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The Oxidative Dehydrogenation of Cyclohexane and Cyclohexene over Unsupported and Supported Molybdena Catalysts Prepared by Metal Oxide Vapor Deposition

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A novel molybdena catalyst has been prepared by metal oxide vapor synthesis (MOVS) and used to promote the vapor phase oxidative dehydrogenation of cyclohexane and cyclohexene. At temperatures in excess of 553 K, the conversion of cyclohexane over γ-alumina supported and unsupported MOVS catalysts and a commercial MoO_3/Al_2O_3 sample yielded cyclohexene, benzene, carbon monoxide, and carbon dioxide as the only detected products. The unsupported MOVS sample behaves as an active heterogeneous catalyst but the specific activities are increased by a factor of up to 8 upon supporting the precursor on alumina. The supported MOVS system also exhibits appreciable higher activity than the commercial catalyst and this is attributed to the unique dual dioxo-molybdenum sites present in the active MOVS catalyst. The oxidative dehydrogenation of cyclohexane is viewed as occurring in a stepwise fashion with cyclohexene appearing in the product mixture and the generation of carbon oxides occurring principally from the direct combustion of cyclohexane. Oxygen consumption, specific activities, and molar selectivities for the conversion of both reactants in the overall temperature range 488 K $\leq T \leq$ 673 K over the three molybdena systems are provided. Cyclohexene conversion to benzene exhibits zero and first-order behavior with regard to the hydrocarbon and oxygen concentrations, respectively, and apparent activation energies are recorded for the supported (89 kJ mol^{-1}) and unsupported (126 kJ mol^{-1}) MOVS and commercial (103 kJ mol^{-1}) catalysts. The nature of the reactive oxygen and catalytic sites are considered and the reactivity and stoichiometry of the deep oxidation of both cyclic hydrocarbons are presented.

INTRODUCTION

In dehydrogenation reactions, a hydrocarbon molecule is converted into a more unsaturated hydrocarbon by breaking C—H bonds and forming C=C bonds. The heterogeneous catalytic dehydrogenation of cycloalkanes is normally achieved in anaerobic media and has served in some instances (1–4) as a model reaction to probe the metallic activity of unsupported and supported transition metal systems. The use of gaseous oxygen as oxidant yields water as a by-product and provides the thermodynamic driving force which permits the reaction to be conducted at a lower temperature than a simple dehydrogenation without oxygen (5). The oxidative dehydrogenation of cyclohexane has been reported using vanadate (6) and zeolite (7–11) based catalysts. Molybdena catalysts have also been successfully employed in the conversion of cyclohexane but in a hydrogen atmosphere (12–14) and the published oxidative dehydrogenation studies have largely been limited to olefins (15–17) and alcohols (18–20) as the feedstock. Previous documented research conducted in this laboratory revealed that an alumina-supported molybdenum catalyst prepared by metal oxide vapor synthesis (MOVS) exhibits considerably higher activities in the oxidative dehydrogenation of methanol (21) and ethanol (22) when compared with a conventional iron molybdate/molybdenum trioxide catalyst. The focus has now been switched to the oxidative dehydrogenation of cyclohexane and cyclohexene, and reproducible catalytic data are reported herein for unsupported and supported MOVS molybdena systems and a commercial MoO_3/Al_2O_3 sample prepared by impregnation. This comparative study is based on reactivity, so discussion of detailed characterization data is deemed outside the scope of this paper. The response of the activity/selectivity data to a range of catalytic parameters is shown to be diagnostic of the unique structural properties of the MOVS system and the nature of the active sites and reactive oxygen are addressed.

EXPERIMENTAL

Catalyst Preparation and Activation

The metal oxide vapor syntheses were carried out using the Torrovap apparatus that has been described in full detail elsewhere (23). Molybdenum trioxide (Aesar/Johnson Matthey, 99.95%) vaporization was achieved by resistive heating at a pressure of 3×10^{-6} torr and the oxide vapors were cocondensed at 77 K with a 250-fold molar excess

