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K.J. Zhen, M.M. Kahn, C.H. Mak, K.B. Lewis, and G.A. Somorjai

October 1984

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# PARTIAL OXIDATION OF METHANE WITH NITROUS OXIDE OVER $V_2O_5$-$SiO_2$ CATALYST

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## Abstract

The partial oxidation of methane to methanol and formaldehyde can be achieved selectively on silica-supported vanadium pentoxide catalysts in the 460-500°C temperature range in a reactant mixture of $CH_4$, $N_2O$ and $H_2O$ at 1 atm total pressure. The selectivity to $CH_3OH$ and HCHO can be 100 percent at 460°C at low conversions (~0.2%) and contact time (1.2 sec), and decreases to produce more CO with increasing temperature, contact time and conversion. The activation energies are 22 ± 2 kcal/mole, 40 ± 4 kcal/mole and 47 ± 4 kcal/mole for the production of HCHO, $CH_3OH$ and CO, respectively. The rate equations are Rate$(CH_3OH) \sim (CH_4)^{1/2}(N_2O)^{1/2}(H_2O)^{1/2}$, Rate $(HCHO) \sim (CH_4)^{1/2}(N_2O)^{1/3}$ and Rate $(CO) \sim (CH_4)^{1/2}\,(N_2O)(H_2O)^{-1}$. Oxygen does not react when it is added to the reaction mixture. The products form by parallel reaction paths which are different from the sequential oxidation mechanism of methane on molybdena and in a lower temperature range than on molybdenum oxide.

## Introduction

The partial catalytic oxidation of methane to methanol or to formaldehyde provides intriguing new opportunities for the production of liquid fuels and chemicals. Recent studies in our laboratory and elsewhere have shown that molybdenum oxide appears to be a suitable catalyst for these processes.[1-3] In the temperature range of 550-580°C and at 1 atm total reactant pressure methane can be oxidized selectively to $CH_3OH$ and HCHO in the presence of $N_2O$ and $H_2O$ at low conversions (1-2%) and at low contact times. The fraction of formaldehyde increases with increasing contact time and its activation energy of formation is identical to that of $CH_3OH$ at the higher temperatures. This indicates that formaldehyde is the product of a secondary reaction involving the further partial oxidation of methanol on the molybdena catalyst which is known to be an excellent catalyst for this reaction.

Our continued investigation uncovered that silica supported vanadium pentoxide is also a good catalyst for the partial oxidation of methane and the purpose of this paper is to report our findings. $V_2O_5$ produces methanol and formaldehyde selectively and at comparable conversions in the temperature range of 460-500°C. This is a significantly lower temperature range than that employed when using molybdenum oxide catalysts. The activation energies of HCHO and $CH_3OH$ formation are different, 22 ± 2 kcal/mole and 40 ± 4 kcal/mole respectively, indicating that their formation is by parallel reaction paths instead of the consecutive reaction sequence found on molybdena. The

rates of $CH_3OH$, HCHO and CO production are all ~1/2 order in methane partial pressure and they also depend significantly on the partial pressures of $N_2O$ and $H_2O$. The rate equations can be rationalized assuming the presence of a methoxy, $-OCH_3$, reaction intermediate that may hydrolyze to form methanol or may lose one or more hydrogen atoms to yield HCHO or CO. Carbon dioxide is not detectable during the reaction and oxygen does not react when present in the reaction mixture.

## Experimental

Materials: The catalyst, 2.0% $V_2O_5$-$SiO_2$, was prepared by impregnation from a basic solution of ammonium metavanadate at a pH of 10.5 and a subsequent drying followed by heating in air at 550°C. The support, Cab-O-Sil HS-5 fumed silica, had a reported surface area of 350 ± 25 $m^2g^{-1}$. The finished catalyst was pressed and sifted to 30-60 mesh particles. The final surface area, as determined by BET measurement, was found to be 230 ± 10 $m^2g^{-1}$. The active vanadium surface area was not determined, but it is well below the loading reported to be necessary for a monolayer coverage. The reactant gases, methane (99.9%), nitrous oxide (99.0%), oxygen (99.8%), and the carrier gas, helium (99.9%) were used as received.

