

CATALYTIC EFFECT OF SODIUM 12-MOLYBDSILICATE AND SODIUM 12-MOLYBDOPHOSPHATE ON CALCINATION OF CALCIUM CARBONATE

ALI I. SAFA, PAK L. LEUNG and KENNETH E. DAUGHERTY *

Department of Chemistry, North Texas State University, Denton, TX 76203 (U.S.A.)

WILLIAM A. MALLOW and JERRY J. DZIUK

Department of Materials Sciences, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78284 (U.S.A.)

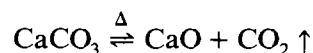
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ABSTRACT

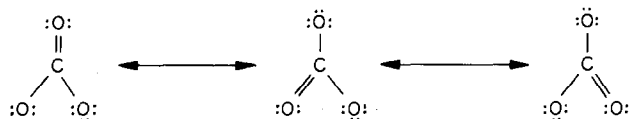
Several catalytic systems have been used to enhance the calcination rate of calcium carbonate using a differential thermal analysis/thermogravimetric analysis (DTA–TGA) system. The sodium salts of 12-molybdosilicic acid and 12-molybdophosphoric acid ($\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$ and $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$, respectively) were mixed with calcium carbonate (calcite) at weight ratios ranging from 1:5 to 1:200 and were studied at constant temperatures of 650, 700, 750 and 800 °C. The calcination rates (mg h^{-1}) have shown marked increases when compared with a blank of calcium carbonate at these temperatures.

INTRODUCTION

Calcination is the direct conversion of calcium carbonate into calcium oxide with the liberation of carbon dioxide. The calcination reaction is represented by



The structure of calcium carbonate is shown in Fig. 1. The Carbonate ion has the three resonance structures below. This resonating structure dictates



* Author to whom correspondence should be addressed.

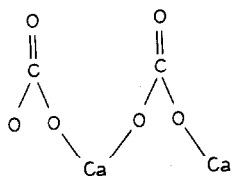


Fig. 1. The structure of calcium carbonate.

that the carbonate ion is planar with bond angles of 120° and three C–O bonds of 1.32 Å [1]. Bragg found that the carbonate ion has a trigonal planar configuration by X-ray analysis of the calcite crystals [2]. The planarity, bond angles and the stability of the resonance structures of the carbonate ion as well as the thermal stability of calcium carbonate supports the postulate of a polymeric or highly coordinated and ordered molecular arrangement of the calcium carbonate species.

The calcination of calcium carbonate (calcite) has been studied by numerous investigators and the kinetics, as well as the thermodynamics, are well known. However, the calcination of calcium carbonate requires approximately two to four times the theoretical quantity of energy predicted from thermodynamic analysis.

It has been previously shown [3] that catalysts can bring about the calcination of calcium carbonate at lower temperatures and/or cause an increase in the calcination rate; thus the energy requirement can be reduced by using different types of catalysts. These catalysts intrude into the crystal lattice and interact electronically with the associated ion species, especially in a polar environment.

This investigation examines the potential of sodium 12-molybdosilicate and sodium 12-molybdophosphate as catalysts for increasing the calcination rate of calcium carbonate. If the calcination rate can be increased, the energy requirements of calcination processes in industries such as lime, cement, glass and paper may be reduced. Calcium carbonate is a major ingredient in products manufactured by these industries.

EXPERIMENTAL

The catalysts used for this study were the sodium salts of 12-molybdosilicic acid and 12-molybdophosphoric acid, because of their well-known catalytic effects on several chemical reactions [4]. The spatial and polyhedral diagrams for 12-molybdophosphate(V) anions were also reported by Tsigdinos [4].

These catalysts were obtained in pure fine-powdered form from Southwest Research Institute, San Antonio, Texas, and were mixed manually to a

homogeneous mixture with reagent grade calcium carbonate with weight ratios 1:5, 1:10, 1:50, 1:100 and 1:200. Specimens of 90–100 mg of each ratio contained in deep platinum sample holders were weighed and individually introduced into a Mettler thermal analysis unit with a Mettler HE20 balance unit under an air environment.

