

Activity of Ru/Fe₂O₃ Catalysts in the Process of NO Reduction with Propane

A. Basińska¹, T. Machej², F. Domka^{1*}, J. Janas²

¹Department of Kinetics and Catalysis, Faculty of Chemistry, Adam Mickiewicz University,
ul. Grunwaldzka 6, 60-780 Poznań, Poland

²Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek 1, 30-239 Kraków, Poland

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Abstract

The activity of supported ruthenium catalysts (Ru/Fe₂O₃) in the reaction of NO reduction with propane was studied. The iron oxides used as support of the ruthenium phase differed only in the type of oxide-hydroxide (α -, β -, γ -, δ -FeOOH) used in synthesis of the support. It has been established that the precursor Fe₂O₃ determined the activity of the catalysts studied in the process of NO reduction with propane. It has been shown that the catalysts Ru/Fe₂O₃ precipitated on the properly prepared iron oxide permit obtaining high NO conversion at temperatures from 400 to 500°C in reducing conditions.

Keywords: NO reduction, Ru/Fe₂O₃ catalysts

Introduction

Increasing air pollution with nitrogen oxides emitted during fuel combustion in industrial installations and motor vehicles has become a source of serious environmental problems [1,2] and has stimulated much effort towards its minimisation. One of the most effective solutions proposed has been to treat exhaust emission gases using catalysts [3]. The process requires the catalysts characterised by high activity and selectivity, resistant to poisons and working in a wide range of temperatures.

In this study the Ru/Fe₂O₃ catalysts, known to be successful in the water-gas-shift reaction [4], and made of components known to be active in nitrogen oxide reduction [3, 5], have been tested. In these catalysts iron oxides of different origin were applied as supports of the ruthenium phase. The reducing agent applied was propane, which, along with ammonia [6-9], CO [10-17] and

hydrocarbons [18-25] was expected to be an attractive and less aggressive reducing agent.

Experimental

Catalyst Preparation

The iron oxides used as supports for the Ru/Fe₂O₃ catalysts were obtained from iron oxide-hydroxides of α -, β -, γ - and δ -FeOOH types as follows [26].

α -FeOOH was obtained by aging freshly precipitated ortho-iron hydroxide (precipitation by ammonia from a solution of Fe(NO₃)₃ · x 9H₂O) in 1M solution of NaOH.

β -FeOOH - by oxidation of a solution containing FeSO₄ · x 7H₂O and NH₄F in the air (24h),

γ -FeOOH - by oxidation of Fe(OH)₂ precipitated from a solution of FeSO₄ · x 7H₂O with ammonia in the air (3h),

δ -FeOOH - by oxidation of Fe(OH)₂ precipitated from a solution of FeSO₄ · x 7H₂O with a solution of NaOH by a 15% solution of H₂O₂.

*Corresponding author

The precipitates of iron oxide-hydroxides were washed out to eliminate the accompanying ions and dried. Then they were subjected to 3-hour calcination at 600°C at air atmosphere. The supports were labelled as α , β , γ and δ respectively. The symbols assumed in the work do not refer to the phase composition of the support. The ruthenium catalysts, 2% Ru/Fe₂O₃, which showed the greatest differences in activity, were prepared by incipient wetness impregnation of the supports α , β , γ and δ with solution of RuCl₃ in acetone and then activation at 400°C for 3 hours in the air atmosphere. These catalysts were labelled as Ru/ α , Ru/ β , Ru/ γ and Ru/ δ .

Catalyst Characterisation

The porous structure and surface area of the catalysts were determined by the method of low-temperature nitrogen adsorption on an ASAP 2010 sorptometer (Micromeritics USA).

Temperature programmed reduction (TPR_{H₂}) was carried out in hydrogen. Measurements of TPR_{H₂} were performed in Micromeritics Chemisorb 2705 apparatus using the reduction mixture of 10% H₂ + 90% Ar. The rate flow of the gas was 60 cm³/min. The TPR_{H₂} measurements were performed from RT to 900°C at the linear temperature increase of 20°C/min. The catalyst samples were taken in the amount of about 0.05 g.

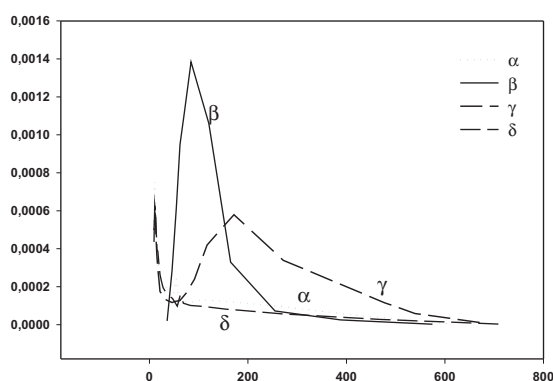


Fig. 1. Pore volume distribution in the iron oxide supports obtained by calcination of α -, β -, γ - and δ -FeOOH (α , β , γ and δ).

