Oxidative Coupling of Methane over the Oxides of Group IIIA, IVA, and VA Metals

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The conversion of methane to C_2 hydrocarbons by oxidative coupling was studied on the oxides of group IIIA (3), IVA (4), and VA (5) metals over a temperature range of 550-700 °C. The effect of the preparative method of the catalyst, of alkali promoters, and of supports was investigated in more detail with bismuth oxide. The addition of alkali, up to a concentration of 8×10^{20} ions/g, promoted alumina-supported Bi₂O₃ catalysts, and a maximum was observed for the total carbon conversion and the C₂ selectivity at Bi₂O₃ concentrations of 3-10 wt % in the Bi₂O₃-K₂CO₃-Al₂O₃ catalysts. It was also found that the yield of C₂ hydrocarbons on the Bi₂O₃ catalysts strongly depended on the support: alumina was most efficient, followed by magnesia, while Bi₂O₃ supported on silica and titanium oxide was inactive under the present conditions. When supported on alumina and promoted by potassium, Bi₂O₃ was most active and selective followed by SnO₂ and PbO in that order but Ga₂O₃, In₂O₃, Tl₂O₃, GeO₂, and Sb₂O₄ gave practically no C₂ hydrocarbons at 640 °C. The results of the present study and of the hydrogen-exchange reaction between CH_4 and CD_4 suggest that the $Bi_2O_3-K_2CO_3-Al_2O_3$ catalysts catalyze the oxidative coupling reaction as bifunctional catalysts.

1. Introduction

A predicted shortage in the supply of conventional oil has given natural gas an important position as an alternative source of hydrocarbons, and various processes have been proposed to convert natural gas into higher hydrocarbons. There are difficulties, however, in the direct conversion of natural gas mainly due to two factors: the high stability of the methane molecule and the thermodynamic disadvantage. The oxidative coupling of methane, $2CH_4 + \frac{1}{2}O_2 = C_2H_6 + H_2O$, is one of the processes that surmounts these difficulties. For example, ΔG , the free energy change, at 900 K for $2CH_4 = C_2H_6 + H_2$ is 17.0 kcal vs. -30.3 kcal for the oxidative coupling reaction of methane. Keller and Bhasin¹ investigated the reaction over a number of metal oxides by feeding air and methane alternatively. They found that some metal oxides, mostly those of the low-melting metals, showed higher selectivity for the formation of C_2 hydrocarbons at temperatures between 800 and 1000 °C. Hinsen et al.² used a continuous-flow system to study the oxidative coupling of methane on supported lead oxide catalysts mainly at 740 °C and reported the effect of the support, alkali promoter, and loading of PbO. Recently, a number of rare earth metal oxides were tested by Otsuka et al.^{3,4} However, more study is necessary to understand this reaction fully as the direct conversion of natural gas attracts increasing attention.

In an attempt to obtain further information on the oxidative coupling of methane, the reaction was investigated in this report on the oxides of metals in group IIIA (3), IVA (4), and VA (5) of the periodic table⁹ with a continuous-flow reactor. These oxides were supported on potassium-promoted alumina, and their catalytic performance was compared. The effect of the method of catalyst preparation, alkali promoters, and supports was studied in more detail with bismuth oxide. The reaction temperatures (<700 °C) employed in the present work were much lower than those used by the previous investigators.

2. Experimental Methods

The apparatus used in the present study consisted of electronic mass flow controllers and a tubular reactor, the outlet of which was connected to two gas sampling valves of a gas chromatograph. The reactor was made of stainless steel and had an i.d. of 0.9 cm and a 15-cm-long heated zone, consisting of a 12-cm preheating zone and a 3-cm catalyst bed. Most of the reactions were carried out with a gas mixture of 50% methane, 25% air, and 25% helium. The main products were carbon dioxide, water, and C₂ hydrocarbons with a trace of C₃ hydrocarbons, which were neglected

in the calculations of this study. No carbon monoxide was found under the reaction conditions employed in the present study. The ratio of ethane to ethylene varied depending on the reaction conditions and the catalyst, but ethane always predominated (90% typically). The selectivity toward C_2 hydrocarbons was calculated as 100 × (carbon conversion to C_2)/(total carbon conversion).

