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The Mechanism of Dehydrogenation of Cyclohexane on MoO_3/Al_2O_3 Catalysts

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The conversion of cyclohexane in the dehydrogenation reaction over $MoO_3/\gamma\text{-}Al_2O_3$ catalysts, measured in a pulse reactor, increases with the metal oxide content. Up to 15 wt% MoO_3 only dehydrogenation products are observed (cyclohexene and/or benzene) with cyclohexene being present in limited amounts only and completely absent on catalysts with more than 10% MoO_3. Above 15 wt% MoO_3 combustion products are formed at the expense of benzene. On oxidized catalysts the reaction proceeds through oxodehydrogenation: carbon oxides mainly stem from octahedral oxomolybdenum configurations, while formation of benzene is favored by a tetrahedral molybdenum stereogeometry. For reduced catalysts an alternative simple dehydrogenation scheme is required in which the catalytic activity is directly related to the *d*-electron configuration of the metal in its various valence states. The proposed mechanisms are sustained by observations on the influence of reductants [H_2, CO), oxidants (O_2, CO_2) and water and by a study of the catalyst deactivation.

INTRODUCTION

Information in the literature on dehydrogenation of cyclohexane over MoO_3/Al_2O_3 catalysts is mainly concerned with the kinetic aspects of the reaction (*1*, *2*). It is the purpose of this paper to discuss the dehydrogenation mechanism of such catalysts after various pretreatments and, as in case of the transformation of propylene (*3*, *4*) and acetone (*5*), to discuss the relation between catalytic activity and the stereogeometry and valence state of the metal.

According to Erofeev *et al.* (*6*) dehydrogenation over several metallic oxides (Cu, Mo) is enhanced by supports having a crystal structure with octahedral symmetry of the cationic vacancies, such as MgO and $\gamma\text{-}Al_2O_3$. In fact, for spinel-type Al_2O_3 the structure $Al^{3+}(Al_{5/3}^{3+}\square_{1/3})O_4^{2-}$ has been proposed (*7*).

The coordination of molybdenum on $\gamma\text{-}Al_2O_3$ has been the subject of various studies (*8*, *9*). According to Asmolov and Krylov (*10*) and Giordano *et al.* (*11*) the oxomolybdenum environment gradually changes from tetrahedral to octahedral on increasing the MoO_3 content of the catalyst. The tetrahedral molybdenum species mainly occupy the vacancies at the surface whereas octahedral molybdenum coordinations also involve the bulk.

EXPERIMENTAL

Materials. Catalysts were prepared by impregnation of $\gamma\text{-}Al_2O_3$ (Akzo Chemie

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B-type, surface area 350 m^2/g, V_p 1.6 cm^3/g) with an aqueous solution of $(NH_4)_6MO_7O_{24} \cdot 4H_2O$ (C. Erba), followed by drying for 14 hr at 125°C and activation for 8 hr at 500°C.

Cyclohexane (R.P., C. Erba) was dried over anhydrous Na_2SO_4 before use. Transport gases were dried products of SIO S.p.a.

Pulse experiments. Catalytic activity measurements were performed in a pulse-microreactor (Fig. 1), similar to the one described in previous work (*12*), in which the carrier gas (He), after passing the detector of an analytical unit (Fractovap Mod. C, C. Erba), is regulated by two valves in such a way as to vary the contact time τ at a constant overall flux in the chromatographic column. After injection of the reactant pulse (1 μl), the gaseous mixture is passed through a Pyrex reactor, loaded with 0.25 to 0.35 g of catalyst in the 50 to 300 μm size. Temperature control of the reactor and heating unit was effected by means of Fe-constantan thermocouples.

Product analysis. The reaction products (cyclohexane, benzene, cyclohexene, CO, and CO_2 were analyzed gas chromatographically with a column (∅ 4 × 2 mm, length 1.0 m) loaded with di-*n*-decylphthalate on Chromosorb P (20 wt%) or Chromosorb 102 (for detection of H_2O) at 90°C with a He gas flow of 1.7 liters hr^{-1}.