Catalytic Reaction

The reaction of NO reduction with propane was conducted in a flow-through quartz microreactor coupled with a gas chromatograph. The catalyst in the portion of 0.5 cm³ and mesh size 0.5-0.2 mm was placed in the microreactor and its activity was studied in the range 250 - 500°C (every 50°C), in the stationary state reached after 1h. The reaction mixture composed of 0.1% mol NO, about 0.25% mol propane and 1.2 - 1.6% mol oxide [see: Tables 2 and 3] was introduced into the reactor at a volume rate of 10,000 h⁻¹.

Results and Discussion

In an earlier study on phase transitions in α -, β -, γ -, δ -oxide-hydroxides it was established that the products of iron oxide-hydroxides type α -, β -, γ -, δ -FeOOH calcination at 600°C, used as supports, are composed of the α -Fe₂O₃ phase with traces of Fe₃O₄ [27]. The freshly made Ru/Fe₂O₃ catalysts on these supports preserve their phase composition after impregnation with ruthenium and after thermal activation. The textural characteristics of the catalysts and supports tested is given in Table 1.

The surface area of the pure supports varies from 19 to 31 m²/g and is the greatest for the supports obtained from β - and γ -FeOOH. Moreover, the oxides based on β - and γ -FeOOH are characterised by a great contribution of larger pores, whose maximum radius is 100Å and 200Å, respectively, (Fig. 1).

The deposition of ruthenium on these oxides has practically no effect on their surface area (Table 1).

The pore volume distribution of the supports based on α - and δ -FeOOH are similar and their maximum is in the range close to micropores. The deposition of ruthenium also does not result in significant changes in the pore volume distribution. In conclusion, the supports based on β - and γ -FeOOH are characterised by greater surface area and greater pore size (Fig. 1), whereas those based on α - and δ -FeOOH ensure greater dispersion of the supported ruthenium phase (Fig. 3) [29]. Taking into regard the fact that in the process of NO reduction with propane a partial reduction of the iron oxides and the catalysts Ru/Fe₂O₃

Table 1. Characterisation of the iron oxide supports and Ru/Fe₂O₃ catalysts.

Preparation	Surface area [m ² /g]	Mean radius of pores [Å]	Total volume of pores [cm ³ /g]
α	22	31	0.06
β	30	100	0.15
γ	31	42	0.17
δ	19	63	0.05
Ru/ α	17	31	0.05
Ru/ β	32	91	0.14
Ru/ γ	33	40	0.16
Ru/ δ	20	34	0.05

can be expected, they have been tested in the thermally programmed reduction with hydrogen (TPR_{H₂}). The results are given in Figs. 2 and 3.

The reduction profiles of pure iron oxides type δ , α , γ in hydrogen differ by the number of maxima on the TPR

curves and the reduction of Fe₂O₃ begins in them at the temperatures 330°C, 340°C and 360°C. Only for the support based on β -FeOOH is reduction slower and begins at 480°C, and clear maximum appears at 562°C. The maxima of iron oxide reduction observed on the TPR_{H₂}

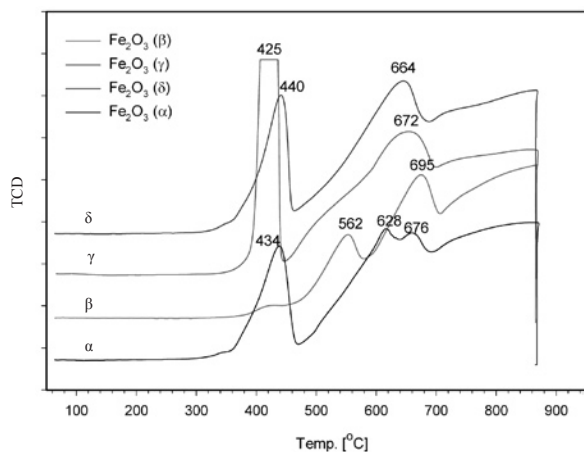


Fig. 2. TPR_{H₂} profiles recorded for Fe₂O₃ supports obtained from α -, β -, γ - and δ -FeOOH.