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of anhydrous methanol (Aldrich, 99.9+%). The cocondensate was allowed to slowly come to room temperature and formed a clear colorless solution which was removed from the reaction flask via a cooled Schlenk tube. The evaporation/cocondensation reaction can be simply expressed as

$$2MoO_3 + 4CH_3OH \rightarrow Mo_2O_5(OCH_3)_2 \cdot 2CH_3OH + H_2O.$$

After 6 to 8 h at room temperature the condensate became cloudy and a white precipitate eventually formed which may be denoted as the unsupported catalyst precursor. Alternatively, a γ-alumina (Aesar/Johnson Matthey, 99.99%, 188 $m^2\ g^{-1}$) support was introduced to the cocondensate prior to precipitation. The combined mixture was then stirred for 36 h to ensure an even deposition throughout the carrier at which point the solution volume was reduced by vacuum evaporation to recover the supported catalyst precursor. Both precursors were lightly ground, dried at 383 K and exposed to UV radiation ($\lambda = 350$ nm) for 7 days; photoactivation produced formaldehyde and methanol as byproducts to generate the core molybdena species. The resultant solids were then calcined by heating in a 120 $cm^3\ min^{-1}$ stream of dry air at a rate of 5 K min^{-1} to a final temperature of 673 K which was maintained for 18 h prior to catalysis. A sample of a commercial 10% w/w MoO_3 on γ-alumina (Aesar/Johnson Matthey) catalyst was likewise calcined for comparative purposes.

Catalytic Procedure

All the catalytic reactions were carried out under atmospheric pressure in a fixed bed glass reactor (i.d. = 15 mm) over the temperature range 488 K $\leq T \leq$ 673 K. The catalysts, sieved in the mesh range 125–150 μm, were diluted by an equal amount of silica and supported on a glass frit where a layer of glass beads above the catalyst bed ensured that the reactants reached the reaction temperature before contacting the catalyst. The reactor temperature was monitored by a thermocouple inserted in a thermowell within the catalyst bed; reactor temperature was constant to within ±1 K. A Sage pump (model 341 B) was used to deliver the cyclohexane and cyclohexene feed via a syringe at a fixed rate which had been carefully calibrated. The hydrocarbon vapor was carried through the catalyst bed in a stream of dry air, the flow rate of which was set using Brooks mass flow controllers. Rate measurements were made at a space velocity of $1.5 \times 10^3\ h^{-1}$ (STP) and in the W/F range 6–124 g mol^{-1} h, where W is the weight of activated catalyst and F is the flow rate of hydrocarbon. Reaction rates measured in this W/F range, where W and F were independently varied, were constant to within ±8% at a constant W/F value. The oxygen to hydrocarbon ratio was maintained at 2.7 : 1.0, where the partial pressure of oxygen equalled 140 torr. Oxygen partial pressure in the conversion of cyclohexene was varied from 70 to 210 torr, using purified nitrogen as diluent, at constant hydrocarbon pressure to determine the reaction order with respect to oxygen. Steady state conversions were kept below 30% by varying W in order to minimize heat and mass transfer effects and the carbon balance was within ±6%. Blank runs showed that the reactor walls, diluent, and glass beads were inert with respect to cyclohexane/cyclohexene oxidative dehydrogenation in the temperature range that was investigated. Product analysis was made using a Varian 3400 GC chromatograph employing a 30% Silicone SF96 on 60/80 mesh acid washed Chromosorb *W* (6 ft × 1/8 in.) stainless steel column and FI detector to analyze the C_6 hydrocarbon components and a 60/80 mesh Carboxen 1000 (15 ft × 1/8 in.) stainless steel column and TC detector to analyze O_2, N_2, CO, and CO_2 content in the product stream; data acquisition and analysis was performed using the GC Star Workstation. Mol% conversion of cyclohexane/cyclohexene is defined as $(m_i - m_o)/(m_i) \times 100$, where m_i is the initial concentration or number of moles of cyclohexane/cyclohexene entering the reactor per unit time and m_o is the number of moles of cyclohexane/cyclohexene exiting the reactor per unit time. Molar selectivity in terms of product x is defined by $m_x/m_{tot} \times 100$, where m_{tot} is the total number of moles of product. The cyclohexane and cyclohexene (Aldrich, 99+%) reactants were thoroughly degassed by purging with purified helium followed by a series of freeze/pump/thaw cycles and were stored over activated molecular sieve type 5A.

