

## The Role of Surface Acidic Centers in the Extensive Oxidation of 1-Butene over Molybdenum Oxide-Based Catalysts

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In order to study the role of surface acidic properties on isomerization and extensive oxidation reactions, the catalytic behavior of a large series of poorly selective molybdates and selective tellurium-doped molybdates in the oxidation of 1-butene was investigated at different reaction temperatures. This study was carried out both in the presence and absence of steam in the feed. Strong analogies within the series of the investigated catalysts were observed: (i) The more active a catalyst is in the isomerization at low temperature (usually 330°C), the higher the amounts of carbon oxides it produces at high temperature (usually 390°C); (ii) the decrease with temperature of the isomers yield is related to the corresponding increase of the carbon oxides yield within the class of both selective and poorly selective catalysts; and (iii) the addition of steam increases the isomers yield and decreases the yield of carbon oxides. Again the two changes are related within the class of both selective and poorly selective catalysts. It is assumed that these effects come about by the transformation of the Brønsted sites (responsible for low temperature isomerization) into Lewis sites at high temperature (responsible for the formation of carbon oxides). It is proposed that the extensive oxidation to CO and CO<sub>2</sub> involves an interaction between an acidic center, an activated hydrocarbon molecule, and oxygen. It is advanced that the difference in the catalytic behavior between poorly selective and selective catalysts is due to the fact that the Brønsted sites are destroyed by the addition of tellurium.

### INTRODUCTION

The extensive oxidation of olefins and alcohols over oxide-based catalysts is usually ascribed to the presence of reactive adsorbed species of oxygen (1-3), to lattice oxygen (4, 5), or to the strength of the bond between the olefin and the cation on the catalyst surface, according to the classical picture of  $\pi$  complexes (6). In a recent paper (7) one of us pointed out that a large class of molybdenum-based oxidation catalysts is highly active in the isomerization of the double bond at low temperatures and not selective in the

oxidation at high temperatures. For these catalysts it was proposed that the isomerization occurred through a carbocation which in the presence of oxygen could give rise to carbon oxides.

For the purpose of better understanding the relationship between the sites responsible for 1-butene isomerization and those responsible for extensive oxidation and also to throw light on the nature of these centers, we studied the effect of steam addition in the oxidation of 1-butene over a series of pure and tellurium-doped molybdate-based catalysts. Steam can be a

powerful tool in modifying the surface acidic properties which could be involved in the isomerization process.

From scientific and technical literature it appears that the presence of steam allows for high process capacities outside the explosion limits (8). It also appears that steam increases the selectivity to partially oxidized products (9). However, in spite of its large use in commercial olefin oxidation processes, its role and mechanism of action are not yet at all clear.

To ensure that the effect of the steam was not due only to a stricter temperature control, the oxidation runs were done in a stirred tank reactor of the Carberry type which eliminates the possibility of external temperature gradients being present.

#### METHODS

Pure Cd, Co, and Mn molybdates were prepared according to Ref. (10) and Fe-molybdate according to Ref. (11). They were dried at 110°C and calcined at 500°C for 2 hr. Pure  $\text{CaMoO}_4$  was prepared as follows: Both solutions containing 159 g of  $\text{NH}_4$ -*p*-molybdate, "Merck zur Analyse," in 5 liters of deionized water (solution A) and a solution containing 236 g of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , "Merck zur Analyse," in 4.5 liters of water (solution B) were heated at 80°C. Solution B was dropped into solution A under vigorous stirring. The pH was brought to the final value 8 by adding diluted ammonia, and the precipitate was heated and boiled inside the mother liquor for 1 hr. Drying (12 hr at 110°C) and calcination (2 hr at 500°C) followed.

The doped catalysts with Te contents of 2, 3.81, and 8% of body weight, relative to pure molybdate, more prepared by heating at 500°C for 2 hr an intimate mixture of  $\text{MoO}_3$ , "Merck zur Analyse," or pure molybdate (dried but not calcined) and of adequate amounts of orthorhombic

$\text{TeO}_2$  (Merck laboratory reagent; purity, 99.999%). They will be referred to for brevity as M-0, M-2, M-3.81, and M-8, where M is molybdenum in the case of  $\text{MoO}_3$  or the second metal (Ca, Cd, Mn) in the case of molybdates. The number is the Te content as weight percent.

