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TiO_2–Al_2O_3 as a support for propane partial oxidation over Rh

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We show that supports prepared by addition of TiO_2 to Al_2O_3 improves hydrogen yield from propane partial oxidation by 30%. An optimal hydrogen yield is obtained with a TiO_2–Al_2O_3 composite of 0.54:0.46 ratio deposited with Rh operating at 900 °C. Long-term operation shows that TiO_2 delays catalyst deactivation, only up to 25 hrs.

KEY WORDS: propane; partial oxidation; TiO_2; Al_2O_3; TiO_2–Al_2O_3; rhodium; hydrogen.

1. Introduction

Hydrogen production has been the focus of much research as a possible alternative fuel source [1,2]. Hydrogen can be used effectively as a fuel to power systems producing energy over a range from mW (portable systems) to KW (on site power generation). Several reviews have discussed hydrogen generation from hydrocarbons at high temperatures [3,4]. A general process for hydrogen generation involves hydrocarbon oxidation over a catalyst deposited on an oxide support. One example of such a process is propane conversion by steam reforming and partial oxidation at high temperatures [5]. Partial oxidation (POx) of propane is an exothermic process and occurs at temperatures between 500 °C and 1000 °C [6]. In general, high temperature process such as POx result in problems such as coking (of support) and sintering (of catalyst) [7]. Since precious metals are used as the catalyst, efforts to minimize these problems are necessary, as is the long-term stability of the catalyst and its support.

So far, propane POx to produce hydrogen has been performed over oxides such as Al_2O_3 [4–6,8,9]. It has been found that TiO_2 favorably yields particularly low CO generation [10] and higher selectivity toward hydrogen [11]. Mixed oxide supports in principle may display the beneficial properties of the parent oxides. Indeed, a few reports discuss the application of mixed oxides as supports for catalytic conversion of propane (oxidation [12], dehydrogenation [13]).

In an earlier report, we showed that TiO_2–Al_2O_3 mixed oxides prepared by a sol–gel process can be stable up to 900 °C [14]. No transformation of the TiO_2 phase from anatase to rutile is observed up to 900 °C, over long-term exposure. It is important to maintain the TiO_2 in anatase phase because it assists in maximizing and retaining the dispersability of the metal by delaying the sintering of the metal. This promising result, led us to examine the applicability of the TiO_2–Al_2O_3 mixed oxide as a support for the catalytic partial oxidation of propane over Rh. In this communication we have shown that the presence of TiO_2 with Al_2O_3 improves the hydrogen yield compared to using Al_2O_3 alone as a support, and does so over periods up to at least 25 hrs. Further, long-term studies show that Rh deposited on Al_2O_3 leads to a rapid decrease in hydrogen yield, while presence of TiO_2 with Al_2O_3 improves the hydrogen yield at high temperatures under otherwise similar operating conditions.

2. Experimental

2.1. *Tiitania–Alumina–Rhodium catalyst synthesis and characterization*

TiO_2 was prepared by the sol–gel method from a titanium isopropoxide precursor (Aldrich). Al_2O_3 (Degussa® corporation) was added to the TiO_2 sol in various proportions to obtain the mixed oxide support. The mixed oxides were fired in air at 900 °C to transform the phases from amorphous to crystalline. Synthesis details of the mixed oxides and their properties after calcination have been elaborated elsewhere [14]. A ~10 mL solution of rhodium chloride (Aldrich) in water (1 mg Rh salt/1 mL of water) was prepared to impregnate the mixed oxide powder. A small amount (0.3 mL) of the salt solution was added to 0.8 g of mixed oxide powder. Subsequently, 2 mL of deionized water was added, and the mixture was sonicated to ensure homogeneity. The water was then evaporated by slow drying

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at ~80 °C overnight. The oxide – Rh mixture was loaded onto a quartz tube and reduced at 600 °C for 2 hr in a 100 sccm flow of 8.5% hydrogen – 91.5% Helium. Helium flow was always maintained during cooling to keep atmospheric oxygen from contacting the reduced Rh until room temperature was reached.

