AN OVERVIEW OF RECENT ADVANCES IN CATALYTIC DECOMPOSITION OF N_2O ON NOBLE METAL AND METAL OXIDE CATALYSTS

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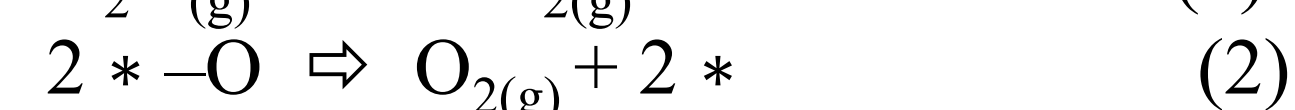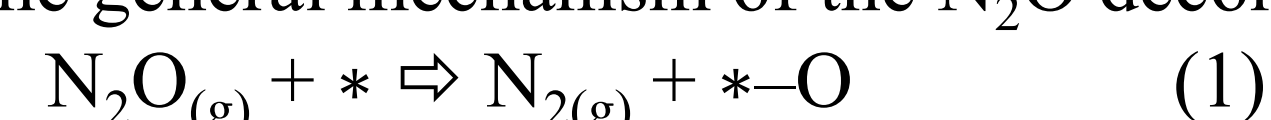
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1. Summary

The catalytic decomposition of nitrous oxide (N_2O) into N_2 and O_2 has attracted intense research interest in the past decades due to the fact that large amounts of N_2O are currently produced by anthropogenic activities, such as stationary or mobile combustion processes of fossil fuels and/or biomass, certain chemical industries (e.g. adipic and nitric acid production plants) and the use of fertilizers in land cultivation. However, nitrous oxide is a powerful greenhouse gas, which has recently also been recognized as the dominant stratospheric ozone-depleting substance. It is estimated that N_2O emissions will double by around 2050, if the appropriate methods for N_2O abatement from anthropogenic emissions are not applied urgently and widely. Therefore, the control of N_2O emissions is of great environmental importance. The catalytic decomposition of N_2O into N_2 and O_2 is the most promising and cost-effective technique to reduce its emissions, due to the simplicity, the high efficiency and low energy requirements of the process compared to other methods like thermal decomposition and selective absorption. To this purpose, a wide variety of catalytic materials for N_2O decomposition has been developed and studied in recent years. The main aim of the present work is to comprehensively and comparatively review the recent advances on the research for developing effective deN_2O catalytic materials involving both supported noble metal (NM) and NM-free metal oxide catalysts. Particular attention is paid to the main factors influencing the de-N_2O activity and stability of the catalysts, among others the preparation method, the nature and the oxidation state of the active phases under reaction conditions, possible metal-support interactions and crystallite shape or size effects, as well as imposed reaction conditions (temperature, presence of other reactants, etc) in order to gain a deep understanding of structure-activity relationships that promote the de-N_2O efficiency of the catalytic systems.

The general mechanism of the N_2O decomposition reaction comprises three elementary steps :

$$N_2O_{(g)} + * \Rightarrow N_{2(g)} + *{-}O \qquad (1)$$
$$2* {-}O \Rightarrow O_{2(g)} + 2* \qquad (2)$$
$$N_2O_{(g)} + *{-}O \Rightarrow N_{2(g)} + O_{2(g)} + * \qquad (3), \text{ where (* represents a catalytically active site)}$$