The products were analyzed with two GC columns: a 3-m Porapak R column connected with a FID and a TCD in series for the analysis of CH_4 , CO_2 , H_2O , and C_2 and C_3 hydrocarbons; a 3-m molecular sieve 5A column with a TCD for N_2 and O_2 . The nitrogen peak in both reactant and product was used as an internal standard, thus material balances within $\pm 3\%$ were achieved for carbon, hydrogen, and oxygen.

Most of the catalysts were supported on Alon alumina (Cabot Corp., Boston, MA) as will be described in the following section. Other supports tested were silica (Cab-O-Sil M-5, Cabot Corp.), titanium oxide (P25, Degussa Corp., Teterboro, NJ), and magnesia, which was coprecipitated from magnesium nitrate. Most of the metal oxides were precipitated on the supports from their nitrate solution with ammonium hydroxide. Bismuth nitrate supplied from Anachemia, Champlain, NY, was used. Also bismuth oxide (99.8%) was purchased from Alfa Products, Danvers, MA, and used without support or mechanically mixed with support. The compositions of the catalysts are expressed in weight percent in this report.

All catalysts were crushed and sieved to a particle size of 0.5-0.7 mm. The amount of catalyst used was 35 mg, which was diluted with 350 mg of inert silica to keep the temperature gradient along the catalyst bed to less than 10 °C. The catalysts were pretreated in the reactor with a flow of the reactant mixture for about 2 h at 670 °C until the reaction proceeded steadily. Unless otherwise described, all reaction results reported in this paper were obtained with 35 mg of catalyst and a total flow rate of 200 mL/min $(CH_4:air:He = 50:25:25)$. Ultrahigh-purity methane (99.97%) and ultrazero air were purchased from Linde. Helium was ultrahigh-purity grade (99.999%) from Matheson.

3. Results

3.1. Effect of Preparation Method. Three methods were used to prepare the supported bismuth oxide catalysts.

(a) Precipitation with Ammonia (PA). Alon alumina was suspended in a bismuth nitrate solution and a 5% ammonia solution

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TABLE I: Comparison of Preparation Method for 7% Bi₂O₃-9% K₂CO₃-Al₂O₃ Catalysts at 640 °C

method of	convsn, ^b %		C,	surface
preparation ^a	carbon	oxygen	selectivity, %	area, m^2/g
PA	6.6	87	23.9	78
PU	6.7	88	23.2	70
MI	3.4	50	13.4	72
MM	6.0	85	18.9	77

^a PA, precipitation with ammonia; PU, precipitation with urea; MI, multiple impregnation; MM, mechanical mixing. ^b Total carbon or oxygen reacted on 35 mg of catalyst at a total flow rate of 200 mL/ min.



Figure 1. Effect of Bi_2O_3 concentration in $Bi_2O_3-9\%$ $K_2CO_3-Al_2O_3$ catalysts. Reaction temperature 640 °C: X_c, total carbon conversion; S_2 , C_2 selectivity; SA, surface area.

was slowly added until the pH reached 8. The precipitate was filtered, washed, and dried at 110 °C. The catalyst was then impregnated with potassium carbonate and finally calcined at 600 °C for 3 h. This method was used to prepare all the catalysts in the present work unless otherwise stated. Also one catalyst was prepared by homogeneous precipitation with urea (PU). Alumina was suspended in a solution of bismuth nitrate and urea. The mixture was then heated to 90-100 °C for precipitation. Finally potassium carbonate was added as above.

(b) Multiple Impregnation (MI). Alon alumina was first alkalized by impregnation with potassium carbonate followed by calcination at 600 °C. A dilute bismuth nitrate solution (0.04 M) was added to just cover the alumina powder, and the slurry thus made was subsequently dried at 110 °C. This step was repeated until the concentration of Bi₂O₃ reached the desired level. The catalyst was finally calcined at 600 °C.

(c) Mechanical Mixing (MM). A calculated amount of bismuth oxide was mixed with the alkalized alumina by grinding, followed by the addition of water to form a slurry. The slurry was dried and finally calcined in air at 600 °C.

Results obtained at 640 °C with the catalysts prepared by the above methods are summarized in Table I, which shows that the catalysts prepared by the precipitation method are the most active and selective. Unexpectedly, the catalyst prepared by the mechanical mixing performed rather closely to the precipitated ones, while the multiple impregnation resulted in the poorest catalyst in the group. Table I also shows that the differences in activity are not due to the surface area.