Chemisorption measurements were performed by a Micromeritics® system (Pulse Chemisorb 2705) using ~200–300 mg of the catalyst-support mixture. Before the measurements, the support-catalyst composite was pretreated under a 50:50 N_2–H_2 mixture for 2 hr at 400 °C, followed by cooling to room temperature under N_2 flow. Hydrogen was pulsed intermittently to titrate the active Rh surface; and specific metal area was estimated using standard expressions found elsewhere [15]. Images were obtained by a Philips CM200 transmission electron microscopy (TEM).

2.2. *Propane partial oxidation*

Propane, oxygen, and nitrogen were obtained from S. J. Smith and used without further purification. A customized quartz tube with a ceramic frit was used as the reactor for propane POx. A condenser was attached to the exit of the quartz tube to remove water formed as a reaction product from the gas stream. All experiments employed 0.8 g of oxide support. Metal loading was always maintained at 3.5 ± 0.02 wt%. The flow of the gas was controlled with a mass-flow controller (MKS®) attached to each gas stream. The reacted gas mixture was collected in a gas-sampling chamber, and the contents were analyzed with an SRI 8610C gas chromatograph. The feed was a gas mixture consisting of propane, oxygen, nitrogen, and helium with a composition in the ratio: 10:19:5:271 (in sccm). Nitrogen was used as an internal standard for calibration purposes. The temperature was varied between 500 and 900 °C in a Lindberg/Blue tube furnace. Each reaction was run for 0.5 hr prior to sampling to ensure steady state. The samples were injected in a 100/120 20 ft Hayesep D Restek® column. Helium was the carrier gas at a flowrate of 40 mL/min. The oven of the gas chromatograph was operated at 40 °C for the first 5 minutes, followed by ramping up to 200 °C at 6 °C/min.

