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Effect of γ-Irradiation on Methanation of Carbon Dioxide over Supported Ru Catalysts

N. M. GUPTA, V. S. KAMBLE, AND R. M. IYER

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400085, India

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In situ γ-irradiation has been found to enhance the activity of Ru/molecular sieve and Ru/alumina catalysts for the CO_2 methanation reaction in the temperature range 400–600 K. The extent of radiation enhancement in catalytic activity was inversely related to temperature. The activation energy for the formation of CH_4 from 2% CO_2 in H_2 was reduced in the presence of radiation from 13.8 to 7.7 kcal mole^{-1} for Ru/alumina and from 7.3 to 4.2 kcal mole^{-1} for Ru/molecular sieve. The results indicate that γ-irradiation gives rise to energy storage in support materials. It is suggested that the energy released on thermal stimulation weakens the metal–CO_2 bonds resulting in an accelerated rate of reduction of CO_2 to active carbon and its subsequent methanation.

1. INTRODUCTION

The effect of electromagnetic radiations on the catalytic activity of solids with different band gaps has been widely investigated (see reviews (*1–5*)). In general, it has been observed that while radiation enhanced the catalytic activity of insulating materials, the activity of metal catalysts remained more or less unaffected, though in some cases a reduction in activity was observed (*3, 4*). Very few efforts (for example (*6, 7*)) have been made to investigate the effect of radiation on metal catalysts supported on insulating materials. In an earlier communication from this laboratory (*8*), it has been shown that *in situ* γ-irradiation causes a large increase in the activity of Ru/molecular sieve catalyst for methanation of carbon monoxide. In continuation of this work, studies have been carried out on the effect of *in situ* γ-irradiation on chemisorption of CO_2 and its methanation in the temperature range of 400–625 K using alumina- and molecular-sieve-supported Ru catalysts, and the results are reported in this paper.

2. EXPERIMENTAL

A continuous-flow microcatalytic reactor was employed to study the CO_2–H_2 reaction before, during, and after γ-irradiation. In all experiments the reacting gases were at about 1.2 atm. The reaction products were analyzed by gas chromatography. Thermoluminescence studies on the support materials were carried out to evaluate the stored energy, if any, as a result of γ-irradiation.

The experimental methods have been described elsewhere in detail (*8, 9*) and only salient features will find mention here.

2.1. CATALYSTS

Two ruthenium catalysts were used, one with molecular sieve-13X support (RM) and the other with activated γ-alumina support (RA). The catalysts were prepared by soaking 60- to 80-mesh support material in an aqueous solution of $RuCl_3$ followed by drying in air at 375 K. The reduction of catalysts RM and RA by H_2 was carried out at 625 and 675 K, respectively. Both catalysts contained ~1.8 wt% Ru. The surface areas of RM and RA were estimated to be 293 ± 5 and 177 ± 5 m^2 g^{-1}, respectively, as measured by the BET method using N_2 gas. Active catalyst areas, determined by the temperature-programmed desorption method using H_2 (*9*), were found to be 13 ±

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1 and 8 ± 1 m^2 g^{-1} for RM and RA, respectively.

For each experiment 2.2 ml of catalyst was taken in a 0.4-cm-i.d. S.S. tube reactor and was activated *in situ* by heating in H_2 at 600 K for 1 hr.

2.2. IRRADIATION

The catalytic reactor was so designed that it could be lowered or retrieved automatically from a ^{60}Co γ-source within 10 sec. One end of the reactor was at all times connected to He/H_2 carrier gas and the other to a gas chromatograph. The estimated dose rate was 0.63 Mrad hr^{-1}.

2.3. METHANATION EFFICIENCY OF CATALYSTS

Catalytic efficiency at different temperatures was measured by two methods: (i) pulses of 40 μl CO_2 (at NTP) were injected at regular intervals into H_2 gas flowing through the reactor (at 820 ml ml^{-1} hr^{-1}) and effluent gases were analyzed; (ii) a continuously flowing (437 ml ml^{-1} hr^{-1}) gas mixture of 2% CO_2 in H_2 was used and the product gases were periodically sampled and analyzed.

Analogous experiments were carried with the catalytic reactor in the γ-source. At the stage when methane yields reached a saturation value under radiation, the catalyst reactor was taken out of the γ-source and experiments were continued until constant yields of methane were again obtained. The experimental conditions such as temperature and gas flow rate remained undisturbed during a particular set of experiments.

