

CATALYSIS AND ENVIRONMENTAL
PROTECTION

Selective Reduction of Nitrogen Oxides by Hydrocarbons on Hydrotalcite Co and Ni Catalysts

V. F. Tret'yakov^{a*}, A. G. Zakirova^a, A. A. Spozhakina^b,
M. V. Gabrovska^b, R. Edreva-Kardzhieva^b, and L. A. Petrov^c

^a Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

^b Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria; SABIC Chair in Catalysis, King Abdulaziz University, Jeddah, Saudi Arabia

^c SABIC Chair in Catalysis, King Abdulaziz University, Jeddah, Saudi Arabia

*E-mail: tretjakov@ips.ac.ru

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Abstract—Hydrotalcitelike Co–Al and Ni–Al catalysts of different compositions (with the atomic ratio $M^{2+}/Al^{3+} = 0.5–3.0$) were studied in the reaction of selective reduction of NO by propane, propylene, and *n*-decane in the presence of O₂. The higher activity of the catalysts with $M^{2+}/Al^{3+} = 0.5$ is connected with high dispersity of Ni or Co cations stabilized by a significant amount of Al³⁺ ions. Propylene was shown to be the most efficient reducing agent for nitrogen oxide. The highest degree of conversion to the extent of 90–99% was attained at 400 and 420–440°C for Ni–Al and Co–Al samples, respectively. When propane and decane were used as reducing agents, the conversion of both catalysts was characterized by the volcano-shaped dependence on temperature due to the fact that the catalyst took part in the concurrent reaction of hydrocarbon (reducing agent) oxidation. Hydrotalcitelike materials are promising representatives of inexpensive bi- and multicomponent systems. The design strategy for new active catalysts for processes of purification of gas exhausts from NO_x, that are stable in the presence of water and sulfur oxides, may be based on usage of hydrotalcites with modified ions introduced into them.

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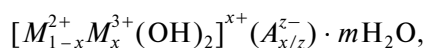
INTRODUCTION

Protection of air from pollutants, among them nitrogen oxides (NO_x) is a problem for modern society, which is gaining urgency. Nitrogen oxides have a negative effect on human beings and the environment [1, 2]. Automobile transport and heat power plants are the main sources of NO_x emissions.

Many ways to reduce NO_x concentration in gas emissions are known. Hydrogen, carbon oxide, ammonia or urea, methane, and even diesel fuel are used as reducing agents. CH–SCR NO_x—the selective catalytic reduction of NO_x by hydrocarbons, which typically are present in products of incomplete combustion of hydrocarbon fuels is of particular interest. Propane, propylene, and *n*-decane are commonly used as reducing agent hydrocarbons in simulating the composition of exhaust gases of gasoline and diesel engines. Various catalysts are utilized in processes of reduction of nitrogen oxides, namely, simple and complex oxides, zeolites, montmorillonite pillar clays and transition metals applied on them [1, 3–9].

Multicomponent catalysts prepared using hydrotalcitelike (HTL) materials that are also called layered double hydroxides or anionic clays and represent a novel class of synthetic layered materials are of intense

interest. Generally, the formula of HTL materials appears as:



where M^{2+} stands for Mg²⁺, Ni²⁺, Zn²⁺, Co²⁺, Cu²⁺ ...; M^{3+} stands for Al³⁺, Fe³⁺, Ga³⁺, ...; and A^{z-} stands for CO₃²⁻, NO₃⁻, Cl⁻, ...

Some of them are widespread in nature in form of minerals, such as hydrotalcite Mg₆Al₂(OH)₁₆CO₃ · 4H₂O, takovite, Ni₆Al₂(OH)₁₆CO₃ · 4H₂O, pyroaurite Mg₆Fe₂(OH)₁₆CO₃ · 4H₂O, reevesite Ni₆Fe₂(OH)₁₆CO₃ · 4H₂O, etc. [10–13].

Hydrotalcites are characterized by nanodimensionality of crystallites and homogeneous distribution of cations within the layers. Under calcination, hydrotalcites transform into highly disperse, thermally stable mixed oxides of nonstoichiometric composition with a developed surface, that allows one to use them in catalysis [14–16], in particular, in catalytic reduction of NO_x to N₂ [17, 18].