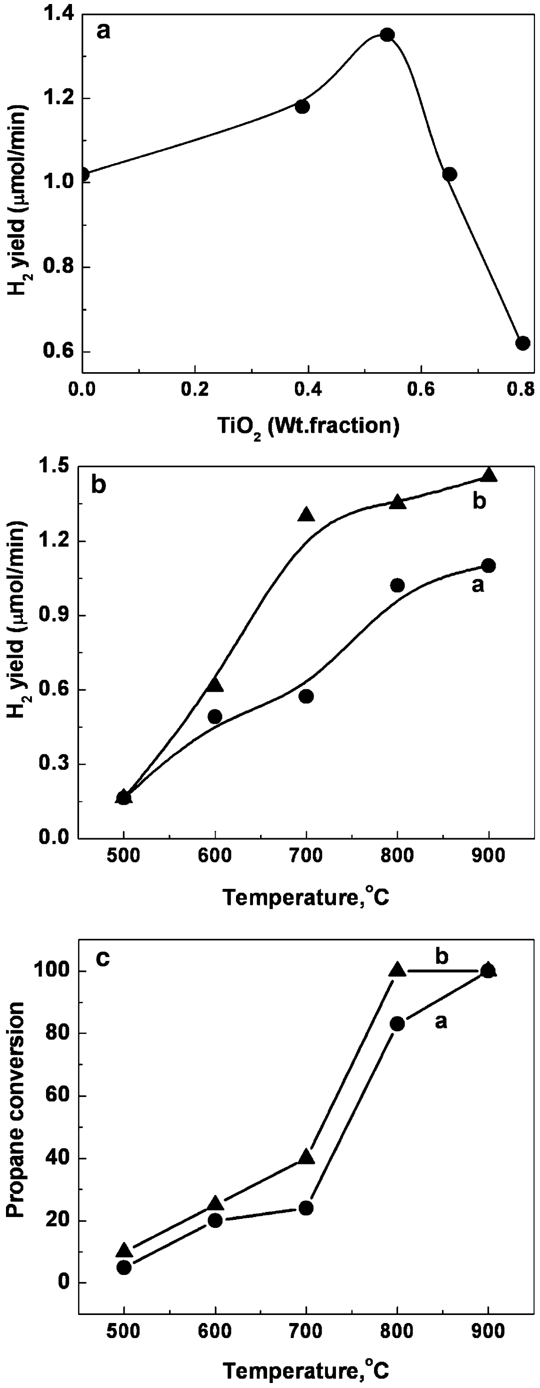

Figure 1. (**a**) Hydrogen yield per minute from propane partial oxidation over TiO_2 – Al_2O_3 composite of different ratios. Operating conditions: Rh – 3.5 ± 0.02wt %, Temperature – 800 °C, flowrate 305 sccm. (**b**) Hydrogen yield per minute from propane partial oxidation over (a) Al_2O_3, (b) TiO_2–Al_2O_3 (TiO_2 wt.% 54) at different temperatures. Operating conditions: Rh – 3.5 ± 0.02wt %, flowrate 305 sccm. (**c**) Propane consumption over (a) Al_2O_3, (b) TiO_2–Al_2O_3 (TiO_2 wt.% 54) at different temperatures. Operating conditions: Rh – 3.5 ± 0.02wt %, flowrate 305 sccm.

3. Results

3.1. *Effect of support*

Figure 1(a) shows the hydrogen yield over Al_2O_3 and TiO_2–Al_2O_3. The hydrogen yield improves when TiO_2 is present. As the concentration of TiO_2 increases up to 54 wt %, the hydrogen yield increases. Above this TiO_2 concentration, however, the hydrogen yield decreases rapidly, and becomes to less than that of Al_2O_3 alone above 65 wt %. At the optimum composition of 54 wt % TiO_2, 30% improvement in hydrogen yield is possible. This result was for 0.8 g of the total mixed oxide support weight. It is noteworthy to mention that similar results of higher hydrogen yield at 54wt% TiO_2

were obtained at different total weights (1 g and 1.2 g) of TiO_2–Al_2O_3 loading compared to different weights of just Al_2O_3. Figures 1(b and c) shows the effects of temperature. As the temperature increases from 500 °C to 900 °C, the hydrogen yield increases. Propane conversion and hydrogen generation become significant at similar temperatures (500 °C), and their rates increase with temperature. Figure 1(b) also shows that the hydrogen yield is higher with Al_2O_3 – TiO_2 (TiO_2 wt.% 54) compared to Al_2O_3 at all temperatures. It can be noted that all the propane supplied in the feed is consumed (100% conversion) by the time temperature reaches 800 °C. Below 900 °C, Rh deposited over TiO_2 – Al_2O_3 generally gives slightly higher conversion than Al_2O_3.

3.2. *Effect of long-term operation*

For commercial applications, it is essential that catalyst and catalysts supports maintain reasonable operation over 100 s of hours [16]. Besides ~100% conversion of propane is effective only at high temperatures. For example, 900 °C for partial oxidation [6] and from 750–900 °C [17,18] for steam reforming. Therefore the goal here is to examine the activity of the catalyst – support complex to achieve propane to hydrogen conversion at 900 °C for as long as possible. Since 100% conversion of the propane was observed between 800 and 900 °C, this analysis focused on evaluating the properties of the Rhodium–TiO_2–Al_2O_3 composite at 900 °C. The results from figure 1 indicate maximum hydrogen generation at 900 °C for a TiO_2–Al_2O_3 composite with 54 wt% TiO_2. These experiments were performed after a steady state reaction time of 30 minutes. Often, longer-term catalyst operation can lead to a decrease in catalytic activity. To investigate this possibility, hydrogen generation was monitored at 900 °C over 25 hrs of operation for the TiO_2–Al_2O_3 composite. Figure 2 shows these results along with the hydrogen yield over Al_2O_3 as a reference. The hydrogen yield decreases by 70% in 12 hr in this reference case. By contrast, the yield over 54 wt% TiO_2 shows a decrease of only 35% over the same period. However, at the end of 25 hr, the hydrogen yield over both materials continues to decrease in such a way that the yield for TiO_2–Al_2O_3 is identical to that over Al_2O_3. A similar observation is also made for the 40wt% TiO_2.