Due to the preparation method, Te-doped systems were originally available as powder substances. The stirred tank reactor of the Carberry's type already described (12) requires that catalyst pellets of hard consistency be used, in order to avoid weight losses during working operations. For this reason hard granules with 1-mm dimensions, obtained by pressing the catalyst at 250 kg/cm<sup>2</sup> for 5 min, were used in the oxidation runs. This procedure was followed for homogeneity also in the case of  $\text{MoO}_3$  and pure molybdates.

The experimental conditions were: *T*, variable; feed flow, 120 ml/min (in the entrance); and catalyst weight, 1.9 g.

Feed composition in the absence of steam was 1% 1-butene and 13%  $\text{O}_2$ , the balance being  $\text{N}_2$ ; in the presence of steam,  $\text{N}_2$  was lowered from 86 to 53%, 1-butene and  $\text{O}_2$  percentages being kept at the same values.

Steam was added to the feed by using a peristaltic pump (Watson-Marlow MHRE) which allows for a wide flow range.

The gas-chromatographic analysis of reagents and reaction products has already been reported elsewhere (12).

#### RESULTS AND DISCUSSION

The catalytic behavior of a large series of poorly selective molybdates and selective tellurium-doped molybdates in the oxidation of 1-butene were investigated within the 300–450°C temperature range both in the presence and absence of steam in the feed. At low temperature large amounts of 2-butenes always formed; at high temperature carbon oxides and, fre-

quently, butadiene formed in considerable quantities.

As the main interest of the discussion is the isomerization and extensive oxidation properties of the investigated catalysts in Table 1, only the data relative to two temperatures are reported (330 and 390°C, respectively, for all the catalysts with the exception of Co-O). As the lower temperature, 330°C was chosen since it is just under the level where complete oxidation becomes important; Fe-O and Mn-O are the only cases where carbon oxides are already formed in large quantities at 330°C. The higher temperature was chosen at a level where the conversion to carbon oxides is already of some importance and the maximum in the butadiene yield has not yet been reached; beyond this maximum it is possible for other mechanisms of bulk oxidation to operate.

The data given in the table are not affected either by external effects or by intraparticle transfer limitations. As it was checked experimentally (see Methods), the Carberry reactor eliminated external effects, while the dependence of 1-butene conversion on the reaction temperature indicated that intraparticle limitations could play a role in the most active catalysts over 400°C. We estimated the apparent energy of activation of 1-butene consumption rate in the temperature range below 400°C, assuming pseudo-first-order kinetics. The calculated values were always higher than 15 kcal/mol, which suggests that in this temperature range the reaction is controlled by chemical factors. For this reason also the high temperature was taken at 390°C. Only in the case of Co-O were high and low temperatures above 390°C (430 and 390°C, respectively) chosen. This was done in order to keep the effects of temperature and steam addition separate from the effect caused by a phase change of  $\text{CoMoO}_4$ . Actually, it is known from the literature that  $\text{CoMoO}_4$  changes from the green to the violet form

at about 390°C (where a strong rise in activity can be observed) and that violet  $\text{CoMoO}_4$  is the active phase (13).

2-Butenes, butadiene, and carbon oxides were the only reaction products observed, although some of the investigated systems (Co-O and Mn-O) had been previously found to form maleic anhydride (10, 12, 14). The pressing procedure adopted in this case should be responsible for the different behavior since Co-O and Mn-O, when tested simply after drying and calcination (without pressing), again formed maleic anhydride in appreciable quantities.

The following points can be derived from the data shown in Table 1:

(1) As a general rule, the catalysts which are highly active in the extensive oxidation at high temperature are also highly active in the isomerization at low temperature. In Fig. 1, the yield of carbon oxides at 390°C (430°C for Co-O) is displayed against the yield of isomers at

