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NOTE

Catalytic Hydrogenation of Propylene over Perovskite-Type Oxides $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Mn, Fe, Co, or Y)

In a previous study, Carberry *et al.* (1, 2) have reported that strontium-doped solid oxide solutions of the formula $La_{1-x}Sr_xCrO_{3-\delta}$ exhibit similar catalytic activity to the Pt/Al_2O_3 catalyst. The level of strontium doping at about 20 mole% in the perovskites resulted in the maximum catalytic activity for oxidation reactions. In continuation of our earlier work (3, 4), we decided to examine the catalytic activity of $La_{0.8}Sr_{0.2}MO_{3-\delta}$ oxides (M = Cr, Mn, Fe, Co, or Y) for hydrogenation reactions. Matthias *et al.* have shown the A site substituted manganese perovskite of the type $La_{1-x}A_xMnO_3$ (A = Pb, Sr, Ca, or Ba) to exhibit promising catalytic activity for treating the internal combustion engine exhaust gases (5). They showed that the catalysts were efficient in both oxidation reaction of CO and reduction reaction of NO by H_2. Many published results on the hydrogenation and hydrogenolysis of hydrocarbons were centered around the ethylene hydrogenation over $LaCoO_3$ (6, 7). The propylene hydrogenation activity over $La_{0.8}Sr_{0.2}MO_{3-\delta}$ has not been reported, so far, in the literature. The objective of the present work is to monitor the catalytic efficiency of $La_{0.8}Sr_{0.2}MO_{3-\delta}$ in reducing atmosphere viz., propylene hydrogenation and the choice of propylene as reactant have no bearings on any practical applications.

The catalysts $La_{0.8}Sr_{0.2}MO_{3-\delta}$ (M = Cr, Mn, Fe, Co, or Y) were all prepared by solid-state processing techniques as described elsewhere (3). X-ray diffraction studies were performed before and after the reaction on all catalysts, using a Diano X-ray diffractometer with Cu$K\alpha$ radiation. The surface area of the sample was measured with a Quantachrome single-point BET surface area analyzer using N_2 as the adsorbate.

The catalytic hydrogenation experiments on all catalysts were carried out at atmospheric pressure in a gradientless recycle reactor designed by Serrano *et al.* (8). The reactant gas mixture containing 1% propylene in H_2 was fed over 0.2 g of the catalyst at a total constant flow rate of 100 cm^3/min. A recycle ratio of 30 was maintained to obtain the gradientless condition in all catalytic runs. The gas composition was analyzed before and after reaction by on-line gas chromatography with Poropak Q 80/100 (Alltech) packed column. The reaction was followed by monitoring the fraction of propylene converted as a function of temperature from 25 to 300°C. Each reading was obtained at constant temperature under steady-state conditions. Although the number of products formed during the reaction were identified, no quantitative analysis on the product distribution was made in the present study; this aspect will be given due attention in later kinetics studies.

The reaction conditions and rate data on the propylene hydrogenation activity are listed in Table 1. The light-off temperature curves obtained on all catalysts for the hydrogenation of propylene from 25 to 300°C are shown in Fig. 1. A maximum propylene conversion of about 95% was observed on $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ at 260°C, and of all the catalysts, $La_{0.8}Sr_{0.2}YO_{3-\delta}$ showed the lowest propylene conversion of about 9.0%. The activity of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ was found to decrease toward propylene conversion above 180 and 160°C, respectively. The global rate of the reaction was computed using the equation [1] suggested for a recycle reactor operating under CSTR conditions.

$$\text{Global rate} = C_f \cdot \chi/\theta, \qquad [1]$$

where C_f = concentration of propylene (mole/cm^3) in the feed, χ = fraction of propylene converted, and θ = holding time (weight of the catalyst (g)/total flow rate (cm^3 sec^{-1}). $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ and $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ have shown high activity for propylene conversion and also exhibited both hydrogenation (propane) and hydrogenolysis reaction products (methane and ethane), the amounts being a function of temperature. The other three catalysts (Mn, Fe, and Y perovskites) reveal only hydrogenation activity. The Mn and Fe perovskites were found to deactivate rapidly with increasing temperature. Deactivation of $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ was noticed at reaction temperatures greater than 300°C. Regeneration studies on $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ has been attempted since these were reported to show good activity for NO reduction by H_2 (5) and for CO oxidation reaction (2). The hydrogenation reaction was carried out over $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ above 300°C for several hours to produce

