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RESEARCH NOTE

Nonselective Reduction of NO by CO under Oxidizing Conditions on Supported Rhodium Sol–Gel Catalysts

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Currently the reduction of nitrogen oxides formed by mobile sources is widely studied to control atmospheric pollution. To remove the NO from automobile exhaust, the nonselective reduction of NO by CO using supported rhodium catalysts is one of the most promising technologies (1). However, the current catalyst is not able to reduce NO_x in excessively lean (O_2-rich) exhaust. For instance, the three-way catalytic converter loses its activity in converting nitric oxide in oxidizing conditions, even though the concentration of the reducing agents (CO, H_2, and HC) exceeds the concentration of nitric oxide (2).

Cho *et al.* (3, 4), report that the overall NO + CO reaction involves the following reaction pathways:

$$NO + CO \rightarrow \tfrac{1}{2} N_2 + CO_2 \quad [1]$$

$$2\,NO + CO \rightarrow N_2O + CO_2 \quad [2]$$

$$N_2O + CO \rightarrow N_2 + CO_2. \quad [3]$$

Where reaction three plays a very important role on supported rhodium catalysts (5). They have shown that the rate for the intermediate N_2O with CO can be faster than the NO + CO overall reaction, eventhough the isolated N_2O + CO reaction is slow (6). In the same way, Tauster and Murrell (7) propose the partitioning of the reducing agents between NO and O_2, when the reduction of NO by CO is done under oxidizing conditions, as follows:

$$CO + NO \rightarrow \tfrac{1}{2} N_2 + CO_2 \quad [1]$$

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2. \quad [4]$$

On the other hand, McCabe *et al.* (8), have examined the activity of Rh/Al_2O_3 catalysts, in the reduction of NO by CO under oxidizing conditions, for the three more important reactions (CO + O_2, CO + NO, and CO + N_2O), and found the onset temperature reaction for each one is 150, 225, and 370°C, respectively.

Likewise, support or doping effects on this reaction have also been observed with regard to support. Oh *et al.* (9) have shown that CeO_2 added to Rh/Al_2O_3 can enhance the rate of both CO + O_2 and CO + NO reactions under steady-state conditions. Moreover, there is a certain discrepancy about the activity of the noble metals (Pt, Rh, Pd, Ir, etc.) for the reduction of NO by CO in presence of oxygen. For instance, Lester *et al.* (10) have reported high activity for Ir, Rh, and Pt, when supported on alumina; however, Nakurama *et al.* (11) have shown that Rh, Pt, and Pd supported on titania are more active than when they are supported on alumina or silica.

The storage and transport capability of oxygen in various supports has been studied (3, 12). Generally, the most studied has been cerium oxide (1, 13) since, as a additive in the automotive three-way catalytic converter, it acts as follows: it stabilizes the dispersion of noble metals on alumina support and it stores and releases oxygen under net-oxidizing and net-reducing conditions, respectively (14).

In an alternative support like titania, the adsorption of the oxygen on TiO_2 leads to the formation of electron-deficient oxygen species such as O_2^- or O^- anions, where both participate in the surface reactions (15). Pure titania with large crystallite sizes is stoichiometric, dielectric, and not useful as a catalytic support; however, its catalytic properties change when it is doped with other atoms; for instance, when oxygen vacancies are created or when the valence of some Ti atoms is reduced from 4+ to 3+ (16). Thus, its chemical and electronic properties depend on the local defect density and on the type of impurities introduced into its crystalline structure (17).

Another way to change the chemical properties of titania is through the method of preparation and thermal treatment (18), and a method to obtain titania nanoparticles is the sol–gel process (19). Sol–gel titania was made

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with titanium alkoxide (20). The hydrolysis product, however, is not fully hydrolyzed nor can it ever be pure oxide (19). Through this method it can only be $Ti_nO_{2n-(x-y)/2}(OH)_x(OR)_y$, where n is the number of titanium atoms polymerized in the polymer, and x and y are the number of terminal OH and OR groups, respectively. Since the sol–gel method is associated with a hydrolysis reaction, OH groups are deposited on the surface or in the bulk of the support; thus the active metal can also be supported by an impregnation method. The results, however, can differ from those obtained by co-gelling active metal and support (21).

In this work we have studied the effect of rhodium supported on titania and alumina catalysts prepared by the sol–gel method. Impregnated rhodium reference catalysts were also prepared and their activity in the reduction of NO by CO with and without oxygen were compared (5, 22). These kinds of sol–gel catalysts have not been reported before in experimental work concerning the NO decomposition reaction.