The conditions for this investigation included a heating rate of $10^{\circ}\text{C min}^{-1}$, a chart speed of 8 cm h^{-1} and a $200\text{-}\mu\text{V}$ range for the DTA. The reference material was alumina. The dissociation of calcium carbonate is independent of the geometry of the sample holder since the reaction is reversible [5].

A typical thermogram was allowed to run for 2–4 h after reaching the desired temperature, depending on the time necessary for the completion of the decomposition of the sample. The thermogram obtained of weight vs. temperature depicted the rate of decomposition at each specific temperature.

The IR spectra were obtained by preparing a 2% (by weight) sample homogeneously mixed with potassium bromide and compressed using a Carver Press at 25 000 pounds for 10–20 s without vacuum. This procedure produced a transparent disc. The discs were scanned in a Perkin-Elmer infrared spectrometer model 1330.

RESULTS AND DISCUSSION

Table 1 summarizes the data obtained using the sodium 12-molybdosilicate at temperatures ranging from 650 to 800°C with catalyst concentration weight ratios varying from 1:5 to 1:200 with a blank of pure calcium carbonate. Figures 2–5 show that the rate of decomposition increases with the increase of the percent of catalyst, until reaching the ratio of 1:10. At this ratio, the rate begins to decrease, but not below the pure calcium carbonate.

These catalysts are unstable at temperatures over 400°C [6]. Therefore, it may be suspected that the rate increase may be due to the decomposition of the molybdate complexes thus increasing the overall rate.

However, Table 2 and Fig. 6 indicate that the rate of decomposition of the pure catalyst is minor. Moreover, the low rate of the 12-molybdosilicate at high concentration may prevent the evolution of carbon dioxide from the crucible, thus causing reduction of the overall rate. Tables 3 and 4, with Figs. 7 and 8 confirm the assumption that the rate of decomposition is dependent on the quantity of sample used. If the sample weight is increased, more carbon dioxide will be evolved.

Table 5 shows the data obtained using the sodium 12-molybdophosphate. Figures 9–12 show the same effect as the sodium 12-molybdosilicate except that the rate reaches a plateau at 700 and 800°C . The reason for this plateau cannot be explained until further investigations are pursued.

TABLE 1

Data for $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$

Temperature (°C)	Ratio (by wt)	% Catalyst (by wt)	Rate (mg h ⁻¹)	Sample weight (mg)
650	Pure CaCO ₃	—	5.40	91.6
	1:5	16.67	7.27	91.5
	1:10	9.09	6.45	91.5
	1:20	4.76	6.79	91.4
	1:50	1.96	6.00	91.3
	1:100	0.99	5.83	91.8
	1:200	0.50	5.42	91.6
700	Pure CaCO ₃	—	20.00	91.6
	1:5	16.67	23.16	91.4
	1:10	9.09	26.67	91.4
	1:20	4.76	27.69	91.8
	1:50	1.96	27.50	91.3
	1:100	0.99	21.86	91.5
	1:200	0.50	21.33	91.4
750	Pure CaCO ₃	—	57.14	91.7
	1:5	16.67	66.67	91.8
	1:10	9.09	80.00	91.6
	1:20	4.67	91.43	91.5
	1:50	1.96	76.67	91.7
	1:100	0.99	73.33	91.6
	1:200	0.50	62.86	91.3
800	Pure CaCO ₃	—	150.00	91.7
	1:5	16.67	160.00	91.4
	1:10	9.09	200.00	91.4
	1:20	4.76	200.00	91.8
	1:50	1.96	180.00	91.5
	1:100	0.99	173.00	91.6
	1:200	0.50	160.00	91.7

There are two features of heteropolymolybdate compounds that contribute to their catalytic properties:

(1) molybdenum oxidation states, especially (VI) and (V) are easily inter-converted;

TABLE 2

Rate of decomposition of $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x \text{H}_2\text{O}$ at different temperatures

