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Reactions of Alkenes on Lanthana

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Reactions of ethene, propene, butenes, 2-methylpropene, cyclopentene, 2,3-dimethylbut-1-ene, and 3,3-dimethylbut-1-ene have been studied with hydrogen, and sometimes deuterium, on lanthana catalysts. Many alkene/lanthana systems show evidence of self-poisoning which is more marked with straight-chain hydrocarbons than with branched hydrocarbons and at higher temperatures; the catalysts are also highly sensitive to impurities. The temperature required to attain a fixed rate of hydrogenation (10^{16} molecules s^{-1} m^{-2}) varied from 220 K for ethene to over 373 K for the 2,3-dimethylbutenes. Fast hydrogenation without accompanying deuterium exchange was observed with alkenes which cannot form allylic species. The ability to form such species led to rapid isomerization of the butenes below 273 K and of 2-3-dimethylbut-1-ene at 373 K, and to exchange rates with deuterium which were comparable to (propene) or faster than (2-methylpropene) addition reactions at 380 K. Deuterium NMR spectroscopy was used for analysis of the products from the reactions with deuterium. Although the hydrogenation of 3,3-dimethylbut-1-ene occurred readily at 245 K, no isomerization was detected even at 510 K. © 1987 Academic Press, Inc.

INTRODUCTION

Rosynek (*1*) has given a general review of the catalytic properties of lanthana and his report showed that the oxide was an effective catalyst for the hydrogenation and isomerization of selected alkenes. Minachev *et al.* (*2*) reported some results for the hydrogenation of ethene at low temperatures as part of a study of the catalytic activities of rare-earth oxides. High activity for hydrogenation was found at 195 K and rates were dependent on the temperature at which the catalyst was pretreated. A maximum rate of about 1.7×10^{17} molecules s^{-1} m^{-2} after pretreatment at 1073 K was reported but activities were estimated only by taking rates at 50% conversion. Khodakov *et al.* (*3*) used thermal programmed desorption to provide evidence for at least two adsorbed forms of ethene on the surface after exposure to the gas at 195 K and the amounts of these species were dependent on pretreatment temperatures. They also showed that carbon monoxide, carbon dioxide, and water reduced the rate of hydrogenation of ethene. Topchieva and Ibragimova (*4*) reported that the hydrogenation of propene took place on lanthana between 415 and 483 K but gave no detailed results. The most extensive work involving alkene hydrogenation was carried out by Jensen (*5*) who used ethene, propene, and but-1-ene and showed that at 273 K the rate of reaction of ethene was about 10^4 times faster than the rates for the other molecules.

The isomerization of but-1-ene and related reactions have been studied by a number of groups (*5–10*). There is a high initial preference for the formation of *cis*-but-2-ene and this demonstrates a kinetic control of selectivity which has been attributed to a mechanism involving π-allylic intermediates. Similar results have been found on other basic oxide catalysts such as calcium oxide (*11*) and magnesia (*12*). Experiments with mixtures of undeuterated and deuterated butenes on lanthana showed that double-bond movement occurred by intramolecular transfer of H or D with little contribution from intermolecular reaction.

More recently mechanistic studies of the reactions of 2-methylpropene and deuterium were reported (*13*). Reactions were followed by gas chromatography and prod-

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ucts examined by ^{2}D NMR spectroscopy. Exchange of the alkene occurred about 10 times faster than addition at 414 K and the distribution of deuterium atoms in 2-methylpropene was consistent with a π-allyl species as intermediate. The NMR results showed that the chances of acquiring D or H at the primary and tertiary positions of 2-methylpropane in the addition process were not the same. It was suggested that the species adding to these positions originated from different pools of H or D on the surface with different partial charges.

The original intention of this research was to obtain information on the hydrogenation of a wider range of alkenes on lanthana and also to examine the isomerization of 3,3-dimethylbut-1-ene on the catalyst. Preliminary results showed that two complicating features were important. The first of these was a tendency for self-poisoning to occur with alkene/hydrogen mixtures on lanthana and the extent of this depended not only on temperature but also on the alkene. The second complication was the sensitivity of the catalysts to aging as a result of uptake of water or carbon dioxide. With some of the alkenes, experiments were carried out using deuterium instead of hydrogen and, where appropriate, products were examined by ^{2}D NMR spectroscopy.

EXPERIMENTAL

Materials. The source of the various alkenes (all at least 99% pure) and the conditions used to analyse the alkene/alkane mixtures by gas chromatography are listed in Table 1. The hydrocarbons were distilled under vacuum before use. The second sample of cyclopentene(II) was further purified by passage through a column packed with basic γ-alumina to remove peroxide impurities. Deuterium (99.5%) from Matheson Chemicals and hydrogen from BOC were dried over a bed of molecular sieve 4Å at 77 K and then diffused through a palladium–silver alloy thimble.

The oxide catalyst was prepared using the method described by Imizu *et al.* (*14*). This involved precipitation of $La(OH)_3$ from an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$ (99.999%, Aldrich Chemical Co.) by addition of ammonia. The hydroxide was washed with deionized water, dried at 373 K, and ground to 24–42 mesh. Two preparations were made; $La(OH)_3$(I) was stored in the atmosphere and $La(OH)_3$(II) was kept under vacuum in a desiccator. Weighed amounts of hydroxide (usually in

TABLE 1

Source of Alkenes and Conditions Used for Gas Chromatography

Compound	Supplier	GC conditions			
		Column[a]	Length (m)	T (K)	Total P (kPa)
Ethene	Matheson	A	2	293	177
Propene(I)	Air Products	A	2	348	308
Propene(II)	Matheson	A			
2-Methylpropene	Matheson	A	2	368	342
3,3-Dimethylbut-1-ene	Fluka AG	B	50	273	163
2,3-Dimethylbut-1-ene	Fluka AG	B			
cis-But-2-ene	Fluka AG	C	4	318	239
But-1-ene	Matheson	C			
Cyclopentene (I) and (II)	Aldrich	D	2	313	225

[a] A = 3% squalane on activated alumina; B = squalane capillary; C = 13.5% bis-2-methoxyethyl adipate + 6.5% di-2-ethylhexylsebacate on Chromosorb P; D = 15% squalane on Chromosorb P.

the range from 15 to 60 mg) were outgassed at 873 K for 3 h for catalytic runs to give La_2O_3(I) or La_2O_3(II). Fresh samples were used for each experiment except where indicated in the text.