Apparatus and Methods: The fixed bed reactor and the continuous flow manifold were the same as used in a study reported earlier.[1] Reactant and carrier gases from the manifold and water vapor from a steam boiler were adjusted to the desired composition and passed through the catalyst bed at a total flow rate of 80 $cm^3min^{-1}$. Typically, a molar composition of 0.15 $CH_4$, 0.30 $N_2O$, 0.40 $H_2O$ and 0.15 He at 1 atm total pressure was employed for most of the experiments. The entire reaction manifold was heated to 120°C to prevent condensation of water vapor. The analysis of the gas mixture before and after reaction was carried out gas chromatographically using a thermal conductivity and a flame ionization detector. The reaction temperature was controlled and monitored with a probe thermocouple embedded in the catalyst bed. The reaction was initiated by flowing 80 $cm^3min^{-1}$ of the

reaction mixture of a desired composition through the catalyst bed preset to the reaction temperature, usually between 460 and 500°C. One to two hours was allowed for the system to reach a steady state and be ready for sample analysis.

Analytical Procedure: An in-line gas chromatograph, equipped with a ten-port sampling valve, a flame ionization (FI) detector, a thermal conductivity (TC) detector, and two analytical columns was used for alternate injections into the two columns, one leading to the TC detector and the other to the FI detector. The pre- and post-reaction samplings were made possible by incorporating a six-port switching valve into the reaction manifold. Separation and detection of ($N_2$+$O_2$), CO, $CO_2$, $CH_4$, $N_2O$ and $H_2O$ were accomplished with a Carbosieve S-II (Supelco) column and a TC detector. For $CH_3OH$, HCHO, $CH_4$ and higher hydrocarbons, a Porapak-QS column and a flame ionization detector at a sensitivity of 12 pAFS were used. For quantitative analysis the measured peak areas were corrected for the molar response factors of the various components as reported by Dietz.[4]

The products, HCHO and $CH_3OH$, were collected by stripping the exit gas stream in a cold trap maintained at -5°C. Since there was a considerable amount of steam in the reaction mixture, the condensate was trapped in the form of an aqueous solution of a mixture of HCHO and $CH_3OH$ with better than 99% efficiency. The analysis of the condensate was carried out gas chromatographically as described in a previous paper[1] and the rates of formation of $CH_3OH$ and HCHO were calculated on the basis of the weight of the condensate collected over a timed

interval. The rate of formation of CO was calculated as the product of the flux and the mole fraction of CO as determined by the GC analysis of the exit gas stream.

The reported rate data are based on the assumption of a 100% dispersion of vanadium over the support, since at a 2% loading, vanadium is known to have submonolayer coverage over a support of similar surface area.[5]

## Results

Yield and Product Distribution: Figure 1 summarizes the effects of temperature and contact time on the overall conversion of methane and the relative product distribution of $CH_3OH$, HCHO and CO expressed as a mole percent of the total. At a contact time of 1.2 sec, the overall conversion varied from 0.2% at 460°C to 0.8% at 500°C. Both $CH_3OH$ and HCHO selectivities dropped and CO selectivity increased with the increase in temperature. For example, at 460°C $CH_3OH$ and HCHO formed with selectivities of 38% and 62% respectively. These decreased to 16 and 36% respectively at 500°C, while the CO selectivity increased from zero to 48% over the same temperature range. No $CO_2$ formation was observed at a contact time of 1.2 sec over this temperature range. Increased contact time had a more adverse effect on the product selectivities towards $CH_3OH$ and HCHO. Higher temperature and contact time resulted in the formation of increased amounts of CO and $CO_2$ at the expense of $CH_3OH$ and HCHO. As shown in the hatched bar graphs in Fig. 1, the formation of $CH_3OH$ and HCHO were marked with substantially lower selectivities of 12 and 29% respectively at 460°C when the contact time was increased to 4.6 sec. At higher temperatures, especially in the range of 480-500°C, CO was the major product, with an 80% selectivity. Moreover, this increase in contact time to 4.6 sec even led to the formation of a small amount of $CO_2$, a product which was not detected under the flow conditions of a 1.2 sec contact time. It is also to be noted from Fig. 1 that the overall conversion of $CH_4$ more than doubled with the increase in contact time from 1.2 sec to 4.6 sec.