These catalysts were stable unless they were heated above 700 °C, and the conversion was reproducible within 2%.

3.2. Effect of Oxide Loading. Figure 1 presents the effect of the concentration of Bi₂O₃ in the K₂CO₃-promoted Bi₂O₃-Al₂O₃ catalysts. The activity (total carbon conversion) and the C₂ selectivity increased sharply with a small amount of bismuth oxide added but went through a maximum as seen in Figure 1. The activity and selectivity both became constant between 3% and 10% of Bi_2O_3 but decreased beyond 10%. The descending part of the activity curve (X_c) is probably due to the decreasing surface area. A similar dependency on the Bi₂O₃ concentration was observed



Figure 2. Effect of potassium promoter for 7% Bi₂O₃-K₂CO₃-Al₂O₃ catalysts. Reaction temperature 640 °C. X_c, S₂, and SA are the same as in Figure 1.

TABLE II: Effect of Support on Bismuth Oxide Catalysts

	convsn, ^b		C ₂	surface	
catalyst ^a	carbon	oxygen	selectivity, %	area, m ² /g	
Bi ₂ O ₃	1.2	19		2	
68% Bi ₂ O ₃ -32% KOH	1.3	22			
7% Bi ₂ O ₃ -9%	6.6	87	23.9	78	
K ₂ CO ₃ -Al ₂ O ₃					
7% Bi ₂ O ₃ -9%	7.3	88	29.0	64	
$K_2CO_3 - Al_2O_3^c$					
7% Bi ₂ O ₃ -9%	6.9	92	20.7	178	
$K_2CO_3 - Al_2O_3^d$					
$7\% \operatorname{Bi}_2\operatorname{O}_3-\operatorname{MgO}$	5.2	81	5.7	78	
$7\% \operatorname{Bi}_2 \operatorname{O}_3 - \operatorname{SiO}_2$	0.6	12	2.1	140	
7% Bi ₂ O ₃ -9%	0.8	14	1.9		
K ₂ CO ₃ -SiO ₂					
$7\% \text{ Bi}_2 \text{O}_3 - 7\%$	0.9	17	1.5	51	
KOH-SiO ₂					
$7\% \operatorname{Bi}_2 \operatorname{O}_3 - \operatorname{Ti} \operatorname{O}_2$	1.5	26	0.9		
7% Bi ₂ O ₃ -11%	1.2	21	0.5	35	
Cs ₂ CO ₂ -TiO ₂					

^aAll catalysts had the same concentration of alkali ions (8 \times 10²⁰ ions/g) except for Bi_2O_3 -KOH (3 × 10²¹) and Bi_2O_3 -Cs₂CO₃-TiO₂ (4 \times 10²⁰). ^bTotal carbon or oxygen reacted at 640 °C with 35 mg of catalyst and a total flow rate of 200 mL/min. ^cAlumina was γ -alumina from Strem Chem. Inc., Newburyport, MA. ^d Alumina and Bi₂-O3 were coprecipitated from their nitrates.

for the unpromoted Bi_2O_3 -Al₂O₃ catalysts, but their activities were much lower than those of the promoted ones.

A blank test showed that the formation of carbon dioxide and C2 hydrocarbons without catalyst was negligible. Therefore, the results of Figure 1 indicate that the 9% K₂CO₃-Al₂O₃ support itself has some activity. It is, however, much lower than the Bi₂O₃-containing catalysts, suggesting that bismuth oxide is an essential part of the active sites.

Maxima for the activity and selectivy similar to those in Figure 1 were also observed with the content of tin oxide in $SnO_2-9\%$ K_2CO_3 -Al₂O₃ catalysts.

3.3. Effect of Alkali Promoter. Potassium was added to Bi₂O₃-Al₂O₃ catalysts as potassium carbonate by impregnation as described in method a in section 3.1. Figure 2 shows the effect of potassium added to 7% Bi₂O₃-Al₂O₃ catalyst. The activity and selectivity both increased with the amount of potassium but reached a plateau at about 10%. Krupay and Amenomiya⁵ found that below surface saturation K2CO3 on alumina decomposed on heating below 600 °C and that the K ions were likely to replace the surface protons to form OK groups. Furthermore, K₂CO₃ added beyond about 9% did not decompose.⁶ Indeed, 7% Bi₂- O_3 -Al₂ O_3 catalyst impregnated with KBr at about the same ion concentration (8 \times 10²⁰ K⁺ ions/g) showed similar activity and

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Figure 3. The order of reaction on 7% $Bi_2O_3-9\% K_2CO_3-Al_2O_3$ catalyst at 550 °C. Reaction rate = kp^x (hydrocarbon) p^y (oxygen).

selectivity to those of the K_2CO_3 -promoted catalyst. Also sodium and cesium at the same ion concentration promoted the Bi₂O₃-Al₂O₃ catalyst as effectively as potassium. The impregnation of lithium, however, resulted in a less active and less selective catalyst.