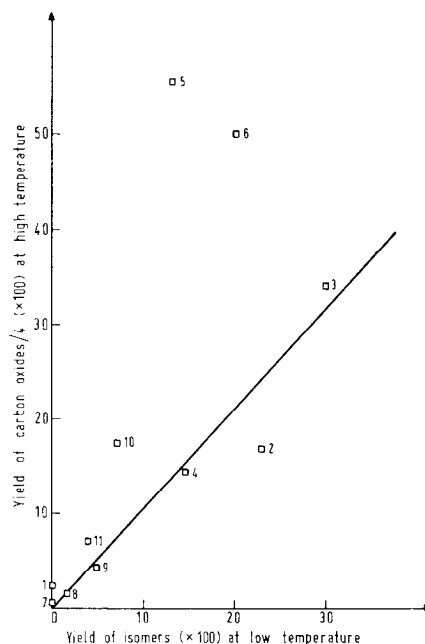


FIG. 1. Yield of carbon oxides divided by 4 at high temperature vs the yield of isomers at low temperature for the oxidation of 1-butene in the absence of steam. Numbers as in Table 1.

TABLE 1  
Oxidation of 1-Butene over Molybdenum-Based Catalysts at Different Temperatures in the  
Absence and in the Presence of Steam in the Feed

Catalyst	Number	Temperature (°C)	Presence of steam	Yield of butadiene (× 100)	Yield of isomers (× 100)	Yield of (CO + CO <sub>2</sub> )/4 (× 100)	Selectivity to butadiene (× 100)
MoO <sub>3</sub>	1	330	No	—	Traces	1.51	—
			Yes	—	2.2	0.40	—
		390	No	1.10	—	2.30	32.4
			Yes	0.71	1.93	0.87	44.9
Ca-O	2	330	No	0.42	23.0	1.23	25.5
			Yes	0.95	30.1	0.83	53.0
		390	No	4.84	18.2	16.7	22.5
			Yes	5.54	27.0	8.97	38.2
Cd-O	3	330	No	2.30	30.0	4.53	33.6
			Yes	0.79	35.2	6.07	11.5
		390	No	3.86	15.5	34.3	10.1
			Yes	3.24	21.1	27.1	10.7
Co-O	4	390	No	4.05	14.5	3.63	52.7
			Yes	3.38	17.6	2.48	57.6
		430	No	6.58	9.1	14.6	31.0
			Yes	6.25	14.9	10.2	38.0
Fe-O	5	330	No	—	13.2	41.0	—
			Yes	1.49	15.5	40.5	3.54
		390	No	—	4.1	55.6	—
			Yes	0.805	6.82	50.98	1.55
Mn-O	6	330	No	4.74	20.31	14.8	24.25
			Yes	3.05	32.52	12.57	24.25
		390	No	1.72	5.45	49.92	3.3
			Yes	2.5	21	33.2	7
Mo-3.81	7	330	No	6.02	—	0.377	91.3
			Yes	2.17	0.2	0.20	91.5
		390	No	4.7	—	0.4	92.1
			Yes	3	—	0.26	92
Ca-3.81	8	330	No	5.5	1.56	0.52	91.3
			Yes	4.3	4.2	0.47	96
		390	No	16.2	2.93	1.67	90.1
			Yes	12.85	4.17	0.79	94.2
Cd-8	9	330	No	5.5	4.7	0.745	88.0
			Yes	2.69	8.5	0.27	90.8
		390	No	13.5	3.27	4	77.1
			Yes	7.4	7.05	1.45	83.6
Mn-2	10	330	No	15.6	7.17	1.44	91.5
			Yes	17	14	1.04	94.2
		390	No	21.68	5.67	17.66	55.1
			Yes	25	9	14	64.1
Mn-3.81	11	330	No	13.1	3.8	1.3	90.9
			Yes	17	13.85	1.01	94.3
		390	No	20.18	3.5	7.11	73.9
			Yes	22.3	10.57	3.7	85.7

330°C (390°C for Co-O), for oxidation runs performed in the absence of steam. From the figure it appears that a gross but still significant correlation exists between the low temperature isomerization and the high temperature oxidation properties. The exceptions of Mn-O and Fe-O could be due to the fact that these systems produce significant quantities of carbon oxides at 330°C, and consequently the catalytic behavior at this temperature can no longer be described in terms of isomerization properties only.

(2) The addition of steam always affects both isomerization and extensive oxidation properties in opposite directions: It increases the yield of 2-butenes and decreases the yield of carbon oxides. These facts further show that the above properties are mutually related within the series of the investigated catalysts.