Apparatus and procedure. Surface areas of the catalysts were determined using nitrogen adsorption and the BET method. Further characterization of the catalysts was obtained by thermogravimetry (TG) using a Stanton Redcroft TG770 analyzer with a heating rate of 10 K min^{-1}. Samples (5 mg) were treated in flowing air with full-scale deflection set at 50% of the starting weight.

Reactions were followed in a greased-tap recirculation system containing a silica vessel with a 1-cm sinter, a Metal Bellows (240 V) recirculation pump, and a flow meter. Gas samples (~1%) were removed by means of a three-way tap connected by a Carle valve to a Perkin–Elmer F11 gas chromatograph with flame ionization detector. The columns and conditions used have been given in Table 1. The total volume of the recirculation system was 355 cm^3 and usually reactant mixtures consisted of a 5 : 1 ratio of hydrogen (or deuterium) : hydrocarbon with a pressure of 2.4 kPa of alkene corresponding to a charge of about 2.0×10^{20} molecules of hydrocarbon.

Samples for analysis by NMR spectroscopy were obtained by condensing the hydrocarbons in a liquid-nitrogen trap and subsequently distilling them into an NMR tube containing 5% D-chloroform. The examination of the samples followed procedures already described (*15, 16*).

RESULTS

Catalyst Characterization

Thermograms for various catalyst samples showing the percentage weight changes with temperature are given in Fig. 1. Since the samples contained different but significant amounts of carbonate, it was preferable to convert observed weight changes to percentages of the final weight attained around 1173 K as this was assumed to correspond to La_2O_3. Trace A shows the sequence of events when a sample of $La(OH)_3$(II) which had been stored under vacuum was heated. A loss of 3 to 4% occurred at 353 to 393 K. Since a monolayer of water would amount to only 1.1% of the oxide weight, it is likely that some water is lost from the bulk in this temperature region. The substantial loss between 573 and 683 K can be attributed to completion of the decomposition of the hydroxide. By 700 K the loss of weight of 15% was approaching the expected value of 16.6% for conversion of hydroxide to oxide. The significant further loss between 823 and 1073 K was ascribed to decomposition of carbonate. Since a monolayer of carbon dioxide would only account for a decrease of 1.6% the fall of 10.5% observed provides strong evidence for the presence of some bulk carbonate.

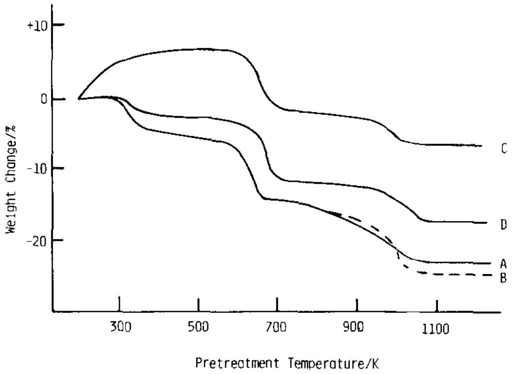

FIG. 1. Thermograms for samples of lanthanum hydroxide. (A) $La(OH)_3$(II); (B) $La(OH)_3$(II) exposed to 67 kPa CO_2 for 48 h; (C) La_2O_3(II) fresh from vacuum line after degassing at 873 K for 3 h; (D) La_2O_3(II) treated as for (C) but after 24 h in the atmosphere.

Traces B, C, and D show the effect of treating the samples in various ways. Exposure of $La(OH)_3$(II) to 67 kPa of carbon dioxide for 48 h gave trace B which was similar to A except for a larger weight loss in the high-temperature region. Trace C corresponds to a sample evacuated at 873 K for 3 h and then rapidly transferred to the TG apparatus. There was a significant increase in weight observed up to 400 K which shows the rapid uptake of atmospheric water by this sample. In contrast, there was a smaller weight loss in the high-temperature region, indicating that the sample contained less carbonate after evacuation at 873 K. A sample treated as for C but allowed to stand in the atmosphere for 24 h gave trace D which showed characteristics which were more similar to those for the hydroxide.

There was a good correlation between the age of catalyst samples and the percentage loss of weight in the high-temperature region due to carbonate decomposition and the results are given in Table 2. Infrared studies carried out for us by Professor Rochester and Mr. Anderson at Dundee University on a sample of our catalyst confirmed that temperatures of 1000 K were necessary to free the surface of carbonate species. After evacuation of the sample at 873 K bands were detected in the range 1300 to 1600 cm^{-1} but these disappeared when the catalyst was degassed at 1023 K.

The BET plots for nitrogen adsorption were linear in the range of relative pressure (p/p_0) from 0.05 to 0.20 and the derived surface areas are given in Table 3 for a number of pretreatment temperatures.

