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Catalysts for NO_x selective catalytic reduction by hydrocarbons (HC-SCR)

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ABSTRACT

This short review concerns the efficient catalysts for HC-SCR discovered more than 20 years ago. In 1990, Iwamoto proposed Cu ion-exchanged ZSM-5, and it was the first powerful catalyst for HC-SCR. This paper presents first metal ion-exchanged zeolites and the influence of various parameters on the catalysts activities (acidity, O_2 content, etc.). In the second part, this paper reviews supported metal catalysts, base metal oxides, hybrid catalysts and the possible reducing agents to remove NO_x. It can be inferred that the most active catalysts for HC-SCR should have acidic sites, an active phase like copper or cobalt, or for a wider activity, elements such as silver or a mixture of metals. For low deactivation, they should contain noble metals such as platinum, rhodium or tin.

1. Introduction

Large quantities of pollutants are released to the environment from the combustion of biomass and fossil fuels. Among these contaminants are nitrogen oxides (NO_x) which are the source of severe environmental problems. Research in the field of NO_x abatement has grown significantly in the last two decades [1]. The general approach has focused on developing new catalysts with complex materials in order to meet the stringent environmental regulations. Nowadays, two main methods for the removal of NO_x from emission gases are employed: the selective catalytic reduction of NO_x with NH_3 (ammonia-SCR) which is applied for stationary sources such as power plants, and the three-way catalysts (TWC) used for mobile sources, such as automobiles [2]. In spite of the intense research in this former, the outcomes present partial solutions and include serious drawbacks for ammonia-SCR. Alternatively, selective catalytic reduction of NO_x using hydrocarbons as a reductant (HC-SCR) is currently attracting a great deal of interest because of the main advantage of the use of a gas mixture very similar to that found in exhausts.

The aim of this review is to gain knowledge on the selective catalytic reduction of NO_x with hydrocarbons in order to contribute to the development of suitable catalysts for NO_x abatement. This review discusses briefly the sources, the emission levels of NO_x, their influence on the environment and on public health, and their regulation and above all, it focuses on the efficient catalytic materials for selective reduction of NO_x using hydrocarbons.

2. Effects, sources, legislation of NO_x and the advantages of HC-SCR

The abbreviation NO_x usually relates to nitrogen monoxide (NO) and nitrogen dioxide (NO_2), which are produced during combustion at high temperatures. NO is the most important nitrogen–oxygen product of combustion, but it is further oxidized to NO_2. NO_x from engine exhaust typically consists of a mixture of about 95% NO and 5% NO_2 [1].

The toxicity of NO on human health would be four times lower than the toxicity of NO_2. However, in the presence of oxygen, NO is quickly oxidized into NO_2 which is a potent pulmonary irritant that can cause severe burns when in contact with the skin or the eyes. Gaseous NO_2 is associated with adverse effects on health, and its presence of it in high concentrations causes inflammation of the airways and reduced lung function [2]. Moreover, NO_x contribute to acid deposition, eutrophication as well as the formation of secondary inorganic particulate matter and tropospheric O_3 [2].

Anthropogenic activity is the main source of NO_x emissions, while biogenic sources constitute only a small fraction [1]. NO_x

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Table 1
NO_x emissions and projections of European Union Member States.

Member State	NO_x emission ceilings for 2010 (kT) [4]	NO_x final emission data 2010 (kT) [4]	NO_x final emission data 2011 (kT) [4]	NO_x provisional emission data 2012 (kT) [4]	2020 Gothenburg protocol (GP) reduction commitment for NO_x [5]
France	810	1067.1	1008.0	983.0	705
Germany	1051	1328.1	1293.6	1273.4	961
UK	1167	1117.4	1045.0	1061.6	707
European Union	9003	8942.1	8581.5	8361.3	6694

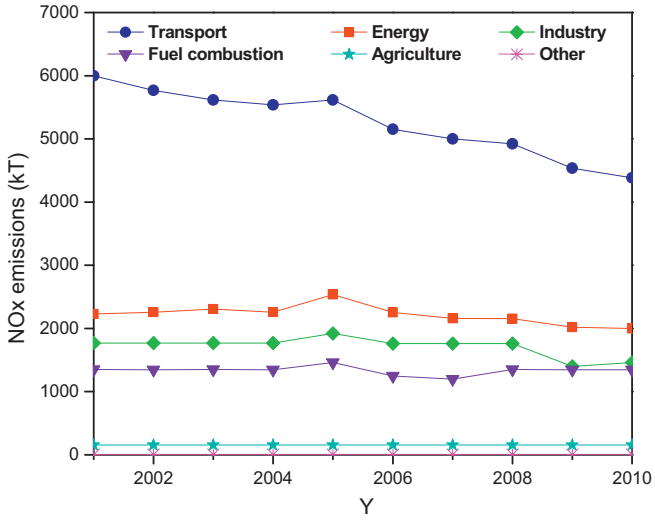

Fig. 1. Illustration of NO_x emission by source category in European countries after [3].