3.4. Effect of Support. Results obtained with bismuth oxide supported on various oxides are listed in Table II. As is clear from Table II, the catalytic performance of bismuth oxide strongly depends on the support. Unsupported bismuth oxide did not produce any C_2 hydrocarbons, within experimental error, whether it was promoted by alkali or not. Use of 1.1 g of bismuth oxide, which had 450 times more Bi₂O₃ than the supported 7% Bi₂O₃ catalysts listed in Table II, also resulted in poor conversion and selectivity, although a trace of C_2 hydrocarbons was detected in this case. KOH and Cs_2CO_3 were used as promoters for silica and titanium oxide supports, respectively, because K_2CO_3 might not decompose on these surfaces.

The results of Table II show that the alumina support gives the best results, followed by magnesia. The carbon conversion of magnesia-supported Bi_2O_3 catalyst was comparable to that of alumina-supported catalysts, but the C_2 selectivity was much lower. Silica and titanium oxide supported catalysts with or without alkali promoter were almost inactive. These results clearly indicate that the increase in the surface area of bismuth oxide by the support does not contribute to the catalytic performance but rather that the chemical property or the interaction of the support is an important factor for the activity and selectivity.

3.5. Kinetics. If one ignores a trace of C_3 hydrocarbons, five reactions may occur, either in parallel or in series, under the present reaction conditions.

$$2CH_4 + \frac{1}{2}O_2 = C_2H_6 + H_2O$$
(1)

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
 (2)

$$C_2H_6 + 1/2O_2 = C_2H_4 + H_2O$$
 (3)

$$C_2H_6 + \frac{7}{2}O_2 = 2CO_2 + 3H_2O$$
 (4)

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$
(5)

Ethylene is assumed to be formed by the oxidative dehydrogenation of ethane as expressed by reaction 3 rather than by the direct formation from methane. The results of the exchange reaction between CD_4 and CH_4 carried out in our laboratories over a bismuth catalyst showed that only one hydrogen atom was exchanged per adsorption-desorption cycle. This supports the above assumption.

The order of reaction was obtained on 7% Bi₂O₃-9% K₂C-O₃-Al₂O₃ by varying the partial pressure of one reactant while keeping the other's pressure constant. The ranges of pressure variation were 190-350 Torr for CH₄, 70-170 Torr for C₂H₆ and C₂H₄, and 40-110 Torr for O₂. The reaction temperature was also lowered to 550 °C to keep the conversion low, and the reactor was regarded as a differential reactor. Results are shown in Figure 3, where x and y are the reaction orders for the hydrocarbon and oxygen, respectively. In spite of the low reaction temperature,

TABLE III: Effect of Partial Pressures on C2 Selectivity at 640 °C

partial pressure, torr		C,		
	CH ₄	O2	selectivity, %	
	348	40	23.3	
	348	81	23.8	
	185	81	20.9	

TABLE IV: Comparison of Metal Oxides at 640 °C

oxide on 9%	conv	sn, %	C ₂ selectivity, %
K ₂ CO ₃ -Al ₂ O ₃ ^a	carbon	oxygen	
Ga ₂ O ₃	1.4	25	
In_2O_3	2.4	41	
Tl_2O_3	0.9	17	
GeO ₂	1.5	29	
SnO_2	6.4	85	14.7
PbO	4.2	63	7.6
Sb ₂ O ₄	1.8	28	
Bi ₂ O ₃	6.6	87	23.9

^a The concentration of all oxides was 7 wt %.



Figure 4. Temperature dependence of carbon conversion and C_2 selectivity on 7% Bi₂O₃-9% K₂CO₃-Al₂O₃.

the conditions still deviated from those of a differential reactor so that the reaction orders obtained in the present work are approximate.