TABLE 2

Carbonate Weight Loss from Lanthana Samples

Treatment	Weight loss in range 823–1023 K (as % of La_2O_3 weight)
(1) La_2O_3(II) after degassing at 873 K for 3 h	4.4
(2) As for (1) after 24 h in atmosphere	7.4
(3) $La(OH)_3$(II) one week after preparation and storage under vacuum	10.5
(4) As for (3) exposed to 67 kPa CO_2 for 48 h	13.9
(5) $La(OH)_3$(I) six weeks after preparation and storage in atmosphere	21.6
(6) As for (5) but exposed to 67 kPa CO_2 for 48 h	22.9

TABLE 3

Surface Areas of Lanthana(I)

Outgassing temperature (K)	Area of La_2O_3 ($m^2\,g^{-1}$)
673	40 ± 1
823	35 ± 1
873[a]	29 ± 1
923	16 ± 1
973	8.4 ± 0.6
1073	1.4 ± 0.3

[a] A sample of La_2O_3(II), outgassed at 873 K, had an area of 42 ± 2 $m^2\,g^{-1}$.

Reactions with Alkenes and Hydrogen

A general feature observed with most of the catalytic reactions was a fall in rate during the course of the reaction. Such a decrease may arise from an approach to equilibrium which is easily recognized, from a kinetic dependence on the pressure of alkene which will only become appreciable after more than 15% conversion, or from some poisoning of the catalyst. When a reduction in rate was observed at low conversions the most probable cause was self-poisoning of the system.

n-Butenes. As there are many results in the literature, we carried out only a few experiments to show that our catalysts were comparable to those of other workers for the isomerization of the butenes. Reactions of but-1-ene and *cis*-but-2-ene at 273 K are shown in Fig. 2. There was a fast isomerization of but-1-ene which decreased by a factor of about 10^3 after a few minutes even though the amount of reactant was still well in excess of the equilibrium percentage (1.4%). On the other hand, with *cis*-but-2-ene there was a decrease in rate in the first 10 or 15 min which was largely associated with the establishment of the equilibrium between *cis*-but-2-ene and but-1-ene and

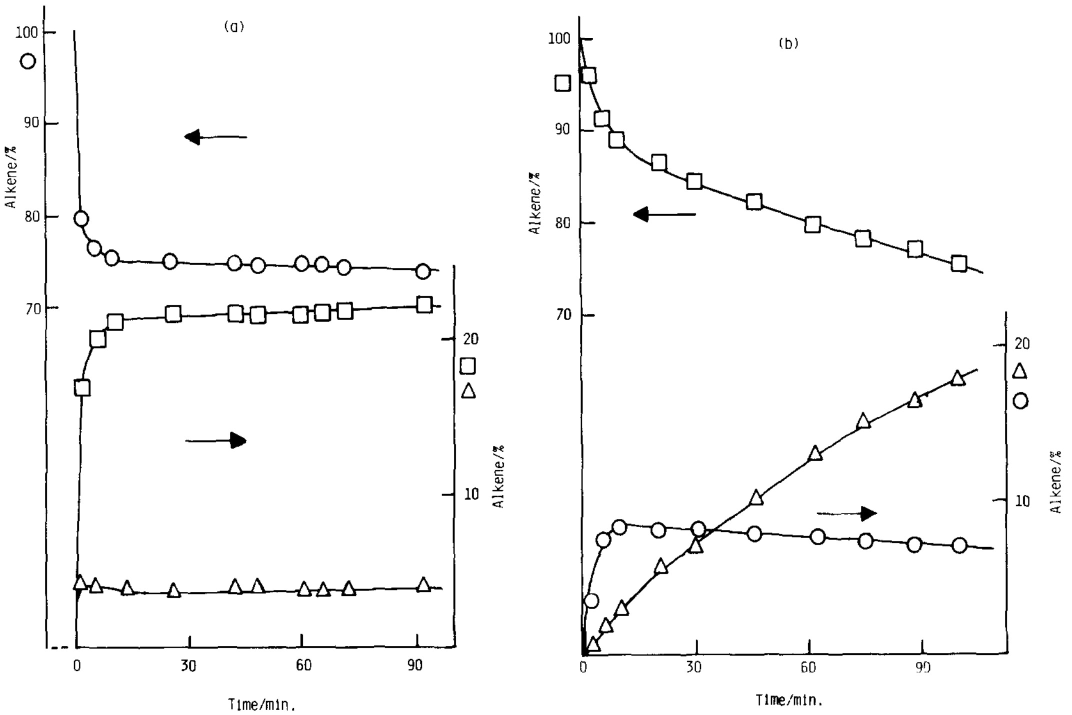

FIG. 2. Isomerization of butenes over 13 mg La_2O_3(II) at 273 K. (a) Reaction of but-1-ene, (b) Reaction of *cis*-but-2-ene. ○, but-1-ene; □, *cis*-but-2-ene; △, *trans*-but-2-ene.

the subsequent conversion to *trans*-but-2-ene continued at a steady rate which was about one-tenth of the rate of the initial reaction. Rates are given in Table 4.

Ethene. Figure 3 shows successive hydrogenations of ethene at 247 K. Between each experiment the reaction mixture was pumped away at 293 K and the catalyst evacuated for 30 min. The catalytic activity was high but fell by more than 50% between runs and during each run there was a decrease in rate even in the case of the third reaction when the conversion was only about 25%.

In order to study the influence of temperature, it was decided to measure initial

TABLE 4

Rates of Isomerization of *n*-Butenes at 273 K

Reaction	Rate (10^{18} molecule s^{-1} m^{-2})		
	La_2O_3(I)	La_2O_3(II)	Ref. (*10*)[a]
but-1-ene → but-2-enes	1.6	5.3	6.7
cis/*trans* ratio	7–8	4–5	7–8
cis-but-2-ene → but-1-ene	—	0.5	0.4
cis-but-2-ene → *trans*-but-2-ene	—	0.05	—

[a] The rates taken from Ref. (*10*) refer to catalysts outgassed at 873 K, the temperature used in the present work.