2.4. EVALUATION OF METHANE PRECURSOR SPECIES

To study the effect of γ-irradiation on methane precursor species, a 40-μl CO_2 pulse and eight successive pulses of 2 ml H_2 were sequentially injected into He carrier gas flowing over the catalyst (820 ml ml^{-1} hr^{-1}) using the experimental setup described in Ref. (*8*). The effect of time lapse between CO_2 and H_2 injections on the yield of CH_4 was investigated both in the presence and in the absence of γ-radiation. The radiation experiments were started after keeping the catalyst in the γ-source for 90 min (maximum time required for achieving saturation CH_4 yield in the presence of radiation).

2.5. THERMOLUMINESCENCE (TL) STUDIES

The TL glow peaks of metal-free alumina and molecular sieve samples exposed to different doses of γ-radiation were recorded in the range 296–750 K using the experimental setup described elsewhere (*10*). A 27-mg sample was heated over a 0.25-mm-thick kanthal strip at a uniform rate of 5 K sec^{-1}. The emitted light was measured using an EMI 6255B photomultiplier tube coupled with a Keithley 610C electrometer amplifier and recorded as a function of temperature. Both the alumina and the molecular sieve samples were annealed at 425 K for 1 hr prior to γ-irradiation at 296 K.

3. RESULTS

3.1. EFFECTS OF γ-IRRADIATION ON CATALYTIC ACTIVITY

a. Pulse Injections of CO_2 in H_2 Carrier Gas

Curves 1 and 2 of Fig. 1 show the observed methane yields in the absence of γ-irradiation from catalysts RA and RM, respectively, and their dependence on catalyst temperature when 40-μl pulses of CO_2 were injected into the H_2 stream. When the catalysts were under γ-irradiation, higher methane yields per CO_2 pulse were obtained for both catalysts, the enhancement being dependent on catalyst temperature and γ-ray dose. Methane yields as a function of γ-dose are shown in Figs. 2a and b for catalysts RM and RA, respectively. The methane yields shown in these figures at zero time represent the values obtained in the absence of γ-radiation and the vertical dashed line indicates

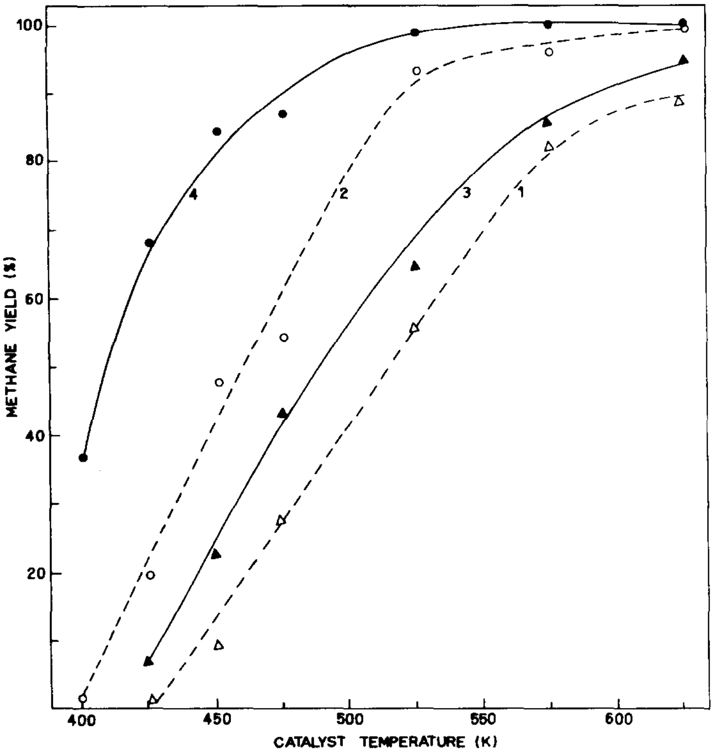

FIG. 1. Effect of γ-irradiation on activity of Ru/alumina (curves 1, 3) and Ru/molecular sieve (curves 2, 4) catalysts for the methanation reaction when 40-μl CO_2 pulses were injected into H_2 carrier gas. Curves 1 and 2, without irradiation; curves 3 and 4, in the presence of γ-radiation.