The orders of the primary reactions (reactions 1 and 2) observed in this work generally agreed with those obtained by Hinsen et $al.^2$ In order to check the validity of the reaction orders at higher temperatures, the reaction was carried out at 640 °C with varying partial pressures as shown in Table III. As predicted from the values of x and y in Figure 3, the change in the C₂ selectivity was minimal for the variation of oxygen pressure but it changed more when the methane pressure was varied. The latter change was, however, much smaller than expected from the difference in the values of x in Figure 3.

The temperature dependence of the total conversion of methane and of the C₂ selectivity is presented in Figure 4. The selectivity increases more rapidly with temperature, suggesting that the activation energy of reaction 1 is larger than that of reaction 2. The 7% Bi₂O₃-9% K₂CO₃-Al₂O₃ catalyst did not show any change in the activity and selectivity for 100 h at 640 °C. At 730 °C, however, a slow deactivation of the catalyst was observed.

3.6. Comparison of Metal Oxides. The activity and selectivity of metal oxides from group IIIA (3), IVA (4), and VA (5) are summarized in Table IV. All metal oxides were supported on 9% K_2CO_3 -Al₂O₃ at the same concentration (7 wt %) prepared by method a as described in section 3.1. In the case of SnO₂ and Sb₂O₄, the precipitation was made from chloride solution instead of nitrate solution. As seen in Table IV, the activity of the oxides of Sn, Pb, and Bi for the total methane conversion are distinctively higher than the others and comparable between themselves. For the C₂ selectivity, however, bismuth oxide is by far the best under the present reaction conditions.

As described earlier, Hinsen et al.² studied the oxidative coupling of methane on supported PbO catalysts primarily at 740 °C. They found the maximum selectivity at a much higher loading of PbO, 36 wt % when supported on alumina. They also found that the silica-supported catalysts gave generally higher selectivities. The reaction conditions employed in their study were, however, different from those used in the present work, in particular the temperature range was much higher. We also tested a 34% PbO-Al₂O₃ catalyst, but the results at 640 °C were about the same as those of the 7% PbO catalyst shown in Table IV. Recently, Driscoll et al.⁷ reported the formation of methyl

Recently, Driscoll et al.' reported the formation of methyl radicals on the surface and their subsequent release into the gas phase, by passing methane over magnesia at 500 °C. They also found that the radical formation increased when MgO was doped with lithium. We prepared a 10% Li-doped MgO catalyst and tested it under our reaction conditions (35 mg of catalyst at a total flow rate of 200 mL/min). The C₂ selectivity was about 25% at a total carbon conversion of 2% at 640 °C. At 700 °C, the selectivity and the carbon conversion reached 29% and 2.5%, respectively, but both decreased rapidly with time.

4. Discussion

The present investigation has shown that a highly selective catalyst for the oxidative coupling of methane is prepared by supporting the oxides of Bi, Sn, or Pb on alkali-promoted alumina. The selective oxidation of hydrocarbons catalyzed by metal oxides is generally throught to take place by the redox cycle of the catalyst. For the oxidative coupling of methane (reaction 6), the redox cycle of a metal oxide, M_mO_n , is written as

$$2CH_4 + M_mO_n = C_2H_6 + H_2O + M_mO_{n-1}$$
(6a)

$$M_m O_{n-1} + \frac{1}{2} O_2 = M_m O_n$$
 (6b)

The free energy change for the overall reaction 6 is the sum of the free energy changes for reactions 6a (ΔG_a) and 6b (ΔG_b). In order for $M_m O_n$ to catalyze reaction 6, both ΔG_a and ΔG_b must be either negative or close to zero. On the basis of these criteria, metals whose oxide may catalyze the oxidative coupling of methane are Tl, Pb, Sb, and Bi, while Ga and In have a large positive ΔG_{a} . ΔG_a values of germanium and tin oxides (mono- and dioxide) are 12-18 kcal/mol between 900-1000 K so that they are not favorable catalysts either. Lead and bismuth oxides, listed above as favorable catalysts, were found to be active in the present study (Table IV). The temperature-programmed reduction of the Bi_2O_3 -Al₂O₃ catalysts carried out in a stream of He + CH₄ showed that the reduction of the catalyst by methane occurred above 500 °C, coinciding with temperatures at which the oxidative coupling reaction was observed. The exception is tin-tin oxide, which showed a high activity and selectivity is thermodynamically unfavorable.