(3) Steam always increases the selectivity to butadiene. This is essentially due to the fact that fewer carbon oxides form while there is either a decrease in the yield of butadiene (in the case of a few very selective catalysts such as Mo-3.81, Co-3.81, and Cd-8 the decrease can be significant) or an increase which is not very significant anyway. In the case of a decrease, steam acts as a poisoning agent.

Based on significant differences in the catalytic behavior, the investigated catalysts can be classified in two groups: poorly selective molybdates (MoO<sub>3</sub>, Ca-O, Cd-O, Co-O, Fe-O, and Mn-O) and selective Te-doped molybdates (Mo-3.81, Ca-3.81, Cd-3.81, Mn-2, and Mn-3.81). These will be dealt with separately.

In the case of poorly selective systems, a rise of the reaction temperature in the absence of steam always produces a strong decrease in the yield of isomers together with a strong increase in the yield of carbon oxides.

The values of the two variations compared against one another are shown in Fig. 2 (open symbols). It is interesting

to note that for all the poorly selective catalysts, including Mn-O and Fe-O, the decrease in the yield of isomers is twice as low as the corresponding increase in the yield of carbon oxides. The addition of steam restores the isomerization power to the detriment of the formation of carbon oxides. In Fig. 3 the variation of the isomer yield is given as a function of the variation of the carbon oxide yield at the same temperature, in this case high temperature (open symbols). From the figures it appears that again a strict correlation exists between the increase in the isomer yield and the decrease in the carbon oxide yield, which are both due to the addition of steam (the two variations are equal one to the other). It is also interesting to observe that the effect on the yield of 2-butenes is less relevant at low temperature (see Table 1).

The strong analogies in the effects of temperature rise and steam addition on the isomerization and complete oxidation reactions within the series of the investigated poorly selective catalysts likely imply strong analogies in the mechanisms involved and in the chemical reasons for such effects.

Concerning the mechanism of extensive

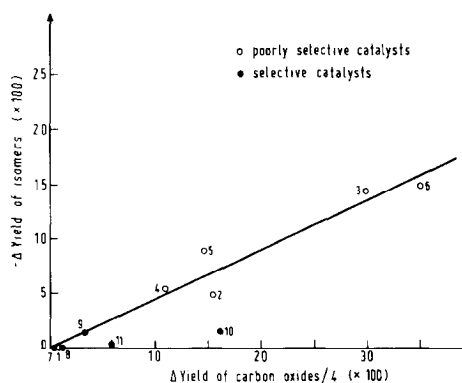


FIG. 2. Decrease in the yield of isomer ( $-\Delta Y$ ) vs increase in the yield of carbon oxides divided by 4 [ $\Delta Y(\text{CO} + \text{CO}_2)/4$ ] for the oxidation of 1-butene at both high and low temperatures, in the absence of steam. Numbers as in Table 1.

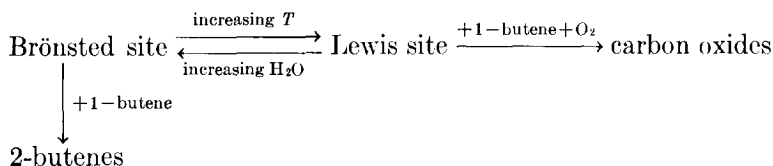
oxidation, it is useful to recall that in the case of Cd-O, Co-O, Fe-O, and Mn-O a variation in the partial pressure of oxygen was previously found to affect the distribution of products during the oxidation of 1-butene (10, 12, 14). By lowering the oxygen level in the gaseous phase a strong decrease in the formation of carbon oxides together with an increase in both 2-butenes and butadiene were observed. The distribution of products at low oxygen level depends on the different catalysts. Gaseous oxygen was proposed as being responsible for extensive oxidation and lattice oxygen for selective oxidation to butadiene.

The actions of temperature, steam addition, and oxygen partial pressure on the isomerization and extensive oxidation reactions of 1-butene within the class of investigated poorly selective catalysts are summarized in Table 2.