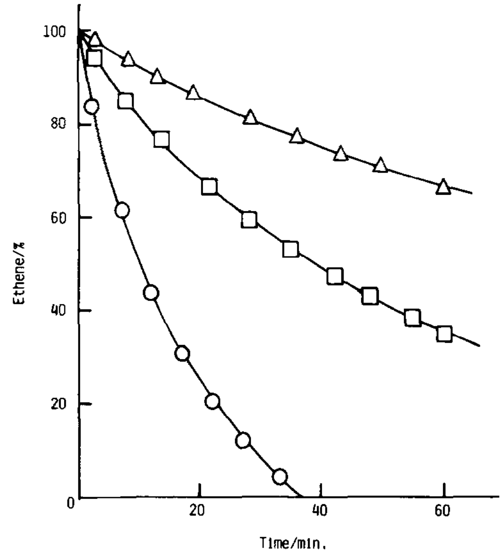

FIG. 3. Hydrogenation of ethene over 22 mg La_2O_3(I) at 247 K. ○, first reaction; □, second reaction; △, third reaction.

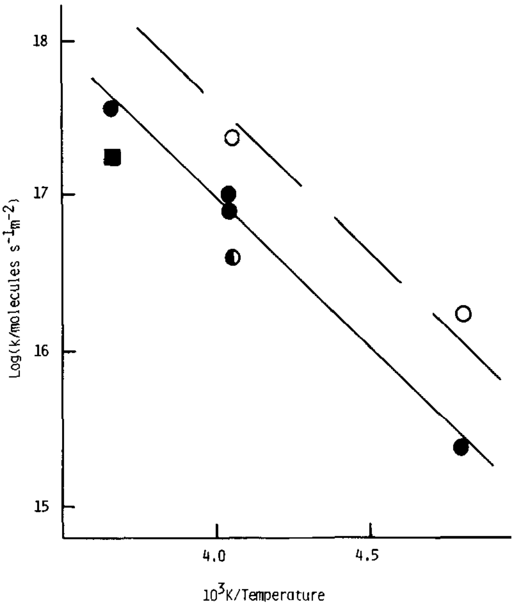

FIG. 4. Arrhenius plots for the hydrogenation of ethene. ○, ● and ◐, results on La_2O_3(I) used as fresh catalyst or after one or two "conditioning" reactions at 247 K, respectively; ■, La_2O_3(II) after one "conditioning" reaction at 247 K.

rates between 208 and 273 K for a series of second reactions. Prior to each of these, the catalyst sample was "conditioned" by running a first reaction at 247 K. Rates obtained in this way are shown by an Arrhenius plot in Fig. 4, which also includes some rates on fresh catalysts and on a twice-conditioned catalyst. Arrhenius parameters for ethene and other alkenes are presented in Table 5. Experiments were carried out on the hydrogenation of ethene on catalyst samples which had been used for the hydrogenation of 2-methylpropene and propene at 414 K. Subsequent rates of reaction of ethene were 12 and 15 times slower, respectively, at 273 K than for the reaction at this temperature after the catalyst had been used for hydrogenation of ethene at 247 K.

The effect of catalyst aging was examined by using a sample of La_2O_3(I) which had been stored in the atmosphere for 18 months. The rate of hydrogenation of

TABLE 5

Arrhenius Parameters for Hydrogenation

Alkene	Temperature range (K)	Activation energy (kJ mol^{-1})	Frequency factor log(A/ molecules s^{-1} m^{-2})
Ethene[a]	208–273	36 ± 2	24.6 ± 0.4
3,3-Dimethylbut-1-ene	245–273	23 ± 2	21.1 ± 0.3
Propene	311–414	43 ± 3	22.6 ± 0.4
2-Methylpropene[b]	335–414	42 ± 2	22.3 ± 0.3

[a] Results for a reaction on catalysts "conditioned" by hydrogenation of ethene at 247 K.

[b] Results from Ref. (*13*).

ethene at 273 K was more than 10^2 times slower than for reaction on fresh lanthana and there was more significant poisoning during the course of the reaction.

3,3-Dimethylbut-1-ene. The vapor pressure of this compound was too low to permit experiments with the usual pressures to be carried out below 245 K but hydrogenation was followed between this temperature and 273 K. Only a small decrease in rate was observed after high conversion had occurred as shown by the plot in Fig. 5. This was attributed to a kinetic dependence on the pressure of alkene and the course of the reaction conformed to an equation based on a power-rate law. Following the procedure used by Brown *et al.* (*17*), the effect of changes in the pressure of hydrogen are ignored so that the rate is given by

$$\frac{dx}{dt} = -k_r\left(\frac{x}{100}\right)^n, \qquad (1)$$

where x is the percentage of alkene present at time t, k_r is the initial rate of reaction expressed as a percentage per unit time, and n is the order of reaction with respect to alkene. Integration of Eq. (1) gave

$$x^{(1-n)} - x_0^{(1-n)} = -(1-n)k_r t/(100)^n \qquad (2)$$

where x_0 is the percentage of alkene at $t = 0$. A satisfactory linear plot was obtained for the reaction of 3,3-dimethylbut-1-ene at 273 K by using $n = 0.4$, as shown in Fig. 5. The rates for the reaction at different temperatures are given as an Arrhenius plot in Fig. 6.