At 460°C, for example, the conversion increased from 0.2 to 0.8% with this increase in contact time but the selectivity of $CH_3OH$ and HCHO dropped from 38 and 62% to 12 and 29% respectively with the increase in selectivity of CO from 0 to 59%.

Temperatures below 460°C were too low for the detection of $CH_3OH$ and HCHO with any reliability. Above 500°C CO and $CO_2$ were the predominant products and therefore this temperature region was not investigated.

Reaction Rates and Kinetic Parameters: The turnover rates of $CH_3OH$, HCHO and CO observed over the temperature range of 460°C to 500°C and contact times of 1.2 sec and 4.6 sec are presented in Table I. At a contact time of 1.2 sec and an 80 $cm^3min^{-1}$ flow of 0.15 $CH_4$ + 0.30 $N_2O$ + 0.40 $H_2O$ + 0.13 He + 0.02 $O_2$ through the catalyst bed at 490°C, $CH_3OH$, HCHO and CO were formed at turnover rates of $1 \times 10^{-4}$, $1.2 \times 10^{-4}$ and $1.1 \times 10^{-4}$ molec.$s^{-1}$.$atom^{-1}$ respectively, with an overall yield of 0.6%. However, at a higher contact time of 4.6 sec the net rates of formation of $CH_3OH$ and HCHO dropped to $0.08 \times 10^{-4}$ and $0.18 \times 10^{-4}$ respectively, whereas, that of CO increased to $1.2 \times 10^{-4}$ with an overall yield of 1.8% at the same conditions of reactant composition and temperature. This increased rate of CO formation with concomitant decreases in $CH_3OH$ and HCHO formations as a function of increased contact time was reflected in the product distribution data discussed in the previous section.

As shown in Fig. 2, the temperature dependence of the rates of formation of $CH_3OH$, HCHO and CO were found to give an Arrhenius fit

within the limits of experimental uncertainty over the entire temperature range of 460-500°C. The activation energies were 22 ± 2, 40 ± 4 and 47 ± 4 kcal/mole for the formation of HCHO, $CH_3OH$ and CO respectively. Due to the scatter in the data, the latter two values are probably not significantly distinct.

The kinetic order determination, carried out at 500°C, revealed the following rate laws.

$$\text{Rate } (CH_3OH) \propto [CH_4]^{1/2} [N_2O]^{1/2} [H_2O]^{1/2}$$

$$\text{Rate } (HCHO) \propto [CH_4]^{1/2} [N_2O]^{1/3}$$

$$\text{Rate } (CO) \propto [CH_4]^{1/2} [N_2O]^{1} [H_2O]^{-1}$$

The logarithmic plots of the various rates vs. the mole fraction of the reactant of interest were obtained as shown in Figures 3 through 6, with the relevant composition data specified therein.

The order with respect to $CH_4$ was one-half for the rates of formation of all three products over a $CH_4$ mole fraction range of 3 to 14. At lower concentrations the rate was too low to be measured accurately and at higher concentration deactivation due to excessive coking was observed. For $N_2O$ pressure dependence a $N_2O$ mole fraction range of 4 to 25 was found suitable for the measurement. $CH_3OH$, HCHO and CO formed with respectively one-half, one-third and first order kinetics with respect to $N_2O$. The steam pressure dependence was respectively one-half, zero, and negative first. For the measurement of kinetic order with respect to $H_2O$, a much lower concentration of methane of 4% instead of the usual 13-14% was necessary to prevent cracking of $CH_4$ at the lower range of steam pressure. The purpose

of including a small quantity of oxygen in the kinetic measurements was to investigate its possible role in reoxidizing the surface and thus confining the use of $N_2O$ solely to the oxidation of methane. All three rates, as shown in Figure 6, had slightly negative dependence (0.1 to 0.2) on the oxygen partial pressure.