RESULTS

Cyclohexane Pulses

Experimental results were collected using γ-Al_2O_3 loaded with 10, 20 and 30 wt% MoO_3. The conversions of cyclohexane, reported in Figs. 2–4 as a function of the number of "slugs" (pulses), refer to catalysts after various pretreatments in the temperature range 350 to 460°C for 3 hr following outgassing with helium at 350°C for 14 hr. The total conversions decrease sharply with time at a reaction temperature of 460°C both on oxidized and outgassed catalyst samples; this is different from reduced samples where the conversion does not greatly vary for several hours after an initial induction period. Initial conversions (first slug) depend upon the degree of oxidation and temperature and time of pretreatment; the reaction is selective toward benzene on reduced catalysts and on oxidized and outgassed 10 wt% MoO_3 samples (Fig. 5). In the latter case, CO and CO_2 are formed at the expense of benzene, especially at higher loads of the active phase. Selectivity to CO_x increases with the degree of oxidation, in particular for the catalyst with the highest MoO_3 content (Fig. 4); it also increases toward higher conversions of cyclohexane (Fig. 6). The diminution in activity as a function of the number of slugs leads to

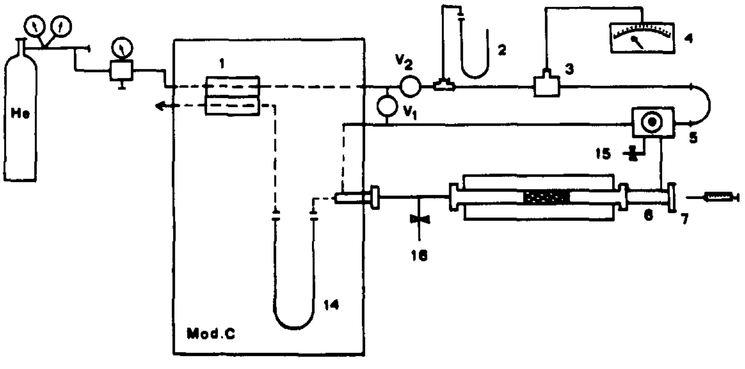


FIG. 1. Schematic view of the apparatus with thermal conductivity detector (1), valves V_1 and V_2, manometer (2), Hastings gas flow detector (3, 4), Carlo Erba device for mounting an external column (5), preheating chamber (6), followed by microreactor and analytical column (14).

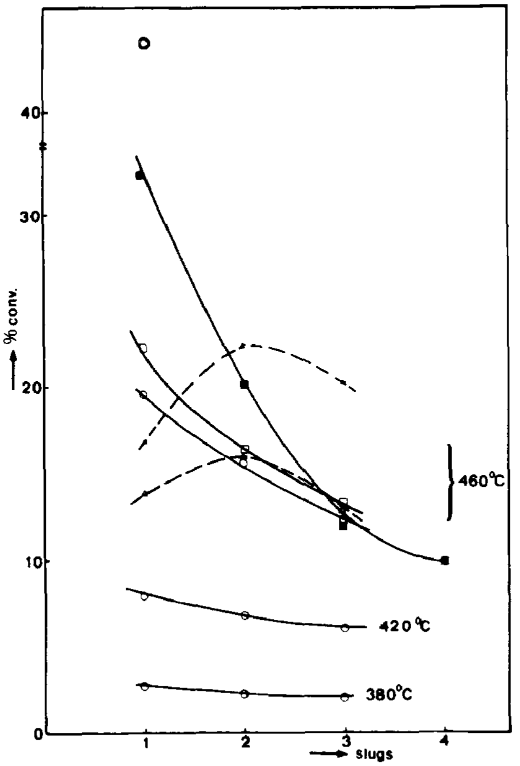


FIG. 2. C_6H_{12} conversions at various reaction temperatures over 10 wt% MoO_3/Al_2O_3 catalysts (τ = 2.6 sec), preheated at 460°C in O_2 (◎), air (■), He (○), H_2 (×), and at 350°C in air (□) or H_2 (△).

higher selectivity in benzene, which reaches almost 100% after five or six pulses of cyclohexane.

The catalyst surface is not deactivated homogeneously, as may be derived from the fact that data referring to subsequent slugs do not agree with those of the first pulse reported in Fig. 6.

Effect of O_2, H_2, CO, CO_2, and H_2O

Table 1 reports the effect on the reaction of cyclohexane when alternating pulses, O_2 or air, and hydrocarbon, are introduced. This treatment favors the total conversion and selectivity to carbon oxides, especially the latter for the oxidized and outgassed catalysts containing more than 10 wt% MoO_3. The capacity of replenishing oxygen and of reestablishment of the initial activity is higher for catalysts at lower molybdenum contents.