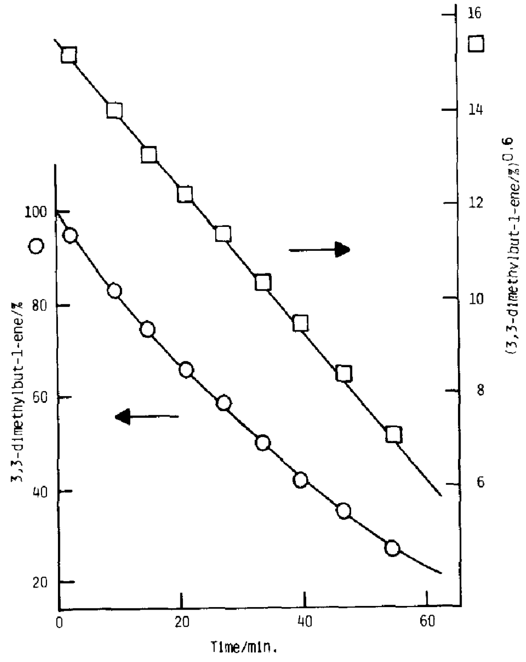

FIG. 5. Hydrogenation of 3,3-dimethylbut-1-ene over 52 mg La_2O_3(I) at 273 K. ○, percentage alkene; □, plot to test Eq. (2) using $n = 0.4$.

Since the hydrogenation of this compound seemed to be a well-behaved catalytic reaction which was not subject to self-poisoning, it was used as a test reaction to study the influence of pretreatment temperature on the activity of lanthana. The results shown in Fig. 7 indicated that maximum activity was obtained after pretreatment at 950 K.

An attempt was made to follow the isomerization of 3,3-dimethylbut-1-ene to 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene, a reaction which is thought to require acidic catalytic sites (*18*). However, on 85 mg of La_2O_3(I) less than 1% reaction was observed in 2 h at 510 K.

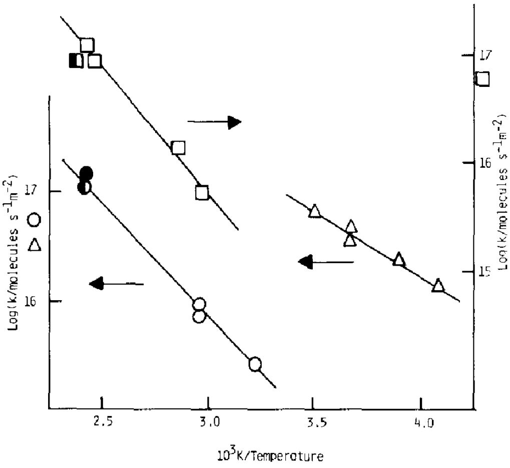

FIG. 6. Arrhenius plots for the hydrogenation of the alkenes. □, 2-methylpropene; ○, propene(I); ●, propene(II); △, 3,3-dimethylbut-1-ene on La_2O_3(I); ◧, 2-methylpropene; ◐, propene(II) on La_2O_3(II).

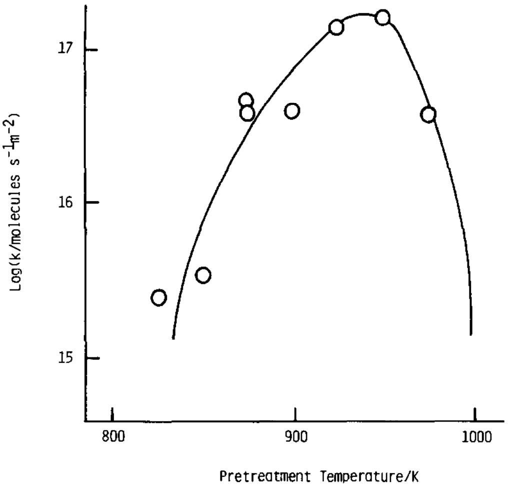

FIG. 7. Effect of pretreatment temperature on the rate of hydrogenation of 3,3-dimethylbut-1-ene on 52 mg La_2O_3(I) at 273 K.

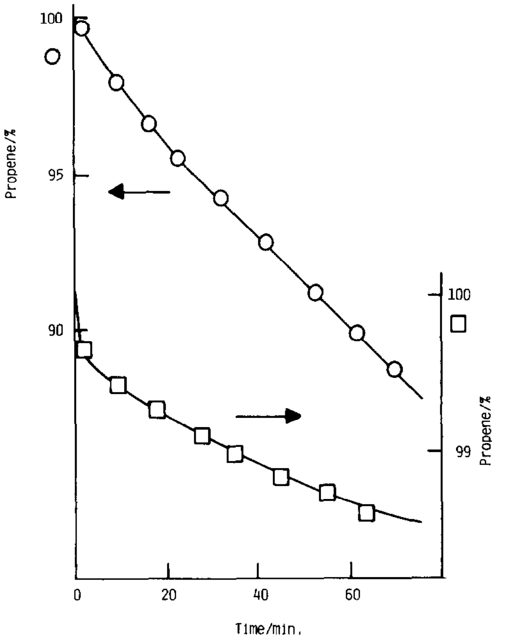

FIG. 8. Hydrogenation of propene(I) over 22 mg La_2O_3(I) at 338 K; ○, first reaction; □, second mixture.

2-Methylpropene. As reported elsewhere (*13*), the hydrogenation of 2-methylpropene was studied in the temperature range 335 to 414 K. The reaction was well behaved and second runs on the same catalyst sample gave rates only slightly lower than those for first runs. An Arrhenius plot is included in Fig. 6 for comparison with the other alkenes. A sample of La_2O_3(I) stored for 18 months gave a rate 10^2 times less than the rate for a fresh catalyst at 414 K.