2. Decomposition of N_2O on noble metal catalysts

Noble metals mostly studied in N_2O catalysis are platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), and iridium (Ir). Among them, Rh was generally found to be the most active, although it is the most expensive due to its scarcity and extensive use in three-way catalytic converters (TWCs). The less expensive Ir and especially Ru, have found to be almost as good as Rh on N_2O decomposition activity. However, a drawback of both Ru and Ir nanodispersed catalysts is their inferior thermal stability compared to that of Rh and Pt. The use of Au and Ag-based catalysts has been less reported for the deN_2O process. The choice of support is very important and various supports have been studied for the N_2O decomposition, such as metal oxides (e.g. Al_2O_3, SiO_2, TiO_2, CeO_2, Fe_2O_3), perovskites and mesoporous materials. It is worth to note that the impact of H_2O, CO, CO_2, O_2, NO, and NO_2 on N_2O reduction is particularly important, since these substances are usually present in excess in N_2O containing gas streams. Especially, the addition of oxygen to the gas feed limits the conversion of N_2O and decreases reaction rates over supported noble metal catalysts in most cases, because the oxygen presence oxidizes the active sites of the catalysts (see Fig 1). The catalytic performance in the decomposition of N_2O is also correlated with different noble metal particle sizes. The structure–activity relations seem to be very complex, however small nanoparticles are more active species. Furthermore, the effect of preparation method and the addition of electropositive promoters, such as alkali or alkaline earth metals, have also been reported to play a key role on de-N_2O process over several catalytic systems.
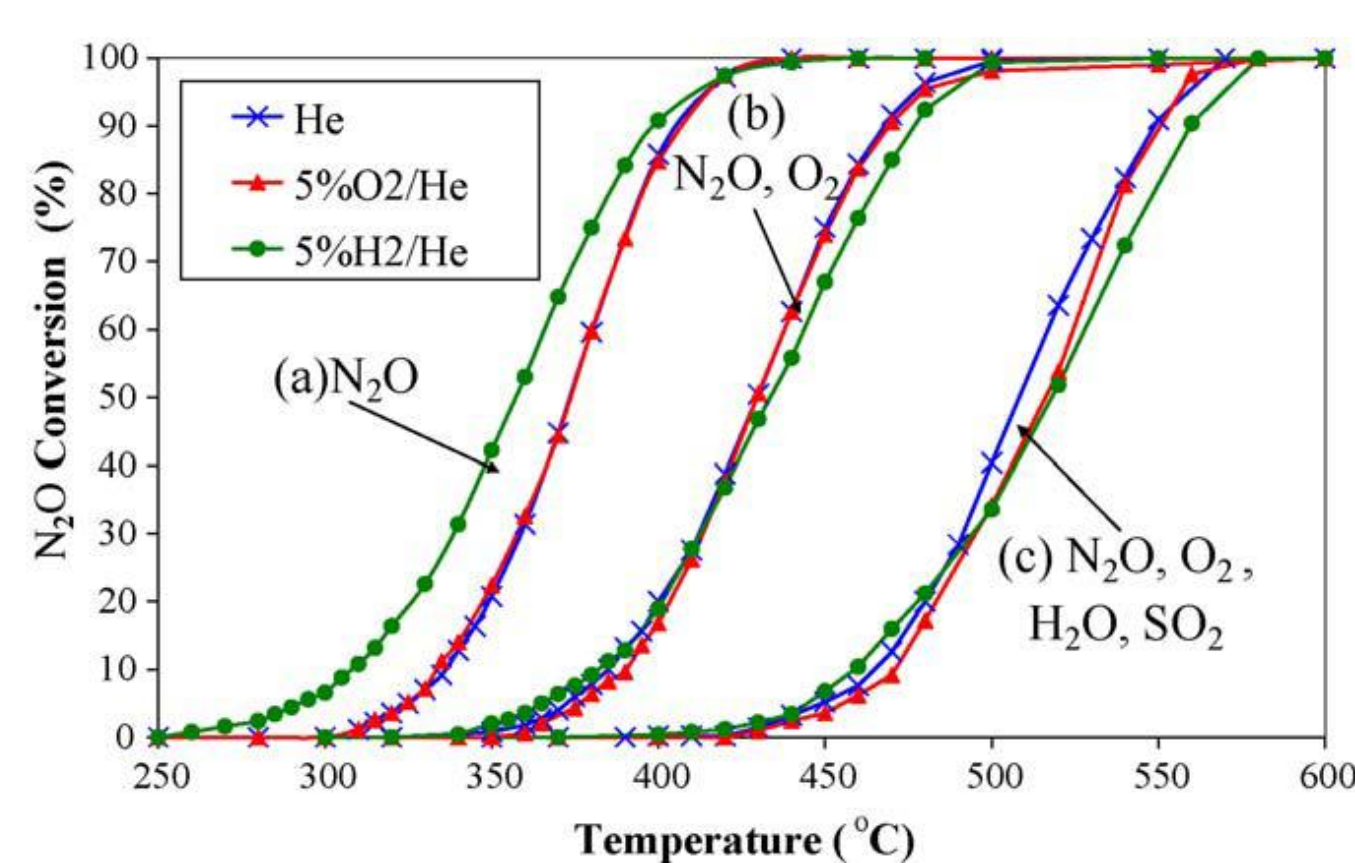

Fig 1: N_2O decomposition activity of Ru/γ-Al_2O_3 catalyst for various feeds: (a) 500 ppm N_2O in He, (b) 500 ppm N_2O, 5%O_2 in He, and (c) 500 ppm N_2O, 5% O_2, 50ppm SO_2, 10%H_2O in He. Total flow rate: 500 cm3/min, catalyst weight: 0.5 g, GHSV: 56,000 h^{-1} [7].