RESULTS AND DISCUSSION

The photoactivated unsupported MOVS sample is composed of α-MoO_3 and an amorphous component and is characterized by a particle diameter in the range 15–50 nm, a surface area of 25 $m^2\ g^{-1}$ and pore radii ranging from 0.8–6.2 nm (21). The commercial MoO_3 sample or catalyst precursor used in the MOVS synthesis is characterized by a particle size distribution from 1 to 15 μm and a surface area of 1–2 $m^2\ g^{-1}$. The supported (10% w/w MoO_3/Al_2O_3) MOVS system exhibited no apparent crystallinity, a surface area of 77 $m^2\ g^{-1}$, which is higher than that exhibited by the commercial 10% w/w MoO_3 on γ-alumina catalyst (64 $m^2\ g^{-1}$), and a narrow pore radius distribution (0.8–1.8 nm). Stability of the catalysts to 673 K was assured by prior testing results to this temperature (21). Additionally, differential scanning calorimetry (DSC) and thermalgravimetric analysis (TGA) to 773 K show that the unsupported MOVS catalyst gives a continual endothermic energy absorption with no significant weight loss, whereas the DSC profile of the supported MOVS catalyst matches well that of MoO_3 itself, with the 7% weight loss (TGA) that occurs below 553 K being attributable to loss of physisorbed methanol.

Passage of cyclohexane or cyclohexene in a stream of air over the three molybdena systems only yielded dehydrogenation and combustion products in the temperature range 488 K ≤ T ≤ 673 K; oxidation products such as cyclohexanone or cyclohexanol or the partially dehydrogenated cyclohexadiene were not observed. The activity/selectivity data presented in this paper were reproducible to better than ±6% and represent the average of at least five separate test samples. The γ-Al_2O_3 carrier alone was found to exhibit negligible oxidative dehydrogenation activity as observed previously by Minachev *et al.* (10).

The products of cyclohexane conversion were cyclohexene, benzene, carbon monoxide, carbon dioxide, and water. Steady state conversions were achieved after 0.8–2.0 h on stream, the time necessary to attain steady state decreasing with increasing reaction temperature. The slow continuous deactivation reported for dehydrogenation in hydrogen (1) was not evident in this study. The relationship between conversion and selectivity is illustrated in Fig. 1. The degree of conversion to benzene noticeably increased with increasing conversion apparently at a loss to the selective formation of cyclohexene. As the reaction progressed, combustion to CO_x also proceeded with increasing selectivity. The relationships plotted in Fig. 1 are characteristic of a sequential reaction mechanism where cyclohexane is dehydrogenated stepwise to benzene via cyclohexene as a stable intermediate which desorbs from the catalyst to appear in the product stream. Combustion occurs at all degrees of conversion but is clearly promoted at higher conversions. Carbon oxides may then result from the oxidation of (a) the cyclohexane reactant which occurs from the outset of the reaction, (b) the partially dehydrogenated cyclohexene which may account, at least in part, for the observed drop in selective cyclohexene formation, or (c) the fully dehydrogenated benzene, as the degree of combustion mirrors the increase in selective benzene formation. It is not, however, possible to identify the principal source of CO_x from the data presented in Fig. 1.

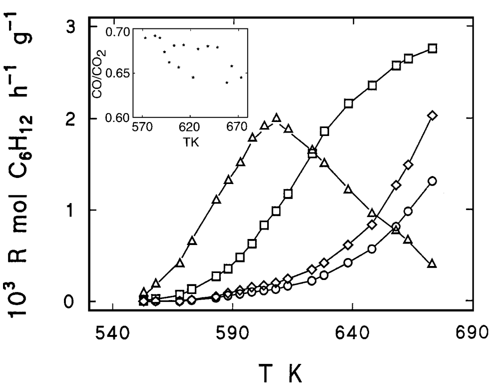

FIG. 2. Rate of conversion of cyclohexane over the supported MOVS catalyst to cyclohexene (△), benzene (□), CO (○), and CO_2 (◇) as a function of reaction temperature. Inset: the effect of temperature on the product CO/CO_2 ratio.

Steady state activity as a function of reaction temperature for the supported MOVS catalyst is illustrated in Fig. 2. The rate of oxidative dehydrogenation of cyclohexane to cyclohexene passes through a maximum at 608 K while the rate of benzene and CO_x formation increases with increasing temperature over the entire temperature range that was considered. The effect of temperature on the CO/CO_2 product ratio is shown in the inset to Fig. 2. Carbon dioxide was the preferred combustion product with a CO/CO_2 ratio in the range 0.65–0.70. The combustion product composition exhibits no discernible temperature dependence and deep oxidation stoichiometry can be approximated by

$$5C_6H_{12} + 39O_2 \rightarrow 18CO_2 + 12CO + 30H_2O.$$

The influence of temperature on the four sets of molar selectivity data at steady state is presented in Fig. 3. At temperatures less than 628 K cyclohexene was the preferred product but was produced with continually decreasing selectivity as the temperature was elevated from 553 to 673 K. Selective formation of benzene passes through a maximum at 628 K while deep oxidation proceeded with increasing