Propene. The hydrogenation of propene occurred in the same temperature range and at rates similar to those found for 2-methylpropene, but the behavior of the two alkenes differed in other respects. Some decrease in rate with time was noted with all propene reactions and second runs were usually at least 10 times slower than first runs. These points are illustrated in Fig. 8 and an Arrhenius plot for first runs is included in Fig. 6.

Cyclopentene. Little hydrogenation, less than 1% in 1 h, was found at 312 K for cyclopentene(I), i.e., the sample not treated to remove peroxides. With cyclopentene(II) a rapid reaction was observed at 312 K with some decrease in rate at higher conversions. The results conformed to Eq. (2) with $n = 0.6$ and the initial rate of reaction of 5.9×10^{16} molecules s^{-1} m^{-2} was an order of magnitude larger than the extrapolated rate for 2-methylpropene at the same temperature. Different behavior was found for cyclopentene(II) at 382 K as shown in Fig. 9. The initial reaction was faster than at 312 K but poisoning became obvious after a few minutes so that conversions at times greater than 40 min were actually lower than at 312 K.

2,3-Dimethylbut-1-ene. Results for reaction of this compound with hydrogen at 373 K are shown in Fig. 10. A very rapid ($>10^{18}$ molecules s^{-1} m^{-2}) isomerization to 2,3-dimethylbut-2-ene took place in the first few minutes and then hydrogenation of the two alkenes to 2,3-dimethylbutane followed at a steady rate of 5.5×10^{15} molecules s^{-1} m^{-2}.

Reactions with Alkenes and Deuterium

Experiments using deuterium instead of hydrogen were carried out with ethene, propene, and 3,3-dimethylbut-1-ene. The

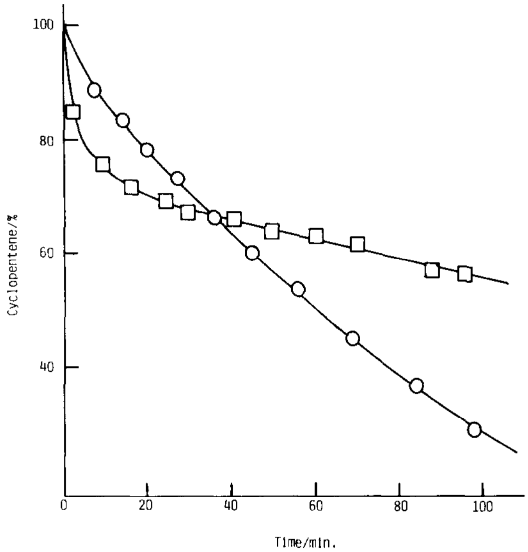

FIG. 9. Hydrogenation of cyclopentene(II) over 22 mg La_2O_3(I). ○, 312 K; □, 382 K.

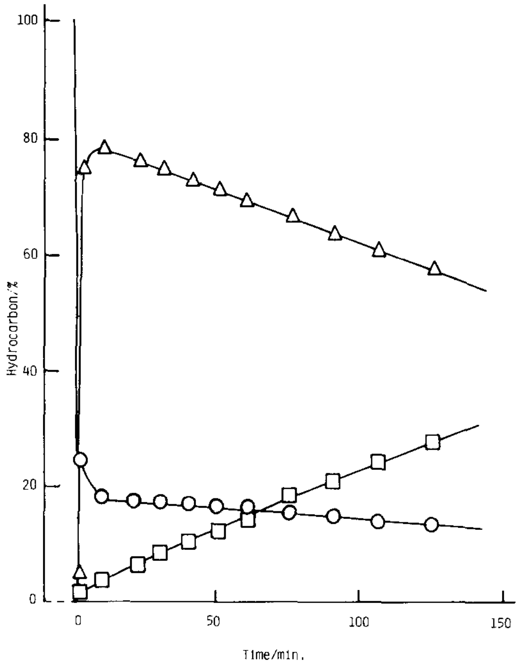

FIG. 10. Isomerization and hydrogenation of 2,3-dimethylbut-1-ene over 52 mg La_2O_3(I) at 373 K. ○, 2,3-dimethylbut-1-ene; △, 2,3-dimethylbut-2-ene; □, 2,3-dimethylbutane.

procedure in each case involved following reactions at a selected temperature by gas chromatography until about 20% of the alkene had been converted to alkane and then the hydrocarbons were condensed and subsequently analyzed by NMR spectroscopy. In this way, it was possible to determine the amount and position of the deuterium atoms in the alkanes and, when exchange occurred, in the alkenes as well. In some cases it was possible to identify grouping of deuterium atoms in the products because the resonances were displaced by isotopic shifts caused by other deuterium atoms in neighboring positions (*15*, *16*).

Ethene and 3,3-dimethylbut-1-ene. In both cases deuterium was observed only in the alkanes formed and not in the alkenes. Reaction of ethene at 222 K to 30% conversion gave a simple NMR spectrum with a single resonance at $\delta = 0.834$ ppm. This position corresponds closely with the expected value (*15*), $\delta = 0.836$ ppm, for the compound CH_2DCH_2D in which the two deuterium atoms are equivalent but are subject to a β-shift due to the neighboring deuterium. Clearly, the reaction involved simply the addition of deuterium to the alkene without any detectable alkene exchange.

Two experiments were carried out at 243 K using 3,3-dimethylbut-1-ene with conversions of 14 and 27% to 2,2-dimethylbutane, respectively. In both cases the spectra had two resonances of similar size with $\delta = 0.811$ ppm and $\delta = 1.196$ ppm. These positions suggested that the product of the deuteration contained one primary and one secondary deuterium atom so that again the reaction involved simply addition of deuterium across the double bond to give $(CH_3)_3CCHDCH_2D$ and no exchange of the alkene.

