

Comparative Study of the Oxygen Storage Capacity of Pt/M_xO_y/Al₂O₃ Systems

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Abstract—The oxygen storage capacity of 1% Pt/15% M_xO_y/Al₂O₃ systems containing a rare-earth or an alkaline-earth metal oxide or TiO₂ as the oxygen-storing component was studied. Oxygen storage capacity was evaluated as the amount of C₃H₈ reacting at 400°C with oxygen that was taken up by the catalyst during oxidative treatment. The systems containing a rare-earth metal oxide or TiO₂ possess the highest oxygen storage capacity among the catalysts examined (80 and 75 μmol C₃H₈/g Cat, respectively). Of the BaO and SrO systems, the latter is of interest, although its oxygen storage capacity (~27 μmol C₃H₈/g Cat) is somewhat lower than the oxygen storage capacity of any rare-earth metal oxide or the TiO₂ system.

The conversion of C₁–C₃ paraffins into valuable products by partial oxidation is one of the challenging problems of heterogeneous catalysis. Along with the search for new selective and active catalysts, an interesting approach to this problem is the conduction of heterogeneous catalytic processes under unconventional conditions, including hydrocarbon oxidations in which reactants are alternately admitted to the catalyst. In conventional processes, both oxygen and hydrocarbon are present in the gas phase, causing branching free-radical oxidation that rapidly yields complete combustion products. By contrast, the alternating admission of air and a hydrocarbon allows one to oxidize the hydrocarbon with oxygen stored in the catalyst, in the absence of gaseous O₂, thereby substantially enhancing the selectivity of the reaction [1].

In the oxidative dehydrogenation of propane, propylene selectivity can be increased by a factor of 3 (from 30 to 90%) by changing from the simultaneous (continuous) feeding of the reactants to alternating (periodic) feeding [2].

Oxidative dehydrogenation of methane into heavier hydrocarbons [3], oxidative dehydrogenation of propane into propylene [2], and butane oxidation to maleic anhydride [4] are candidate processes to be conducted in the alternating-feed regime.

Note that passing to this regime will markedly decrease the process rate.

The main factor responsible for the decrease in the process rate is the insufficient amount of lattice oxygen capable of reversibly leaving the catalyst surface or, in other words, the low oxygen storage capacity of the catalyst. Oxygen capacity determines the amount of hydrocarbon that can be converted in one redox cycle, so that increasing this parameter is an urgent task.

The problem of enhancing the oxygen storage capacity of a selective oxidation catalyst can possibly

be solved by introducing an oxygen-storing component into the catalyst. Oxides of metals that are capable of changing their oxidation state depending on the composition of the reaction medium can serve as an oxygen-storing component.

Here, we present a comparative study of catalytic systems containing various metal oxides as O₂-storing components. The purpose of this study is to find the system with the largest amount of stored oxygen capable of reversibly reacting with hydrocarbons.

Ceria is a classical oxygen-storing component. In view of this, CeO₂ is widely used as an oxygen buffer in three-way catalysts for exhaust gas neutralization [5]. Note that the oxygen storage capacity of other rare-earth metal oxides has received little attention [5, 6]. In view of this, we attempted to estimate this parameter for La, Pr, and Nd oxides.

Other O₂-storing components tested in this study are alkaline-earth metal oxides, which are interesting for their capacity for forming peroxides [7, 8]. These compounds are appropriate oxygen sources for selective oxidation processes [9].

Titanium(IV) oxide is of interest as a catalyst component since it possesses catalytic properties and is capable of storing oxygen.

The oxygen capacity of catalysts is evaluated by various methods, including determination of the amount of oxygen chemisorbed on the surface of a pre-reduced sample [10], measurement of the amount of CO reacted with oxide oxygen in a pulsed regime [11, 12], and temperature-programmed reduction with hydrogen [10, 12, 13] or carbon monoxide [14].

In this work, the amount of oxygen reactive toward hydrocarbons was estimated by measuring the amount of C₃H₈ reacted with oxide oxygen in a pulsed regime.

EXPERIMENTAL

Preparation of Catalysts

To promote propane oxidation, Pt was introduced into the catalysts. The reference catalysts were 1% Pt/Al₂O₃ and 15% CeO₂/Al₂O₃, which were prepared by impregnation of Al₂O₃ ($S_{\text{BET}} = 184 \text{ m}^2/\text{g}$) with an aqueous solutions of H₂PtCl₆ and Ce(NO₃)₃, respectively.