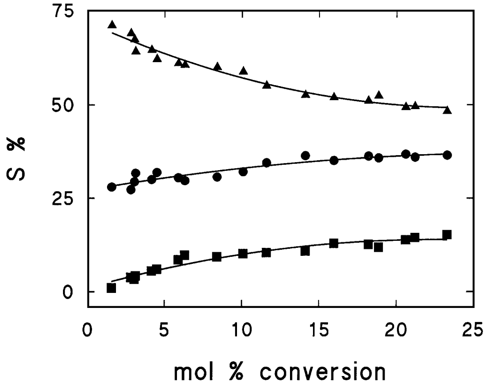

FIG. 1. Variation in the selective formation of cyclohexene (▲), benzene (■), and carbon dioxides (●) with increasing conversion of cyclohexane over the supported MOVS catalyst.

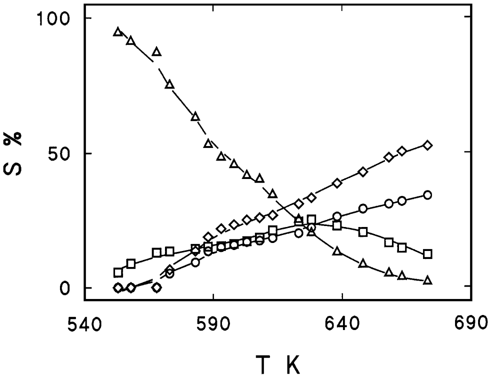

FIG. 3. The effect of temperature on the selectivity with which cyclohexene (△), benzene (□), CO (○), and CO_2 (◇) are formed from the conversion of cyclohexane over the supported MOVS catalyst.

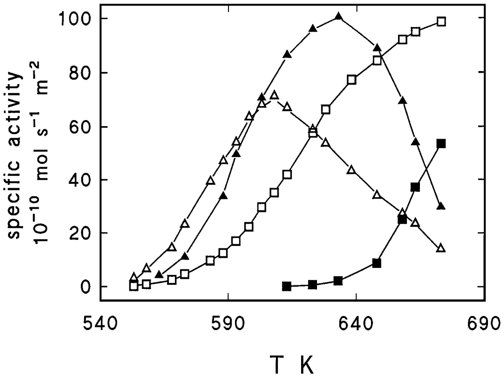

FIG. 4. Temperature dependence of specific activity in the conversion of cyclohexane to cyclohexene (△, ▲) and benzene (□, ■) over the commercial (solid symbols) and supported MOVS (open symbols) catalysts.

selectivity to attain a combined CO_x selectivity of 87% at 673 K. The selectivity data are again indicative of a stepwise dehydrogenation of cyclohexane, where the further conversion of cyclohexene was promoted with increasing temperature, the formation and dehydrogenation of cyclohexadiene appears facile at all temperatures and reactant combustion was ultimately the preferred process.

The specific activity, or number of moles of cyclohexane converted per unit time per surface area, in the conversion of cyclohexane to cyclohexene and benzene, obtained using the laboratory prepared and commercial catalyst is compared in Fig. 4. The MOVS catalyst is certainly the more active and the oxidative dehydrogenation products, cyclohexene and benzene, were generated at temperatures 10 and 60 K lower, respectively, than observed for the commercial catalyst. In addition, the turnover of cyclohexane to cyclohexene over the impregnated sample passed through a maximum ca. 25 K higher than that recorded for the MOVS system. At temperatures greater than 603 K the commercial sample generated a higher concentration of cyclohexene in the product stream but the level of benzene formation was consistently and appreciably (by up to a factor of 10^2) lower. Catalyst preparation by impregnation is known to generate a nonuniform distribution of active sites and a heterogeneous active phase under certain calcination conditions (24). However, the enhanced dehydrogenation activities achieved using the laboratory prepared MOVS catalyst can not be attributed merely to an enhanced dispersion of active sites but may be accounted for by the unique structural properties of the MOVS system. The unsupported MOVS precursor has been shown to possess "dual dioxo molybdenum sites" and the unique bridging Mo–O–Mo moieties persist after its deposition on the support and calcination (23, 25). Earlier ESR, FTIR, FT-Raman, and DSC data suggest that the coordination geometry in the active MOVS catalyst may be predisposed to five coordination (25, 26), whereas it is known that Mo (VI) species predominate on the surface of calcined catalysts prepared by impregnation (27). The MOVS system can be said to possess active sites in a different environment from the conventional impregnated catalyst. Oxidative dehydrogenation normally proceeds via a hydrogen abstraction step involving the lattice oxygen of the metal oxide (28). In molybdena systems, the molybdenum to oxygen (Mo=O) terminal bonds are the principal source of hydrogen abstraction (28, 29). Goddard and Allison (30), on the basis of thermochemical measurements and *ab initio* quantum calculations, have shown that reactant activation at a catalytic site composed of two adjacent surface dioxo sites has a lower enthalpy of activation than that associated with a single molybdenum dioxo site. The greater lability of the terminal Mo=O bonds in the coordinatively unsaturated MOVS molybdenum species can be expected to interact more strongly (31) with the adsorbed cyclohexane reactant, providing a more energetically favorable pathway for hydrogen abstraction. While the terminal Mo=O bond initiates hydrogen abstraction, the bridging oxygen of the Mo–O–Mo moiety may participate in the oxydehydrogenation mechanism for the formation of water as has been proposed for V–O–V (32, 33). If hydrogen abstraction takes place at both terminal Mo=O sites and occurs at adjacent carbons in the cyclohexane ring, cyclohexene is then generated from the resultant cleavage of both C–H bonds. In the catalyst reoxidation and water evolution steps some of the cyclohexene must desorb prior to further hydrogen abstraction. The bridging oxide vacancies present in the MOVS system may act as the active sites for a rapid reoxidation of the reduced surface which facilitates a more efficient turnover of the adsorbed reactants than is observed for the impregnated system. The effect of supporting the MOVS precursor on the γ-alumina carrier on specific activity and selectivity is shown in Table 1. The unsupported MOVS catalyst was active also for this reaction but the specific activities are appreciably lower, by a factor of up to 8 and detectable conversion of the reactant only occurred at temperatures