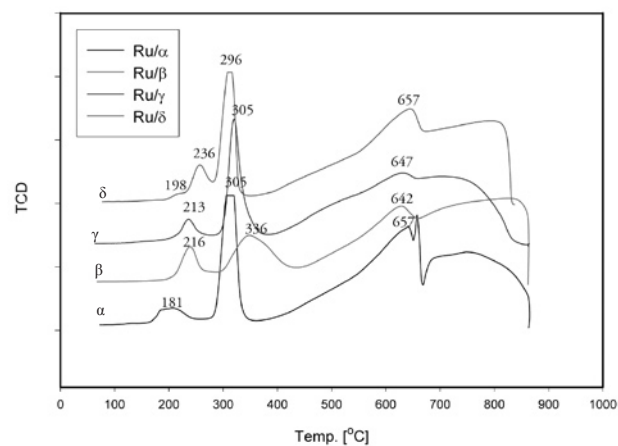


Fig. 3. TPR_{H₂} profiles recorded for the catalysts Ru/ α , Ru/ β , Ru/ γ , Ru/ δ .

Table 2. The degree of NO reduction with propane in the reactions taking place in different conditions in the presence of iron oxide supports obtained from α -, β -, γ - and δ -FeOOH.

Catalyst	Reaction temp. [°C]	Conversion of NO (K _{NO}) [% mol]						
		Strongly reducing conditions		Mild reducing conditions		Oxidising conditions *		
		η_{O_2}	K _{NO}	η_{O_2}	K _{NO}	η_{O_2}	K _{NO}	
α	500	0.78	39.9	0.882	0	1.20	0	
	450		0		0		2.5	
	400		1.0		0		5	
	350						śl	
	300				(0)		0	
β	500	0.60	32.5	0.793	0	1.04	0	
	450		0		0		0	
	400		0		3.5		3.5	
	350				0		2.5	
	300				0			
γ	500	0.68	100	0.833	4.5	1.09	0	
	450		0		0		2	
	400		3		3.5		3	
	350				4.8		0	
	300				3.5			
δ	500	0.58	95.6	0.86	78.3	1.13	0	
	450		5		31.3		18.8	0
	400				20.0		3.5	3.5
	350						0	2.0
	300						0	

η_{O_2} – the ratio of the real oxygen concentration to the oxygen concentration necessary for total combustion of propane in the mixture.
 * In the absence of the reducing agent NO is oxidised to NO₂ (the maximum of 21% at 450°C), at lower temperatures the selectivity of NO conversion to N₂O increases (for K_{NO} below 10% mol., S_{N₂O} takes 88-75% mol.)

Table 3. The degree of NO reduction with propane taking place in different conditions in the presence of Ru/Fe₂O₃ catalysts supported on iron oxide of different origin.

Catalyst	Reaction temp. [°C]	Conversion of NO (K _{NO}) [% mol]						
		Reducing conditions		Neutral conditions		Oxidising conditions		
		η _{O₂}	K _{NO}	η _{O₂}	K _{NO}	η _{O₂}	K _{NO}	
2%Ru/α	500	0.75	100	1.0	100	1.05		
	450		100				100	
	400		100				100	
	350		<1				58.3	14.5
	300		disact.				3.0	3.5
	250		disact.					2.5
2%Ru/β	500	0.66	100	1.0	93.2	1.05	3.2	
	450		100		70.6			
	400		100		25.6			
	350		44.4		3.5			
	300		9.1		6.0			
	250		0					
2%Ru/γ	500	0.75	100	1.0	100	1.05	100	
	450		100		100		14.0	
	400		100		24.1		29.5	
	350		40.9		19.0		24.1	
	300		13.4		14.6		14.0	
	250		0		0		0	
2%Ru/δ	500	0.75	100	1.0	100	1.05	9.8	
	450		100		95.0		33.0	
	400		74.9		0		12.5	
	350		10.0		0		0	
	300		3.5		0			
	250		0					

η_{O₂} – the ratio of the real oxygen concentration to its concentration necessary for total combustion of propane in the mixture.

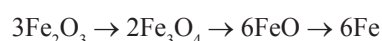
Table 4. Catalytic decomposition of NO on the α support and the 2%Ru/α catalyst.