The influence of alternating pulses, H_2, CO, CO_2 or H_2O, and C_6H_{12}, is illustrated in Table 2. Water rapidly deactivates the catalyst, whereas CO_2 is inert. Hydrogen and CO do not substantially modify the conversion levels of the reduced catalysts. However, in the case of the oxidized catalysts, H_2 and CO block the deactivation or increase the conversion level, depending on the operating conditions; the benzene selectivity here is almost 100%.

Reaction Scheme

The presence of cyclohexene, in small quantities, among the reaction products

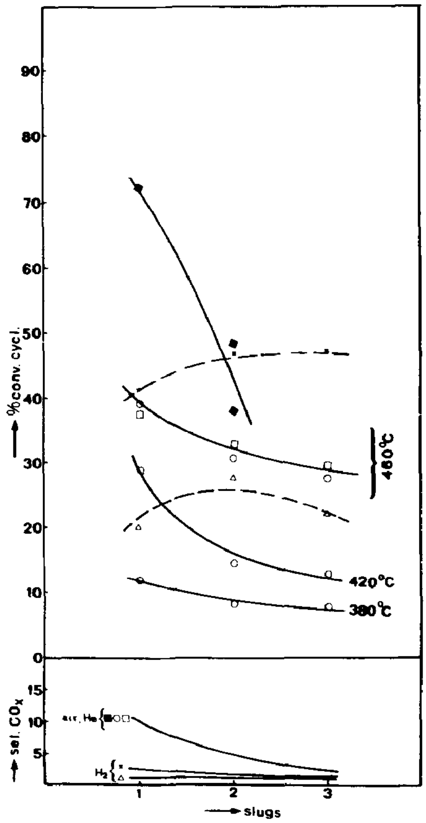


FIG. 3. C_6H_{12} conversions at various reaction temperatures and CO_x selectivity at 460°C over 20 wt% MoO_3/Al_2O_3 catalysts (τ = 2.6 sec), preheated as indicated in Fig. 2.

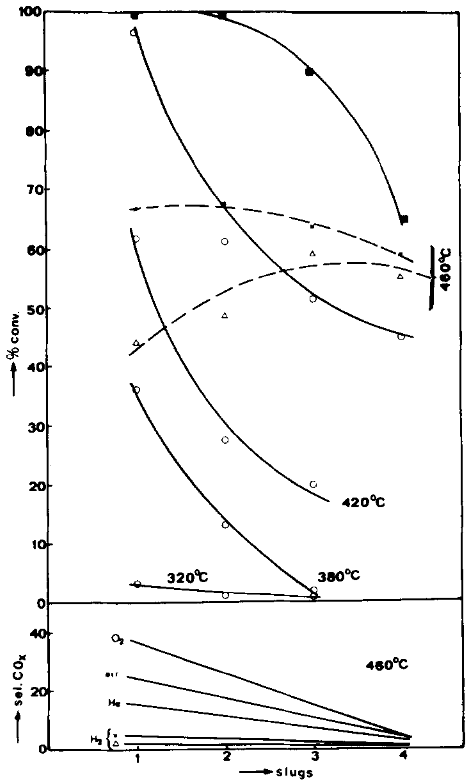
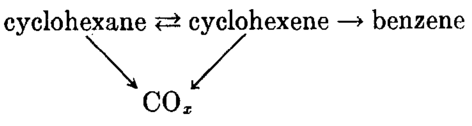


FIG. 4. C_6H_{12} conversions at various reaction temperatures and CO_x selectivity at 460°C over 30 wt% MoO_3/Al_2O_3 catalysts (τ = 2.6 sec), pretreated as indicated in Fig. 2.

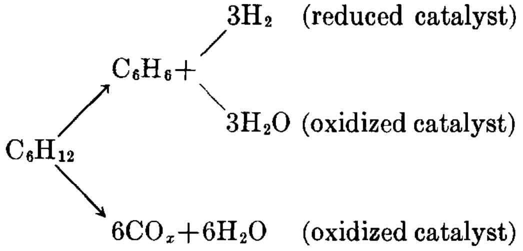
means that it arises as an intermediate in the dehydrogenation of cyclohexane to benzene, as indicated in other papers (*13*, *14*).