the time of cessation of irradiation. It may be noted that for both catalysts the irradiation time required to obtain saturation methane yields and the time taken to return to preirradiation values after cessation of irradiation depend inversely on catalyst temperature, as was observed in the CO–H_2 study (*8*). It is also significant to note that at a particular catalyst temperature the time required to reach the saturation methane yield and the time for its return to the preirradiation value on termination of irradiation are less in the case of the RA catalyst than with RM. The saturation methane yields obtained with the catalysts under irradiation are included in Fig. 1 for comparison (curves 3 and 4 for RA and RM, respectively). It is evident that γ-radiation considerably enhances the activity of both catalysts; for example, in the case of catalyst RM enhancement is 18 times at 400 K and 3.5 times at 425 K under present experimental conditions.

b. Continuous Flow of CO_2 + H_2

When 2% CO_2 in H_2 flowing at 437 ml ml^{-1} hr^{-1} was used, a γ-radiation effect similar to that shown in Fig. 1 was observed. When higher proportions of CO_2 in H_2 were used, a small amount of CO was found in the effluent along with CH_4 at temperatures greater than 525 K. For example, using catalyst RM at 525 K and CO_2 + H_2 in the ratio 1 : 6 flowing at 110 ml ml^{-1} hr^{-1}, 0.2% of CO was found to be present in the effluent. However, catalyst deactivation began after 45 min of starting the gas flow. The rather low proportion of CO_2 was therefore used in present experiments to avoid catalyst fouling.

Arrhenius-type plots of log turnover number values (moles of CH_4 per second

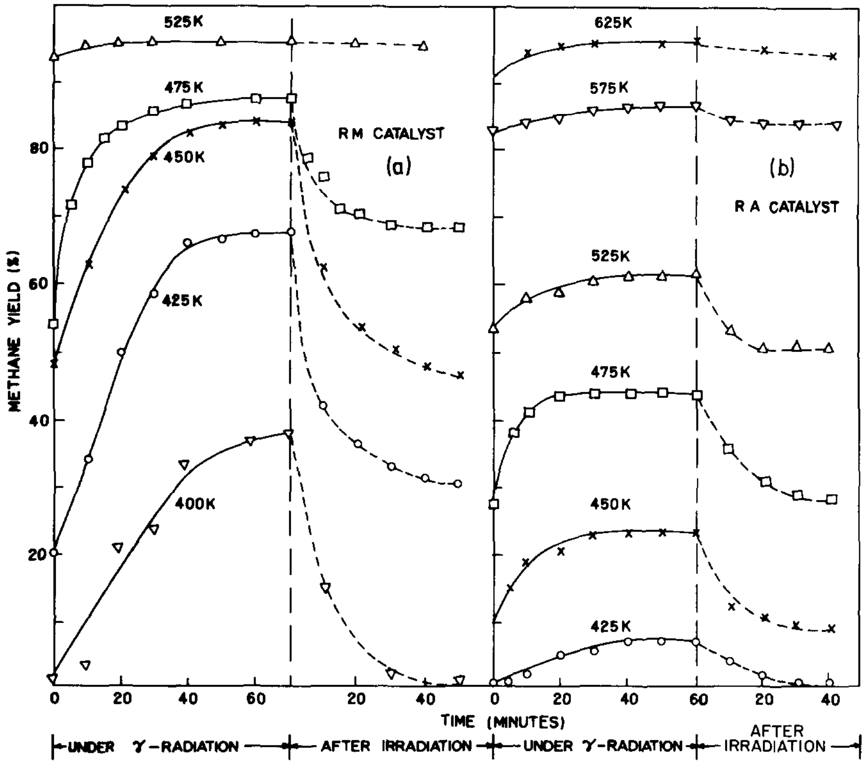

FIG. 2. Growth in methane yields from CO_2–H_2 reaction at different temperatures as a function of γ-dose and its decay with time subsequent to removal of the catalyst from the γ-source. (a) Ru/molecular sieve catalyst; (b) Ru/alumina catalyst. Vertical dashed lines indicate the time of cessation of irradiation.

per metal site) vs T^{-1} for RA gave activation energy (E) values of 13.8 and 7.7 (±0.5 kcal $mole^{-1}$) in the absence and in the presence of radiation, respectively. The corresponding values for catalyst RM were 7.3 and 4.2 kcal $mole^{-1}$. It is apparent that radiation lowers the activation energy for CO_2 methanation of both catalysts.

It may also be mentioned that while the semilog plots of CH_4 yields observed after cessation of radiation as a function of time gave straight lines for data under both the experimental conditions of Sections 3.1.a and 3.1.b, no such straight-line plots could be obtained for growth data. It thereby indicates that while the decrease in yield corresponds to a first-order relaxation process, the growth is probably a multistep process.