Reaction temp. [°C]	Support α		Catalyst 2%Ru/α	
	K _{NO} [% mol.]	S _{N₂O} [% mol.]	K _{NO} [% mol.]	S _{N₂O} [% mol.]
500	8.65	0.0	9.6	traces
450	21.0	2.3	13.6	7.3
400	11.6	45.6	32.65	4.9
350	10.0	88.2	52.5	3.6
300	4.95	75.3	63.6	2.5

K_{NO} – conversion of NO

S_{N₂O} – selectivity to N₂O

profiles can be explained assuming that the reduction process takes place according to the scheme [28]:



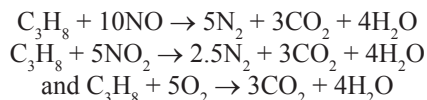
The deposition of ruthenium on the iron oxide supports drastically changes the reduction profiles (Fig. 3).

The maxima assigned to particular iron oxides are shifted towards lower temperatures. The other maxima appearing above 600°C can be interpreted as corresponding to continuing reduction to FeO or Fe, which means that the Ru/Fe₂O₃ catalysts show a greater susceptibility to reduction of iron oxides caused by the presence of ruthenium.

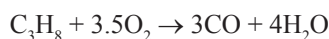
The maxima observed in the range 180-216°C, are as-

signed to reduction of ruthenium oxides [28] and their position depends on the degree of ruthenium dispersion [29]. It is understandable that the greater ruthenium dispersion the lower the temperature of reduction.

At the next stage, the performance of the iron oxide supports and the corresponding ruthenium catalysts (Ru/Fe₂O₃) was tested in the reaction of NO reduction with propane. The strong process was conducted in the reducing (strong or mild reducing conditions), neutral and oxidising atmosphere. In these conditions the following alternative courses of the reaction were considered [25]:



Moreover, in the conditions of oxygen deficit the formation of CO according to the following reaction cannot be excluded:



As follows from the results presented in Table 2, the iron oxide supports in strongly reducing conditions become active only at 500°C. The degree of their activity is correlated with the reducibility of the iron oxides. Below 500°C the activity of the iron oxides type α , β and γ rapidly decreases, especially in mild reducing conditions. At higher temperatures only the support based on δ -FeOOH preserves its catalytic properties. In the oxidising conditions the degree of NO reduction with propane is very low.

As follows from the data presented in Tables 2 and 3, the deposition of ruthenium on iron oxides of different origin significantly changes the catalysts activity relative to the activity of pure iron oxides. The degrees of NO reduction with propane obtained for the ruthenium catalysts are given in Table 3.

In the reducing conditions, between 400 and 500°C, the NO conversion on ruthenium catalysts supported on the α , β and γ types iron oxides takes place 100%. Below 400°C their activity considerably decreases. Moreover, the Ru/Fe₂O₃ catalysts are active in the NO reduction with propane in a range of much lower temperatures than that of the activity of pure supports. The latter observation in particular refers to the reducing atmosphere.

The most effective supports used for synthesis of effective Ru/Fe₂O₃-type catalysts proved the iron oxides based on β - and γ -FeOOH, which by themselves are not very active in this reaction. The tests performed in the oxidising conditions, i.e. above $\eta=1.05$, have shown very low or zero activity, e.g. for the catalyst 2% Ru/A at $\eta=1.1$ and at 500°C, K=0%, at 450°C K=7,4%; for the catalyst 2% Ru/C at $\eta=1.1$ and at 500°C, K=8,0%.

To complete the analysis of the catalytic conversion of NO, its decomposition was studied without the reducing agent, on the support α and the catalysts Ru/ α , the results are presented in Table 4. The process of de-

composition taking place in temperatures 300–450°C on the pure support leads mainly to N₂O, which disappears from the reaction products with increasing temperature. The NO conversion on the Ru/Fe₂O₃ catalyst is different. With increasing temperature of the reaction, the degree of NO conversion decreases and the reaction products begin to show the presence of small amounts of N₂O. This fact implies that in these conditions the dominant reaction is NO oxidation. On the pure support only in high temperatures the NO oxidation reaction rate begins to be higher than the rate of the NO decomposition to N₂O. A comparative analysis of the results of the catalytic performance of the pure support and the ruthenium catalyst indicates that ruthenium increases the rate of NO oxidation to NO₂ but has no effect on the NO reduction to N₂O. In general, a certain correlation has been noted between the iron oxides activity in the NO reduction with propane and their susceptibility to reduction. The iron oxides which are more easily reducible are more active in the reaction of the reduction studied. The deposition of ruthenium increases the catalytic properties of the Ru/Fe₂O₃ catalysts. This increase can also be related to different acid-base properties of the iron oxides studied [30], affecting ruthenium dispersion and electron density of the supported ruthenium.

As follows from the above-presented results, the Ru/Fe₂O₃ catalysts show high activity in the process of NO reduction with propane. The use of appropriate iron supports permits preparation of the optimum and effective catalysts that can be applied in different conditions.

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