The catalysts 1% Pt/15% M_xO_y/Al₂O₃ (where M = Ce, La, Pr, or Nd) were prepared by the incipient-wetness impregnation of alumina ($S_{\text{BET}} = 184 \text{ m}^2/\text{g}$) with an aqueous solution containing M_x(NO₃)_y and H₂PtCl₆.

The catalysts 1% Pt/15% MO/Al₂O₃ and 1% Pt/15% MO/SiO₂ (M = Ba, Sr) were prepared by impregnating a support (Al₂O₃ or SiO₂; $S_{\text{BET}} = 120 \text{ m}^2/\text{g}$) with an aqueous solution containing H₂PtCl₆ and M(NO₃)₂. A support was suspended in the solution, the resulting suspension was stirred at 50°C for 1 h, and the excess water was removed on a rotary evaporator.

The catalyst 1% Pt/TiO₂ was prepared by impregnation of TiO₂ ($S_{\text{BET}} = 85 \text{ m}^2/\text{g}$) with an aqueous solution of H₂PtCl₆.

Pt/TiO₂/Al₂O₃ systems containing 1 wt % Pt and various amounts of Ti (10, 15, or 20 wt %) were prepared in two steps:

(1) impregnation of Al₂O₃ with a solution of C₁₂H₂₈O₄Ti in isopropyl alcohol followed by drying and calcination of the dry material in flowing air at 600°C for 2 h;

(2) H₂PtCl₆ impregnation of the TiO₂/Al₂O₃ obtained in the first step.

All catalysts were dried at room temperature in air. Next, they were calcined in flowing air at 600°C for 2 h, with the temperature raised at a rate of 0.5 K/min. The calcined materials were reduced in flowing H₂ at 400°C for 2 h, with the temperature raised at a rate of 2 K/min.

Determination of the Oxygen Capacity of Catalysts

The capacity of catalysts for reversibly storing oxygen was studied using a flow catalytic setup (schematized in Fig. 1) operated in a pulsed regime according to the following procedure:

(1) The sample is exposed to flowing air for 1 h at 400°C. Oxygen is accumulated in the catalyst at this stage.

(2) The sample is treated with flowing N₂ at 400°C for 30 min to remove the dioxygen from the gas phase and the weakly bound oxygen from the catalyst surface.

(3) A 10-s pulse of N₂ containing 5000 ppm C₃H₈ is fed into the reactor.

(4) The reactor is purged with a 20-s pulse of N₂ to remove the reaction products formed at the previous stage.

(5) Stages 3 and 4 are repeated until propane conversion is no longer observed.

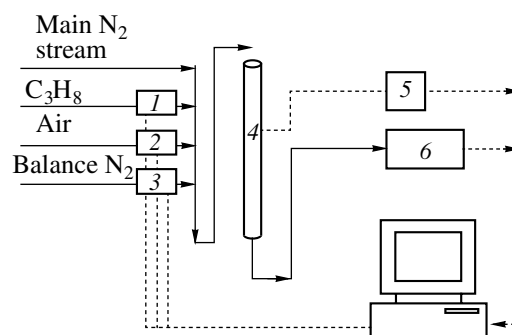
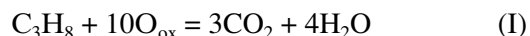


Fig. 1. Schematic of the experimental setup: (1–3) computer-controlled electromagnetic valves, (4) reactor, (5) temperature controller, and (6) C₃H₈ analyzer.

The feed composition was varied by adding propane, air, or nitrogen to the main nitrogen flow using electromagnetic valves 1–3 (Fig. 1). The volume hourly space velocity was 40000 h⁻¹ at all stages, and the catalyst temperature was 400°C.

The catalyst volume was 0.5 cm³. The sample was placed in a quartz reactor with an inner diameter of 7 mm. Outlet propane concentration was determined with a gas analyzer equipped with a flame-ionization detector. The gas analyzer allows one to estimate only the total amount of hydrocarbons in the gas mixture, so oxygen storage capacity was evaluated from total propane conversion.