With regard to the presence of carbon oxides among the reaction products, formation of CO_x from cyclohexene and the absence of reactivity of benzene indicate the following overall process:



$$\text{cyclohexane} \rightleftarrows \text{cyclohexene} \to \text{benzene}$$
$$\text{cyclohexane} \to CO_x \leftarrow \text{cyclohexene}$$

On the completely reduced catalyst no water is detected, in contrast to the case of oxidized catalysts where the amount of H_2O corresponds to that which is formed by dehydrogenation to benzene and oxidation to CO_x. We therefore advance the following reaction scheme:



$$C_6H_{12} \to C_6H_6 + \begin{cases} 3H_2 & \text{(reduced catalyst)} \\ 3H_2O & \text{(oxidized catalyst)} \end{cases}$$
$$C_6H_{12} \to 6CO_x + 6H_2O \quad \text{(oxidized catalyst)}$$

Obviously, an intermediate situation is verified for catalysts with an oxidation state between the extremes.

DISCUSSION

From the results reported, it appears that the catalyst surface of MoO_3/Al_2O_3 contains sites active for dehydrogenation and for complete oxidation. As under the conditions of our experiments alumina is completely inactive, it follows that molybdenum is crucial in the cyclohexane

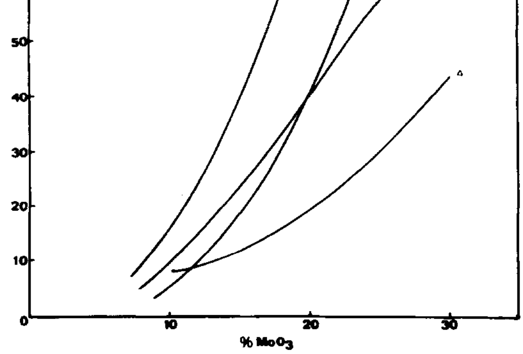


FIG. 5. Conversion of cyclohexane and selectivity in benzene as a function of the composition (wt% active phase) of MoO_3/Al_2O_3 catalysts, pretreated as indicated in Fig. 2. Reaction condtions: T = 460°C, τ = 2.6 sec, carrier He.

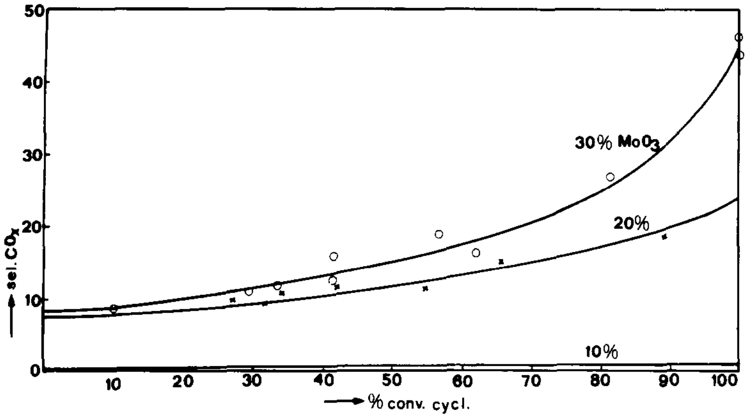


FIG. 6. Selectivity in carbon oxides as a function of the conversion of cyclohexane for various catalysts outgassed at 350°C for 14 hr.

transformation. The results also indicate that the valence state and stereogeometry of molybdenum are important in the interpretation of the reaction mechanism.

In the catalytic dehydrogenation of cyclic hydrocarbons over metal oxide catalysts (*13, 15*) the reaction proceeds by edge-on adsorption of cyclohexane onto

TABLE 1

Conversions of Cyclohexane and Selectivities to Benzene(%)