The oxidation of 1-butene involves a complex reaction network. Isomerization, oxidative dehydrogenation to butadiene, and direct and consecutive extensive oxidations do occur. In the present work we

are not concerned with the mechanism of the formation of butadiene, which has already been discussed and related to the presence of Mo=O groups at the catalyst surface (10, 12, 14, 15). Furthermore the observed effects, due both to steam addition and temperature increase, primarily concern isomerization and 1-butene extensive oxidation, in so far as (i) the temperature range (below 390°C) is such that the maximum in the butadiene yield has not yet been reached. Beyond this maximum the extensive oxidation of butadiene assumes greater relevance; (ii) the main effects of steam and temperature concern the carbon oxide yield and the isomer yield, while the butadiene yield is only slightly influenced. These points suggest that most of the carbon oxides are formed directly from 1-butene and not through butadienes as an intermediate. This is also consistent with the excess of 1-butene among the reaction products.

Therefore, we propose that the observed effects can be explained in the following way:



The experimental data and considerations which agree with what we have just proposed are:

(i) The effect of steam addition strongly suggests that Brönsted acidic centers are involved in the isomerization. In this case a carbocation should occur as an intermediate in the reaction process; such a situation is also consistent with the observed *cis/trans* ratio close to unity (7, 16) and with the 1/*trans* ratio in the isomerization of *cis*-2-butene (lower than 1), as

reported in Ref. (7) for some of the investigated catalysts.

(ii) The decrease in the isomers yield brought about by increasing the temperature could be explained by assuming that centers which are active in the isomerization at low temperature are destroyed by the temperature rise.

(iii) The strict relation between the decrease in isomer yield and the increase in carbon oxide yield (see Fig. 2) likely indicates that centers which are active in the isomerization at low temperature are trans-

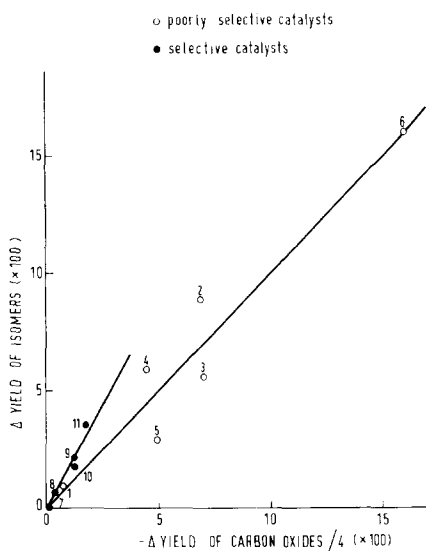


FIG. 3. Increase in the yield of isomers ( $\Delta Y$ ) vs decrease in the yield of carbon oxides divided by 4 [ $\Delta Y(\text{CO} + \text{CO}_2)/4$ ] for the oxidation of 1-butene, both in the presence and in the absence of steam, at high temperature. Numbers as in Table 1.

formed into centers which are active in the extensive oxidation at high temperature.

(iv) A transformation of Brönsted sites due to a thermal dehydration appears quite reasonable, also considering that the reversibility of such a process could explain the effect of steam addition. This also accounts for the greater importance of this effect at high temperature where the isomerization power has been strongly lowered by the temperature rise.

(v) Accordingly, therefore, Lewis sites should be responsible for extensive oxidation. However, the effect of oxygen partial pressure reveals that an essential role is played by gaseous oxygen in this process and suggests that the overoxidation in-

volves an interaction among acidic centers, the olefin, and oxygen (either adsorbed or not on the catalyst surface).

Selective catalysts show the following important differences with respect to the effect of temperature and steam addition:

(i) By increasing the temperature and in the absence of steam a strong increase in the formation of carbon oxides can be again observed, but no appreciable change takes place in the yield of isomers for these catalysts (filled symbols in Fig. 2).

(ii) The addition of steam restores the isomerization power again to the detriment of the formation of carbon oxides. In Fig. 3 the variation of the isomer yield is shown against the variation of carbon oxide yield at high temperature (filled symbols). From the figure it appears that a strict correlation exists also for the selective catalysts which occurs between the decrease in the carbon oxide yield and the increase in the isomer yield. However, the effect of steam addition on the isomerization power is greater than for poorly selective catalysts; this effect is more remarkable at low temperature.

It is likely that the above observations also imply strong analogies within the series of selective catalysts. It is probable that the Brönsted sites present in poorly selective molybdates, which, we suggest, were transformed by increasing temperature into Lewis sites, are no longer present. This hypothesis accounts for the fact that no significant change due to temperature rise occurs in the isomer yield.