Propene. The NMR spectrum of the products from the conversion of 20.2% propene to propane at 380 K was complex but readily interpreted. Significant amounts of deuterium were present in the alkene and the positions of the resonances were identical to those previously found for the exchange of propene with deuterium over calcium oxide (*16*) together with some evidence of a small amount of exchange of the H atom on the central carbon atom. The resonances due to deuterium present in the propane were less well resolved but showed evidence for D atoms in both secondary and primary positions in various groupings which were established from the isotopic shifts (*15*). The full analysis of the spectrum from this experiment is given in Table 6.

We will consider the distribution of deuterium atoms in the propene first. Although some exchange of the H atom had taken place on the central carbon, the percentage

TABLE 6

Analysis of the NMR Spectrum for the Reaction of Propene with Deuterium after 20.2% Conversion to Propane

Deuterium in propene				
Grouping[a]	Chemical shift (ppm)	% D		
		Expt 1	Expt 2[b]	Calculated[c]
X—C—X ‖ CX_3—C—D	5.8551	2.1	—	
D—C—H ‖ CX_3—C—X	5.0570	17.3	17.6	18.1
D—C—D ‖ CX_3—C—X	5.0428	2.1	2.1	1.9
H—C—D ‖ CX_3—C—D	4.9638	19.0	19.4	18.1
D—C—*D* ‖ CX_3—C—X	4.9481	2.6	2.7	1.9
—CH_2X	1.7135	49.1	50.2	49.3
—CHD_2	1.6945	7.8	8.0	10.2
—CD_3	—	—	—	0.5
		100.0	100.0	100.0

Deuterium in propane				
	Grouping[a]	Chemical shift (ppm)	% D	D/molecule
Secondary	$(CH_3)_2CHD$	1.3058	9.4	0.90[d]
	$(CH_3)(CH_2D)CH$*D*	1.2990	40.2	
Primary	—CH_2CH_2D	0.8919	4.4	0.92
	—$CHDCH_2$*D*	0.8831	40.7	
	—$CHXCHD_2$	0.8642	5.3	
			100.0	

[a] X refers to H or D.

[b] Distribution in terminal positions scaled to 100%.

[c] Calculated for a random distribution over the five terminal positions with a chance of a D in each position of 0.095.

[d] Assigned on the relative amounts of the primary deuterium groupings –CH_2CH_2D and –$CHDCH_2D$.

of D in this position was much less than the expected 16.7% for a random distribution of D over all six positions. Thus, the main exchange had occurred in the five terminal positions and the agreement between experimental distribution 2 and the calculated distribution confirmed that exchange over these five positions was random. The relative amounts of the two groupings of primary D atoms in the propane $-CH_2CH_2D$ and $-CHDCH_2D$ showed that only 90% of the propane had a D atom on the central carbon. On this evidence we assigned the value of 0.90 for the number of secondary D atoms in the propane molecules. Comparison of the sizes of the various resonances then indicated that each propane had 0.92 primary D atom and that the propene molecules had an average of 0.30 D atom. Thus in the period of the experiment during which 20% of the propene was deuterated some 30% of the alkene acquired a D atom. It follows that the exchange reaction was some 1.5 times faster than the addition process.

We can also estimate the chances of acquiring D at the secondary and primary positions of propene in the formation of propane. Since the exchange on the central carbon of the alkene was small, the final value of 0.90 secondary D in each propane indicated a 90% chance of acquiring D at the secondary position of the alkene. Some of the 0.92 primary D observed in the propane would have originated from exchange of the alkene. This contribution from exchanged alkene was assumed to be half the final value of the amount of deuterium on the end carbon atoms of the propene, i.e., 0.15 D/molecule. This suggested that the 0.92 value was a sum of 0.15 from exchanged alkene and 0.77 from the addition process, so that only 77% of the atoms adding to the methylene group of the alkene were D. The appreciable chance (23%) of acquiring an H atom at the methylene group on addition explains why 19% of the secondary deuterium in propane had no primary deuterium neighbor.

DISCUSSION

In order to obtain maximum catalytic activity for lanthana a compromise has to be made between removal of surface impurities and loss of surface area as a consequence of a high pretreatment temperature. Treatment at 873 K clearly removed water but some carbonate remained as confirmed by both the thermogravimetric and infrared results obtained. Treatment at 1073 K removed all impurities but gave an oxide with a surface area of $<2\ m^2\ g^{-1}$. The experiments on the hydrogenation of 3,3-dimethylbut-1-ene indicated an optimum pretreatment temperature of 950 K. In terms of characterization our catalyst was similar to the sample prepared by Rosynek and Magnuson (*19*) who used the dehydration/rehydration method. The catalytic activity and the selectivity observed in this work for the isomerization of but-1-ene were comparable to those reported by Rosynek *et al.* (*10*); see Table 4. Furthermore, our extrapolated rate for the hydrogenation of ethene in a first reaction of over 10^{18} molecules $s^{-1}\ m^{-2}$ is in line with the rate of 4×10^{18} molecules $s^{-1}\ m^{-2}$ at 273 K from Jensen's results (*5*).

Much of the emphasis in previous investigations involving reactions of alkenes on lanthana has been on effects of outgassing temperature, on selectivity, and on the influence of poisons on activity. Several groups (*4, 7, 9*) have reported that lanthana was very sensitive to traces of impurities. Rosynek and Fox (*7*) ascribed curvature at low conversions in the kinetic plots to self-poisoning by but-1-ene, and Goldwasser and Hall (*9*) observed stable and reproducible activities only for samples of butene which had been repeatedly purified. Our results confirm the very substantial loss of activity which occurs when lanthana is stored under atmospheric conditions.