wt% MoO_3 on γ-Al_2O_3	State of catalyst	Successive cyclohexane pulses				Alternating pulses,[a] air or O_2, and C_6H_{12}				Successive C_6H_{12} pulses	
10	Oxidized[b]	36.2	16.0	11.6		27.7	30.6	30.9	30.9	14.4	6.0
10	Oxidized	15.2	11.6	9.5	4.4	6.8	6.5				
10	Reduced[c]	22.0	21.6	19.1		32.8	28.2	29.8			
10	Outgassed[d]	31.0	28.3	16.4	12.9	24.7	27.2	27.4	25.7		
20	Oxidized	27.3	24.0	20.5	15.3	19.1	35.6				
		(78)[e]	(96)	(98)	(99)	(97)	(91)				
20	Oxidized	41.0	30.5			41.0					
		(86)	(97)			(91)					
20	Reduced	31.5	32.4	27.3	26.8	32.4				30.0	
20	Outgassed	26.4	20.8	17.5		27.7	30.5	29.6	30.5		
		(91)	(97)	(98)		(91)	(90)	(91)	(90)		
30	Oxidized	6.3	1.3	0.9		6.8					
		(54)	(79)	(82)		(62)					
30	Oxidized	18.6	3.2			14.8	16.6				
		(45)	(84)			(58)	(56)				
30	Oxidized	100.0	64.6	55.2	40.0	47.0	47.1				
		(50)	(74)	(75)	(90)	(58)	(56)				
30	Reduced	63.4	70.0	62.0		57.6	47.0	49.4			
30	Outgassed	100.0	61.3	39.5	34.4	41.4	42.1	46.2	46.1		
		(70)	(74)	(91)	(96)	(81)	(71)	(67)	(70)		

[a] Pulse of C_6H_{12} is preceded by introduction of 15 cm^3 oxygen or air.

[b,c] Catalyst oxidized/reduced for 3 hr at 350 to 460°C.

[d] Catalyst outgassed by He flow for 14 hr at 350°C.

[e] The values in parentheses are selectivities to benzene. When not specified the selectivity to benzene is 100%.

TABLE 2

Conversions of Cyclohexane and Selectivities to Benzene (%)

wt% MoO_3 on γ-Al_2O_3	State of catalyst	Successive C_6H_{12} pulses			Alternating pulses,[a] H_2, CO, CO_2, H_2O, and C_6H_{12}			Successive C_6H_{12} pulses	
						$\underline{H_2}$			
10	Oxidized[b]	24.1	9.2	6.1	6.9	5.5	5.9	5.4	
20	Oxidized	100.0	100.0	51.6	58.4	59.0	58.5	42.0	
		(6)[c]	(43)	(91)	(99)	(99)	(99)	(95)	
10	Outgassed[d]	21.0			12.4	9.3	9.9		
30	Reduced[e]	43.7	43.9	44.4	44.2	47.6			
						$\underline{CO}$			
10	Oxidized	30.7	14.4	10.3	30.1	28.2	31.5	14.3	10.7
10	Oxidized	28.4	10.0	6.8	13.8	15.5	15.6	8.9	
30	Oxidized	100.0	62.1	25.6	33.3	38.9			
		(22)	(77)	(95)	(92)	(93)			
10	Outgassed	28.4	13.0	10.0	13.4	11.2	13.3		
25	Reduced	43.8	41.5	46.0	46.7	46.2			
						$\underline{CO_2}$			
30	Oxidized	35.9	33.5		31.9	34.4	36.4		
		(92)	(97)		(98)	(98)	(98)		
						$\underline{H_2O}$			
10	Oxidized	44.0	18.7	12.6	3.8	2.0			

[a] Pulse of C_6H_{12} is preceded by introduction of 15 cm^3 H_2, CO, CO_2, or H_2O.

[b] See footnote *b*, Table 1.

[c] The values in parentheses are selectivities to benzene. When not specified the selectivity to benzene is 100%.

[d, e] See footnote *d* and *c* in Table 1.

two cations, followed by step-wise hydrogen elimination and formation of the olefinic intermediate, as indicated above; afterward the transformation of the cyclohexene to benzene by intermolecular hydrogen transfer is extremely facile. From a thermodynamic point of view naphthenic hydrocarbons show a tendency to form aromatic hydrocarbons at atmospheric pressure and at temperatures above 250°C.

Russell and Stokes (*16*) report that the dehydrogenating activity of MoO_3/Al_2O_3 increases linearly with the metallic oxide content up to the formation of a monomolecular layer, after which the activity remains unchanged. According to Sonnemans and Mars (*1*) the dehydrogenation rate, referred to unit weight of MoO_3 on Al_2O_3, is constant and independent of the preparation of the catalyst. This contrasts with our results which indicate that the cyclohexane conversion, expressed per unit weight of MoO_3 and surface area (cf. Ref. *17*, in agreement with the present results) increases with the MoO_3 content, as does the selectivity in benzene (Fig. 7). An exception is the catalyst pretreated in air at 460°C, which results in maxima at 20 wt% MoO_3. The CO_x selectivity always increases with the MoO_3 content, whereas on reduced catalysts almost negligible yields are observed.