Temperature (°C)	Sample weight (mg)	Rate (mg h ⁻¹)
650	91.8	0.80
700	91.9	1.60
750	91.5	4.14
800	91.5	6.22

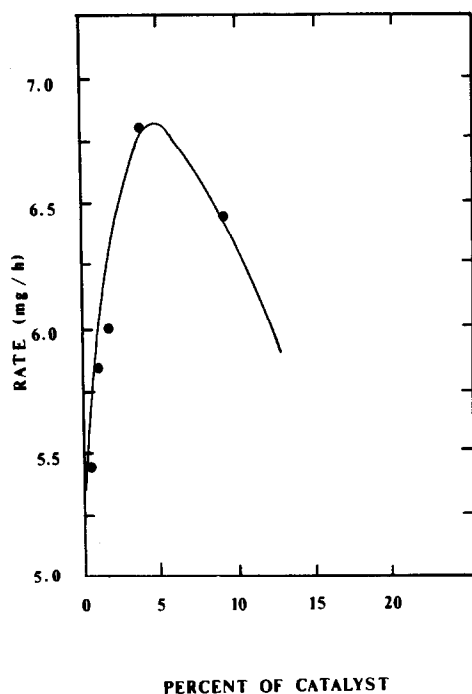


Fig. 2. Percent of catalyst vs. rate of decomposition at 650°C. Catalyst used: $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

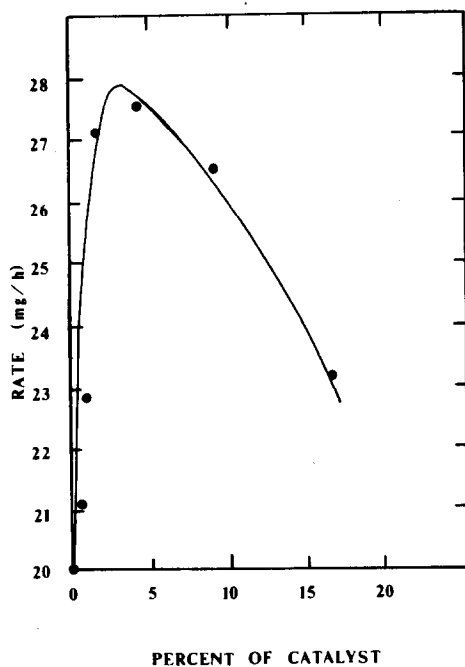


Fig. 3. Percent of catalyst vs. rate of decomposition at 700°C. Catalyst used: $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

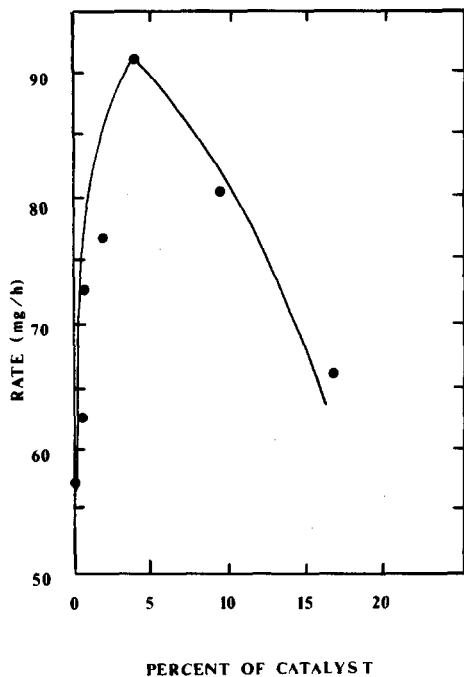


Fig. 4. Percent of catalyst vs. rate of decomposition at 750°C. Catalyst used: $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