are emitted during fuel combustion, of industrial facilities and road transport sector. The major source of NO_x is the combustion of fossil fuels [1]. The origin of NO_x is generally categorized into mobile and stationary sources as described in Fig. 1 [3]. Among the countries of the European Union [4,5], the three largest countries emitting NO_x in 2010 with more than 1000 kT/year were Germany, France and the UK (Table 1). NO_x emissions continue to pose the greatest challenge, with 11 Member States (two of the three largest emitters) exceeding their respective NO_x ceilings for 2010.

Regulations have been proposed by the European Parliament to control NO_x emissions from stationary plants; National Emission Ceilings "NEC" Directive (Directive 2001/81/EC) sets upper limits for each Member State for the total emissions in 2010 of four pollutants among them nitrogen oxides (Table 1) to reduce acidification, eutrophication and the effect of ozone. Updated information related to pollutant emissions could be obtained by the European Environment Agency (EEA) and in the European Pollutant Emission Register (EPER) which is the first Europe-wide register of emissions into air and water from large- and medium-sized industrial facilities [4]. Other directives concerning industrial and agricultural activities include limits for NO_x emissions (such as Integrated Pollution Prevention and Control "IPPC" (Directive 2008/1/EC) and Large Combustion Plants (Directive 01/80/EC)).

With regard to emissions from mobile sources, the Euro V and Euro VI standards limit the reduction of NO_x from light vehicles. The first standard limits the NO_x emission to less than 180 mg/km for diesel and 60 mg/km for petrol-driven engines. In Euro VI, an additional reduction of more than 50% compared to Euro V standard will be applied.

Other programs have been designed in the United States to reduce emissions of nitrogen oxides from power plants, notably the Acid Rain Program (ARP) and the Clean Air Interstate Rule (CAIR) which contributed to significant NO_x reductions (Table 2). From 1990 to 2012, annual NO_x emissions in CAIR and ARP units together dropped by about 4700–1700 kT, a decrease of 73% [6]. Moreover, in Japan, NO_x emissions in Fiscal Year 2010 (FY2010) were 1744 kT. They decreased by 14.6% since FY1990 and decreased by 1.9% compared to the year 2009 [7].

From a thermodynamic point of view, the NO molecule is unstable even at 298 K and 1 atm. Even though NO formation is an endothermic phenomenon, no decomposition is observed at 825 K. This is due to the electronic structure of the bond in NO. However, the reaction is spin-forbidden, and NO is therefore kinetically stable. Thus, the high thermal stability of nitric oxide is due to its high energy of dissociation (364 kJ mol^{-1}) and to corresponding extremely low decomposition rates. Therefore, a catalyst is needed to lower the activation energy in order to facilitate the decomposition. Research in this domain is extensive and can be divided into two major paths of deNO_x activities based on automobile and stationary sources, either in the presence or absence of a reducing agent.

There are advantages of NO_x reduction by a reducing agent. In the presence of a reductant, reactions induce a strong decrease in the Gibbs free energy values. Furthermore, the introduction of oxygen involves an additional reduction in the free energy. This explains that such reactions are used in practical applications. As ammonia reductant has a lot of drawbacks, and the SCR of NO_x by hydrocarbons (HC) seems to be the most promising way to eliminate NO_x.

Moreover, the main advantage is the use of a gas mixture very similar to that found in exhausts. In fact, combustion processes lead to NO_x and HC exhausts which are both controlled pollutants.

Some researchers studied the mechanism of NO_x reduction by hydrocarbons [8]. In this process, the selective reaction of NO to N_2 initially proceeds by the simultaneous oxidation of NO to surface nitrates as strong oxidants and oxidation of hydrocarbons to surface oxygenates, followed by the reaction between these surface intermediates that leads to the formation of NCO and CN species, and finally induce the formation of N_2 and CO_2 via the oxidation or the hydrolysis of these nitrogen-containing species.

Powerful catalysts for selective catalytic reduction of NO_x by HC are important to discover. In 1990, Iwamoto [10] proposed the first powerful catalyst for HC-SCR, Cu ion-exchanged ZSM-5, since metal ion-exchanged zeolites have been the most investigated class of catalysts.

3. Powerful catalysts for selective catalytic reduction of NO_x by HC

3.1. Metal ion-exchanged zeolites

Table 3 presents various zeolite catalysts cited in the literature. The table is divided into catalyst, conditions (composition of gas mixture) and NO reduction efficiency. More specific information can be found in the literature.