4. Discussion

4.1. *Chemisorption measurements*

TiO_2 addition to the Al_2O_3 support is evidently beneficial in improving propane to hydrogen conversion during both short-term and long-term operation. However, long-term operation results in decreased activity with time suggesting, irreversible transformation at the catalyst and/or catalyst–support interface. From the stand point of commercial application, unfortunately, this catalyst deactivates in a much shorter period. We used chemisorption to examine the effect of temperature on the active surface area of the Rh under different conditions. The result of this analysis is reported below.

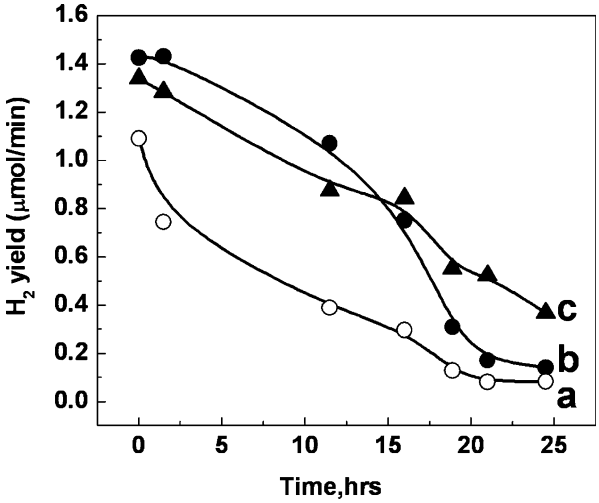

Figure 2. Hydrogen yield per minute from propane partial oxidation over (a) Al_2O_3, (b) TiO_2–Al_2O_3 (TiO_2 wt.% 54), and (c) TiO_2–Al_2O_3 (TiO_2 wt.% 40) composite over 25 hrs. Operating conditions: Rh – 3.5 ± 0.02wt %, Temperature – 900 °C, flowrate 305 sccm.

Table 1 shows these results obtained using hydrogen as the chemisorption gas. The active surface area before high temperature operation, after exposing to a non-reactive gas (nitrogen) at 900 °C, and after subjecting the catalyst to a reactive gas are shown in this table. The specific surface area of Rh after reduction is about 0.83 m^2 for Al_2O_3 and 1.6 m^2 for TiO_2 of 54 wt%. This near-doubling of the surface area has also been reported earlier with respect to Pd dispersion over TiO_2–Al_2O_3 [14]. At this point it is essential to mention that, addition of TiO_2 results in increasing the surface area of the composite TiO_2–Al_2O_3, which can be attributed to improving Rh dispersion. However how much of this increase in surface area contributes to increase in the dispersion of the rhodium is unclear and requires further examination. In a related study, improved dispersion of Platinum over a TiO_2–Al_2O_3 support compared to

Table 1

Rhodium active surface area for Al_2O_3 and TiO_2–Al_2O_3 after various exposures

	Surface area (m^2/g)	
	Al_2O_3	TiO_2 (54wt%)–Al_2O_3
After reduction	0.828	1.608
N_2, 900 °C, 25 hrs	0.3	0.829
C_3H_8,900 °C, 25 hrs	0.02	0.05
Air, 600 °C, 48 hrs	0.064	0.11

Al_2O_3 has been attributed mainly to deposition of platinum over TiO_2 and the ability of TiO_2 to prevent strong metal support interactions of Pt with Al_2O_3 [19]. Detailed surface analysis of the Rhodium using XRD and TEM has to be performed to identify what contributes to Rhodium dispersion on the support.