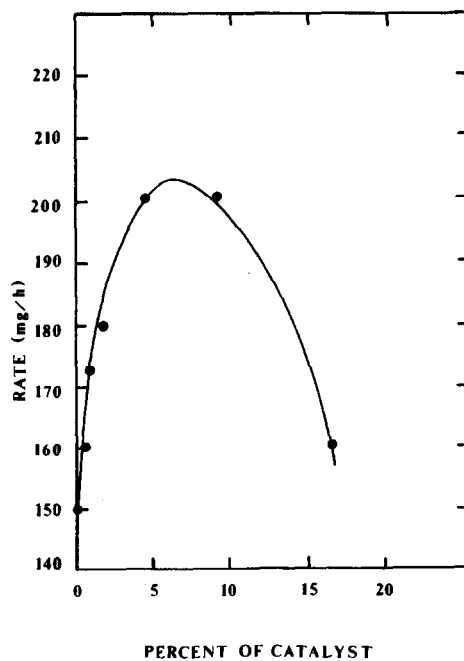


Fig. 5. Percent of catalyst vs. rate of decomposition at 800°C. Catalyst used: $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

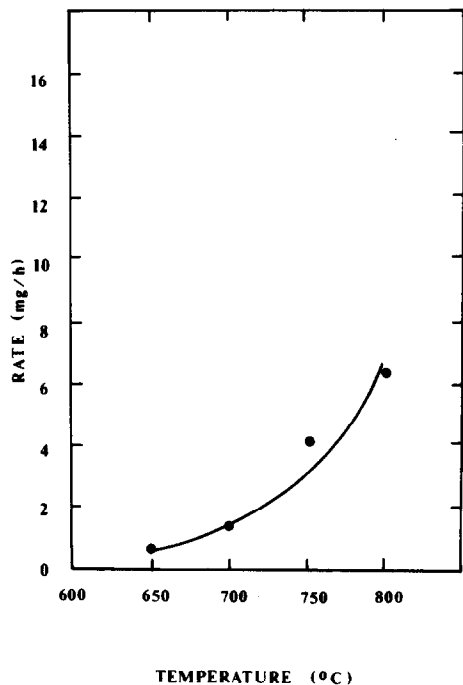


Fig. 6. Rate of decomposition of $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ vs. temperature.

TABLE 3

Relationship between rate of decomposition and amount of sample at 750 °C

Ratio (by wt)	Sample weight (mg)	Rate (mg h^{-1})
Pure CaCO_3	91.7	55.00
	81.6	53.33
	71.5	48.00
	61.7	46.67
	51.6	44.00
1:50	91.4	80.00
	81.6	80.00
	71.5	74.29
	61.4	73.33
	51.7	70.00
1:100	91.7	60.00
	81.5	62.85
	71.5	60.00
	61.7	64.00
	51.5	60.00

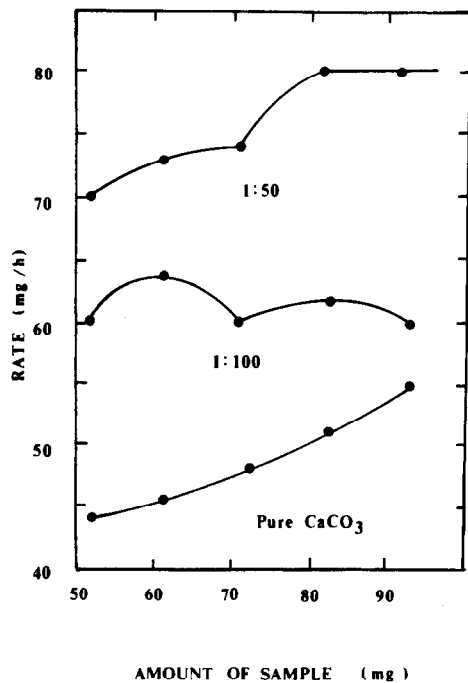


Fig. 7. Amount of sample vs. rate of decomposition at 750°C. Catalyst used $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