It has been shown [19, 20] that HTL materials containing Cu, Mg, and Al are potential catalyst precursors, which are active in reactions of decomposition and reduction of NO_x with propane.

Physicochemical parameters of the samples

Samples	Content of M^{2+} oxide, wt %	After drying at 80°C			After calcination at 550°C		
		S_{sp} , m ² /g	XRD	L_{TL} , nm	S_{sp} , m ² /g	XRD	L_{MO} , nm
Co–Al-0.5	CoO – 42.1	89	TL + G*	11	189	Co ₃ O ₄	5
Co–Al-1.5	CoO – 68.8	60	TL	12	136	Co ₃ O ₄	8
Co–Al-3.0	CoO – 81.3	29	TL	16	87	Co ₃ O ₄	12
Ni–Al-0.5	NiO – 42.3	102	TL + G	–	206	NiO*	–
Ni–Al-1.5	NiO – 68.7	91	TL	4	154	NiO*	–
Ni–Al-3.0	NiO – 81.5	71	TL	7	133	NiO	4

Notes: G is gibbsite, L_{TL} is the size of TL-particles, and L_{MO} is the size of oxide particles.

* Amorphous phase.

During the catalytic decomposition of N₂O, calcined Ni–Al–CO₃ HTL samples with $M^{2+}/M^{3+} = 3$ were proved to be more active compared with the corresponding Co- and Cu-containing hydrotalcites. However, the activity of hydrotalcite Co–Al and Cu–Al catalysts in the reaction specified was higher than that for ZSM-5-based zeolite Co, Cu catalysts [21, 22].

This work was aimed at the utilization of hydrotalcitelike Co–Al and Ni–Al catalysts of different compositions in the reaction of selective reduction of NO_x by propane, propylene, and *n*-decane.

EXPERIMENTAL

For preparation of the catalysts, we used reagents of analytical grade. Hydrotalcitelike Co and Ni samples were prepared by coprecipitation from the solutions of corresponding nitrates: Co(NO₃)₂ · 6H₂O, Ni(NO₃)₂ · 6H₂O, and Al(NO₃)₃ · 9H₂O (with the total concentration of metals in the solution of 0.5 M) and solution of nonaqueous Na₂CO₃ (concentration 0.9 M) at 80°C and pH = 8. A feed rate of nitrate solution of 1 dm³/h was maintained constant. The Na₂CO₃ solution was introduced into the system so that the pH value remained constant. After 1 h, the resultant precipitate was filtered and washed with distilled water at 90°C until the negative reaction to nitrate ions. The content of Na₂O in the precipitation obtained was less than 0.2 wt %. The samples of Co- and Ni-containing catalysts were being dried for 20 h at 80°C and calcined for 2 h at 550°C.

In general form, the catalysts can be presented as M –Al– x , where $M = \text{Co or Ni}$, and x is M^{2+}/Al^{3+} atomic ratio, which varies over a range of 0.5–3.0.

The precipitate composition was determined by atomic adsorption spectroscopy after the precipitate had been dissolved in HCl (in a 1 : 1 proportion) using a Perkin Elmer 360 spectrophotometer.

X-ray diffraction analysis (XRD) of the samples was performed on a TUR-M 62 powder diffractometer using CoK_α-radiation ($\lambda = 179.026$ pm). The phases were identified when compared to the JCPDS

database standards. Crystallite sizes were calculated according to the Scherrer equation using software [23]. We used the most intensive reflexes with indices (003) and (006) for tacovitelike (TL) phases in noncalcined systems, (200) for NiO and (311) for Co₃O₄ for calcined systems.

The catalyst surface was determined based on N₂ adsorption using the single-point method. The samples were preliminarily dried for 16 h at 105°C. The measurement error was less than 10%.

The activity of samples (that were precalcined at 450°C in nitrogen flow for 1 h) in SCR NO_x reaction was determined on a continuous-type setup over the range of 50–500°C at volume rate of gas flow of 11200 h⁻¹ (the catalyst volume was 0.8 cm³).