3.1.1. Influence of the zeolite structure and its acidity

The three main zeolite types studied for more than 20 years are FER, MFI and MOR [9]. Indeed, Iwamoto et al. [10] studied the

Table 2
CAIR and ARP annual NO_x trends [6].

Primary fuel	NO_x emissions (kT)				
	2000	2005	2009	2010	2012
Coal	1.398	695	442	527	452
Gas	79	58	39	49	48
Oil	66	57	13	16	11
Other	1	2	2	2	3
Total	1.545	812	495	594	514

Table 3
Activity of various zeolite catalysts for HC-SCR.

Catalyst	Reaction conditions				T_{max} (°C)	NO reduction efficiency		Ref.
	NO (ppm)	O_2 (%)	Reducing agent	H_2O (%)		NO conversion (%)	N_2 selectivity (%)	
Beta-11-194	750	2.4	470 ppm C_3H_8		350	na	75	[13]
ZSM5-17-195	750	2.4	470 ppm C_3H_8		350	na	70	[13]
CuSiBEA	1000	2	1000 ppm C_2H_6O		380	40	78–90	[15]
CuSiBEA	1000	2	2000 ppm C_3H_8		380	20	90–100	[15]
Co/MFI WIE	1600	2.5	1000 ppm CH_4		450	na	31	[21]
Co/MFI SUB-Cl-a	1600	2.5	1000 ppm CH_4		400	na	29	[21]
Co/MFI SUB-Br-a	1600	2.5	1000 ppm CH_4		425	na	34	[21]
Co/MFI WIE	2000	3	2000 ppm iso-C_4H_{10}		475	na	95	[21]
Co/MFI SUB-Cl-a	2000	3	2000 ppm iso-C_4H_{10}		400	na	99	[21]
Co/MFI SUB-Br-a	2000	3	2000 ppm iso-C_4H_{10}		425	na	99	[21]
Pd-SBA-Imp	150	7	1500 ppm CH_4		300	98	na	[22]
HAlBEA (700)	1000	2	1000 ppm C_2H_6O		450	62	98	[26]
Pt-MFI-97	1000	2	1000 ppm C_2H_4		212	na	19.8	[29]
Co(0.91)ZSM-5	900	2	1000 ppm C_3H_8		450	50	na	[33]
Co(1.13) + Ca/ZSM-5	900	2	1000 ppm C_3H_8		500	54	na	[33]
Co(1.28) + Ba/ZSM-5	900	2	1000 ppm C_3H_8		500	76	na	[33]
Co(Imp)-Pd(WIE)-ZSM-5	500	5	2500 ppm CH_4	5	450	90	na	[35]
2% Pt/MCM-41	1000	14	3000 ppm C_3H_6		200	94	na	[51]
2% Pt/B-MPS	1000	14	3000 ppm C_3H_6		160	100	na	[51]
2% Pt/MPS	1000	1	10,000 ppm C_3H_6		400	100	na	[51]
Ag/Al-SBA-15 (6)	500	10	2500 ppm C_2H_6O		350	35	100	[53]

activity for SCR with C_2H_4 and observed the activity order as follow: Cu-MFI > Cu-MOR = Cu-FER > Cu-Y. The authors explained the best activity of Cu-MFI by the MFI structure that is more favorable for the reduction of NO in the presence of C2 hydrocarbons. Halasz et al. [11] indicated that the bridging of the hydroxyl groups of the MFI structure probably constitute active sites for the oxidation of NO by O_2 to surface nitrates.

Similar trends for Ce-exchanged zeolites are also found by Yokoyama and Misono [12]. However, Corma et al. [13] proved that Cu-exchanged beta zeolites exhibited similar activities compared to Cu-exchanged MFI zeolites for SCR with C_3H_8. In addition, the same team [14] proposed that the adequate zeolitic catalyst for SCR of NO with propane should (i) have a medium pore with 10- or 12-member ring channels, (ii) have no cavities and (iii) contain exchanged metal ions. They proposed a new zeolite structure: ITQ 27 with 12-ring pore dimension, 6.94 Å × 6.20 Å that showed a high activity for SCR with propane of this Co-exchanged zeolite. However, the best zeolite structure also seems to depend on the hydrocarbon reductant (especially its acido-basicity and dimension). The catalytic behaviors often depend on the Si/Al ratios and for this "adequate zeolitic catalyst": Si/Al ratio = 8–35 [14]. Nevertheless, Al atoms are not always needed because dealuminated Cu-exchanged SiBEA prepared by Dzwigaj et al. were active for SCR by EtOH [15].

Moreover, the related acid sites of the zeolites have an important role in the reaction. Many papers are directly based on the acido-basicity behaviors of HC-SCR [16,17]. Szanyi and Paffett [18] explained the role of the acid sites by the use of an in situ FT-IR investigation of the NO with O_2 reaction. Acid sites would nucleate NO by the formation of N_xO_y species (not strongly bonded) leading to surface nitrates.