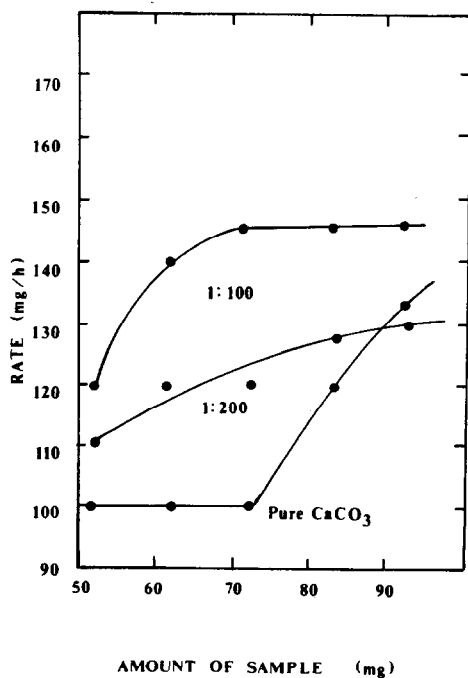


Fig. 8. Amount of sample vs. rate of decomposition at 800°C. Catalyst used: $\text{Na}_4\text{SiMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

TABLE 4

Relationship between rate of decomposition and amount of sample at 800 °C

Ratio (by wt)	Sample weight (mg)	Rate (mg h ⁻¹)
Pure CaCO ₃	91.6	133.33
	81.4	120.00
	71.5	100.00
	61.5	100.00
	51.6	100.00
1 : 100	91.6	146.67
	81.5	146.67
	71.4	146.67
	61.7	140.00
	51.5	120.00
1 : 200	91.7	130.00
	81.7	128.00
	71.4	120.00
	61.4	120.00
	51.4	110.00

TABLE 5

Data for Na₃PMo₁₂O₄₀ · x H₂O

Temperature (°C)	Ratio (by wt)	% Catalyst (by wt)	Rate (mg h ⁻¹)	Sample weight (mg)
650	Pure CaCO ₃	–	5.40	91.6
	1:5	16.67	5.93	91.6
	1:10	9.09	5.71	91.8
	1:20	4.67	5.85	91.7
	1:50	1.96	5.96	91.5
	1:100	0.99	5.71	91.4
700	Pure CaCO ₃	–	16.72	91.7
	1:5	16.67	28.00	91.5
	1:10	9.09	28.00	91.7
	1:20	4.76	26.15	91.4
	1:50	1.96	20.00	91.7
	1:100	0.99	18.06	91.5
750	Pure CaCO ₃	–	57.14	91.7
	1:5	16.67	80.00	91.6
	1:10	9.09	85.71	91.6
	1:20	4.76	80.00	91.3
	1:50	1.96	66.67	91.5
	1:100	0.99	68.57	91.5
800	Pure CaCO ₃	–	150.00	91.7
	1:5	16.67	186.67	91.6
	1:10	9.09	186.67	91.7
	1:20	4.76	186.67	91.7
	1:50	1.96	173.33	91.8
	1:100	0.99	160.00	91.3

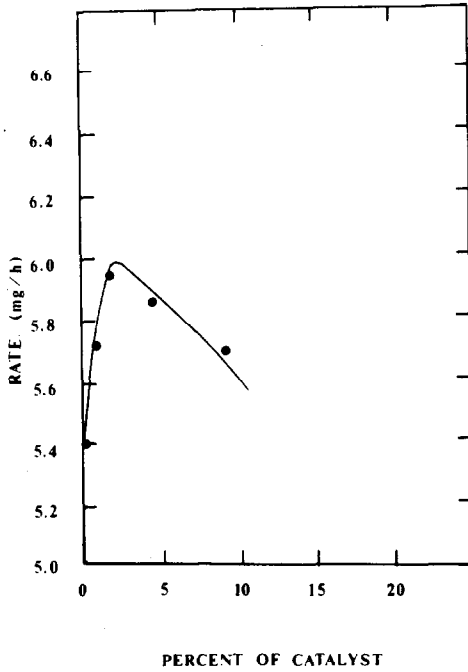


Fig. 9. Percent of catalyst vs. rate of decomposition at 650°C. Catalyst used: $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