3.2. EFFECT OF γ-IRRADIATION ON PRECURSOR SPECIES

To evaluate the effect of γ-irradiation on intermediate steps involved in CH_4 formation, a CO_2 pulse and successive H_2 pulses were admitted into the He stream flowing through the catalyst and the effluents were analyzed at each stage (Section 2.4).

a. Chemisorption of CO_2 on the Catalyst Surface

When 40 μl CO_2 alone was injected, a fraction of the CO_2 was initially adsorbed and the rest was eluted immediately. The amount of immediately eluted CO_2 increased with increasing catalyst temperature. The CO_2 retained on the catalyst was found to be released slowly, the extent of release decreasing with time and temperature. In a typical case of catalyst RM, the slow desorption at 400 K continued for about 2 hr while at a temperature greater than 500 K the desorption was complete within 3 min (cf. Ref. (*9*)).

When the experiments were repeated with the catalyst under γ-irradiation, the initial-burst release of CO_2 was considerably enhanced. The amounts of CO_2 eluted immediately on injection of 40-μl CO_2 pulses over catalysts RM and RA in the presence and in the absence of radiation are given in Table 1 for different catalyst temperatures.

It may be noted that CO_2 is more strongly adsorbed on catalyst RA compared to catalyst RM. Also, at the temperatures where a significant radiation effect on the catalytic activity was observed, the effect on CO_2 desorption is also more pronounced.

b. Methane Formation

Following a CO_2 pulse injection, when 2 ml of H_2 was injected (referred to as first H_2 injection in the text) methane formation was observed on both catalysts, the actual methane yield being dependent on the catalyst temperature and the CO_2–first H_2 time gap. Following the first hydrogen injection, if additional H_2 pulse injections (at intervals of 2 min) were made, further methane formation was observed, the actual CH_4 yields being dependent again on the catalyst temperature and the CO_2–first H_2 time gap. When the catalysts were under γ-irradiation, fewer H_2 injections were required for complete conversion of precursor species to methane and the methane yields from successive H_2 injections were found to be enhanced or reduced depending on

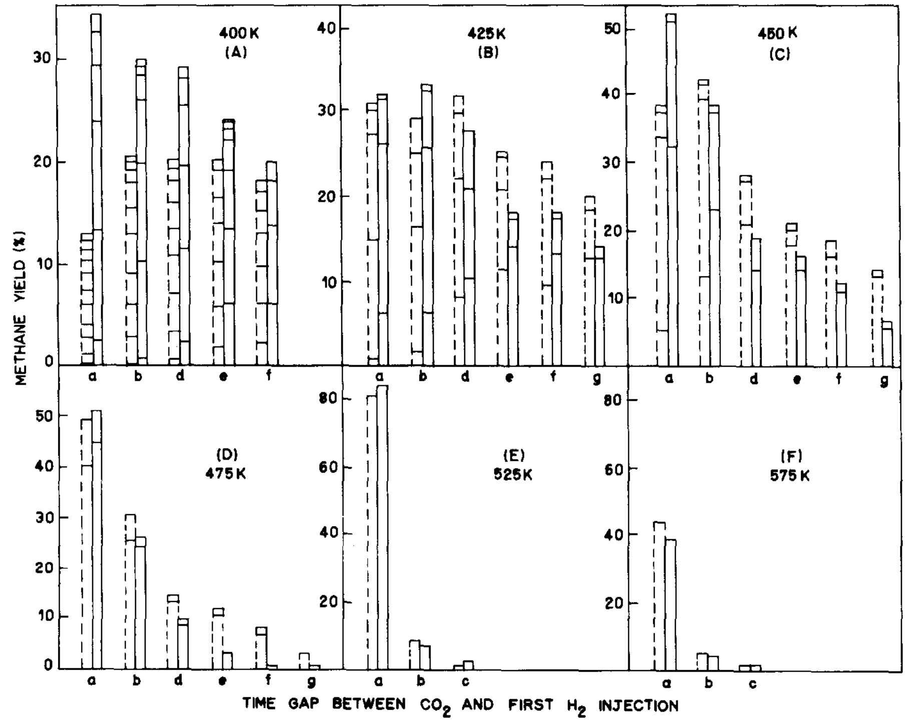

FIG. 3. Methane yields obtained at different temperatures with catalyst RM when a 40-μl CO_2 pulse was injected followed at different time intervals by successive 2-ml H_2 injections. (----) without irradiation; (——) under γ-irradiation. (a) to (g) refer to CO_2–first H_2 injection time gaps of 0 (simultaneous CO_2 and H_2), 10 sec, 40 sec, 1 min, 5 min, 10 min, and 25 min, respectively.