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TABLE 1

Catalytic Data on the Hydrogenation of Propylene over Perovskite Oxides

Catalyst	$S \cdot A$ (m^2/g)	W/F ($g \cdot sec/cm^3$)	Maximum conversion of propylene (%)	Temperature for column 4 (°C)[a]	Global rate ($mole/m^2 \cdot sec$)[a]	Type of reaction observed	Ref.
$La_{0.8}Sr_{0.2}CrO_{3-\delta}$	0.9	0.135	75.7	300	2.76×10^{-6}	hydrogenation and hydrogenolysis	This work
$La_{0.8}Sr_{0.2}MnO_{3-\delta}$	1.4	0.132	40.4	180	9.71×10^{-7}	hydrogenation	This work
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$	0.3	0.127	30.7	160	2.60×10^{-6}	hydrogenation	This work
$La_{0.8}Sr_{0.2}CoO_{3-\delta}$	0.2	0.133	95.6	260	1.60×10^{-5}	hydrogenation and hydrogenolysis	This work
$La_{0.8}Sr_{0.2}YO_{3-\delta}$	0.3	0.134	9.0	300	9.62×10^{-7}	hydrogenation	This work
Pt/Al_2O_3[b]	500	—	—	21	1.14×10^{-7}	hydrogenation	(15)
$LaCoO_3$[c]	0.33	—	—	300	4.06×10^{-9}	hydrogenolysis	(7)

Note. Feed composition = 1% propylene in H_2; total flow rate = 100 cm^3/min.

[a] Data correspond to maximum propylene conversion obtained.

[b] 4.5 mole% propylene over 0.6% Pt/Al_2O_3 commercial catalyst and BET surface area.

[c] Reaction was performed in a static reactor.

a deactivated catalyst. The regeneration of the deactivated catalysts was attempted by heating the material to 550°C in a flowing oxygen atmosphere (100 cm^3/min) for 60 min. Under this reoxidation condition, only the chromium perovskite was found to restore its activity toward propylene conversion but not the manganese containing catalyst (Fig. 1). The chromium perovskite is well known for its stability in a reducing atmosphere (9) and hence the deactivation may be accounted for by the formation of carbon/coke deposits on the catalyst. As the manganese perovskite is susceptible to reduction under a hydrogen atmosphere to manganese oxide, MnO, and La_2O_3, the deactivation in this case could result from both the presence of a carbonaceous deposit as well as the separation of the two oxides. X-ray diffraction analysis on the fresh and spent catalysts showed significant changes in the X-ray patterns on Mn, Fe, and Co perovskites revealing a possible reduction of the metal ion (for example the *d*-spacing for 100, 111, and 133 planes were missing on the Mn spent catalyst). Among the unsubstituted perovskites, the cobaltate has been found by Ichimura *et al.* (7) to show a remarkable hydrogenation activity for ethylene. They concluded that the high activity of $LaCoO_3$ is due to the synergistic effect of La, Co, and O ions in which the Co ion is responsible for the hydrocarbon activation.

Partial information is available for the thermodynamics of the unsubstituted perovskites $LaMO_3$ (M = Cr, Mn, Fe, or Co) and the reduction equilibria at 1000°C (10) show the following pattern: Lanthanum chromite is the most stable compound, being stable down to at least 10^{-20} atm pO_2. Ferrite is the next most stable, being reduced to La_2O_3 and Fe at pO_2 equal to 10^{-17} atm, followed by $LaMnO_3$, which reduces to La_2O_3 and MnO at 10^{-15} atm, and finally $LaCoO_3$, which decomposes to form a compound of the formula $La_4Co_3O_{10}$. It can thus be seen that these perovskites show quite different reduction paths at low oxygen potentials and high temperatures. Using the literature (11) and estimated data, we conclude that the only modification in these patterns which might be expected at the lower temperatures used in the present study would be the formation of Mn_3O_4 instead of MnO for the manganite. The compound $La_4Co_3O_{10}$ can also be written as $2La_2O_3 \cdot Co_3O_4$ and therefore has a mixture of Co^{2+} and Co^{3+} ions. This should lead to a high conductivity