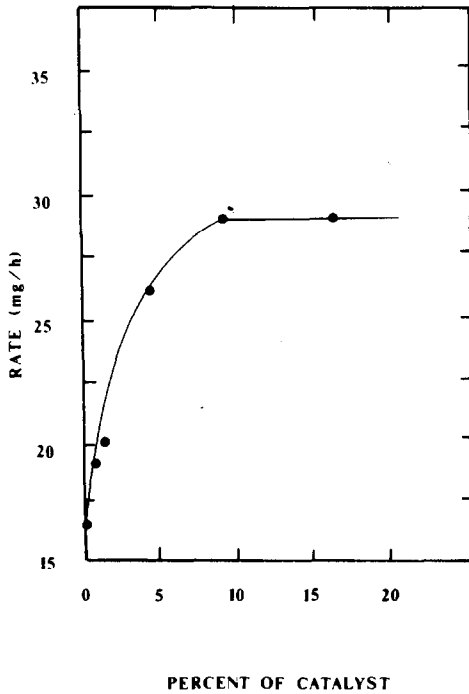


Fig. 10. Percent of catalyst vs. rate of decomposition at 700°C. Catalyst used $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

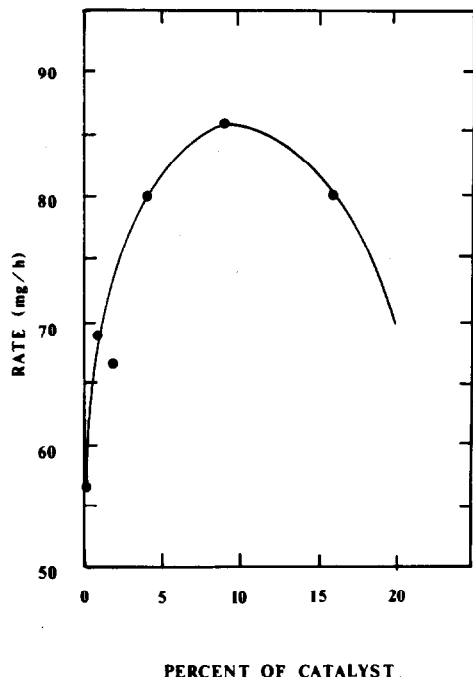


Fig. 11. Percent of catalyst vs. rate of decomposition at 750°C. Catalyst used $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

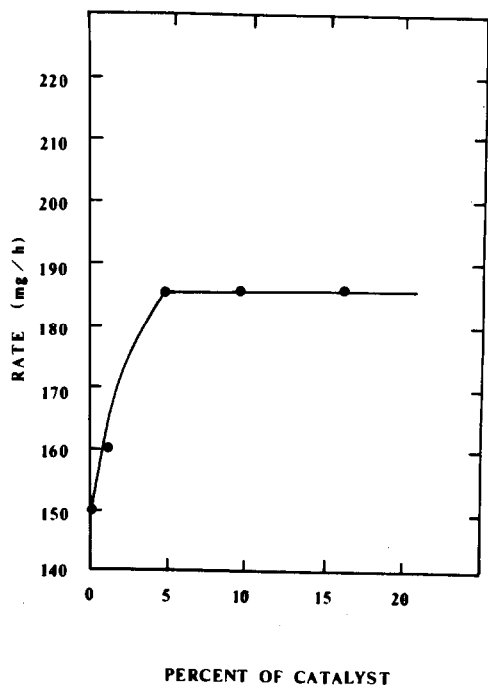


Fig. 12. Percent of catalyst vs. rate of decomposition at 800°C. Catalyst used $\text{Na}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$.

TABLE 6

IR data for sodium 12-molybdosilicate and ammonium 12-molybdosilicate

Sodium 12-molybdosilicate (cm^{-1})	1610	950	895	850	770
Ammonium 12-molybdosilicate (cm^{-1})	996	958	909	856	783

(2) change of coordination number for molybdenum(VI) with coordination numbers of four, five and six are well known.

These two features may be important in providing low activation energy pathways for electron transfer and the creation of anionic vacancies at molybdenum [7]. Tsigdinos reports that the water of hydration plays an important role in providing hydrogen bonding to the individual heteropoly anions [8].