Oxidized Catalysts

The formation of CO_x and the beneficial action of oxygen on partially deactivated catalysts indicate an oxidative dehydrogenation mechanism.

It may be noted that molybdenum catalysts are very efficient in the oxodehydrogenation of olefines; on the other hand, very few data are available on the oxodehydrogenation of cyclohexanes over such catalysts.

According to Naccache *et al.* (*18*) the surface of MoO_3/Al_2O_3 catalysts consists of Al–O–Al groups with low electron affinity and Mo–O–Al groups active in the generation of positive radical ions. On the low molybdenum content catalysts the weak electron affinity of the relatively abundant Al–O–Al groups is enhanced by molecular oxygen which acts as an electron acceptor with formation of O_2^-. The oxidative properties of Mo–O–Al derive from adsorption of the hydrocarbons on the Lewis acid sites (Al ions) with electron transfer to Mo^{6+}. Therefore, Mo^{6+} plays the same role as molecular oxygen. The acidic nature of the surface is also evidenced by the deactivating effect of pyridine on the oxidative properties of these catalysts. On the other hand, MoO_3/Al_2O_3 has electron-donating properties as follows from the formation of anion radicals upon oxygen adsorption.

Therefore, on the basis of the presence of electron accepting and donating sites on $MoO_3/\gamma\text{-}Al_2O_3$ a mechanism for formation of benzene from cyclohexane may be advanced [Uchida *et al.* (*19*)] in which C_6H_{12} is adsorbed on the unsaturated Al ions with weak Lewis acidity; a weak complex is formed and electron transfer to Mo^{6+} occurs through the crystalline lattice.

Below 550°C alumina presents no dehydrogenation activity (*20*), in accordance with our results, in view of its weak electrophilic character. The presence of Mo^{6+} increases the electrophilicity and thus favors the formation of the radical ion $C_6H_{11}^+$. Adsorption of naphthene directly onto Mo^{6+} is improbable, as cyclohexane has no reductive character, in contrast with unsaturated hydrocarbons such as propylene (*21*). Proton loss of $C_6H_{11}^+$ may therefore occur at the terminal anions (*22*) or O^{2-} ions of the oxidized catalytic surface (*23*). Intermolecular hydrogen transfer then leads to formation of benzene.

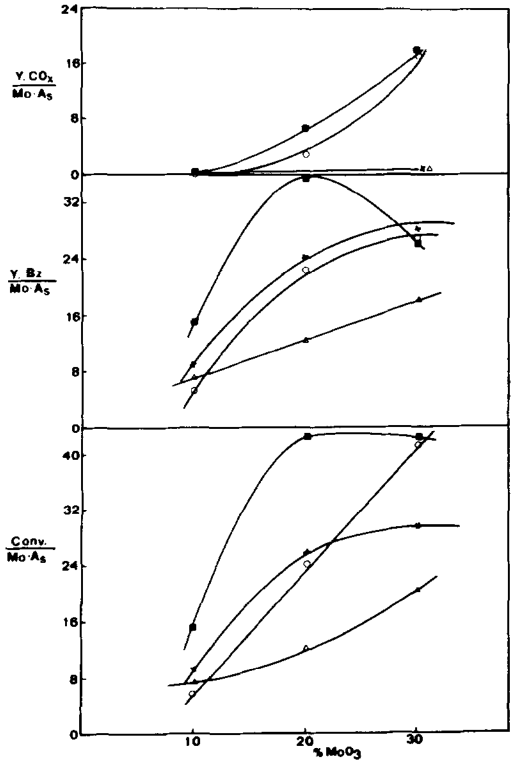


FIG. 7. Conversions of cyclohexane and yields of CO, CO_2, and C_6H_6 per unit weight of MoO_3 and surface area, as a function of the composition in wt% of MoO_3/Al_2O_3 catalysts, pretreated as indicated in Fig. 2. Reaction conditions: T = 460°C, τ = 2.6 sec.