The addition of steam could quite reasonably bring about the transformation of

TABLE 2

Effect of Temperature, Steam Addition, and Oxygen Partial Pressure on the Isomerization and Complete Oxidation of 1-Butene for Poorly Selective Molybdates

	Decreasing $T$		Increasing $T$	
	Increasing $\text{H}_2\text{O}$		Decreasing $\text{H}_2\text{O}$	
	Decreasing $\text{O}_2$		Increasing $\text{O}_2$	
2-Butenes	→	1-Butene	→	$\text{CO} + \text{CO}_2$

Lewis sites into Brönsted sites, thus accounting for the increase in the isomer yield and the decrease in the carbon oxide yield which we observed when steam was added to the feed. This could also account for the greater effect on the isomer yield at low temperature. Keeping in mind that all selective catalysts are made up of a poorly selective molybdate matrix together with small amounts of tellurium, it follows that tellurium modifies the acidic properties of the pure molybdates by destroying the Brönsted sites, which in molybdates are mainly responsible for the extensive oxidation at high temperature.

#### CONCLUSIONS

A large series of molybdates poorly selective in the oxidation of 1-butenes and of selective tellurium-promoted molybdates has been investigated at different reaction temperatures both in the presence and in the absence of steam in the feed. The discussion of the results gives additional insight into the roles of surface acidity, the presence of steam, and the addition of tellurium. The following points have been stressed:

(I) *Role of surface acidity.* The most active catalysts in isomerization are the least selective ones in oxidation. Lewis sites, formed from Brönsted sites at high temperatures, are proposed as being responsible for the extensive oxidation of 1-butene. Thus surface acidity is a factor which decreases the selectivity to partial oxidized products.

(II) *Role of the presence of steam in the feed.* Steam decreases the yield of carbon oxides and increases the yield of isomers. It has a small effect on the butadiene yield, for which it sometimes acts as a poisoning agent. The increase in the selectivity to butadiene is essentially due to a decrease in the formation of CO and CO<sub>2</sub>.

(III) *Role of the addition of Te to the catalysts.* Te destroys surface Brönsted sites present in pure molybdates. The increase in the selectivity to butadiene in Te-promoted molybdates is, at least partially, due to the decrease in surface acidity. It is expected that the formation of new active and selective oxidative dehydrogenation sites also operates in this direction (15).

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#### REFERENCES

1. Trifirò, F., and Pasquon, I., *J. Catal.* **12**, 412 (1968).
2. Cant, N. W., and Hall, W. K., *J. Cat.* **27**, 70 (1972).
3. Kazansky, V. B., Plenary lecture, Sixth International Congress on Catalysis, London, July 1976.
4. Trifirò, F., *Chim. Ind. (Milan)* **56**, 835 (1974).
5. Keulks, G. W., and Krenze, L. D., Paper B20, Sixth International Congress on Catalysis, London, July 1976.
6. Germain, J. E., *Intra-Sci. Chem. Rep.* **6**, 101 (1972).
7. Trifirò, F., and Carrà, S., *React. Kinet. Catal. Lett.* **2**, 411 (1975).
8. Krabetz, R., *Chem. Ing. Tech.* **46**, 1029 (1974).
9. Suvorov, B. V., and Senbaev, D. H., Paper 20, Mechanism symposium, Fourth International Congress on Catalysis, Moscow, 1968.
10. Trifirò, F., Caputo, G., and Villa, P. L., *J. Less Common Metals* **36**, 305 (1974).
11. Patent No. 25545 A74 Ital. Appl. 25.7.74.
12. Trifirò, F., Caputo, G., and Forzatti, P., *Ind. Eng. Chem. Prod. Res. Develop.* **14**, 22 (1975).
13. Boutry, P., Courty, Ph., Daumas, J. C., and Montarnal, T., *Bull. Soc. Chim. Fr.* **10**, 4050 (1968).
14. Trifirò, F., Banfi, C., Caputo, G., Forzatti, P., and Pasquon, I., *J. Catal.* **30**, 393 (1973).
15. Forzatti, P., Villa, P. L., Ercoli, D., Ercoli, G., Gasparini, F., and Trifirò, F., *Ind. Eng. Chem. Prod. Res. Develop.* **16**, 26 (1977).
16. Shannon, I. R., Kembal, C., and Leach, H. F., *Symp. Chemisorp. Catal.* **46** (1970).