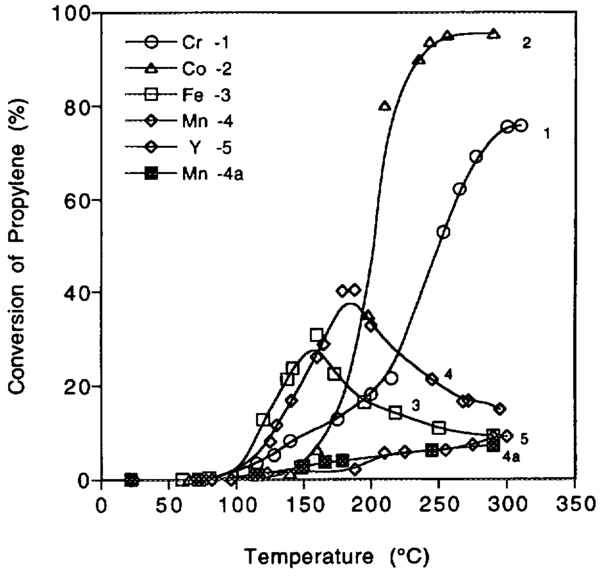

FIG. 1. Light-off temperature (LOT) curves for the propylene hydrogenation over solid oxide solution catalysts. Feed = 1% propylene in hydrogen; total flow rate = 100 cm^3/min; catalyst weight = 0.2 g. (1) $La_{0.8}Sr_{0.2}CrO_{3-\delta}$, (2) $La_{0.8}Sr_{0.2}CoO_{3-\delta}$, (3) $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, (4) $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, (5) $La_{0.8}Sr_{0.2}YO_{3-\delta}$, and (4a) $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (regenerated). Regeneration of the catalyst (4a) was performed by heating to 550°C in flowing oxygen (100 cm^3/min).

similar to that of the perovskites, although experimental evidence is not yet available. It can be tentatively concluded that the reason for the different behavior of the cobalt and chromium catalysts on one hand, and the manganese and iron compounds on the other, is that the latter decompose to form two new major phases, whereas the former retain the properties of perovskites either partially or wholly. No attempt has been made to characterize the active sites of the catalysts in the present study. However, X-ray diffraction studies made on the spent catalysts revealed information on the reduction of valence state of Co, Mn, and Fe in their respective perovskites. The Cr and Y perovskite did not show any significant change in the X-ray pattern on the spent samples corresponding to a possible change in valence.

The activity pattern of propylene hydrogenation in the series follows the order $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ > $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ > $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ > $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ > $La_{0.8}Sr_{0.2}YO_{3-\delta}$. The activity of $La_{0.8}Sr_{0.2}CrO_{3-\delta}$ is also expected to be due to the Cr^{3+} ions as is known for the activation of hydrogen and hydrocarbon bonds (12). The Mn and Fe systems showed less activity corresponding to the poor hydrogen reactivity of MnO and Fe_2O_3, respectively. Among the first row transition metal oxides the activity of Cr_2O_3 and Co_3O_4 is much greater than the others for both H_2–D_2 exchange and ethylene hydrogenation (13, 14). A similar activity pattern is evident from the data presented on the propylene hydrogenation over the $La_{0.8}Sr_{0.2}MO_{3-\delta}$ oxides (Table 1), explaining the general trend in the activity of transition metal ions in different environments. The comparison of the reaction rates observed in the present study with Pt/Al_2O_3 (15) and $LaCoO_3$ (7) has been summarized in Table 1. It should be noted that the reaction conditions and reactant concentrations are very different from each other and hence a quantitative comparative analysis is not possible.

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N. Gunasekaran
J. J. Carberry

Laboratory of Catalysis
Department of Chemical Engineering
University of Notre Dame
Dame, Indiana 46556

R. Doshi
C. B. Alcock

Center for Sensor Materials
Department of Electrical Engineering
University of Notre Dame
Notre Dame, Indiana 46556

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