A Rh/TiO_2-SG sol–gel catalyst was prepared as follows: 50-ml ethanol, 10-ml H_2O, 2-ml NH_4OH (pH 9), and 0.26-g rhodium trichloride ($RhCl_3 \cdot 3\,H_2O$) were refluxed at 70°C with constant stirring. Afterwards, 29-ml titanium tetraethoxide ($Ti(OCH_2CH_3)_4$) were added to the solution dropping for 3 h. The reflux continued until the gel was formed. The gel was dried at 70°C for 12 h and then calcined at 550°C for 6 h. The final metal concentration in the catalyst was 1.0 wt%. A Rh/Al_2O_3-SG sol–gel catalyst was prepared as follows: 100-ml ethanol and 49-ml aluminum tri-*sec*-butoxide ($(C_2H_5(CH_3)O)_3Al$) were refluxed at 70°C with constant stirring for 1 h; afterwards 3-ml NH_4OH (pH 9), 5-ml H_2O, and 0.26-g rhodium trichloride ($RhCl_3 \cdot 3\,H_2O$) were added to the solution. The reflux continued until the gel was formed. The gel was dried at 70°C for 12 h and then calcined at 550°C for 6 h. The final metal concentration of the catalyst was 1.0 wt%.

A Rh/TiO_2-RC reference catalyst was prepared by impregnation of commercial titania (Degussa titanium dioxide, BET area 50 m^2/g). The sample as received by the provider was impregnated with an aqueous solution of rhodium trichloride in the required amount to obtain a metal content of 1.0 wt%. A Rh/Al_2O_3-RC reference catalyst was prepared in a similar way using commercial alumina (Alcoa, BET area 195 m^2/g) as support. The reference catalysts were dried and calcined under the same conditions used for the sol–gel catalyst. All the sol–gel preparations and reference catalysts were reduced at 450°C under pure (UHP 99%) flowing hydrogen for 4 h before characterization.

The specific surface area of the catalysts was determined by the BET method from the nitrogen adsorption isotherms at 77°K in an automated Micromeritics ASAP-2000 apparatus. Apparent Metal dispersion was determined by hydrogen adsorption in a glass volumetric apparatus and by TEM observations from the equation $\%D = 1000/\varphi$, where φ is the particle size from TEM and a constant 1000 for noble metals. The particle size determined by chemisorption (ϕ) was calculated from the equation $\phi = 6/d\,Am$, where d is the density of the metal (g/cm^3) and Am is the metallic area (m^2/g metal), assuming a spherical shape of the particle (23).

The catalytic activity in the nonselective reduction of NO by CO under oxidizing conditions was determined at atmospheric pressure in reduced samples in a fixed bed reactor at low conversion, using nitrogen as a carrier flow gas containing 1.5 vol% CO, 1.5 vol% O_2, and 0.5 vol% NO. Comparative reactions were carried out without oxygen in the feedstream. The experimental conditions were: reaction temperature 200°C, catalyst 50 mg, and reacting mixture flow of 30 $cm^3\ min^{-1}$. The analysis of the products was made by infrared spectroscopy (FT-IR), using a Nicolet-8220 Gas Analyzer and gas chromatography using HP-5890 Chemical Station.

In sol–gel preparations, the particle size determined by H_2 chemisorption or by transmission electron microscopy shown notably differs; for instance, the particle size calculated from volumetry corresponds to a much larger particle than that determined by electron microscopy, this effect is not observed in reference catalysts whose particle sizes are similar. In sol–gel catalysts a SMSI effect could be operating at lower temperature than that usually observed (>550°C) (24, 25). The difference between sol–gel preparations and reference catalysts is that in sol–gel method, the titanium alkoxide and noble metal form a homogeneous solution before gelation, which induces the possibility to find some metal incorporation into the titania network. By heat pretreatment one portion of the particles could be found partially covered by titania support; this would result in a disagreement between the dispersion values obtained by chemisorption and by transmission electron microscopy (Table 1). This effect does not occur in the reference catalysts, where the formation of metallic particles could be limited to the surface of the support; therefore, if the spherical model is adopted for metallic particles, practically all the atoms are available to chemisorb hydrogen. In impregnated catalysts the SMSI effect must be drastically diminished, due to the temperature at which it was done.

TABLE 1

Metal Particle Size of Sol–Gel and Reference Catalysts

Catalyst[a]	Surface area (m^2/g)	Dispersion (%)		$d\phi$ (Å)	$d\varphi$ (Å)
		ϕ	φ		
Rh/TiO_2-SG	110	10	25	108	40
Rh/Al_2O_3-SG	280	20	33	54	30
Rh/TiO_2-RC	50	11	11	103	90
Rh/Al_2O_3-RC	195	22	28	50	35

[a] Reduced at 450°C; ϕ = chemisorption; φ = TEM.