3. Decomposition of N_2O on non-noble metal oxides

The largest amount of NM-free oxides have studied as catalysts in the specific process, includes single metal oxides and spinels, as well as binary mixed oxides, spinels and perovskites. Among the single oxides, the most effective seem to be the mesoporous Co_3O_4, NiO, MnO_2 and CuO oxides. Co_3O_4 spinel is the most active single oxide, that's why is the most well studied. Regarding to the binary oxides, zirconia-based catalysts are nowadays getting much more attention due to the tetragonal ZrO_2 crystal structure sensitivity in the reaction. However, ceria-based catalysts have gained the center of interest because of the high Ce^{3+}/Ce^{4+} redox cycle contribution in N_2O decomposition, especially in combination with other oxides which also possess redox cycle, such as CuO and the spinel Co_3O_4. Furthermore, Co_3O_4 spinel is often partially substituted by other metals so as to improve its physicochemical and catalytic properties. Bivalent transition or alkali earth metals (e.g. Mg^{2+}, Ni^{2+}, Zn^{2+}) are preferred. The most common perovskites have been used for N_2O decomposition are those containing Cobalt because again it seems to be the most active transition metal in such structures. Lastly, it is worth mentioning that the promoting effect of alkali metals has also been examined on the majority of the aforementioned catalyst types and especially on the cobalt-based spinel catalysts. This promoting effect in the process is attributed to an induced electron interaction, improving the electron donation ability of cobalt which finally facilitates the N_2O adsorption and decomposition. Potassium seems to be the best promoter in this field.

4. Conclusions

- ✓ N_2O decomposition is one of the most efficient methods for N_2O abatement.
- ✓ A number of studies reveal the important role of catalytic performance of noble metals and their support materials under a variety of different conditions.
- ✓ Among the metal oxides have been applied in the deN_2O process , cobalt spinel based and ceria based oxides are in the centre of interest.
- ✓ Metal oxides seem to highly compete the activity of the more expensive supported noble metals in the process.

Table 1 summarizes for each noble metal the catalyst composition, its preparation method, reaction conditions, N_2O conversion (%) and/or light off temperature (T_{50}). T_{50} is a characteristic criterion for the estimation of the catalytic activity and is called light-off temperature, which is the temperature where the conversion of the reactant is 50%