IR spectra for the molybdates of sodium were taken and compared with those of ammonium salts as presented by Sharpless and Munday [9] as shown in Table 6. Also, Kasparzak et al. studied these 12-molybdosilicic and 12-molybdophosphoric acids by using Raman spectroscopy in aqueous solutions [10]. The spectra are almost identical in the region $1200\text{--}600\text{ cm}^{-1}$ with a slight upfield shift for the sodium salts which may be solely due to instrumental variations. However, with molybdate samples mixed with calcium carbonate in a 1:1 ratio, the absorptions of the molybdates are masked by the calcium carbonate and cannot be seen except at 950 cm^{-1} , as shown in Table 7.

These results may be interpreted as either the molybdates have or have not reacted with the calcium carbonate so strongly that this vibrational motion no longer exists because of the extreme interaction and bonding of the molybdates to the geometrical matrix of the calcium carbonate lattice structure or, alternatively, due to the strong absorptions of the calcium carbonate, they totally mask the absorption of the molybdates. Other techniques, such as X-ray diffraction, are being investigated in order to study the possible interactions between the molybdates and calcium carbonate.

A suggested explanation for the catalytic effects of the molybdates on the calcination of calcium carbonate can be deduced from bonding theory. In Fig. 1, for the calcination process to occur, bond (b), the O-C bond, and bond (c), the O-Ca bond must break. Bond (b) is covalent, while bond (c) may be either ionic or covalent. However, bond (c) should be a very weak

TABLE 7

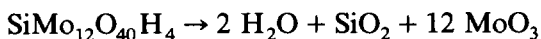
Data for pure CaCO_3 and sodium 12-molybdophosphate with CaCO_3 in a 1:1 weight ratio

Pure CaCO_3 (cm^{-1})	1792	1400	868	706	
Sodium 12-molybdophosphate + CaCO_3 (1:1) (cm^{-1})	1788	1400	950	868	706

bond. Breaking of bond (c) would accelerate the subsequent breakage of bond (b), since the calcium atom is released from the oxygen atom in bond (c). This would then assert a more positive attraction force on the oxygen bond (a). In the molybdophosphate structure, each oxygen atom of the central XO_4 ($X = P, Si$) group is shared with three MoO_6 octahedra. Each MoO_6 octahedron also shares four other oxygen atoms with other MoO_6 groups. The sixth oxygen atom in each MoO_6 group is attached to the molybdenum atom alone. These unshared oxygens project from the anion in all directions. Simply stated, this could be viewed as a P (or Si) atom in the center, covered by a layer of molybdenum, and finally covered by another layer of oxygen.

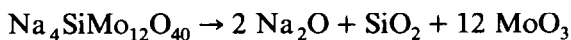
In the sodium salts, the sodium atoms are placed outside the anion with ionic bonding to it. The electrons are drawn closer to the anion leaving some positive forces stretching outside from the sodium atoms. These positive forces help the breaking of bond (c) by attacking any one of the two oxygens attached to the carbon (reaction site p or q).

Alternatively, since the anion is very large compared to the sodium cations, there may also be negative forces stretching out from the center of the anion, which attack the calcium atom helping with the breakage of bond (c). Nevertheless, according to Rabette and Oliver [11], the thermal decomposition of 12-molybdosilicic acid at $730^\circ C$ has the following equation of decomposition



The acid decomposes to amorphous silica and a phase ϕ_A , which is transformed, exothermically in the solid state, into MoO_3 at $705^\circ C$. However, from $680^\circ C$, ϕ_A starts to sublime, and recrystallizes on the cold inner surface in the form of MoO_3 .

For the sodium salt, the above equation could be rewritten as follows



This means that at the temperature of calcination, the huge 12-molybdo anion has broken down into some smaller molecules, i.e., Na_2O , SiO_2 and MoO_3 . Regardless of which molecule plays the important role as the catalyst, the positive and negative charge forces should be important in interpreting the results obtained so far.

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