TABLE 1

Effect of γ-Irradiation on Adsorption of CO_2 on Catalysts RM and RA and on Support Materials[a]

Catalyst temperature (K)	Catalyst RM		Catalyst RA	
	No irradiation	Under γ-irradiation	No irradiation	Under γ-irradiation
400	0 (0)	5.7(18.0)	—	—
425	6.5(30.5)	12.0(35.4)	0	0
450	11.5(32.2)	17.8(37.3)	0	0
475	24.3(37.0)	30.5(39.0)	2.8(0)	5.3(13.5)
525	34.5(38.6)	35.5(39.5)	8.4(12)	16.2(19.0)
575	36.3(39.0)	35.6(39.5)	17.6(20.0)	21.0(23.0)
625	37.5(40.0)	37.0(40.0)	25.2(24.2)	30.8(34.0)

[a] Values are microliters (±1) of CO_2 eluted. Amount of CO_2 injected = 40 μ. The figures in parentheses refer to CO_2 eluted when metal-free support material was used.

the catalyst temperature and the CO_2–H_2 time gap. Typical methane yields thus observed from successive H_2 pulse injections for different CO_2–first H_2 time gaps ranging from zero time (simultaneous CO_2–H_2 injections) to as long as 25 min are shown in Figs. 3 and 4 for catalysts RM and RA, respectively. The bar graphs shown by dashed and solid lines in these figures are for catalysts in the absence and in the presence of γ-irradiation, respectively. The horizontal lines in each bar graph indicate methane yields obtained for each of the successive H_2 injections. Thus, the distance between the abscissa and the first line indicates the CH_4 yield on the first H_2 injection, the distance between the first and the second lines for the second H_2 injection, and so on.

It is significant to note that there is a marked correspondence between the adsorption characteristics of the catalysts (Table 1) and the methane yields given in Figs. 3 and 4. At low temperatures (e.g., 400 and 425 K for RM and 465 K for RA), where adsorption of CO_2 is more significant, a large number of H_2 injections are necessary for complete conversion of precursor species to methane and also γ-radiation-induced enhancement of methane yields is more prominent at these temperatures (Figs. 3, 4).

The effect of γ-irradiation on CH_4 yield obtained on the first H_2 injection (denoted as $CH_4(1)$) is another interesting aspect to be noted. In the typical case of catalyst RM, these values have been plotted in Fig. 5 for a comparative evaluation of the data. At 400 K $CH_4(1)$ yields are higher in the presence of γ-radiation compared to the nonirradiated catalyst for all CO_2–H_2 time gaps studied. At 425 K γ-ray-induced enhancement is observed up to a time gap of 6 min, whereas for longer time gaps $CH_4(1)$ yields in the presence of radiation are less than those for the nonirradiated catalyst. At 450 K the corresponding time gap was 30 sec and at temperatures greater than 450 K $CH_4(1)$ yields from catalysts under irradiation were normally smaller than those from the nonirradiated catalyst for all time gaps (Fig. 3).

3.3 EFFECT OF γ-IRRADIATION ON CHEMISORPTION AND REACTIVITY OF CO_2 ON SUPPORT MATERIALS

To evaluate the role of support materials in the radiation-induced enhancement of catalytic activity, experiments parallel to those mentioned in Sections 2.3 and 2.4 were carried out using metal-free 60- to 80-