However, the criteria for the evaluation of catalysts discussed above are certainly oversimplified. While the thermodynamic calculations were made for the stoichiometric oxides, the X-ray diffraction analysis of promoted and unpromoted Bi₂O₃-Al₂O₃ showed that the compound formed on the alumina was different from Bi_2O_3 . Moreover, the redox mechanism of the metal oxides alone cannot explain some of the present results, the activity of the catalysts in particular. Figure 1 showed that the presence of a small amount of bismuth oxide increases the formation of C_2 hydrocarbons sharply and then the activity remains constant up to a concentration of the oxide of about 10%. The bismuth oxide mechanically mixed with the support gave results close to those obtained with the precipitated catalysts as pointed out earlier (Table I). The mechanically ground Bi_2O_3 had a very small surface area (Table II). These facts all indicate that the activity is not proportional to the amount or to the surface area of bismuth oxide. Also, the strong effect of supports revealed in Table II



Figure 5. Bifunctional mechanism of oxidative coupling of methane.

suggests that the chemical nature of the support or the interaction with the oxide is important for the catalytic performance.

The rupture of the C-H bond of methane is required as the first step in almost any catalytic process for the conversion of methane, including the oxidative coupling reaction. The hydrogen-exchange reaction between CH4 and CD4 was studied on various oxides in our laboratories as a test reaction to evaluate the ability of catalysts to break the C–H bond.⁸ In that study, alumina (Alon alumina) was found to be most active for the exchange reaction followed by 9% K2CO3-Al2O3 and MgO in that order, while SiO₂ and TiO₂ were inactive at least up to 600 $^{\circ}C.^{8}$ Even with active aluminas or magnesia, however, no ethane was formed in the exchange reaction carried out at a low methane pressure. An interesting fact is that, except for nonalkalized alumina, the same order of activity was also found in Table II for the formation of C₂ hydrocarbons when these oxides were used as supports: 7% Bi₂O₃ supported on 9% K₂CO₃-Al₂O₃ is the most active catalyst followed by that supported on MgO, while SiO₂and TiO_2 -supported catalysts are almost inactive. The activity ratio between the magnesia and the alkalized alumina for the exchange reaction at 640 °C is 0.12 and the activity ratio between the MgO- and 9% K₂CO₃-Al₂O₃-supported Bi₂O₃ catalyst for the formation of C₂ hydrocarbons (carbon conversion times selectivity in Table II) is 0.18. The two ratios are in reasonable agreement.

From the present results and the above comparisons, the $Bi_2-O_3-K_2CO_3-Al_2O_3$, Bi_2O_3-MgO , and possibly the PbO-K₂C-O₃-Al₂O₃ catalysts seem to work under the present reaction conditions as bifunctional catalysts; that is, methane is dissociated into CH₃ and H on the alumina or magnesia surface and the hydrogen is oxidized on the metal oxide by a redox mechanism as depicted in Figure 5. When the hydrogen is removed from the adjacent site, methyl radicals would have a better chance to dimerize. The rate of oxidation of hydrogen on bismuth oxide is probably much faster than that of the methane dissociation or the dimerization of methyl radicals so that the presence of a small amount of Bi_2O_3 is enough to activate the catalyst but the activity is not proportional to the concentration of the oxide.

The role of alkali promoter is not clear at this stage. Alkali may promote the oxidation of hydrogen by increasing the electron density of bismuth oxide since the redox cycle of oxide requires an electron transfer. The increase in the C₂ selectivity by the addition of alkali was explained by Hinsen et al.² as being due to the suppression of the acid sites thought to be responsible for the nonselective oxidation of methane. The present results show, however, that alkali increased the conversion to CO₂ as well as C₂ hydrocarbons (Figure 2). High C₂ selectivities were generally found at high carbon conversions in this study (Figures 1 and 2 and Tables II and IV), suggesting that the selective and nonse-

⁽⁸⁾ Li, Q.; Amenomiya, Y. Appl. Catal. 1986, 23, 173.

⁽⁹⁾ In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprises groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

lective oxidation reactions follow the same reaction path to a certain stage. Certainly more information, particularly on the mechanism of the oxidation to CO_2 , is needed to draw a definite mechanism for the oxidative coupling reaction.