## Discussion

Conversion and Product Selectivity: It is worthwhile to draw a comparison between this and the previously reported works on $MoO_x$-$SiO_2$ catalysts.[1-3] Firstly, the working range for vanadium pentoxide (450-500°C) is comparatively lower and narrower than observed in the case of $MoO_x$-$SiO_2$ catalyst, which was 480-590° under similar conditions at reactant composition and contact time. Compared to $MoO_x$-$SiO_2$, $V_2O_5$-$SiO_2$ catalyst was found to be more active for $CH_3OH$ formation at the overlapping temperatures of the above two ranges. For instance at 490°C, the turnover rate for $CH_3OH$ formation on $MoO_3$-$SiO_2$, $0.50 \times 10^{-4}$ molec.site$^{-1}$.s$^{-1}$, was substantially lower than was observed on $V_2O_5$-$SiO_2$, which was $0.97 \times 10^{-4}$ molec.site$^{-1}$.s$^{-1}$. The total conversion was also more favorable on $V_2O_5$-$SiO_2$, 0.10% at 2.3 sec contact time on $MoO_3$-$SiO_2$ as compared with 0.6% at 1.2 sec contact time on $V_2O_5$-$SiO_2$. It appears that $V_2O_5$-$SiO_2$ is a considerably stronger oxidizing catalyst than $MoO_3$-$SiO_2$, which, has the favorable consequence of lower operating temperature. However, $V_2O_5$-$SiO_2$ has an unfavorable product selectivity towards $CH_3OH$.

Kinetics and Mechanisms: A comparison of the rate laws of various product formations and activation energies is provided in Table II. In our previous report on $MoO_3$-$SiO_2$,[1] the two $E_a$ values for HCHO were ascribed to two different mechanisms, a low temperature path leading to the HCHO formation simultaneously with $CH_3OH$ from the same intermediate with an activation energy of 82 ± 2 kcal/mole, and a lower activation energy high temperature process involving further oxidation

of $CH_3OH$. For the methane oxidation on $V_2O_5$-$SiO_2$, however, the mechanism seems to be entirely different. Even though the $E_a$ for $CH_3OH$ formation is very similar (40 kcal/mole) to that on $MoO_3$, the activation energy for HCHO is substantially lower. Furthermore, there is no evidence for any consecutive oxidation of $CH_3OH$ leading to HCHO or CO. It appears that all of the products, $CH_3OH$, HCHO and CO form by parallel reaction paths on the $V_2O_5$-$SiO_2$ catalysts.

Speculation on the Reaction Mechanisms: The chemisorption of methane which occurs with a very low reaction probability produces a methoxy group, $CH_3O$- and a hydroxyl group. Hydrolysis of the methoxy group by water yields methanol and another hydroxyl group on the vanadium oxide surface. However, $CH_3O$ can also undergo sequential loss of hydrogen atoms to produce HCHO and CO molecules which then desorb. Dehydroxylation of the oxide surface can occur by oxidative elimination with the help of dissociatively chemisorbed $N_2O$. While the inertness of molecular oxygen in this reaction is somewhat puzzling, it may be related to its weak interaction with the oxide surface as compared to $N_2O$. The reaction is also likely to be structure sensitive as there are several different oxygen sites on the different vanadium oxide crystal surfaces. These are likely to show different activity toward the production of $CH_3O$- groups. It is possible that twin vanadium-oxygen units are required for the dissociative chemisorption of methane which would make this reaction even more structure sensitive.

Since the formation of $CH_3OH$, HCHO and CO proceeds by parallel reactions it appears possible to block some of the reaction paths by suitable additives thereby increasing the selectivity.

In addition, the selectivity and reaction yield could be further enhanced by increasing the total pressure of the reactants. In this study the total pressure was constant at 1 atm. Further studies are planned to investigate the effect of increased total pressure.