The variation in CO_x selectivity with MoO_3 content is in accordance with the proposed mechanism. In fact, at higher MoO_3 contents not only does the electrophilic character of the catalytic surface increases, but the molybdenum coordination also varies from tetrahedral to octahedral. This obviously leads to a substantial variation in the bond strengths of the Mo–O bonds (*24*), which pass from 1.5 v.u. (valence unity) for regular tetrahedra to 0.2 to 2.0 v.u. for octahedra which are always severely distorted under the influence of crystal field forces. It is reasonable to expect that the border conditions of the surface render these differences even more pronounced. The presence of very weakly bonded oxygen (two oxygens/Mo atom in case of the [2 + 2 + 2] oxomolybdenum coordination) leads to more readily available lattice oxygen and therefore to more facile formation of carbon oxides. This is also in accordance with Akimoto and Echigoya (*25*) who report a preferential tendency to total oxidation rather than formation of intermediate products for the oxidation of butadiene.

The influence of water, as observed in the experiments with periodic pulses of water and cyclohexane, and its formation during the reaction are related to the facile and rapid deactivation of the catalyst. This is sustained by the fact that successive thermal conditioning of the catalyst in an inert atmosphere regenerates the catalytic activity to an extent which depends upon the activation conditions. The presence of water prevents the elimination of the -OH groups formed on the catalytic surface and reduces the surface anions which act as proton acceptors according to

$$O^{2-} + \square + H_2O \rightarrow 2OH^-$$

Moreover, as is well known, water blocks the Lewis acid sites through its oxygen electron lone-pair. As the rate of the decay of the deactivation corresponds to a more rapid diminution in surface electrophilicity, the more rapid decrease of the selectivity in CO_x with respect to benzene is readily understood; moreover, less surface oxygen is available at successive slugs.

Periodic exposure of partially deactivated catalysts to oxygen instantaneously increases the electrophilicity of the catalyst (*18*); the renewed oxygen reservoir renders the dehydrogenation mechanism possible and leads to oxidation to CO_x, as discussed above. In fact, oxygen is adsorbed on $MoO_3/\gamma\text{-}Al_2O_3$ as anion radicals O_2^- and O^- (*26–30*) on anionic vacancies with successive stabilization to O^{2-} on the Mo^{5+} ions (*29, 31*):

$$O_2 + 2e^- \longrightarrow 2O^- \xrightarrow{Mo^{6+}} (Mo^{6+}O^{2-})$$

or directly on reduced Mo ions followed by stabilization (*30, 32, 33*):

$$Mo^{5+} + OH^- + \tfrac{1}{2}O_2 \rightarrow (Mo^{6+}O^{2-}) + \tfrac{1}{2}H_2O$$

Interruption of regular oxygen pulses leads to the immediate deactivation of the catalyst, indicating that its action is the temporary activation of new sites.

As described above, pulses of reductants (H_2 or CO) in alternation to C_6H_{12} arrest the deactivation or increase the conversion depending upon the operating conditions; the selectivity to C_6H_6 increases. This is due to reduction of Mo^{6+} to Mo^{5+}, leading to dehydrogenation to benzene according to a different mechanism, as discussed below:

$$Mo^{6+} + O^{2-} + \tfrac{1}{2}H_2 \rightarrow Mo^{5+} + OH^-$$

$$Mo^{6+} + O^{2-} + CO \rightarrow Mo^{5+}\square + CO_2$$

(The reduction of Mo^{6+} is evidenced by the fact that the color of the catalyst approaches that of reduced catalyst.)

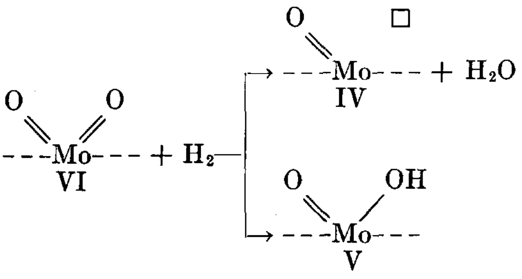
Pretreatment of $MoO_3/\gamma\text{-}Al_2O_3$ with air or oxygen never leads to the complete reoxidation of the molybdenum ions (*34*); the oxidation of the metal increases with the MoO_3 concentration on the support. Consequently, the electrophilicity of the catalyst is not proportional to the Mo concentration. This leads to the increase in C_6H_{12} conversion and C_6H_6 and CO_x selectivity per unit weight of Mo and surface area (Fig. 7). Above 20 wt% MoO_3 the conversions are almost constant, as molybdenum is mainly present as the separate phase MoO_3 (*35*). At the same time the C_6H_6 selectivity decreases and that of CO_x increases, as the latter are preferentially formed at octahedral Mo^{6+} sites.