All studies showed that the activity and the selectivity depend on the presence of acidic sites in the zeolites; both Brønsted and/or Lewis sites are important. Their amount and strength depend on the Si/Al atomic ratio. Bartolomeu et al. [19] showed that, on the one hand, the ability of the HY zeolites to oxidize the HC and, on the other hand, the amounts of NO_x converted into N_2, depend on the availability and strength of acid sites (Brønsted and Lewis) on the different zeolites through their Si/Al range. Zeolites with the most acidic sites have the best oxidizing properties. Moreover, acid sites participate in the dissociation of NO to N_2 and are also expected to be involved in some crucial steps of the $DeNO_x$ mechanism, such as the NO oxidation to NO_2, and/or the secondary reactions of the trapped HC with the NO_2 formed. However, the H-zeolites studied are always not active enough and too water-sensitive.

3.1.2. *Influence of the preparation procedures*

Charjar et al. [20] prepared Cu-ZSM-5 according to three different procedures: exchange (ex), impregnation (imp) and precipitation (prec); the samples were then tested for their activity to SCR by propane. They obtained the following activity order: Cu-ZSM-5(ex) > Cu-ZSM-5 (imp) > Cu-ZSM-5 (prec) and concluded that the ion exchange is the best technique to prepare metal zeolites for this reaction. However, Wang et al. [21] prepared Co/MFI catalysts with Co/Al = 1 by sublimation of $CoCl_2$ and $CoBr_2$ onto H/MFI. The preparation of Co/MFI catalysts by sublimation of $CoBr_2$ produces an equally active but more stable catalyst than sublimation of $CoCl_2$. The higher vapor pressure of $CoBr_2$ resulted in a lower temperature requirement (600 °C instead of 700 °C) during catalyst preparation. As a consequence, the zeolite structure remains intact. They showed that those solids are more active for SCR with CH_4 in a dry feed for a temperature below 450 °C than

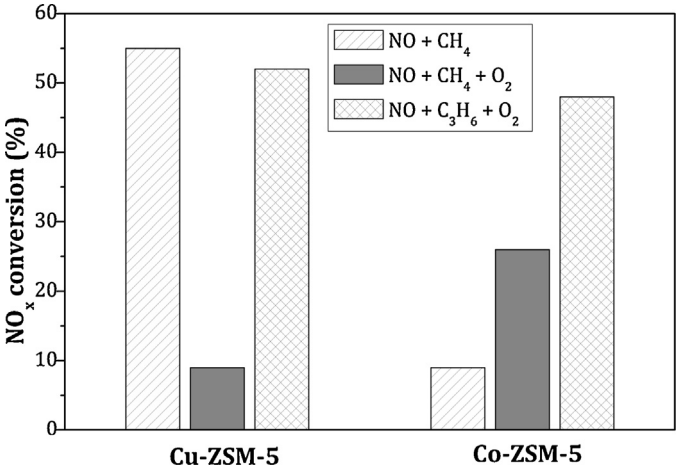

Fig. 2. NO_x conversion over Cu or Co-ZSM-5 with CH_4 (1000 ppm) and/or C_3H_6 (550 ppm) and/or O_2 (2.5%) after Armor [23].

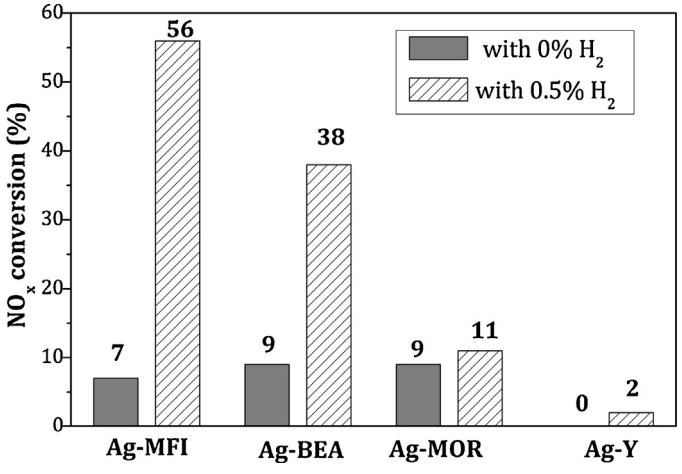

Fig. 3. Conversions over Ag-zeolites for C_3H_8-SCR in the absence and presence of 0.5% H_2 at 300 °C after Shibata et al. [31].

wet-ion exchange. They also used other preparation methods such as solid-state ion exchange and impregnation but they obtained less powerful catalysts. The procedure through which the metal is implanted in the zeolite lattice is then an important factor because the metal is not always totally directly bonded on the exchangeable positions. The higher activity below 450 °C for the Co/MFI catalysts prepared by sublimation would be due to multinuclear Co oxo-ions. The chemisorption of NO_x species would be faster on the multinuclear Co oxo-ions than on Co_3O_4 particles and isolated Co cations and then the rate could be correlated with the catalyst performance in NO_x reduction.