Self-Poisoning in Alkene Reactions

A main conclusion from our results is that stable catalytic activity for reactions of alkenes on lanthana is the exception rather than the norm. One advantage of a recirculation system is that the course of reactions can be followed with time and changes of rate readily determined. Even allowing for kinetic dependence on the pressure of alkene where appropriate, falling rates do appear to be a general feature of the alkene/lanthana systems. The degree to which rates diminish depends on the nature and purity of the alkene, the reaction temperature, and the storage of the catalyst sample.

The overall behavior of reactants with branched structures, such as 3,3-dimethylbut-1-ene and 2-methylpropene, was better than that found with the straight-chain molecules. Hence one possible course of falling rates may be some oligomerization of the alkene on the catalyst surface. Straight-chain molecules would be more likely to exhibit such a reaction than branched molecules. Certainly the most stable catalytic activity was observed with 3,3-dimethylbut-1-ene at 273 K (Fig. 5) and much steadier and more reproducible activity was found at 414 K with 2-methylpropene than with propene. The worst behavior was found with cyclopentene(I) where the presence of peroxide impurities probably enhanced oligomerization.

A further potential course of self-poisoning with alkene/oxide systems is the breakdown of the hydrocarbon by reaction with the surface of the oxide to form surface carboxy entities and adsorbed water. Catalytic activity depends on the formation of adsorbed intermediates which can then be converted to other hydrocarbons. At higher temperatures or on oxides such as lanthana with high affinity for carbon dioxide the intermediates may breakdown irreversibly and the surface become poisoned.

Activity for Hydrogenation and Mechanistic Considerations

Results in Table 7 show the temperatures required to give a rate of hydrogenation of the various alkenes of 10^{16} molecules s^{-1} m^{-2}. The two most easily hydrogenated alkenes are ethene and 3,3-dimethylbut-1-ene and we believe that the one common property linking these compounds is that neither can form an allyl species. The fact that no exchange was detected with either alkene in the experiments using deuterium is another feature in common. The absence of exchange with these alkenes shows that no reversible dissociation occurs to adsorbed vinyl species at low temperatures and also that the formation of the alkyl species is probably rate determining in the addition process. Any alkyl species formed is converted to alkane without any significant back reaction to adsorbed alkene. This behavior is comparable to results reported for ethene (*20*) and cyclopentene (*21*) on zinc oxide for which there was evidence against any contribution from alkyl reversal processes.

TABLE 7

Temperatures Required for Hydrogenation of Different Alkenes on Lanthana

Alkene	Temperature for hydrogenation at 10^{16} molecules s^{-1} m^{-2} (K)
Ethene (second reaction)	222
3,3-Dimethylbut-1-ene	240
Cyclopentene	<312
Propene	342
2-Methylpropene	345
2,3-Dimethylbutenes	>373

The inverse correlation between ability to form allylic species and rate of hydrogenation is further confirmed by the fact that cyclopentene was the next most readily hydrogenated molecule after ethene and 3,3-dimethylbut-1-ene. The formation of a π-allyl species is possible from cyclopentene but does not occur to any appreciable extent on zinc oxide (*21, 22*) or on γ-alumina (*23*). The remaining alkenes studied in this work may dissociate to allyl species without difficulty and the lower rates of hydrogenation observed may be associated with a significant fraction of surface sites being occupied by such species which cannot, of course, contribute to the formation of alkane. The difference between the fast hydrogenation of ethene and the much lower rates for propene and 2-methylpropene on lanthana is in accord with the relative rates reported by Jensen (*5*) for ethene, propene, and but-1-ene. A similar difference was observed between the rates of hydrogenation of ethene and of other alkenes on zinc oxide (*17*) and attributed to the consequences of allyl formation with the C_3- and C_4-alkenes.

The rapid isomerization of 2,3-dimethylbut-1-ene at 373 K probably occurred through the reversible formation of allylic species although the alternative mechanism involving tertiary carbocations cannot be entirely excluded. Further evidence for the role of allylic intermedites came from the exchange of 2-methylpropene with deuterium which takes place at 5 to 10 times the rate of the addition reaction (*13*) and from the present results with propene for which a process leading to the random exchange of the five terminal positions in the molecule exceeds addition at 380 K. The small amount of exchange of the central position found with propene may be due to some alkyl reversal occurring at this temperature which is over 100 K above the temperatures used for the NMR studies on ethene and 3,3-dimethylbut-1-ene. The different chances of acquiring a D atom at the secondary and primary positions of propane in the addition reaction may indicate that two pools of H/D species are present on the surface although the evidence for this was clearer in the previous work with 2-methylpropene (*13*). The suggestion is that the species (possibly with a partial positive charge) acquired at the primary position is more likely to be diluted with hydrogen through the alkene exchange process than the species (partial negative charge) taken up on the secondary carbon atom.

Isomerization

The high initial ratio of *cis*/*trans* products from the fast isomerization of but-1-ene exemplifies the basic nature of lanthana. However, the striking difference between the reaction of but-1-ene and those of *cis*-but-2-ene and of 2,3-dimethylbut-1-ene is the much greater degree of self-poisoning observed. These facts substantiate the suggestion that less self-poisoning is associated with alkenes having more alkyl groups linked to carbon atoms at the ends of the double bond.

The absence of detectable isomerization of 3,3-dimethylbut-1-ene even at 510 K was perhaps not surprising since it is a reaction which occurs readily only on catalysts with acidic sites and is not found to occur on basic oxides (*18*). Our results support the conclusions in the literature that the mechanism of alkene isomerization on lanthana is the reversible formation of carbanionic allylic species, a process which cannot occur with 3,3-dimethylbut-1-ene.

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