Propane, propylene, and *n*-decane were used as reducing agents. The composition of the initial gas mixtures was as follows (vol %): NO—0.13, C₃H₈—0.08, O₂—2.0, N₂—up to 100; NO—0.13, C₃H₆—0.11, O₂—2.0, N₂—up to 100; NO—0.13, *n*-C₁₀H₂₂—0.05, O₂—8.5, N₂—up to 100.

The content of NO in the gas mixture at reactor inlet and outlet was determined using a Testo-33 electrochemical gas analyzer (Germany) with accuracy up to 1 (10⁻⁴%).

The model gas mixtures used were close to the composition of exhaust gases of diesel fuels.

RESULTS AND DISCUSSION

Physicochemical characteristics of samples. The table lists physicochemical parameters of the samples. As seen, the specific surface (S_{sp}) of synthesized catalysts after the drying procedure depends on the nature and content of a two valent cation. Under the same M^{2+}/Al^{3+} ratio, Co–Al samples have less developed surface as compared with Ni–Al. The difference can be explained (based on XRD results) by different crystallinity of the TL phase. Thus, in the Co–Al-0.5, two phases can be identified: explicitly apparent reflexes of TL phase (JCPDS file 15-0087) with 11-n crystallites and weak reflexes of gibbsite (G) (JCPDS file

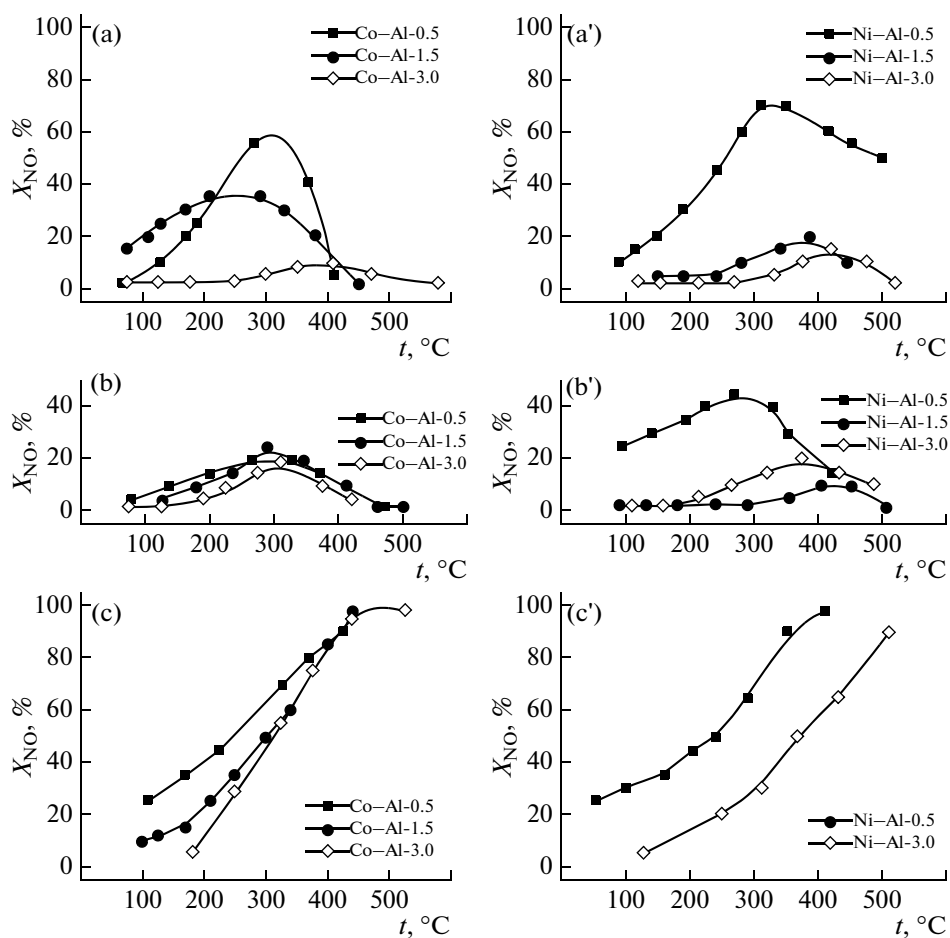


Fig. 1. Temperature dependences of the NO conversion in the reaction CH-SCR NO_x by (a, a') propane, (b, b') *n*-decane, and (c, c') propylene on (a, b, and c) Co-Al and (a', b', and c') Ni-Al catalysts.