Moreover, a recent study by Boutros et al. [22] showed the influence of synthesis parameters on the simultaneous reduction of NO_x and combustion of CH_4. A highest $DeNO_x$ activity was obtained with catalysts synthesized by means of incipient wetness impregnation using an ammine palladium precursor, while the catalyst prepared by means of ion-exchange showed a higher activity in methane combustion [22]. The higher activity of Pd-SBA-Imp is due to a better dispersion of PdO active phase located inside the pores of the silica support and to a relative stronger interaction between the active phase and the support.

3.1.3. Influence of the metal nature and its loading

The nature of the cations in these catalysts is prominent because cations are the active species in the reduction by HC. Cu and Co exchanged zeolites are widely studied due to their activity and selectivity for SCR even though conditions such as the reductant chosen and the presence of oxygen in the feed affect their catalytic activity. Fig. 2 presents the NO_x conversion over Cu or Co-ZSM-5 with CH_4 (1000 ppm) and/or C_3H_6 (550 ppm) and/or O_2 (2.5%) [23]. The presence of O_2 is essential to the reaction. Under oxidizing conditions, Co-ZSM-5 zeolite is an active catalyst for reduction with methane, whereas Cu-ZSM-5 zeolite is almost inactive. However, both catalysts are very active in the presence of O_2 and C_3H_6.

Therefore, under oxidizing conditions, Cu but also Ce-exchanged zeolites [10] are active catalysts in the presence of HC with more than two carbons, whereas other metals like Co, Mn, Fe, Ni, Ga or In exhibit also activity in the reduction with methane and ethane. Among those metals, Mn and Ni exchanged zeolites do not offer advantages over Co, since N_2O is a main product [24]. A special attention is devoted to Fe-zeolite catalysts in SCR for their good activity (Table 3), although CO production is high [25,26].

Ga and especially In-exchanged zeolites [27] are very selective and active in the presence of water for SCR but the maximum of NO conversion is reached at high temperatures (500 °C). Kikuchi and Yogo [28] showed the importance of In-exchanged zeolites in HC-SCR, presenting especially in wet feed, high activity with NO_2 reduction.

Among the platinum group metals, Pt and Pd were widely studied for SCR but they are found to be not very efficient. In fact, Pt is efficient only at low temperatures and N_2O is its main product [29], Pd is often less active than Cu- or Co-exchanged zeolites and Rh is limited to reducing atmosphere as in the case of three-way catalysts. However, as these exchanged zeolites are more stable by adding H_2O and SO_2 in the feed than other metals, they are widely studied.

Ag zeolites are promising catalysts with high performances for NO_x reduction, especially with NO_2 [30] and with addition of small amounts of H_2 in the flow. This can be observed (Fig. 3) with the conversions over Ag-zeolites for C_3H_8-SCR in the presence of O_2 and in the absence or presence of 0.5% H_2 at 300 °C [31].

3.1.4. Effect of the degree of exchange

The degree of exchange is a significant parameter for activity. For Cu, Ce and Co ions [32], the activity for SCR of NO reaches a maximum of 80–100% but a small decrease occurs for higher levels of those metals. Stakheev et al. [33] found that the optimal metal loading for Co-ZSM5 should be correlated with the Al content. They showed that the activity increases with Co content for Co/Al < 0.5 and decreases for a ratio of Co/Al > 0.5. This result was also confirmed by Shibata et al. [31] who observed that the amount of $Ag_n^{\delta+}$ clusters increases with Ag/Al ratio till 0.5 and that the $Ag_n^{\delta+}$ clusters in Ag-MFI catalysts should be responsible of the SCR of NO by C_3H_8. The effect of the degree of exchange on catalysts activity was then discussed for Ag-MFI from the viewpoint of active Ag species (Ag^+ ion, $Ag_n^{\delta+}$ clusters ($2 \le n \le 4$), metallic Ag_m clusters ($3 \le m \le 5$), and Ag metal), whereas the difference of activity for ferrierite containing Co^{2+} exchanged was interpreted as a consequence of the preference of the cations for 8-ring channel sites first and for 10-ring channel sites later.

3.1.5. Supported zeolites containing two different elements

For zeolites containing Cu or Co as their main components, a high number of other metals were tested and among them, only Ce and La [34] added to Cu, earth-alkaline metals to Co [33] and Pd to Co [35,36] seem to exhibit some interesting effect.