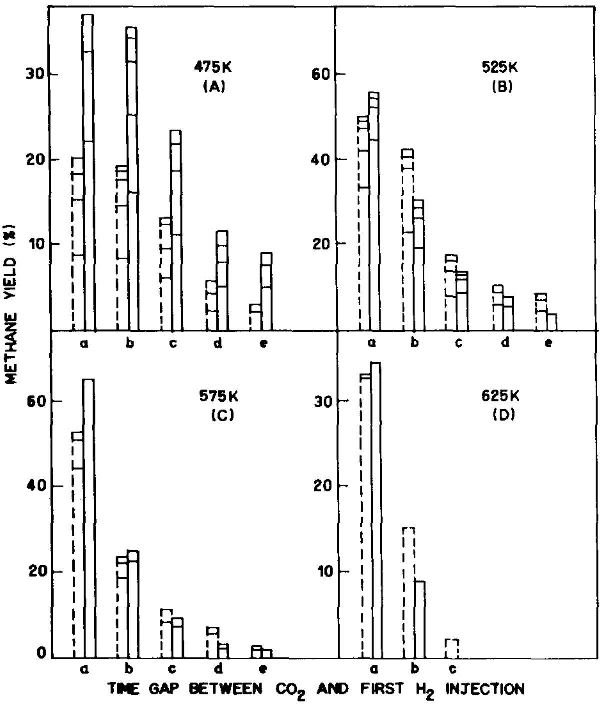

FIG. 4. Methane yields obtained at different temperatures with catalyst RA when a 40-μl CO_2 pulse was injected followed at different time gaps by successive 2-ml H_2 injections. (-----) without irradiation; (——) under γ-irradiation. (a) to (e) refer to CO_2–first H_2 time gaps of 0, 10 sec, 1 min, 5 min, and 10 min, respectively.

mesh γ-alumina and molecular sieve samples.

When pulses of 40 μl CO_2 were injected into the He carrier gas flowing (950 ml ml^{-1} hr^{-1}) over metal-free γ-alumina or molecular sieve, a fraction of the CO_2 was eluted immediately and the adsorbed CO_2 was subsequently released, the rate depending on temperature (cf. Section 3.2.a). However, H_2 injections following a CO_2 pulse did not give CH_4 at all catalyst temperatures studied and for different CO_2–H_2 time intervals ranging from 0 to 1 hr (cf. Section 3.2.b).

In the experiments carried out in the presence of γ-radiation the amount of initially released CO_2 increased progressively with the γ-dose and reached a saturation value after about 90 min of irradiation. No CH_4 was formed from H_2 injections following CO_2. The amounts of CO_2 immediately eluted in the absence of radiation and the saturation yields in the presence of radiation are shown in parentheses in Table 1. The results of this study are in disagreement with the work of Coekelbergs *et al.* (*11*) who observed higher adsorption of CO_2 on X-irradiated alumina in the temperature range 423–583 K.

Replacing He carrier gas with H_2 did not alter the data reported above except that at temperatures above 500 K a small amount of CO was observed in the effluent. In the presence of radiation, the yield of CO increased while that of CO_2 reduced. For example, in the case of molecular sieve at 600 K, the yields of CO and CO_2 were 0.6 and 38.0 μl in the absence of radiation and the corresponding figures in the presence of radiation were 2.1 and 35.0 μl, respectively.

3.4. TL STUDIES

γ-Irradiated molecular sieve and alumina

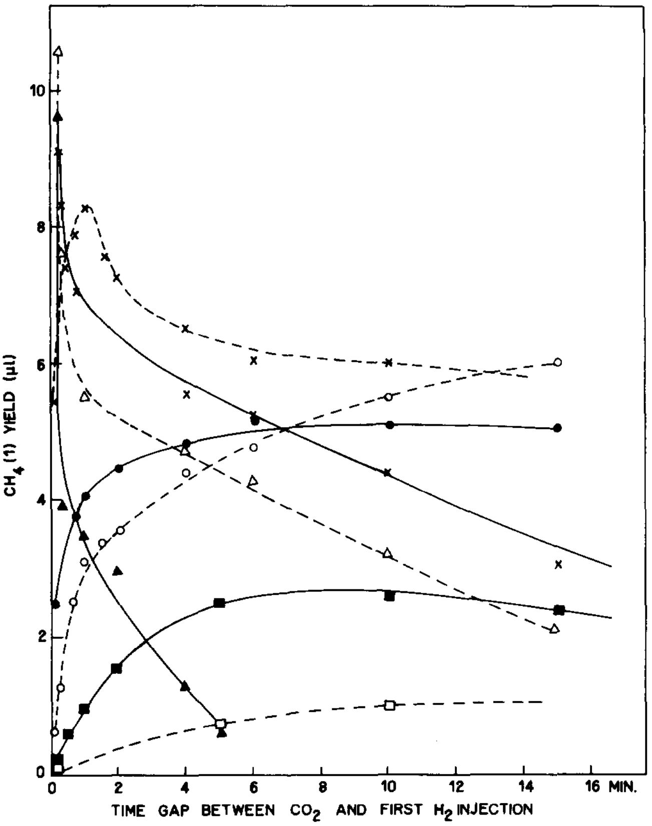

FIG. 5. Effect of γ-irradiation on CH_4 yield obtained on first H_2 injection (CH_4(1)) made at different time gaps subsequent to injection of a CO_2 pulse on catalyst RM surface.