In view of this, the oxygen stored by the catalyst was quantified by two methods based on the stoichiometry of the most probable reactions of propane, namely, complete oxidation,



and conversion to synthesis gas [15],

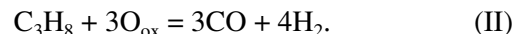


Figure 2 shows a plot of C₃H₈ concentration versus pulse number typical for catalysts pretreated with flowing air at 400°C. The amount of reacted propane decreases rapidly (as indicated by the growing peak concentration of propane in the exit pulse) and reaches zero upon the introduction of approximately ten pulses. The total amount of propane converted during the first ten pulses allows one to evaluate the amount of oxygen capable of leaving the catalyst surface upon interaction with a hydrocarbon.

The reproducibility of data and the reversibility of oxygen storage on the catalyst surface were checked by recovering the catalyst with a flowing oxygen-containing mixture and introducing another series of propane pulses into the reactor.

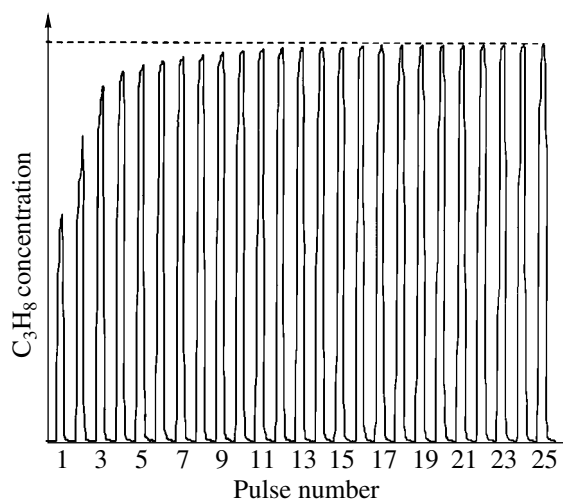


Fig. 2. Propane concentration versus time (number of pulses).

RESULTS AND DISCUSSION

Rare-Earth Oxides

Figure 3 presents oxygen storage capacity data for catalytic systems containing rare-earth oxides. The 1% Pt/Al₂O₃ catalyst was used as the reference.

The oxygen capacity of 1% Pt/Al₂O₃ is 15 $\mu\text{mol C}_3\text{H}_8/\text{g Cat}$. It is obvious that the introduction of a rare-earth oxide significantly increases the oxygen storage capacity of the catalytic system.

Calculated amounts of stored oxygen

Catalyst	Amount of stored oxygen	
	calculated for reaction (I), $\mu\text{mol O}_2/\mu\text{mol M}_x\text{O}_y$	calculated for reaction (II), $\mu\text{mol O}_2/\mu\text{mol M}_x\text{O}_y$
1% Pt/15% CeO ₂ /Al ₂ O ₃	0.373	0.112
1% Pt/15% La ₂ O ₃ /Al ₂ O ₃	0.338	0.101
1% Pt/15% Nd ₂ O ₃ /Al ₂ O ₃	0.339	0.101
1% Pt/15% Pr ₆ O ₁₁ /Al ₂ O ₃	0.268	0.081
1% Pt/10% TiO ₂ /Al ₂ O ₃	0.185	0.056
1% Pt/15% TiO ₂ /Al ₂ O ₃	0.120	0.036
1% Pt/20% TiO ₂ /Al ₂ O ₃	0.087	0.026
1% Pt/15% SrO/Al ₂ O ₃	0.061	0.018

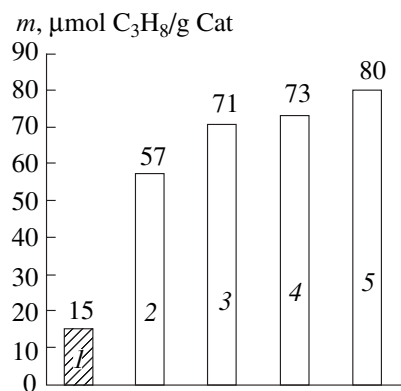


Fig. 3. Oxygen capacity of (1) Pt/Al₂O₃, (2) Pt/Pr₆O₁₁/Al₂O₃, (3) Pt/Nd₂O₃/Al₂O₃, (4) Pt/La₂O₃/Al₂O₃, and (5) Pt/CeO₂/Al₂O₃. *m* is the amount of reacted propane.