The addition of earth-alkaline metals was found to be effective for Co-MFI zeolites in the SCR of NO with propane. However, no clear evidence has been given about the elements facilitating the second element, particularly what is the contribution in the redox

process, in the activation of the reactants or in the scavenging of the products. Nevertheless, the Co–Pd combination supported on zeolite leads to very active and selective catalysts for the SCR of nitrogen oxides with methane or methanol in the presence of oxygen and water. In this case, the activity would be correlated to well-dispersed Pd (ions) inside the zeolite pores that activate the reductant and to the presence of cobalt (Co_3O_4, Co-oxo ions) that enhances the SCR activity by oxidizing NO to NO_2.

3.1.6. Influence of the nature of the reductant

The N_2 yields of NO_x reduction depend on the nature of the reductant, for example, Co/MFI catalysts [21] present selectivities of 100% with *iso*-butane and only of 30% with methane. Moreover, since natural gas (containing more than 90% of CH_4) is widely used as a fuel source, many researches use CH_4 as a reductant even if its activation is difficult [22,37,38].

Matsumoto et al. [39] indicated that, irrespective of the C number, olefins are much more effective than paraffins. Witzel et al. [40] studied the effect of the nature of the HC on the NO conversion on Co/Na-ZSM-5 by the use of saturated HC with lesser reactivity i-C_4H_{10} > n-C_5H_{12} > 2,2,4-tri-methylpentane > neo-C_5H_{12} > 3,3-dimethylpentane > methane > C_3H_8 > 3,3-diethylpentane (neononane). They showed the existence of a strong molecular sieve effect for the SCR reaction with hydrocarbons too bulky to enter the zeolite pores (like neononane) but not for their oxidation. However, in another study, the inverse case [9] is observed because on Fe-MFI, NO should be into the pores with Fe to be transformed to NO_2 whereas the hydrocarbon had to stay outside the porous structure, otherwise it would directly be oxidized.

The activity of oxygenated VOC like alcohols, aldehydes, ketones and ethers is found to be close to that of propene [41]. Therefore, many new works mention the use of ethanol as a reductant [15,42].

Moreover, Iliopoulou et al. [43] showed on Ag catalysts that the use of higher and less saturated hydrocarbons results in an enhanced deNO_x performance. They explained that NO_x is reduced by reacting with intermediates generated from partial oxidation of hydrocarbons used as reductants and that increased availability of these species either by more C atoms in higher hydrocarbons, their easier formation from less saturated hydrocarbons explains the improvement of NO_x reduction.

3.1.7. Influence of oxygen content

The SCR of NO by propene with an oxygen excess over Cu-ZSM-5 produces hydrogen cyanide at $T < 400\,^{\circ}C$ [44]. IR data by Lombardo et al. [37] showed, in the same conditions, the presence of HCN, NH_3 and HNCO.

Moreover, a maximum selectivity is generally obtained for O_2/HC ratio sufficient for total combustion of the hydrocarbon. d'Itri and Sachtler [45] studied the combined effects of O_2 and C_3H_8 on N_2 yield (773 K, 4000 ppm NO, 4000 ppm C_3H_8) and showed that after a maximum of about 2% of oxygen, the N_2 yield decreases.

3.1.8. Stability of metal-exchanged zeolites

All zeolite-based catalysts are very sensitive to water and quickly deactivate. This is mainly due to two effects [46]:

- the modification of the geometry of the metallic active sites namely of their coordination and of their position on the zeolite;
- the dealumination of the structure with a modification of the Brønsted acidity.

Therefore, even though the activity is about three times lower compared to Cu-ZSM-5, Pt-ZSM-5 is less affected by H_2O and SO_2 [47] and then is often studied. The very low sintering of the Pt particles could explain the stability of the catalyst. A high stability to steam [27] is also observed for In-ZSM-5. In fact, a low effect on the indium sites is found by the poisoning of In-ZSM-5 zeolites by water because the phenomenon is reversible. The initial activity can be restored when water is put out of the feed. This can be explained by the fact that H_2O is very likely to be preferentially adsorbed on acid aluminum sites and separate In_2O_3 particles can promote NO_2 formation particularly in wet conditions.

The implanting of cobalt in the beta zeolite structure was reported by Armor and Farris [48] to be also less sensitive to water than the classical exchanged one.

Moreover, a deactivation study of Co–Pd-zeolites [35] showed that MOR zeolite topology is the most appropriate for Pd and Co.