	Without irradiation	Under γ-irradiation
400 K	--□--	—■—
425 K	--○--	—●—
450 K	--X--	—X—
475 K	--△--	—▲—

samples gave a thermoluminescence glow in the temperature range 300–500 K along with a non-radiation-induced peak at ~625 K. The 625 K peak and the TL of the molecular sieve sample have been discussed in detail in another article (*8*). The intensity of the radiation-induced glow peaks in molecular sieve (~410 K) and alumina (~400 and 500 K) increased with γ-dose and attained saturation values in 75 and 45 min, respectively. A typical example of γ-ray dose-dependent variation of the TL glow peak heights in the case of the alumina sample is shown in Fig. 6. For comparison purposes, a glow curve from the molecular sieve sample exposed to 0.8 Mrad γ-irradiation has been included in Fig. 6 (curve 7).

4. DISCUSSION

The catalytic methanation of CO_2 has been widely studied and reviewed (for recent reviews see (*12–16*)). In a recent communication from this laboratory (*9*), the mechanism of formation of methane from CO_2 over Ru/molecular sieve catalyst has been dealt with in some detail. In brief, the

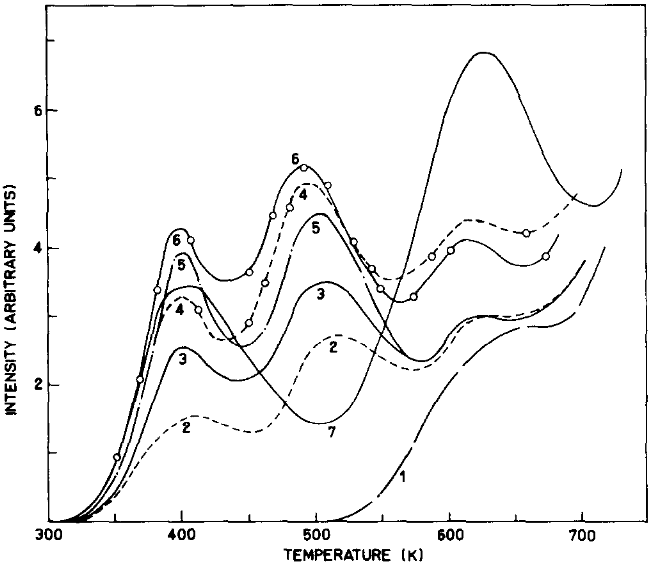

FIG. 6. Thermoluminescence glow curves from alumina (curves 1–6) and molecular sieve (curve 7) samples. Curve 1, nonirradiated; curves 2–7, γ-irradiated for 15, 30, 45, 60, 140, and 75 min, respectively, at a dose rate of 0.63 Mrad hr^{-1}.

suggested mechanism involves reduction of adsorbed CO_2 by H_2 to give CO. The CO thus formed disproportionates on the catalyst to give "active" carbon and CO_2 and the carbon subsequently reacts with H_2 to give CH_4. The experiments of Section 3.3 clearly reveal that although at high temperatures a small fraction of CO_2 may reduce to CO on support materials in the presence of H_2, the disproportionation/methanation of CO occurs at Ru sites alone. Our experiments do not reveal to what extent CO_2 is adsorbed on metal and/or on support. The fact that up to 100% methanation of CO_2 could be achieved with both RM and RA (Fig. 1) suggests that CO_2 is preferably adsorbed on the metal.

γ-Radiation may affect the CO_2–H_2 reaction in following possible ways:

(i) The ionization electrons or the thermally released trapped electrons (as discussed later) may interact with adsorbed CO_2 and cause radiolysis, leading to the formation of CO. Hydrogenation of CO thus produced may provide an alternative route to formation of CH_4.

(ii) Energy transfer to adsorbed CO_2 may enhance its rate of reaction with H_2.

(iii) γ-Radiation may affect the CH_4 desorption from the catalyst surface.

(iv) Radiation may affect the H_2 reactivity with CO or "active" carbon, both formed as intermediate species in CO_2 methanation.

γ-Radiolysis of free or adsorbed CO_2 resulting in the formation of CO has been reported by many workers (*17–20*). However, no CO formation was observed in our radiation experiments when metal-free support materials or Ru catalysts were exposed to CO_2 pulses in the absence of H_2. It may be mentioned that in most of the experiments reported in the literature (*17–20*) static reactors were employed and rather high γ-doses were necessary to obtain detectable amounts of radiolysis product CO. For example, in the experiments of Sutherland and co-workers (*17*), while no CO was observed in the radiolysis of CO_2 adsorbed on molecular sieves, a measurable quantity of CO was found in the radiolysis of CO_2 adsorbed on silica gel only at γ-doses higher than 20 Mrad. Since the γ-doses involved are much less in our experiments (<1 Mrad), a significant contribution from radiation-induced reduction of CO_2 to CO may be ruled out. Also, the gradual decrease in CH_4 yield on cessation of radiation (Fig. 2) clearly indicates that radiolysis of CO_2 plays no role in the observed enhancement of methane yields.