Acknowledgement

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Table I. Conversion and turnover rates at various temperatures and contact times. Reactant composition: 0.15 $CH_4$ + 0.30 $N_2O$ + 0.40 $H_2O$ + 0.13 He + 0.02 $O_2$. Total flow: 80 $cm^3 min^{-1}$.

| Temp °C | Contact time sec | Turnover Rate x $10^4$ molec.$s^{-1}$.$atom^{-1}$ $CH_3OH$ | HCHO | CO | Total Conv. Percent |
|---|---|---|---|---|---|
| 460 | 1.2 | 0.38 | 0.63 | 0 | 0.2 |
| | 4.6 | 0.12 | 0.228 | 0.38 | 0.8 |
| 470 | 1.2 | 0.46 | 0.88 | 0.44 | 0.4 |
| | 4.6 | 0.084 | 0.144 | 0.66 | 1.0 |
| 480 | 1.2 | 0.81 | 1.0 | 0.56 | 0.5 |
| | 4.6 | 0.079 | 0.144 | 0.86 | 1.3 |
| 490 | 1.2 | 0.97 | 1.2 | 1.1 | 0.6 |
| | 4.6 | 0.078 | 0.178 | 1.23 | 1.8 |
| 500 | 1.2 | 0.21 | 1.5 | 1.40 | 0.8 |
| | 4.6 | 0.081 | 0.21 | 1.34 | 2.1 |

Table II. Rate laws and activation energies.

| Product | Rate Law | $E_a$ kcal/mole |
|---|---|---|
| | $V_2O_5$–$SiO_2$ Catalyst | |
| $CH_3OH$ | $[CH_4]^{1/2}\ [H_2O]^{1/2}\ [N_2O]^{1/2}$ | 40 ± 4 |
| HCHO | $[CH_4]^{1/2}\ [H_2O]^{0}\ [N_2O]^{1/3}$ | 22 ± 2 |
| CO | $[CH_4]^{1/2}\ [H_2O]^{-1}\ [N_2O]^{1}$ | 47 ± 4 |
| | $MoO_3$–$SiO_2$ Catalyst* | |
| $CH_3OH$ | $[CH_4]^{1}[H_2O]^{1}[N_2O]^{0}$ | 41 ± 2 |
| HCHO | $[CH_4]^{0}\ [H_2O]^{0}\ [N_2O]^{0}$ | 82 ±2 (low temp), 40 ±2 (high temp) |
| CO | not available | not available |

*Khan and Somorjai (Ref. 1).

Figure Captions

Figure 1. Effects of temperature and contact time on conversion and product distribution. Solid bars: 1.2 sec contact time; hatched bars: 4.6 sec contact time. Composition (mole percent): $CH_4$ 15, $N_2O$ 30, $H_2O$ 40, He 13 and $O_2$ 2.

Figure 2. Arrhenius plots for formation of $CH_3OH$, HCHO and CO. Reactant gas: 80 $cm^3min^{-1}$ flow of 0.15 $CH_4$ + 0.30 $N_2O$ + 0.40 $H_2O$ + 0.15 He, contact time of 1.2 sec.

Figure 3. $CH_4$ pressure dependence of turnover rates at 500°C. Composition (mole percent): $CH_4$ 2.8 to 14; $N_2O$ 22, $H_2O$ 40, $O_2$ 1.6, and balance He.

Figure 4. $N_2O$ pressure dependence of turnover rates at 500°C. Composition (mole percent): $N_2O$ 4 to 25, $CH_4$ 14, $H_2O$ 40, $O_2$ 1.6, and balance He.

Figure 5. $H_2O$ pressure dependence of turnover rates at 500°C. Composition (mole percent): $H_2O$ 14 to 31, $CH_4$ 4, $N_2O$ 28, $O_2$ 1.6 and balance He.

Figure 6. $O_2$ pressure dependence of turnover rates at 500°C. Composition (mole percent): $O_2$ 2 to 11, $CH_4$ 13, $N_2O$ 10, $H_2O$ 37, and balance He.