3.1.9. Other molecular sieves used in the SCR of NO

In order to increase the stability in the presence of water, Inui et al. [49] investigated the activity of MFI and beta-metallosilicate catalysts (H-Fe, H-Co, etc.) and they showed that:

the metal loading, the nature of the reductant, the acidity and the oxygen content have the same influence as in metal-exchanged zeolites;

the best activities are obtained with both average acidity and activity in the oxidation of HC;

the beta and MFI type structures exhibit a high thermal and SO_2 resistance, but carbonaceous deposits are found [50] and these deposits increase with water content.

Transition metals supported on mesoporous silica molecular sieves for HC-SCR have been first studied with MCM-41 due to their low acidity and hydrothermal stability.

Indeed, platinum supported on mesoporous silica and metal-substituted silicates exhibited high NO conversions below 200 °C [51]. The activity is related to support acidity, which is affected by metal substitution of the silicates. The increase in Brønsted acidity of the supports resulted in the low-temperature activity of the catalyst. Nevertheless, new results on more stable SBA15 with Co for CH_4-SCR of NO_2 [52] are showed to be interesting but especially with Ag/Al-SBA15 system [53] which exhibits interesting activity for EtOH-SCR of NO.

3.2. Base oxides and supported metal catalysts

The activity of various base oxides and supported metal catalysts for HC-SCR is shown in Table 4.

4. Influence of the support

The base oxides (SiO_2, TiO_2, Al_2O_3, CoO, ZrO_2, etc.) have a very low or even have no activity for SCR of NO in the presence of the most active reductants (C_2H_4 or C_3H_6) [54,55]; only Al_2O_3 and superacid SO_4^{2-}/TiO_2 SO_4^{2-}/ZrO_2 present some activity due to their acid sites. However, as Al_2O_3 has mainly Lewis acid sites, while SO_4^{2-}/TiO_2 has mainly Brønsted sites, the activity for SCR of NO_x of these oxides does not simply depend on the type of acidity. Kourieh et al. studied the correlation between the catalytic behavior and the samples surface acidity for the SCR of NO_x by *n*-decane over different catalytic systems consisting of zirconia mixed oxides with Me_2O_3 (Me: B, Al, Ga, In, W) and showed that the samples with moderate acidity are the most active and selective towards N_2, because too strong acid sites favor the oxidation of the hydrocarbons that cannot react anymore as a reducing agent [56].

4.1.1. Influence of metal oxides deposition

Only Cu, Co, Fe and Sn on Al_2O_3 exhibit an increasing of the activity and similar influence of the metal loading is obtained for metal exchanged zeolites [55,57]. Indeed, a comparison of the catalytic behavior for SCR of NO by C_2H_4 of transition metal ions in ZSM-5 and in Al_2O_3 showed that the catalytic properties are dictated more

Table 4
Activity of various base oxides and supported metals catalysts for HC-SCR.

Catalyst	Reaction conditions				T_{max} (°C)	NO reduction efficiency		Ref.
	NO (ppm)	O_2 (%)	Reducing agent	H_2O (%)		NO conversion (%)	N_2 selectivity (%)	
Ga_2O_3–ZrO_2	400	9	240 ppm $C_{10}H_{22}$	1.5	300	71	89	[56]
Al_2O_3–ZrO_2	400	9	240 ppm $C_{10}H_{22}$	1.5	300	60	91	[56]
1 wt% Sn/$A1_2O_3$	1000	10	1000 ppm CH_4O	8	350	50	92	[57]
Pt/$A1_2O_3$	1000	10	1000 ppm C_3H_8		350	37	50	[58]
1% Pt/γ-$A1_2O_3$	995	5	870 ppm C_3H_6		250	50	na	[59]
1% Rh/γ-$A1_2O_3$	995	5	870 ppm C_3H_6		300	45	na	[59]
Pt/gamma $A1_2O_3$	400	3	4000 ppm CH_4		300	40	na	[61]
0.17% Au/$A1_2O_3$ DP	1000	10	1000 ppm C_3H_6	10	400	80.7	na	[62]
2.5Ag/Al_2O_3	500	10	2500 ppm C_2H_6O		300	98	60	[64]

Table 5
Activity of various hybrid catalysts for HC-SCR.

Catalyst	Reaction conditions					T_{max} (°C)	NO reduction efficiency		Ref.
	NO (ppm)	O_2 (%)	Reducing agent	H_2O (%)	SO_2 (ppm)		NO conversion (%)	N_2 selectivity (%)	
Pd0.53%/SCZ28	150	7	1500 ppm CH_4			370	35	na	[67]
HBEA + SnO_2 + Mn_2O_3	730	14	385 ppm C_3H_8			350	60	99	[68]
1% Au/Ti–Ce(0.39)	1500	10	1500 ppm C_3H_6			250	42.3	100	[69]
1% Au/Ti–Mn(1.00)	1500	10	1500 ppm C_3H_6			225	40.1	na	[69]
Ag/Al_2O_3 + 6%Ba/ZSM5	500	5	200 ppm $C_{10}H_{22}$	6	1	450	55	na	[71]

by the chemical nature of the metal ions and less by the nature of the support [55]. Tabata et al. [57], using methanol as a reductant, reported also that the addition of Sn led to an important enhancement of the activity of alumina, especially in the low-temperature range ($T < 625$ K) and led to a certain durability of the catalyst in the presence of water and SO_2. The authors suggested that the effect of the addition of Sn was related to the promotion of a reaction step leading to the formation of N_2 and CO_x.

