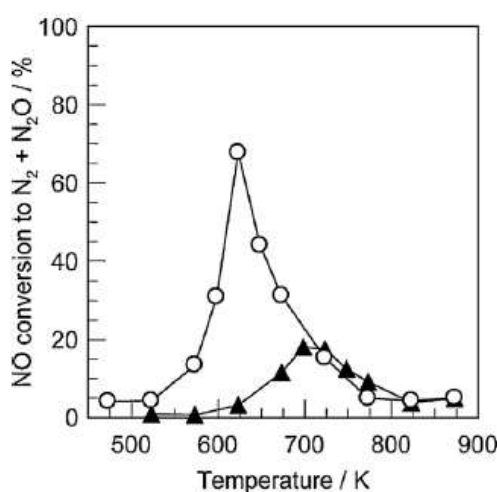

Figure 5. Effect of pretreatment conditions on the activity of 5% Ir/SiO$_2$ for NO reduction with CO in the presence of O$_2$ and SO$_2$ [29]. NO = 500 ppm, CO = 6000 ppm, O$_2$ = 5%, SO$_2$ = 20 ppm, H$_2$O = 6%, W/F = 0.0267 g s cm^{-3}.
(▲) treated in flowing 5% O$_2$/He at 600 °C, (○) treated in flowing 10% H$_2$–6% H$_2$O/He at 600 °C.

Yoshinari et al. [97, 98] and Haneda et al. [29, 40] have examined the effects, in the absence and presence of SO_2, of metal oxide support on the activity of Ir catalysts for CO-SCR. They have found that maximum conversion of 49% for $NO-N_2$ and of 9% for $NO-N_2O$ have been detected at 400°C on Ir/SiO_2 when SO_2 is introduced in the reaction gas, although the maximum NO conversion on Ir/Al_2O_3, Ir/TiO_2 and Ir/ZSM-5 catalysts has been low and reached a value of 15%. The coexistence of SO_2 and O_2 was so essential for NO reduction on Ir/SiO_2 catalyst. Wang et al [28] have investigated Pt, Pd, Rh, and Ir catalysts and reported that an Ir/ZSM-5 (Si/Al = 50) catalyst exhibited high activity for NO reduction with CO in the presence of excess O_2. Shimokawabe et al [37, 96] have measured the catalytic activity of Ir-based catalysts supported on various metal oxides. They have indicated that the use of metal oxides with high oxidation number such as WO_3, Nb_2O_5 and Ta_2O_5 is effective for CO-SCR reaction. Thus, metal oxide would play an important role in the catalytic activity of Ir.

Various supported noble metal catalysts as Pt/Al_2O_3 [99], Pt/SiO_2 [100], Pt/TiO_2 [101], $Pt/WO_3/CeZrO$ [102], $Pd/Ce_{0,6}Zr_{0,4}O_2$ [103] and Rh/Na-Beta zeolite [104], have been reported to show activity for CO-SCR reaction. However, comparison of activities of these various supported metallic catalysts under the identical conditions has revealed that these solids have not been very active compared with that of Ir catalysts. The CO-SCR reaction has been also reported to take place over supported metal oxide catalysts such as Cu/Al_2O_3 [105] and over TiO_2-supported transition metal oxide catalysts (MO_x/TiO_2; M = Cr, Mn, Fe, Ni, Cu) [106]. Comparison of the activity of various supported catalysts under the same conditions, however, revealed that the activity of Cu/Al_2O_3 is not very high, and that supported Ir catalyst is the most active [96]. Taking into account the data cited in the literature, Ir has been found the most probable effective catalytically active metal for CO-SCR in O_2-rich conditions.