TABLE 1

Effect of Supporting the MOVS Precursor on γ-Alumina on the Specific Activity in the Overall Conversion of Cyclohexane and on Reaction Selectivities

Temperature/ Catalyst	10^9 specific activity mol s^{-1} m^{-2}	$S_{\text{cyclohexene}}$ %	S_{benzene} %	$S_{\text{carbon oxides}}$ %
623 K				
Unsupported	1.7	79	9	12
Supported	13.2	25	24	51
648 K				
Unsupported	3.2	45	16	39
Supported	19.2	5	16	79
673 K				
Unsupported	5.2	25	24	51
Supported	23.1	2	12	87

in excess of 593 K. At low conversions (<5 mol%) the oxidative reaction yielded cyclohexene as the sole product. The extent of benzene and CO_x formation were again promoted with increasing temperature and combustion proved the overwhelming reaction at the highest temperatures that were studied. Anchoring the MOVS species to the support serves to greatly enhance activity presumably due to an increase in the dispersion of the active sites which may translate into a greater exposure of the (010) face plane which possesses an arrangement of dual dioxo units that is known to be highly active in oxidative dehydrogenation (34, 35).

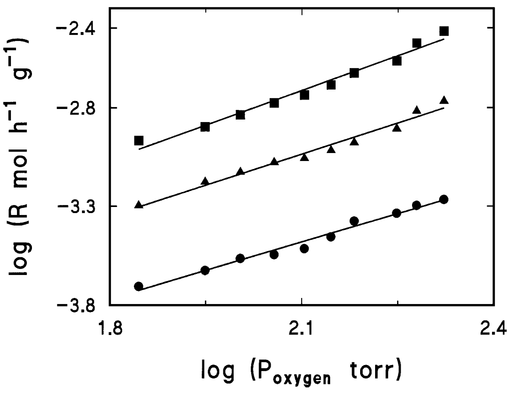

FIG. 6. Rate of cyclohexene oxidative dehydrogenation to benzene as a function of oxygen partial pressure at 493 K (●), 513 K (▲), and 533 K (■).