The largest amount of reacted propane (*m*) is observed for ceria (80 $\mu\text{mol C}_3\text{H}_8/\text{g Cat}$). La₂O₃ and Nd₂O₃ possess nearly the same oxygen storage capacity ($\sim 70 \mu\text{mol C}_3\text{H}_8/\text{g Cat}$) as CeO₂, which is a classical representative of oxygen-storing oxides. The amount of reacted C₃H₈ for Pr₆O₁₁ is somewhat lower, being 57 $\mu\text{mol C}_3\text{H}_8/\text{g Cat}$.

No propane conversion was observed on the Pt-free specimen 15% CeO₂/Al₂O₃.

The estimated amounts of oxygen stored in the catalysts and oxygen reacted with propane are presented in the table. Note that our estimates well exceed the corresponding values reported previously [5, 16]. For example, it was found in an earlier study [5] that the oxygen storage capacity of the catalyst 0.3% Pt/21.63% CeO₂/Al₂O₃ derived from CO conversion at 400°C in a pulsed regime is 0.017 $\mu\text{mol O}_2/\mu\text{mol CeO}_2$. The amount of stored oxygen estimated from oxygen chemisorption is also well below our data. This value for the system 1% Pt/20% CeO₂/Al₂O₃ was reported to be 0.04 $\mu\text{mol O}_2/\mu\text{mol CeO}_2$ [11].

These discrepancies between our results and previous data are unlikely to be due to the fact that propane is a more active reducing agent than carbon monoxide, since alkanes are less reactive and, as a rule, are oxidized at markedly higher temperatures than CO [11].

Note also that oxygen uptake is due to the metal changing its oxidation state in the oxide (for example, through the reaction $\text{CeO}_2 \rightleftharpoons \text{Ce}_2\text{O}_3$). The theoretical oxygen capacity of the systems examined cannot exceed 0.25 $\mu\text{mol O}_2/\mu\text{mol M}_x\text{O}_y$. The oxygen capacities observed in this work are much greater and range between 0.268 $\mu\text{mol O}_2/\mu\text{mol Pr}_6\text{O}_{11}$ for Pt/Pr₆O₁₁/Al₂O₃ and 0.373 $\mu\text{mol O}_2/\mu\text{mol CeO}_2$ for Pt/CeO₂/Al₂O₃.

It is possible that the overestimated amounts of stored oxygen arise from incomplete propane oxidation. The formation of synthesis gas in our experiments

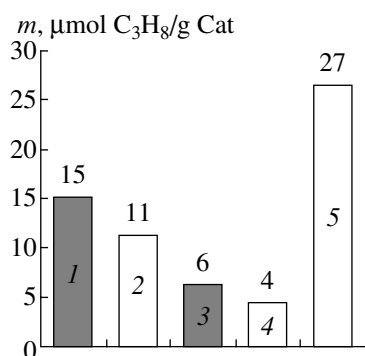


Fig. 4. Oxygen storage capacity of (1) Pt/Al₂O₃, (2) Pt/BaO/Al₂O₃, (3) Pt/SiO₂, (4) Pt/BaO/SiO₂, and (5) Pt/SrO/Al₂O₃. *m* is the amount of reacted propane.

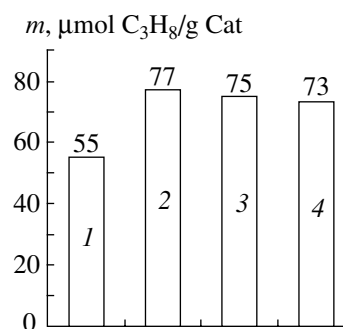


Fig. 5. Oxygen storage capacity of TiO₂ containing systems: (1) Pt/TiO₂, (2) Pt/10% TiO₂/Al₂O₃, (3) Pt/15% TiO₂/Al₂O₃ and (4) Pt/20% TiO₂/Al₂O₃. *m* is the amount of reacted propane.

is most probable, since CO₂, CO, and H₂ cannot be detected with a flame-ionization detector.

The possibility of the conversion of light alkanes into synthesis gas over Pt/CeO₂ under alternating feed conditions was demonstrated in [17, 18].

Considering this source of uncertainty, in order to obtain a more correct estimate of the amount of stored oxygen, we calculated the amount of oxygen reacted with propane to form synthesis-gas (reaction (II)). The values obtained are presented in the table.

These experimental values are in good agreement with the theoretical maximum of stored oxygen (0.25 μmol O₂/μmol M_xO_y), suggesting that, for the catalysts examined, propane oxidation to synthesis-gas dominates over complete propane oxidation.