Finally, Driscoll et al.⁷ demonstrated the formation of methyl radicals on magnesia catalysts and their subsequent release into the gas phase as already described. Therefore, there is the possibility that ethane is formed in the gas phase. The present results, however, can neither support nor deny that possibility.

Registry No. CH₄, 74-82-8; H₃CCH₃, 74-84-0; H₂C=CH₂, 74-85-1; Bi₂O₃, 1304-76-3; K₂CO₃, 584-08-7; Al₂O₃, 1344-28-1; KOH, 1310-58-3; MgO, 1309-48-4; SiO₂, 7631-86-9; TiO₂, 7440-32-6; Cs₂CO₃, 534-17-8; Ga₂O₃, 12024-21-4; In₂O₃, 1312-43-2; Tl₂O₃, 1314-32-5; GeO₂, 1310-53-8; SnO₂, 18282-10-5; PbO, 1317-36-8; Sb₂O₄, 1332-81-6.

Selective Reduction of Nitric Oxide on Nickel Oxide-Copper Oxide Supported Catalysts

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Selective catalytic reduction of nitrogen oxides (NO_x) is one of the main alternatives for reducing atmospheric pollution produced by NO_x emissions from static sources. Experimental results described in this paper were carried out in the framework of a more general study undertaken in order to develop an industrial process for the abatement of NO_x emissions from nitric acid plants. The catalyst used was NiO-CuO/ γ -Al₂O₃ and the reactions studied were NO reduction with NH₃ (in the presence and absence of oxygen) and NH₃ oxidation with oxygen, both at atmospheric pressure and in the temperature range between 200 and 300 °C. A kinetic equation was developed by using three different reaction models. This equation fits the experimental results in the above-mentioned temperature range very well, but at high temperatures experimental values clearly deviate from the model predictions. The paper ends by discussing current data in the literature and the experimental evidence obtained in this work in order to postulate a more complex mechanism for the NO reduction with NH₃ on oxide-supported catalysts. This discussion pointed out possible new lines of research in order to clarify the physical chemistry of the oxidation-reduction system involved in detail.

Introduction

Processes of selective catalytic reduction of nitrogen oxides (NO_x) , using NH₃ as a reducing agent, were extensively studied mainly during the second half of the 1970s. This interest was due to the fact that these processes were one of the main alternatives for reducing the atmospheric pollution produced by NO_x emissions from nitric acid plants.

The work here presented was one of the studies carried out in order to develop an industrial process that is now being successfully used in industrial plants.¹⁻³ In this technology a catalyst formed by oxides of Cu and Ni supported on γ -Al₂O₃ plays an important role.

With this catalyst, the kinetics of the different reactions involved, under conditions as close as possible to those of the industrial process, has been studied.

As the review by Harrison et al.⁴ pointed out, most of the kinetic studies published in the current literature deal with the reduction reaction of NO with $\rm NH_3$ without oxygen. $^{5-8}$ $\,$ In some other papers the reaction is studied in the presence of oxygen,⁹⁻¹⁶ but

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the catalysts used seem to be quite different from the one used in this work.

In order to obtain a design equation for a reactor working under industrial conditions, it was considered necessary to study the influence of the concentration of the different reactants involved in the process.

The study described in this paper was carried out with the above-mentioned catalyst for the reduction of NO with NH₃ at reaction temperatures of 200-300 °C, atmospheric pressure, in the presence of oxygen, and in the absence of SO_2 . Under these conditions, the catalytic reactions of the NO reduction with NH₃ with and without oxygen and the NH₃ oxidation with oxygen were studied.

Experimental Section

Catalyst. The catalyst used in this study was formed with oxides of Cu and Ni, in the atomic proportion 10:1, supported on lowsodium-content γ -Al₂O₃ spheres of diameter between 2 and 4 mm. The preparation method has already been described.¹⁷ It is based on the γ -Al₂O₃ impregnation with an aqueous solution of highpurity nitrates followed by a heat treatment in air for 4 h at 500 °C in order to decompose the nitrates to the corresponding oxides. The final catalyst has a surface area of approximately 180 m² g⁻¹ and a pore volume 0.66 cm³ g^{-1} .

The uniformity in the impregnation of the catalyst and of the distribution of both species inside the sphere was proved by EDAX. The characterization of this type of catalyst was studied in depth

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