Selective catalytic reduction with hydrogen (H_2-SCR)
It has been long believed that H_2 cannot reduce selectively NO_x in oxygen-rich environment because it is used as a reductant in the stoichiometric three-way catalyst system as well as hydrocarbons. However, it has been well proved that H_2 can also act as an effective reductant for SCR of NO_x. Selective Catalytic Reduction of NO_x with H_2 (H_2-SCR) appears to be a promising alternative technology to NH_3-SCR and HC-SCR, with high NO conversion and selectivity towards N_2 since it proceeds at relatively low temperatures. In 1971, Jones et al [107] have pointed out that H_2 can react preferentially with NO over O_2 in the reaction system NO-H_2-O_2 on commercially supported Pt catalysts suggesting the possibility of H_2-SCR although the reaction has not been performed in excess oxygen conditions. Fu and Chuang [108] have published probably the first report to confirm the H_2-SCR reaction in net-oxidizing conditions. They have reported that stable NO_x conversions of 60–80% have been obtained at temperatures above 55°C under reaction mixture composition of 1000 ppm NO_x, 1% H_2 and 3,2% O_2 in N_2 by using noble metal catalysts supported on styrene-di-vinylbenzene (SDB). Supported noble metals as well as various single or mixed metal oxides have been extensively studied towards H_2-SCR of NO_x. [33, 97, 98, 109, 110]. Burch and Coleman [110], have examined the catalytic behavior of Pt, Pd, Rh and Ir supported on Al_2O_3 and SiO_2 towards the reduction of NO by H_2 under strongly oxidizing conditions (500 ppm NO, 2000 ppm H_2, 6% O_2). The authors have reported that Pd, Rh and Ir catalysts (1 wt% loading) have been all found to be inactive towards NO reduction, since they simply oxidize NO to NO_2. On the contrary, both Pt/Al_2O_3 and Pt/SiO_2 have showed significant activity in the 50–250°C range: 50% conversion of NO at 140°C over Pt/Al_2O_3 and 75% conversion at 90°C over 1% Pt/SiO_2. It has been noted that N_2O was also formed in large amounts in addition to N_2 by H_2-SCR reaction over Pt catalysts. In 2001, Yoshinari et al [97], have reported that Ir/SiO_2 exhibited a remarkable activity for H_2-SCR. When O_2 was suppressed from gas feed, the Ir/SiO_2 has showed high activity for NO reduction with H_2 above 300°C. However, NO reduction decreased with increasing O_2 concentration and this evolution of the activity was completely changed when SO_2 has been newly introduced in the reaction gas. An amount of 20 ppm has been found to be sufficient to make the Ir/SiO_2 inactive and couldnot catalyze NO-H_2 reaction at 600°C since NO conversion has been near 10% indicating the poisoning effect of SO_2. NO conversion to N_2 and N_2O has been found around 73% at 300°C with O_2 amount of 0,63% and it decreased at higher O_2 concentrations. This experimental behavior clearly indicates that H_2-SCR occured on Ir/SiO_2 when SO_2 coexists. Pd/SiO_2 has been found also active for H_2-SCR but the presence of SO_2 considerably inhibited NO reduction on Pt/SiO_2 and Pd/SiO_2 [98]. As well as Ir/SiO_2, Rh/SiO_2 catalyst reduced NO in the presence of SO_2 but not in its absence. The catalytic activity of Ir/SiO_2 has been also studied with gas feed containing various components (NO, NO_2, O_2, H_2, SO_2). NO_2 was not reduced in these conditions as compared to NO indicating that NO_2 is probably not a reaction intermediate for H_2-SCR of NO (Table 4).

Table 4: Several unit reactions over 0,5% Ir/SiO_2 [33].

Reaction	NO_x conversion to N_2 (N_2O) (%)		
	300°C	400°C	500°C
NO-H_2	44 (0)	89 (0)	98 (0)
NO-H_2-SO_2	0 (0)	1 (1)	2 (3)
NO-H_2-O_2	4 (0)	11 (2)	11 (1)
NO-H_2-O_2-SO_2	45 (28)	35 (8)	17 (1)
NO_2-H_2-O_2	1 (0)	2 (0)	5 (0)
NO_2-H_2-O_2-SO_2	3 (0)	9 (0)	11 (1)

NO: 1000 ppm, NO_2: 1000 ppm, H_2: 3000 ppm, O_2: 0,65%, H_2O: 10%, W/F = 0,0267 g.s.cm^{-3}.