Catalysts code (Metal loading/wt%, precursor, preparation method)	Reaction conditions	N_2O conversion %/°C	T_{50} (°C)	Ref.
Rh/MgO (1.21%, w/w, Rh(NO3)3, impregnation)	1000 ppm N_2O, 5vol% O_2 in He, GHSV=12000 h^{-1}	100 (300)	249	[1]
Rh/SiO2 (1.11%, w/w, Rh(NO3)3, impregnation)	1000 ppm N_2O, 5vol% O_2 in He, GHSV=12000 h^{-1}	100 (300)	249	
Rh/CeO2 (0.19%, w/w, Rh(NO3)3, impregnation)	1000 ppm N_2O, 5vol% O_2 in He, GHSV=12000 h^{-1}	82 (450)	289	
Rh/Al2O3 (0.58%, w/w, Rh(NO3)3, impregnation)	1000 ppm N_2O, 5vol% O_2 in He, GHSV=12000 h^{-1}	100 (450)	341	
Rh/TiO2 (0.38%, w/w, Rh(NO3)3, impregnation)	1000 ppm N_2O, 5vol% O_2 in He, GHSV=12000 h^{-1}	90(450)	342	
Rh/CeLaZr (0.5%/wt, Rh(NO3)3·xH2O, impregnation)	2000 ppm N_2O in He, GHSV=67000 h^{-1}, over O_2 pre-oxidized	100 (450)		[2]
Rh/CeLaZr (0.5%/wt, Rh(NO3)3·xH2O, impregnation)	2000 ppm N_2O in He, 5% O_2, GHSV=67000 h^{-1}, over O_2 pre-oxidized	98.8 (450)		
Rh/CeLaZr (0.5%/wt, Rh(NO3)3·xH2O, impregnation)	2000 ppm N_2O, 2000 ppm NO in He, GHSV=67000 h^{-1}, over O_2 pre-oxidized	37.7 (450)		
Rh/CeLaZr (0.5%/wt, Rh(NO3)3·xH2O, impregnation)	2000 ppm N_2O in He, GHSV=67000 h^{-1}, over C_3H_6 pre-reduced	100 (450)		
Rh/CeLaZr (0.5%/wt, Rh(NO3)3·xH2O, impregnation)	2000 ppm N_2O in He, 5% O_2, GHSV=67000 h^{-1}, over C_3H_6 pre-reduced	100 (450)		
Rh/CeLaZr (0.5%/wt, Rh(NO3)3·xH2O, impregnation)	2000 ppm N_2O, 2000 ppm NO in He, GHSV=67000 h^{-1}, over C_3H_6 pre-reduced	100 (450)		
Ru/MgO (0.93%, Ru(NO)(NO3), impregnation)	1000 ppm N_2O in He, GHSV=24,000 h^{-1}		>500	[3]
Ru/CeO2 (0.19%, Ru(NO)(NO3), impregnation)	1000 ppm N_2O in He, GHSV=24,000 h^{-1}		483	
Ru/SiO2 (1.14%, Ru(NO)(NO3), impregnation)	1000 ppm N_2O in He, GHSV=24,000 h^{-1}		348	
Ru/TiO2 (0.4%, Ru(NO)(NO3), impregnation)	1000 ppm N_2O in He, GHSV=24,000 h^{-1}		307	
Ru/Al2O3 (0.64%, Ru(NO)(NO3), impregnation)	1000 ppm N_2O in He, GHSV=24,000 h^{-1}		330	
Ir/γ-Al_2O_3 (1.0wt%, IrCl3, impregnation)	0.1%N_2O, He balance, catalyst mass, w_{cat} = 50 mg, WHSV=180 l g^{-1} h^{-1}	100 (~490)	417	[4]
Ir/YSZ (1.0wt%, IrCl3, impregnation, 8 mol% yttria stabilized zirconia)	0.1%N_2O, He balance, catalyst mass, w_{cat} = 50 mg, WHSV=180 l g^{-1} h^{-1}	100 (~510)	435	
Ir/GDC (1.0wt%, IrCl3, impregnation, 10 mol% gadolinia doped ceria)	0.1%N_2O, He balance, catalyst mass, w_{cat} = 50 mg, WHSV=180 l g^{-1} h^{-1}	80 (~575)	490	
Ir/ACZ (1.0wt%, IrCl3, impregnation, (80 wt%Al_2O_3-10 wt% CeO_2-10 wt% ZrO_2 mixed oxide)	0.1%N_2O, He balance, catalyst mass, w_{cat} = 50 mg, WHSV=180 l g^{-1} h^{-1}	80 (~575)	515	
Pd-Al_2O_3 (2 wt. %, Pd(NO3)2·2H2O, dry impregnation)	0.12% N_2O, balanced with He, catalyst mass, w_{cat} = 150 mg, GHSV= 35000 h^{-1}	100 (450)	350	[5]
Pd-Al_2O_3 (2 wt. %, Pd(NO3)2·2H2O, dry impregnation)	0.12% N_2O, 5%O_2, balanced with He, catalyst mass, w_{cat} = 150 mg, GHSV= 35000 h−1	100 (450)	370	
Pd-Al_2O_3 (2 wt. %, Pd(NO3)2·2H2O, dry impregnation)	0.12% N_2O, 0.17% C_3H_6, balanced with He, catalyst mass, w_{cat} = 150 mg, GHSV= 35000 h^{-1}	100(400)	275	
Pd-Al_2O_3 (2 wt. %, Pd(NO3)2·2H2O, dry impregnation)	0.12% N_2O, 5%O_2, 0.17% C_3H_8, balanced with He, catalyst mass, w_{cat} = 150 mg, GHSV= 35000 h^{-1}	100(450)	335	
Pt/ Al_2O_3 (0.5 wt%, Pt(NH3)2(NO2)2, co-precipitation)	0.1% N_2O, balance He, GHSV = 10,000 h^{-1}	33 (600)		[6]
Pt(0.5K)/ Al_2O_3 –CeO_2 –La_2O_3 (0.5 wt%, Pt(NH3)2(NO2)2, co-precipitation)	0.1% N_2O, balance He, GHSV = 10,000 h^{-1}	100 (480)		
Pt(1K)/ Al_2O_3 –CeO_2 –La_2O_3 (0.5 wt%, Pt(NH3)2(NO2)2, co-precipitation)	0.1% N_2O, balance He, GHSV = 10,000 h^{-1}	100 (450)		