Subjecting the catalyst to long-term exposure to nitrogen at 900 °C decreases the surface area for both the supports. This observation suggests that in spite of the absence of the reactants, Rh surface area decreases. Thus, the Rh catalyst nanoparticles aggregate, growing in size and lead to a decrease in active available surface area. The much more rapid decrease in Rh active area over Al_2O_3 compared to the TiO_2–Al_2O_3 composite clearly indicates the stabilizing role of TiO_2 dispersed over Al_2O_3. After actual reaction (propane partial oxidation at 900 °C for 25 hr) both Al_2O_3 and TiO_2–Al_2O_3 have negligible active Rh surface area.

On examining the powder after long-term partial oxidation reaction, both Rh–Al_2O_3 and Rh–TiO_2–Al_2O_3 composites showed deposits of a black residue. If this were a carbonaceous residue, they should be removable by treatment in air. To examine this, we treated the composite materials in an air flow of 200 sccm at 600 °C for 48 hrs. This treatment removed most of the black residue. The chemisorption measurements were performed again after this treatment. Approximately 3 times and ~2 times increase in the Rh surface area over the Al_2O_3 and the 54 wt% TiO_2 was observed respectively (refer table 1). This procedure also resulted in a 15% decrease in weight of the composite, suggesting that the carbonaceous residue is removed by oxidation. This analysis shows that the residue contributes to decrease in the active surface area of the Rh and its removal can restore part of the active catalyst area.

4.2. Surface analysis

To further understand the effects of the high temperature on the support - catalyst complex, we examined the surface with TEM following different treatments. Figures 3(a and b) show the TEM images of TiO_2–Al_2O_3 with Rh after exposure to nitrogen and propane, respectively, for 25 hrs at 900 °C. Statistical analysis of several micrographs showed that the particle sizes of rhodium were 11 ± 3 nm and 8 ± 2 nm over Al_2O_3 and TiO_2–Al_2O_3 after reduction. After subjecting the support – catalyst complex to 900 °C for 25 hrs under a nitrogen flow, the respective particle sizes increased to 15 ± 2 nm and 10 ± 2 nm. The increase in the size of Rh nanoparticles confirms the chemisorption results, which suggest a decrease in area. Thus, the size obtained from the TEM images complement the data obtained from the chemisorption measurements shown in table 1. It can therefore be inferred that the heat treatment at 900 °C results in sintering of the metal nanoparticles, even in the absence of the reactants. Although the increase in particle size occurs over both the supports, more sintering (~35% over Al_2O_3 vs. ~25% over TiO_2–Al_2O_3) is observed in the absence of TiO_2. An earlier report [20] on the effect of temperature on the metal sintering (Pt, Pd) over the oxide supports has shown that the metal crystallites indeed show an increase in size due to heating. This is mainly attributed to the sintering by coalescence. From figure 3(b) it is evident that the particles aggregate to form a composite material of indeterminate composition. In addition to the Rh particles, there are several impurities in the systems (mainly carbonaceous deposits formed as a result of the propane partial oxidation which were removed by post reaction treatment in air).

The chemisorption and TEM measurements indicate a greater dispersion of the Rh over TiO_2–Al_2O_3 than the Al_2O_3, leading to increased hydrogen production. In general catalytic oxidation reactions, the presence of TiO_2 as one of the support constituents leads to improvement in selectivity [11], and higher turnover frequency for the oxidation of the feed [21,22]. For example, a related work on propane oxidation suggests that improvement in selectivity and lower production of intermediate byproduct amounts can be achieved with TiO_2 addition and Pt as the catalyst [12]. This improvement is attributed to the presence of more oxygen-containing support on TiO_2 (TiO_2, has 2 oxygen atoms per Ti) compared to Al_2O_3 (which has 1.5 oxygen per Al atom). Catalytic activity, particularly over mixed oxides, depends upon oxide reducibility and surface acidity [23]. These properties of the oxides can alter the oxidative mechanism of the primary feed component. The presence of TiO_2 has been reported to produce alkene as byproducts while its absence leads to CO as the major intermediate [12]. As far as the role of Pt is concerned, it is reported to function as a propane adsorption site. The overall mechanism involves propane adsorption onto the Pt site to form oxidized byproducts and the oxidation of these byproducts by the support [12]. In our case we believe the function of the Rh is similar to that of the Pt. Several factors can cause deactivation: sintering, coking, and poisoning. The support-catalyst composite revealed possible carbonaceous residue after long-term operation which can be removed by treating in an oxidizing atmosphere. Besides, heating TiO_2–Al_2O_3–Rh just in nitrogen (24 hr, 900 °C) has shown a decrease in surface area due to sintering. Based on these observations, we believe that both sintering and coking occur during propane partial oxidation, which results in lower hydrogen yield under long-term operation. Interestingly however, in a related study, Pt supported on Al_2O_3 and TiO_2 for another alkane (methane) showed deactivation (immediately when TiO_2 is used with Al_2O_3 and a little later for Al_2O_3 alone) after start of oxidation reaction. With both these supports, decay was attributed to formation of carbon deposits over the metal [24]. Although the results