As cyclohexene has been identified as a principal reaction product and possible reaction intermediate, the oxidative dehydrogenation of cyclohexene as the reactant was also considered. Cyclohexene conversion over the three molybdena systems yielded benzene and carbon oxides as the only detected products. The steady state conversion of cyclohexene to benzene, where the degree of combustion accounted for less than 1 mol% of the total feed concentration, is directly proportional to the catalyst weight/feed concentration quotient as shown in Fig. 5 for two representative temperatures. The reaction can therefore be considered zero order with respect to cyclohexene concentration. The reaction order with respect to oxygen partial pressure was determined by means of logarithmic plots illustrated in Fig. 6, where the reaction orders increased from 0.96 to 1.16 as the temperature was raised from 493 to 533 K but the reaction can essentially be said to exhibit first-order behavior with regard to the oxygen partial pressure. Such reaction orders support a mechanism involving a strong adsorption of cyclohexene and molecular adsorption of oxygen. Indeed, the stoichiometric conversion of cyclohexene directly to benzene requires the consumption of one mole of oxygen for every mole of cyclohexene converted. The variation of logarithmic oxidative dehydrogenation rate with reciprocal temperature where deep oxidation was negligible yields the three Arrhenius plots shown in Fig. 7. The computed apparent activation energies with 95% confidence limits for the dehydrogenation of cyclohexene to benzene over the unsupported and supported MOVS and commercial catalysts are 126 ± 5, 89 ± 6, and 103 ± 4 kJ mol^{-1}, respectively. The plotted rates reflect the increasing activity of the catalysts in the order MOVS unsupported < commercial < MOVS supported. The unsupported system only generated an overall specific activity in excess of 10^{-10} mol s^{-1} m^{-2} at temperatures higher than 593 K. The difference in total specific activity (dehydrogenation and combustion combined) between the supported MOVS sample and the commercial catalyst, shown in Fig. 8, is less evident at the higher reaction temperatures as the combustion reaction was increasingly preferred. Molar selectivity as a function of temperature in the conversion of cyclohexene to benzene, carbon monoxide, and carbon dioxide over the supported MOVS system is illustrated in Fig. 9. At $T \leq 538$ K, benzene was the sole reaction product. At higher temperatures the selectivity with which benzene was formed noticeably declined as deep

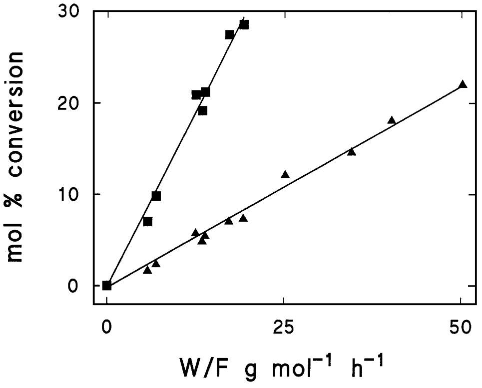

FIG. 5. Linear dependence of conversion on *W*/*F* for the oxidative dehydrogenation of cyclohexene to benzene over the supported MOVS catalyst at 498 K (▲) and 533 K (■).

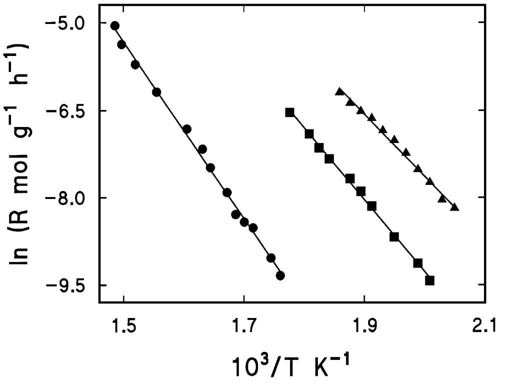

FIG. 7. Apparent Arrhenius plots for the oxidative dehydrogenation of cyclohexene to benzene over the unsupported (●) and supported (▲) MOVS and commercial (■) catalysts.

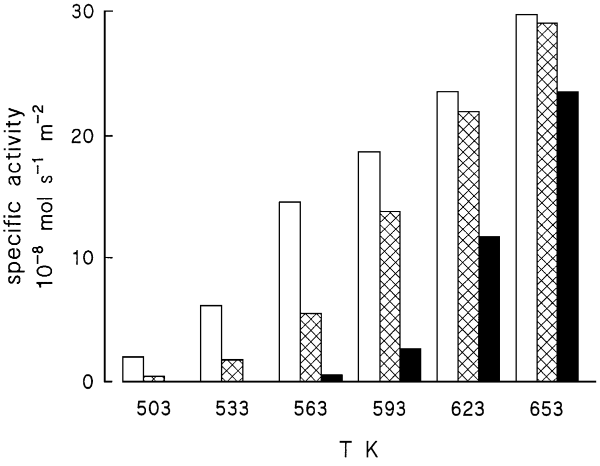

FIG. 8. Representative temperature dependencies of specific activity in the conversion of cyclohexene over the unsupported (solid bar) and supported (open bar) MOVS and commercial (cross-hatched bar) catalysts.