33-00178). On the diffraction pattern of Ni-Al-0.5 the gibbsite phase is also registered, however, TL reflexes are very weak. The lower crystallinity of TL-Ni impedes the determination of particle size and stipulates the higher developed surface. The crystallinity of the TL phase grows (crystallite size increases to 16 nm) with increasing Co content in the samples, which is accompanied by a decrease in the specific surface. Meanwhile, the gibbsite phase is not registered. A similar pattern is observed in the case of Ni-Al samples, where the TL phase in Ni-Al-1.5 and Ni-Al-3.0 samples has lower crystallite sizes (4 and 7 nm, respectively). That indicates that the dispersity of nickel is higher than that in Co-Al analogs by a factor of 2–3.

After calcinations, the surface of all samples increases significantly, and for Ni-Al samples it increases to a larger extent. This effect is associated with the decomposition of the TL phase and CO₂ and H₂O emission, the formation of mixed metal oxides and formation of micro- and mesopores [25]. As cobalt and nickel concentration in the samples increases, the specific surface decreases simulta-

neously with the growth of oxide crystallites. Co₃O₄ (JCPDS file 09-0418) and NiO (JCPDS file 4-850) phases were ascertained in Co- and Ni-containing catalysts, respectively, while the Al₂O₃ phase does not emerge in all the samples, probably, due to its amorphous state. The Co₃O₄ phase with 5 nm crystallites was observed in Co-containing samples even at low Co content (Co-Al-0.5). When cobalt content is increased (Co-Al-3.0), the crystallite size goes up to 12 nm. Ni-containing samples show lower crystallinity compared to Co-analogs both after drying and calcinations, which impedes the determination of crystallite sizes for the NiO phase in Ni-Al-0.5 and Ni-Al-1.5 samples with low Ni content. Only in the Ni-Al-3.0 sample the NiO phase with nanosized (4 nm) particles is registered. A trend toward the formation of higher dispersity of Ni-containing phase remains after drying, similar to the TL samples. The higher dispersity supposes the greater number of active sites on the surface of samples.

Catalytic activity. The temperature dependences of the conversion of nitrogen oxide (X_{NO}) under reduc-

tion by hydrocarbons on Co- and Ni-containing hydrotalcite catalysts are shown in Fig. 1.

In CH-SCR NO, by propane on all catalysts the temperature dependences of NO conversion are characterized by the volcano-shaped maximum, whose height depends on the content of active component (Figs. 1a, 1a'). Ni(Co)-Al-0.5 show the highest activity. The maximum degree of NO conversion at 300°C attains 70% and 55% on Ni- and Co-containing catalysts, respectively. The conversion of nitrogen oxide decreases with increasing cobalt and nickel contents, so that it is lower than 10% on the Co-Al-3.0 sample.

When using *n*-C₁₀H₂₂ (decane), all cobalt samples have low and almost identical activity in NO conversion. The volcano-shaped curves with the maximum of degree of conversion ($X_{\text{NO}} = 20\text{--}25\%$) at 280–320°C are observed (Fig. 1b).

In the case of Ni-containing samples, in the presence of *n*-decane reducing agent, the change in degree of NO conversion is volcano-shaped; however, the temperature corresponding to the maximum changes with the composition (Fig. 1b'). The most active sample, Ni-Al-0.5, attains 42–45% of NO conversion at $t \approx 300^\circ\text{C}$. With nickel content increasing (Ni/Al = 1.5 and 3.0), the activity decreases and becomes comparable with that of cobalt catalysts, the maxima shifting to the high-temperature region (375–400°C).