Table 2 summarizes for each metal oxide the catalyst composition, its preparation method, reaction conditions, light off temperature (T_{50}), as well as an estimated temperature for its full conversion (T_{100})

Catalyst	Preparation method	Reaction conditions	T_{100} (°C)	T_{50} (°C)	Reference
Single metal oxides and spinels					
Co_3O_4	Solution combustion, Hydrothermal, Coprecipitation	10%N_2O in Ar, WHSV= 7.200cc/g*h	430 , 530, >>650	~290, ~350, ~570	[8]
Co_3O_4	Thermal decomposition	0.05%N_2O in N_2, WHSV= 24.000cc/g*h	>>510	>510	[9]
NiO	Hydrothermal	0.2%N_2O/ 2.0%O_2 in He,WHSV= 60.000cc/g*h	>500	392	[10]
MnO_2	Hydrothermal	0.5%N_2O in He, WHSV= 7.200cc/g*h	>>400	~380	[11]
CuO	Hydrothermal	0.2%N_2O/ 2.0%O_2 in He,WHSV= 60.000cc/g*h	550	~460	[12]
CeO_2	Hydrothermal	0.2%N_2O/ 2.0%O_2 in He,WHSV= 60.000cc/g*h	>>600	~550	[12]
ZrO_2	Sol-gel	0.1%N_2O in He, WHSV= 18.000cc/g*h	>>550	>550	[13]
Binary mixed oxides					
NiO/CeO_2 , Ni/Ce=8	Hydrothermal	0.2%N_2O in He,WHSV= 60.000cc/g*h	~450	~350	[10]
NiO/CeO_2 , Ni/Ce=8	Hydrothermal	0.2%N_2O/2.0%O_2 in He, WHSV= 60.000cc/g*h	~450	367	[10]
CuO/CeO_2 , Cu/Ce=1	Hydrothermal	0.2%N_2O in He,WHSV= 60.000cc/g*h	500	~380	[12]
CuO/CeO_2 , Cu/Ce=1	Hydrothermal	0.2%N_2O/ 2.0%O_2 in He,WHSV= 60.000cc/g*h	550	~425	[12]
10%wt. Fe_2O_3/ZrO_2	Sol-gel	0.1%N_2O in He, WHSV= 18.000cc/g*h	>550	~490	[13]
10%wt. NiO/ZrO_2	Sol-gel	0.1%N_2O in He, WHSV= 18.000cc/g*h	>>550	~520	[13]
Binary Spinels					
Co_3O_4/10%wt.CeO_2	Solution combustion	10%N_2O in Ar, WHSV= 7.200cc/g*h	350	230	[8]
$MgCo_2O_4$	Thermal decomposition	0.05%N_2O in N_2, WHSV= 24.000cc/g*h	>525	467	[9]
Alk-$MgCo_2O_4$, Alk=Cs,Li,Na,K , Alk/Co=0.05	Incipient wetness impregnation	0.05%N_2O in N_2 , WHSV= 24.000cc/g*h	>500, >500, >500, ~475	332, 405, 374, 308	[9]
Binary Perovskites					
$LaCoO_3$, $LaFeO_3$, $LaMnO_3$, $LaCrO_3$	Solution combustion	0.5%N_2O in He, WHSV= 120.000cc/g*h	~550, ~750, ~900, ~750	455, 645, 651, 660	[14]
$LaFeO_3$, $SrFeO_3$	Sol-gel auto-combustion	10%N_2O/5%O_2 in He, WHSV= 18.000cc/g*h	~620, >620	485, 540	[15]

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