oxidation was increasingly promoted and at temperatures greater than 633 K the combined CO_x selectivity exceeded 50%. The relationship between temperature and the composition of carbon oxides in the product is displayed in the inset to Fig. 9. The ratio CO/CO_2 varies in the range 0.30–0.35 with no obvious temperature dependence. Deep oxidation of cyclohexene over the supported MOVS catalyst can be adequately described by the stoichiometric equation

$$4C_6H_{10} + O_2 \rightarrow 18CO_2 + 6CO + H_2O.$$

Both supported systems essentially behave as combustion catalysts at the higher reaction temperatures. It is becoming increasingly apparent in the literature that selectivity in terms of dehydrogenation, oxygen insertion, and combustion depends on both the catalyst and the reactant (36, 37). Bridging oxygens have been proposed in a number of catalytic systems (36, 38–40) to be the source of selective oxidation, in that such oxygens ions are more easily removed from the lattice to form C–O bonds. Nevertheless, the higher reaction temperatures involved in the conversion of cyclic hydrocarbons over the molybdena catalysts probably favor combustion to oxygenate formation. It is instructive to note that while the hydrocarbon to oxygen molar ratio for the combustion of both cyclohexane and cyclohexene equals 7.8, the carbon oxide composition generated by both reactants is different. The combustion of the more saturated cyclohexane feed produced a higher fraction of carbon monoxide in the combustion products. Such a finding suggests that the principal source of CO_x is the direct combustion of the reactant rather than the additional attack of reaction intermediates or the benzene product.

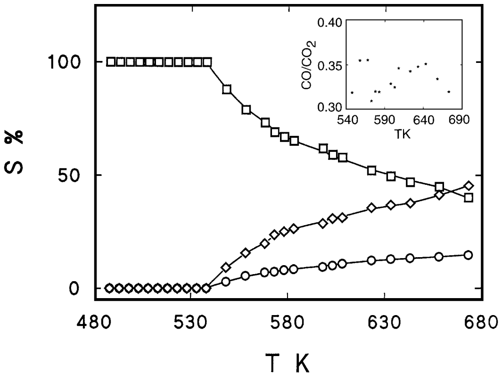

FIG. 9. The effect of temperature on the selectivity with which benzene (□), CO (○), and CO_2 (◇) are formed from the conversion of cyclohexene over the supported MOVS catalyst. Inset: the effect of temperature on the product CO/CO_2 ratio.

The reactivity of the two cyclic hydrocarbon reactants is compared in Table 2 on the basis of two chosen catalytic parameters. The temperature at which a specific activity of 2×10^{-9} mol s^{-1} m^{-2} was achieved was at up to 75 K higher in the case of the cyclohexane feed. The same parameter also reflects the greater efficiency of the supported MOVS system, compared with the commercial catalyst, but the 15–35 K differential observed in this study is lower than the 50 K difference reported earlier for the oxidative dehydrogenation of alcohols (21, 22). The second parameter, the temperature at which mol% conversion to carbon oxides exceeds 1 mol% (T_{CO_x}) also mirrors the higher activity of the alumina supported MOVS catalyst. Although the value of T_{CO_x} is the same for the conversion of both reactants over the relatively inactive unsupported MOVS sample, T_{CO_x} is lower for cyclohexene conversion over the supported systems. Indeed, the amount of oxygen consumed in the conversion of cyclohexene was consistently greater than that recorded for the cyclohexane transformation as is illustrated in Fig. 10. Detectable depletion of the oxygen component in the carrier gas stream occurred at temperature ca 50 K lower in the case of the conversion of cyclohexene. Under identical conditions, cyclohexene is considerably more reactive than cyclohexane and is an intermediate

TABLE 2

Comparison of the Temperature at Which (a) mol% Conversion to CO_x Exceeds 1 and (b) the Specific Activity Equals 2×10^{-9} mol s^{-1} m^{-2} in the Conversion of Cyclohexane and Cyclohexene over the Three Molybdena Systems

	T_{CO_x}		$T_{2 \times 10^{-9}\ \mathrm{mol\ s^{-1}\ m^{-2}}}$	
Catalyst	Cyclohexane	Cyclohexene	Cyclohexane	Cyclohexene
MOVS unsupported	623 K	623 K	623 K	553 K
MOVS supported	573 K	538 K	563 K	488 K
Commercial	583 K	553 K	578 K	503 K