It follows from the above data that rare-earth metal oxides are promising oxygen-storing components for the alternating-feed oxidation of hydrocarbons.

Alkaline-Earth Oxides

The results of our study of the BaO- and SrO-containing catalysts are presented in Fig. 4. Here, 1% Pt/Al₂O₃ was used as the reference catalyst.

First of all, note that the amount of propane that is oxidized over Pt/Al₂O₃ (15 μmol C₃H₈/g Cat) is much larger than the amount of propane that can be completely oxidized (reaction (I)) by the oxygen adsorbed on platinum. (Calculations were based on the assumption that one Pt atom is capable of adsorbing one oxygen atom.) The calculated value is 5.11 μmol C₃H₈/(g Cat), ~35% of the observed value. At the same time, for Pt supported on SiO₂, the amount of converted propane (6 μmol C₃H₈/(g Cat)) correlates well with the amount of oxygen that can be adsorbed on Pt.

The above experimental data suggest that, over Pt/Al₂O₃, partial propane oxidation (reaction (II)) can occur along with the oxidative dehydrogenation of propane, followed by the formation of condensation products on the catalyst surface [19]. The fact that the catalyst changes from white to black during the reaction is

indirect evidence of the formation of condensation products. Unlike Pt/Al₂O₃, Pt/SiO₂ does not darken or lose activity as it works.

The oligomerization process is likely due to the presence of strong Lewis acid sites on the surface of the Al₂O₃ support [18].

The introduction of BaO into Pt/Al₂O₃ or Pt/SiO₂ decreases the amount of converted propane instead of increasing it. It is likely that BaO both increases the platinum particle size and suppresses the oligomerization processes on Pt/Al₂O₃ by the partial neutralization of Lewis acid sites.

Interesting results were obtained for the SrO-containing system. Unlike barium oxide, strontium oxide is capable of storing oxygen. However, it is somewhat inferior to the rare-earth oxides in terms of oxygen storage capacity. This is likely because of the small extent of the peroxide formation reaction (2SrO + O₂ = 2SrO₂). Calculation of the amount of oxygen stored by strontium oxide shows that at most 12% of the SrO is converted to SrO₂.

It is well known from the literature [16] that BaO₂ is obtained by passing air over BaO at 520°C in the presence of small amounts of water vapor. It is quite likely that barium peroxide did not form under the experimental conditions examined. The formation of SrO₂ was observed at a lower temperature of 400°C [16], which is in agreement with the results of the present study.

Titanium(IV) Oxide

According to our data (Fig. 5), the catalysts containing TiO₂ have a high oxygen storage capacity comparable to that of the rare-earth oxides. Note that the deposition of TiO₂ on Al₂O₃ increases the amount of converted propane over that observed for Pt/TiO₂. It is possible that this effect arises from the buildup of reactive oxygen due to TiO₂ dispersion.

For all specimens examined, the amounts of reacted oxygen calculated for reactions (I) and (II) do not exceed the amount of oxygen that can be stored owing

to the transition $\text{Ti}^{3+} \rightleftharpoons \text{Ti}^{4+}$. The values obtained for the specimens containing 10, 15, and 20 wt % TiO_2 (table) are, respectively, 74, 48, and 35% of the stoichiometric value corresponding to the complete transition $\text{TiO}_2 \rightleftharpoons \text{Ti}_2\text{O}_3$ ($0.25 \mu\text{mol O}_2/\mu\text{mol TiO}_2$).

This decrease in the relative amount of stored oxygen with an increase in the TiO_2 content of the system is likely due to the coarsening of titania, which makes part of the O^{2-} ions inside TiO_2 particles inaccessible. This assumption is speculative and requires further investigation.

CONCLUSION

Thus, introducing, into a catalytic system, an oxide of a metal capable of changing its oxidation state allows the oxygen capacity of this system to be increased.

Among the catalysts studied, the systems containing a rare-earth oxide or TiO_2 have the greatest oxygen storage capacity. Partial hydrocarbon oxidation is believed to be possible over rare earth-containing catalysts in the alternating-feed regime.

Among the systems containing alkaline-earth metal oxides, the system with SrO is of interest, although the oxygen storage capacity of SrO is somewhat lower than that of rare-earth metal oxides or TiO_2 .

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