As seen from the curves presented in Figs. 1c and 1c', when propylene is used as a reducing agent, the highest values of nitrogen oxide conversion are attained on all Co- and Ni-containing samples studied. The degree of conversion at low temperatures below 250°C depends on the cobalt content in the catalyst, being the highest for Co/Al = 0.5 (Fig. 1c). At 420–440°C the activity of the samples becomes even and reaches the maximum values: $X_{\text{NO}} = 90\text{--}99\%$. The degree of nitrogen oxide conversion depends on nickel content in the catalyst for all temperatures of the reaction, being the highest for Ni/Al = 0.5 (Fig. 1c'). The maximum values $X_{\text{NO}} = 90\text{--}99\%$ are attained at 400°C.

The decrease in catalytic activity of the samples at temperatures specified for the case of utilizing propane and decane illustrates the role of reducing agent nature (C₃ and C₄) in SCR [24]. Hydrocarbons with greater number of carbon atoms in a molecule are known to show higher reactivity [27]. That refers both to the activity of hydrocarbons in the reaction of reduction of nitrogen oxides and coke formation. The selective reduction of NO_x by hydrocarbons in the presence of oxygen may be considered as a concurrent reaction of hydrocarbon oxidizing by nitrogen oxide or oxygen [25]. The latter reduces the amount of the reducing agent in the reaction medium by decreasing the activity of samples in SCR reaction for producing N₂. All these factors determine the volcano-shaped dependence of the activity on temperature.

As opposed to propane and decane, for propylene there is no volcano-shaped dependence of the activity on temperature for Co and Ni catalysts: activity increases up to 400°C (probably, due to the low activity of these catalysts in oxidizing of the reducing agent—propylene by oxygen at this temperature with high activity of nitrogen oxide conversion, which follows from [26]).

The higher activity of the catalysts with M^{2+}/Al^{3+} ratio is 0.5 is connected with the high dispersity of Ni- or Co-containing mixed oxides. This effect appears more explicitly for the Ni-Al-0.5 sample.

With increasing content of Ni²⁺ and Co²⁺ ions, the size of transition metal oxides increases, with corresponding decrease in the dispersity of the active phase, and, therefore, the number of active sites, which leads to the decrease in activity of the samples under investigation in CH-SCR NO_x reaction.

The further rising of the catalyst activity may be attained by the introduction of various modifying ions into hydrotalcite.

Therefore, being the inexpensive bi- and multi-component systems after modifying additives are introduced into them by various methods, HTL materials are promising for the design of new active highly disperse catalysts.

CONCLUSIONS

(1) The examination of the activity of Co- and Ni-containing hydrotalcite catalysts, which were coprecipitated in the model reaction mixture close to composition of exhaust gases of diesel engines, has demonstrated the prospectivity of their utilizing in the reaction of selective reduction of nitrogen oxides by hydrocarbons.

(2) Under the same M^{2+}/M^{3+} ratio, coprecipitated Ni-Al samples have the higher developed surface as compared to Co-Al samples. The difference observed can be explained by a lower crystallinity and, therefore, smaller nanocrystallite sizes of Ni-Al samples both in the initial hydrotalcite phase and in mixed oxides after the calcination.

(3) The crystallites grow with nickel and cobalt content increasing after the drying procedure and during the calcinations stage, which is accompanied by a decrease in the surface area, and, therefore, in dispersity.

(4) The higher activity of catalysts with $M^{2+}/\text{Al}^{3+} = 0.5$ is due to the higher dispersity of Ni- or Co-containing mixed oxides. This effect can be connected with the lower phase sizes, higher dispersity of the active phase, and, as a result, the number of active sites for the conversion of nitrogen oxides.

(5) Propylene is a more efficient reducing agent than propane and *n*-decane. It is probably connected with the low activity of Co-Al and Ni-Al catalysts in the concurrent reaction of oxidizing the reducing

agent (propylene) by oxygen in the temperature range under examination.

(6) Tacovitellike Ni–Al materials (with Ni/Al = 0.5) have been recommended as promising catalysts in CH–SCR NO_x reaction at 350–400°C.

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