TABLE 2

Catalytic Activity of Sol–Gel and Reference Catalysts in the Nonselective Reduction of NO by CO

Catalyst[a]	NO[b] Conv. (%)		Specific rate (10^5 mol/s g cat)		Activity per site (mol/size s)	
	A	B	A	B	A	B
Rh/TiO_2-SG	4.6	3.7	1.44	1.16	1.47	1.19
Rh/Al_2O_3-SG	3.7	2.1	1.17	0.67	0.59	0.34
Rh/TiO_2-RC	1.5	0.12	0.48	0.03	0.46	0.03
Rh/Al_2O_3-RC	1.3	0.09	0.40	0.02	0.18	0.01

[a] All catalysts reduced at 450°C; A = without oxygen; B = with oxygen.
[b] NO conv. = $([NO])_{react} - [NO]_{prod})/[NO]_{react} \times 100$; activity at 200°C.

The specific rates were calculated in the steady-state region, and activity per site was calculated using the hydrogen chemisorption values (Table 2). Different behavior with and without oxygen in the reduction of NO by CO compared to the reference catalysts was shown by the sol–gel preparations. The sol-gel preparation method plays an important role on the activity in the reduction of NO by CO, mainly in oxidizing conditions, since the sol–gel catalysts do not lose activity in the presence of oxygen, whereas the reference catalysts do lose their activity (Table 2). An effect of the support was observed, given that the rhodium sol–gel catalyst supported on titania was more active than the alumina-supported catalyst.

The consumption of CO during the reduction of NO under oxidizing conditions with sol–gel catalysts was less than reference catalysts, mainly with Rh/TiO_2-SG. Probably the role of TiO_2 could be considered in a similar way to that shown by CeO_2-promoted oxidation catalysts, as proposed by Cuif *et al.* (26), where the cerium oxide acts as an active oxygen storage solid and its oxidation state is regenerated by the oxygen of the following feedstream: oxygen release $xCO + CeO_2 \rightarrow xCO_2 + CeO_{2-x}$; oxygen storage $\frac{1}{2}\,xO_2 + CeO_{2-x} \rightarrow CeO_2$.

In our case, TiO_2 sol–gel support is deficient (21), so it has great capacity to release oxygen from its network, and to store it in a catalytic process. Therefore, the sol–gel method shows a strong effect on titania and alumina oxygen-release properties for NO decomposition (Table 3).

TABLE 3

Consumption of CO in the Reduction of NO with and without Oxygen

Catalyst[a]	CO[b] (% Conv.)		Specific rate (10^5 mol/s g cat)		Activity per site (mol/site s)	
	A	B	A	B	A	B
Rh/TiO_2-SG	4.2	73	1.31	22.7	1.33	23.2
Rh/Al_2O_3-SG	3.3	76	1.0	23.7	0.52	12.0
Rh/TiO_2-RC	1.6	85	0.49	26.5	0.48	25.7
Rh/Al_2O_3-RC	1.5	91	0.46	28.3	0.21	13.3

[a] All catalysts reduced at 450°C; A = without oxygen; B = with oxygen.
[b] Activity at 200°C.

TABLE 4

Influence of Sol–Gel Method on Product Selectivity during Nonselective Reduction of NO by CO

Catalyst	S_{N_2O}[a]	S_{NO_2}[a]	S_{N_2}[a]	S_{N_2O}[b]	S_{NO_2}[b]	S_{N_2}[b]
Rh/TiO_2-SG	39	5	57	36	13	51
Rh/Al_2O_3-SG	32	8	60	38	15	47
Rh/TiO_2-RC	57	10	33	49	27	24
Rh/Al_2O_3-RC	66	9	25	52	29	19

[a] Without oxygen.
[b] With oxygen.

The selectivity to N_2 at low temperature (200°C) shown by sol–gel rhodium catalysts supported on titania and alumina in the reduction of NO by CO, with and without oxygen, was higher than reference catalysts (27, 28) (Table 4). Moreover, the selectivity to N_2 of sol–gel rhodium supported on titania (Rh/TiO_2-SG) with oxygen was better (51%) that when was supported on alumina (47%), but in the reaction without oxygen, this catalyst (Rh/Al_2O_3-SG), was more active for N_2 formation (60%), therefore, there is also an effect of the support over selectivity (Table 4).

Therefore, use of the sol–gel method for developing catalysts provides interesting results, since it offers an enormous potential for obtaining new materials with specific properties difficult to obtain by others methods; for instance, the results presented in this work show that in the nonselective reduction of NO by CO at low temperature with oxygen, the sol–gel preparations were considerably more active than reference catalysts; the same behavior was observed in the selectivity of reaction products, since the sol–gel catalysts are more selective to N_2 than reference catalysts. Finally, the high activity showed for the sol–gel rhodium catalysts in the reduction of the NO by CO in oxygen could be in its application in environmental catalysts, specially in the wash coat monoliths of catalytic converters.

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