Li et al [111] have studied TiO_2-supported monometallic and bimetallic catalysts for H_2-SCR reaction. The bimetallic Pd–Ir/TiO_2 catalyst exhibits much higher H_2-SCR activity than monometallic Pd/TiO_2 and Ir/TiO_2. It has been shown that TiO_2 supported monometallic catalysts were active in H_2-SCR reaction and the H_2-SCR activity was observed as $Ir/TiO_2 > Pd/TiO_2 > Rh/TiO_2$. Pd species were found highly active for H_2 activation, while Rh and Ir species were highly active for NO dissociative activation [112, 113]. To improve the H_2-SCR catalytic performance, the authors have combined the functions of Pd with Rh or Ir and strong synergistic effects

have been observed between Pd and Ir, then, excellent deNO$_x$ activity has been obtained on bimetallic Pd–Ir/TiO$_2$. NO$_x$ conversion of > 80%, with N$_2$ selectivity > 80%, was observed in the temperature range of 413–473 K [111]. The catalytic performances of Pd–Ir/ TiO$_2$ for H$_2$-SCR reaction are comparable with most active Pt catalysts reported in literature under similar conditions [114]. In contrast, the synergistic effects between Pd and Rh are not so obvious, and bimetallic Pd–Rh/TiO$_2$ does not exhibit improved deNO$_x$ activity compared with monometallic Pd/TiO$_2$ and Rh/TiO$_2$. More recently, Goula et al [109] have investigated the lean NO$_x$ reduction by propene, H$_2$ and by propene + H$_2$ over 0,5 wt% Pt/γ-Al$_2$O$_3$, 0,5 wt% Pd/γ-Al$_2$O$_3$ and 0,5 wt% Ir/γ-Al$_2$O$_3$ catalysts. They have carried out various experiments to evaluate the catalyst performance activity with the following reaction mixtures: NO + C$_3$H$_6$ + O$_2$ (R#1), NO + C$_3$H$_6$ + O$_2$ + H$_2$ (R#2) and NO + H$_2$ + O$_2$ (R#3) in the wide temperature range (50–400 °C). It has been reported that the C$_3$H$_6$-SCR reaction catalyzed by all metals is significantly promoted by H$_2$. The comparison of the three reactions: R#1, R#2 and R#3 over 0,5% Ir/γ-Al$_2$O$_3$ catalyst (Figure 6) has showed interestingly very different trends than those recorded on 0,5% Pt/γ-Al$_2$O$_3$ catalyst. The propene oxidation efficiency of 0,5% Ir/γ-Al$_2$O$_3$ is not affected by H$_2$, however, H$_2$ has been found to enhance notably the NO reduction efficiency: the maximum NO conversion of 33% during the reaction R#1 is increased to ~ 70% during the reaction R#2, accompanied by a shift to lower temperatures (T = 280 °C for R#2 instead of 340 °C for R#1). The H$_2$- assistance on C$_3$H$_6$-SCR of NO$_x$ is more substantial on Pt, then on Ir and less on Pd. The influence of H$_2$ on the oxidation state of the noble metals is considered to be a key factor for this promotion [109].
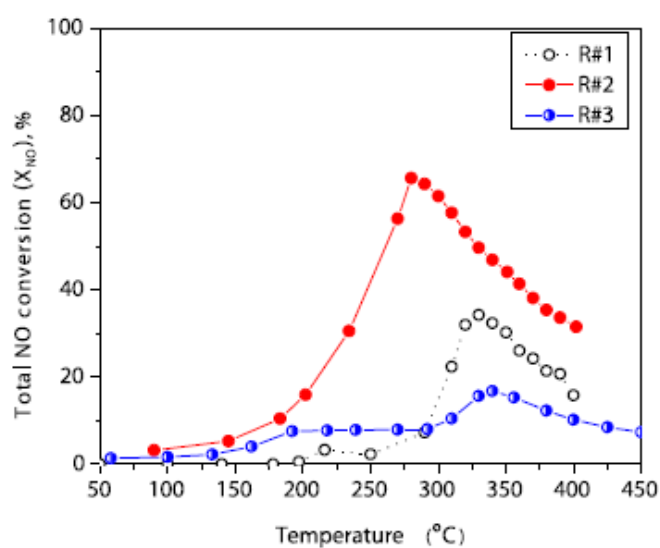