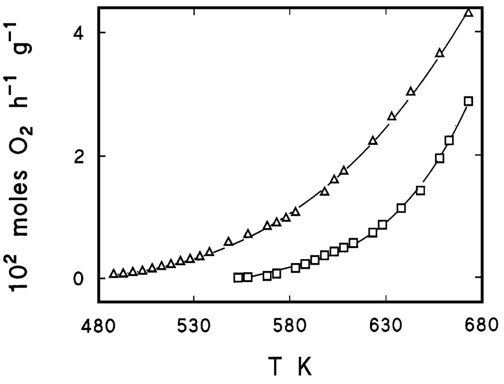

FIG. 10. Oxygen consumption as a function of reaction temperature in the conversion of cyclohexane (□) and cyclohexene (△) over the supported MOVS catalyst.

in the conversion of the latter. The oxidative dehydrogenation of cyclohexane to cyclohexene must therefore represent a rate-demanding step in the formation of benzene from cyclohexane. The molar selectivity with which carbon oxides were formed from both reactants and over both supported catalysts is depicted in Fig. 11. After the initiation of combustion, the more active MOVS catalyst promoted carbon oxide formation to a greater extent than is the case for the commercial sample. The lattice oxygens in the impregnated catalyst which do not possess bridging linkages are less reactive with the result that the degree of combustion is lower. The values of S_{CO_x} are initially higher for the more reactive cyclohexene feed, but at temperatures in excess of 623 K selectivity in the production of carbon oxides is greater from the cyclohexane feed. The adsorbed cyclohexane molecule must therefore require a higher reaction temperature for activation, but as the temperature is increased the rate-limiting partial dehydrogenation to cyclohexene favors the alternative route to CO_x. The more reactive cyclohexene feed, although undergoing combustion at a lower temperature, is dehydrogenated more facilely to benzene with the result that the selectivity with which deep oxidation proceeds is ultimately lower.

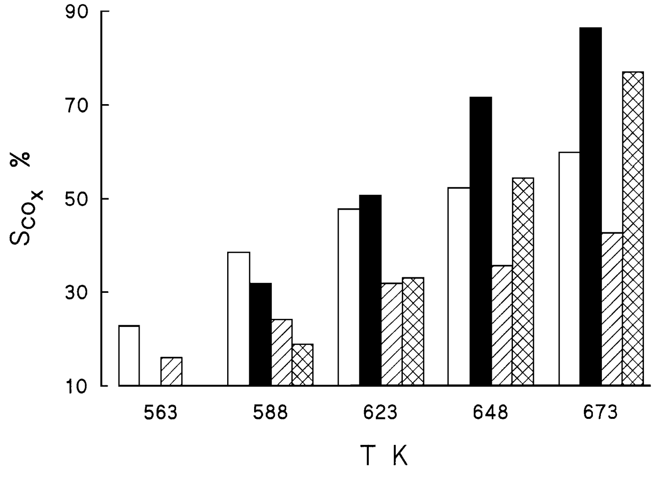

FIG. 11. Representative CO_x selectivity temperature dependencies for the conversion of cyclohexane (solid bar) and cyclohexene (open bar) over the supported MOVS catalyst and the conversion of cyclohexane (cross-hatched) and cyclohexene (hatched) over the commercial catalyst.

CONCLUSIONS

The data presented in this paper support the following conclusions:

(a) the gas phase treatment of cyclohexane and cyclohexene in air over the unsupported and supported MOVS and commercial molybdena catalysts in a continuous flow reactor at $488\ K \leq T \leq 673\ K$ only generates dehydrogenation and combustion products with no detectable oxygenate formation;

(b) at steady state, the oxidative dehydrogenation of cyclohexane proceeds in a stepwise fashion where cyclohexene is produced with decreasing selectivity; the selectivity with which benzene is formed passes through a temperature-related maximum and combustion to carbon oxides, which arises principally from the direct attack of the feed, is ultimately the preferred process;

(c) supporting the MOVS precursor on γ-alumina increases the specific activity in the conversion of cyclohexane by up to a factor of 8;

(d) in the oxidative dehydrogenation of cyclohexene to benzene, strong adsorption of the hydrocarbon and molecular adsorption of oxygen prevail where the apparent activation energies for the three molybdena systems are in the range 89–126 kJ mol^{-1};

(e) the supported MOVS system generates considerably higher dehydrogenation rates than the commercial sample due to the dual dioxo molybdenum sites present in the former which are more effective in the hydrogen abstraction step;

(f) the supported MOVS system also generates higher combustion rates which are attributed to the action of reactive oxygen in the bridging Mo–O–Mo linkages;

(g) combustion of cyclohexane and cyclohexene generates different carbon oxide compositions with the more saturated cyclohexane yielding (i) higher CO/CO_2 ratios at every reaction temperature and (ii) higher reaction selectivities in terms of overall CO_x formation at $T > 623$ K.

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