4.1.2. Influence of platinum group metals deposition

Noble metals investigation is due to the low stability of other metals. Among them, Pt and Rh seem to be better than other metals, especially against deactivation. However, they must also be preferentially deposited on Al_2O_3 for the same reason as metal oxides.

Indeed, Hamada et al. [58] reported a cooperative effect between platinum and alumina in the reaction of NO with propane. Other studies by Obuchi et al. [59] reported that, for the same reductant, there is a relationship between the activity and the nature of the platinum metal. At low temperatures (about 525 K), platinum catalysts present higher activities than other platinum group metals, while at 625 K their activity is inferior to that of Rh-Al_2O_3. In all temperature ranges, the activity of Ir or Pd on the same support is lower than Pt or Rh catalysts. However, N_2O is mainly formed on Pt (only one-third of the NO is converted into nitrogen) [60], whereas more than 90% of the NO consumed is converted into N_2 on Rh-supported catalysts. Moreover, Kim et al. investigated the effect of impregnating Pt on different Al_2O_3 phases (α-Al_2O_3 and γ-Al_2O_3) for the SCR of NO_x by CH_4 and showed that also a good activity is obtained while mixing by mortar the two catalysts [61].

4.1.3. Influence of the deposition of other noble metals

Nano-sized Au/Al_2O_3 catalyst was found to have some interesting activity for HC-SCR [62] but Ag/Al_2O_3 was found to be one of the most active and selective catalysts with a wide operating window for the SCR of NO_x [63–65]. Moreover, Kim et al. [66] studied Ag/Al_2O_3 in hard conditions (400 ppm NO, simulated diesel, 800 ppm EtOH, 6% O_2, 2.5% H_2O), even though high performances are still obtained for NO_x reduction.

Therefore, the catalyst of choice has to perform well over a wide range of temperatures, under different reactant mixtures and has low sensitivity toward deactivation. Therefore, a combination of different metals and/or of different catalysts seems to be the better choice. That is why a great interest is increasingly given to hybrid catalysts.

4.2. Hybrid catalysts

Activities of various hybrid catalysts for the selective catalytic reduction of NO are shown in Table 5.

The combination of different metals is found, for example, in the reduction of NO_x by CH_4 on Pd-sulfated $CeZrO_2$ [67] and those materials present interesting catalytic behavior. However, the combination of different catalysts seems to be more powerful since the mixture of Mn_2O_3, SnO_2 and H-BEA for SCR of NO_x by propane [68], or the mixture of MO_x (M = Ce, Mn) and Au/TiO_2 for SCR of NO_x by propene [69] present almost ideal performances. For instance, a shift of 100 °C towards lower temperatures and a wider window of activity are obtained when Mn_2O_3 is added to Au/TiO_2 in comparison with Au/TiO_2 alone. Other interesting combination catalysts can be observed through "dual bed configuration" with Ag/Al_2O_3 and Cu-ZSM-5 catalysts [70] used one after the other. Another study [71] have shown the interest of mixing Ag/Al_2O_3 with M-ZSM-5 (M: W, In, Ba, Ga) for NO_x reduction with decane, the highest NO_x conversion was obtained with Ag/Al_2O_3 mixed with Ba-ZSM-5.

NO_x storage reduction by the use of mixture or dual bed configuration [72] over hybrid Pt–Ba/Al_2O_3 and Fe-ZSM-5 systems is particularly efficient for NO_x removal.

5. Conclusion

HC-SCR is an interesting way for NO_x reduction and during this last two decades many efficient catalysts were investigated, especially metal ion-exchanged zeolites. The catalyst of choice for HC-SCR would be rather a combination of different metals (with Co, Ag, Pd, etc.) and/or of different mixed catalysts to perform well over a wide range of temperatures and reactant mixtures and without any significant deactivation. In conclusion, an active and selective catalyst for HC-SCR needs some acidity from the support, an adequate active phase (like Cu or Co), silver (or a mixture of metals)

for a wide range of efficiency and, for low sensitivity toward deactivation, Sn or some noble metals could be useful.

Furthermore, articles are trying increasingly to explain how to remove simultaneously the NO_x and the HC (VOC) [60,72–76], whereas single catalyst should be able to destroy directly both NO_x and VOCs.

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