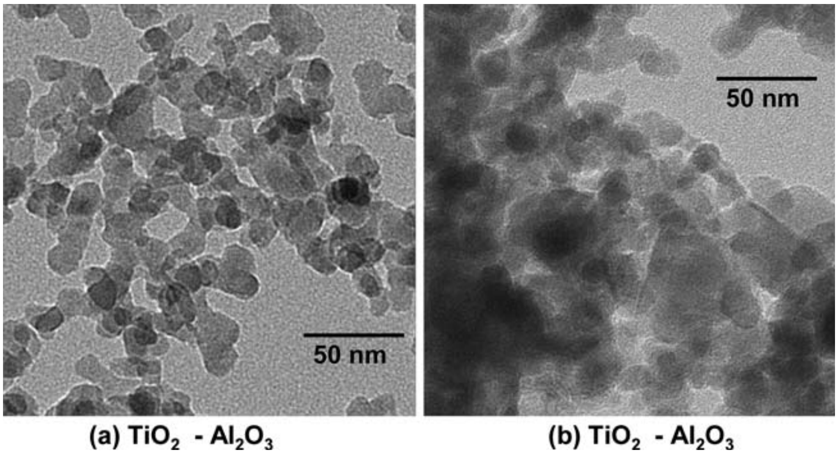

Figure 3. TEM images of (a) TiO_2–Al_2O_3–Rh (TiO_2 wt.% 54), 900 °C, N_2 exposure 25 hrs. (b) TiO_2–Al_2O_3–Rh (TiO_2 wt.% 54), 900 °C, propane partial oxidation over 25 hrs.

reported here are promising, there is still room for performance improvement particularly in long-term operation. Manipulation of process variables, alternate synthesis methodologies, catalyst loading, residence time, feed ratio, and intermediate analysis are some of the parameters that have to be optimized.

This work shows that the presence of TiO_2 is essential for improving Rhodium dispersion. Only limited recovery of active Rh surface was possible as shown earlier by treatment in air. One alternate pathway to improve rhodium dispersion would be improve the dispersion of TiO_2 over Al_2O_3. This could be achieved by synthesizing titania and Alumina sols from their respective precursors separately and mixing them together to form a composite oxide. Unlike the current method, the proposed method would offer an opportunity to ensure an intimate mixing between the TiO_2 and Al_2O_3 before the calcinations step and potentially improve Rh dispersion. Another alternative that can be examined is to use carbon nanotubes as an additive in the support to improve the immobilization [25] of the catalyst and prevent its sintering, and/or prepare Rh nanoparticles and then deposit them over the nanotube–oxide composites [26].

5. Summary

Addition of small amounts of TiO_2 to Al_2O_3 improves the hydrogen yield from propane partial oxidation. This effect results from the doubling in the dispersion of the rhodium catalyst over the mixed oxide support. An optimal ratio of 54 wt% TiO_2 and 46 wt% Al_2O_3 shows maximum hydrogen yield. However, the hydrogen yield decreases to almost zero over 25 hrs of continuous operation at 900 °C. TEM images and chemisorption measurements indicate that this decrease results from coking and sintering of the active rhodium catalyst.

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