On the basis of the product distribution, i.e., benzene up to about 10–15 wt%

MoO_3 and CO_x at higher contents of the active phase, it can be stated that tetrahedral oxomolybdenum sites are mainly selective in benzene and the octahedral sites in carbon oxides.

Reduced Catalysts

Reduction of MoO_3/Al_2O_3 with hydrogen at $T \leqslant 500°C$ leads to tetrahedral Mo^{6+}, tetrahedral and octahedral Mo^{5+}, and octahedral Mo^{4+} and Mo^{3+} (*36*). The distribution of these species depends upon T, p_{H_2}, the MoO_3 content of the catalyst, and the reduction time. The interaction between the metal and the support decreases at higher molybdenum concentration and therefore such catalysts are more easily reduced and oxidized (*35*). In particular, at 550°C and above 20 wt% MoO_3, molybdenum trioxide is present as a separate phase which is reducible to the zerovalent state (*37*, *38*). The reduction can occur at the surface (for mild operating conditions):



or in the bulk. In the latter case, the oxygen bridge between Al and Mo is removed and tetrahedral Mo(VI) passes to lower oxidation states with octahedral configuration; the increase in coordination number leads to the formation of anionic vacancies (*39*).

It has already been noticed that reduction of MoO_3/Al_2O_3 favors the dehydrogenation of cyclohexane and derivatives (*1*, *2*, *16*) and it is independent of the MoO_3 content of the catalysts. Inoyatov *et al.* (*40*) indicate Mo^{5+} as the active site together with Ni on Mo–Ni–Al catalysts. According to Richardson and Rossington (*41*), the catalytic activity of numerous transition metal oxides in the dehydrogenation of cyclohexane is related to the 3*d*-electron configuration of the metal ion, with the activity increasing in the order $d^1 < d^2 < d^3$; no relation exists with the semiconductor properties of these oxides (*42*).

The higher conversions obtained at higher temperature and reduction times in our experiments (Fig. 2–5) indicate that the molybdenum atoms are directly responsible for the dehydrogenation reaction to benzene and that the reduced species are the more active ($Mo^{3+} > Mo^{4+} > Mo^{5+}$). The greater reducibility of the catalyst at higher molybdenum concentration explains the trend of Fig. 7, namely, the greater number of octahedral Mo cationic sites favors the dehydrogenation of cyclohexane.

The results described may be interpreted by the mechanism proposed by Richardson and Rossington (*41*), namely, chemisorption of C_6H_{12} on two cations by means of covalent bonding, then abstraction of hydrogen atoms with formation first of the intermediate monolefine and then benzene. The mechanism thus involves elimination of molecular hydrogen. In fact, at variance with the results on the oxidized catalysts, water is not among the reaction products. This leads to the greater stability of the catalytic activity with time.

Periodic oxygen pulses, which lead to O^{2-} and O^- anions and oxidation of Mo^{5+} to Mo^{6+}, temporarily activate the sites for oxidative dehydrogenation with a consequent increase in conversion, which is higher at the low molybdenum concentrations (easier access to Al–O–Al groups).

Adsorption of water blocks the active Mo^{5+} sites (*43*) with a consequent decrease in catalytic activity. The inertness of the catalyst in the presence of CO, CO_2, and H_2 is easily understood on the basis of the proposed mechanism.

Outgassed Catalysts

Thermal pretreatment of MoO_3/Al_2O_3 in an inert atmosphere has the same effect as a reduction or outgassing (*44*) when performed at high temperatures. Therefore, such catalysts show the presence of various intermediate oxidation states (mainly Mo^{5+}) depending upon the operating conditions.

On the basis of our experimental results, it may be concluded that pretreatment with He at 350°C for 14 hr varies the molybdenum oxidation state only slightly. Therefore, the catalyst behaves like the oxidized one, although at a somewhat lower conversion level. This is another indication of the lower activity of Mo^{5+} with respect to the more reduced cations.

Similar considerations may be applied to oxidized or reduced catalysts in mild operation conditions, for which we have the juxtaposition of two mechanisms (oxodehydrogenation and simple dehydrogenation); the behavior of such catalysts depends upon the distribution of the cationic molybdenum species.

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