Figure 6. The effect of temperature on NO conversion performance of 0.5Ir/Al$_2$O$_3$ catalyst under the following conditions: R#1: 1000 ppmv NO + 1000 ppmv C$_3$H$_6$ + 2% O$_2$; R#2: 1000 ppmv NO + 1000 ppmv C$_3$H$_6$ + 2% O$_2$ + 0.5% H$_2$; R#3: 1000 ppmv NO + 2% O$_2$ + 0.5% H$_2$. Catalyst loading in the reactor w = 335 mg. Ft = 500 cm^3/min (GHSV = 40,000 h^{-1}) [109].

CONCLUSION

The selective catalytic reduction of NOx by hydrocarbons (HC-SCR) on supported and unsupported iridium catalysts has been shown to exhibit high activity and N$_2$ yields in excess oxygen. The HC-SCR process was found to be influenced by several factors as iridium particle size, kinds of support, promoters and reducing agent, and also by sulfur and water tolerance. Various studies showed that the catalytic performance of iridium catalysts strongly depends on the pretreatment (activation, conditioning). Supported iridium catalysts in the calcined and prereduced state exhibit good activity for the selective reduction of NO$_x$ and the catalyst activation can be achieved by high temperature hydrothermal pretreatment or by in situ activation (conditioning). The presence of both CO and O$_2$ in the activation mixture appears essential to the HC-SCR process. The NO–N$_2$ conversion over Ir/Al$_2$O$_3$ catalysts starts at a temperature close to that at which the NO$_2$ formation is maximum and that N$_2$ forms under conditions where reductants are fully converted into CO$_2$. The mechanism for HC-SCR reaction on iridium-based catalysts was not clear. Compared to Pt-based catalysts for which two mechanisms of dissociation and reduction of NO by propene have been proposed, nitrate and acetate species were detected on Al$_2$O$_3$ under mixture [C$_3$H$_6$-O$_2$] during the SCR of NO by C$_3$H$_6$ on Ir-based catalysts. The reduction process has as a first step the formation of nitrate species (oxidation of NO to NO$_2$ adsorbed on basic sites) and then reaction with C$_3$H$_6$ to form acetate species which reduce NO into N$_2$.

Supported platinum-group metals are active for the selective reduction of NO with hydrogen (H$_2$-SCR) and CO (CO-SCR). For CO-SCR, only Ir shows high activity. Coexisting SO$_2$ is essential for the SCR process of NO on

Ir/SiO$_2$. The role of SO$_2$ for both H$_2$-SCR and CO-SCR is to reduce Ir species even in O$_2$-rich atmospheres and to keep Ir in the form of catalytically active Ir metal state. The addition of WO$_3$ and Nb$_2$O$_5$ promotes the catalytic activity of Ir/SiO$_2$. Ir-WO$_x$ species is the active site on the WO$_3$-promoted Ir/SiO$_2$, which enables NO reduction even in the absence of SO$_2$. In the case of H$_2$-SCR, Pt and Pd show high activity for NO reduction to N$_2$ and N$_2$O. The activities of the two metals are much affected by support materials. While coexisting SO$_2$ inhibits H$_2$-SCR reaction on Pt and Pd, it promotes NO reduction on Ir and Rh catalyst especially when metals are supported on SiO$_2$. Other additives improve the activity of Ir/SiO$_2$ and Rh/SiO$_2$, respectively, by maintaining the active metal species on the catalysts. The H$_2$- assistance on C$_3$H$_6$-SCR of NO$_x$ is more substantial on Pt, then on Ir and less on Pd. The influence of H$_2$ on the oxidation state of the noble metals is considered to be a key factor for this promotion.

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