The data in Table 1 and in Figs. 1, 3, and 4 indicate that at temperatures at which γ-radiation caused a significant increase in the desorption of CO_2 i.e., weakened the metal–CO_2 bond, an enhancement of methanation efficiency was also observed. This is in agreement with the generally observed phenomenon that weakly bound molecules require less energy to participate in a reaction (*21, 22*).

It is pertinent to note that at lower temperatures (e.g., at 400 K for RM and 475 K for RA), although γ-irradiation results in faster desorption of CO_2 (Table 1) and the number of H_2 injections required to convert adsorbed CO_2 to CH_4 are less (Figs. 3, 4), the methane yields from successive H_2 injections were higher in the presence of radiation compared to nonirradiated catalysts. For example, in a typical case of catalyst RM at 400 K, while amounts of initially adsorbed CO_2 on the catalyst surface were about 40 and 34 μl for nonirradiated and irradiated catalysts, respectively (Table 1), the methane yields obtained from the first H_2 injection 10 min after injection of CO_2 were 0.9 and 2.6 μl and the methane yields from the second injection were 1.4 and 2.8 μl from nonirradiated and irradiated catalysts, respectively (Fig. 3). This therefore indicates that irradiation results in a higher reaction rate of CO_2 with H_2, giving rise to higher CH_4 yields. The data in Fig. 5 show that two competing processes, namely, the desorption rate of CO_2 and the reactivity of CO_2 toward H_2, are mainly responsible for the observed CH_4 yields. Depending on temperature and radiation the desorption rate and reactivity would be affected. At lower temperatures the radiation-enhanced reactivity of CO_2 toward H_2 seems to be responsible for the higher CH_4 yields; at higher temperatures and large CO_2–H_2 time intervals, the net amount of CO_2 remaining on the catalyst being small, the yields of CH_4 would necessarily be small and in the presence of radiation it will be still smaller, as has been observed (Figs. 3, 4).

The TL data (Fig. 6) show that γ-irradiation results in energy storage (as trapped electrons and holes) in molecular sieve and alumina and the energy is released on thermal stimulation. The electron–hole recombination energy may be dissipated either in the form of photons having a maximum energy equivalent to the band gap of the support material (~10 eV) or as enhanced lattice vibrations (phonons). In both these cases the energy transfer will occur to Ru atoms and/or to adsorbed CO_2, affecting primarily the vibrational modes in Ru–CO_2. However, the transfer of energy in the form of phonons would result in a significant enhancement in the methane yield only if it results in an increase in lattice temperature. In the experiments reported here, the catalyst temperature was maintained within ±0.5 K of the desired value and hence no bulk temperature rise is feasible.

The temperature ranges in which photon energy is released from the support materials as shown in the TL glow peaks (Fig. 6) correspond with the temperatures at which a significant enhancement in the methanation activity was observed from catalysts RM and RA (Fig. 1). Similarly, the time required for achieving saturation catalytic activity of RM and RA under irradiation and the growth behavior of catalytic activity at different temperatures have an apparent parallelism with the corresponding TL growth in support materials (Section 3.4) (for detailed discussion see (*8*)). It can therefore be suggested that thermally induced transport of radiation energy from the support material to the metal surface weakens the chemisorption of CO_2 and thereby results in an accelerated reaction rate of CO_2 with H_2, giving rise to higher yields of "active" carbon via CO. Coekelbergs *et al.* (*11*) similarly observed that X-irradiation enhanced CO oxidation on alumina by affecting O_2 chemisorption.

Experiments using pulse injections of CH_4 showed that methane was not adsorbed on the catalysts in the temperature range of our study.

There is as such no direct evidence to indicate whether the other two steps involved in the formation of CH_4, i.e., disproportionation of CO and hydrogenation of active carbon, are affected by γ-irradiation. However, the results of the CO methanation study (*8*) show that γ-radiation enhances the reactivity of "active" carbon toward H_2. It is therefore likely that a similar phenomenon may be operative in the CO_2–H_2 reaction in which "active" carbon is postulated as an intermediate.

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