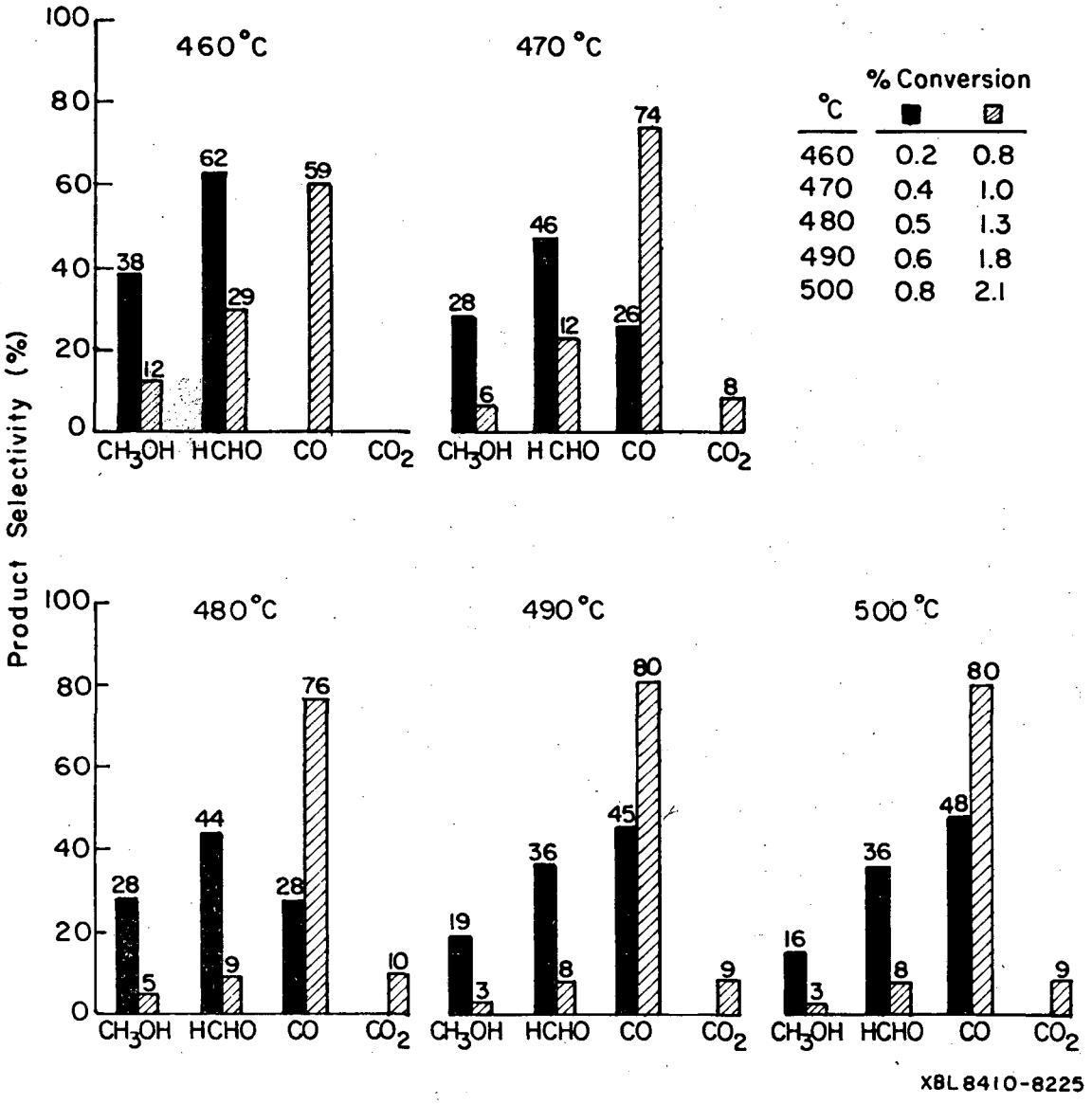
460 °C
470 °C
480 °C
490 °C
500 °C
Product Selectivity (%)
100
80
60
40
20
0
38
12
62
29
59
28
6
46
12
74
26
8
28
5
44
9
76
28
10
19
3
36
8
80
45
9
16
3
36
8
80
48
9
CH3OH
HCHO
CO
CO2
% Conversion
°C
460 0.2 0.8
470 0.4 1.0
480 0.5 1.3
490 0.6 1.8
500 0.8 2.1
XBL 8410-8225

Fig. 1

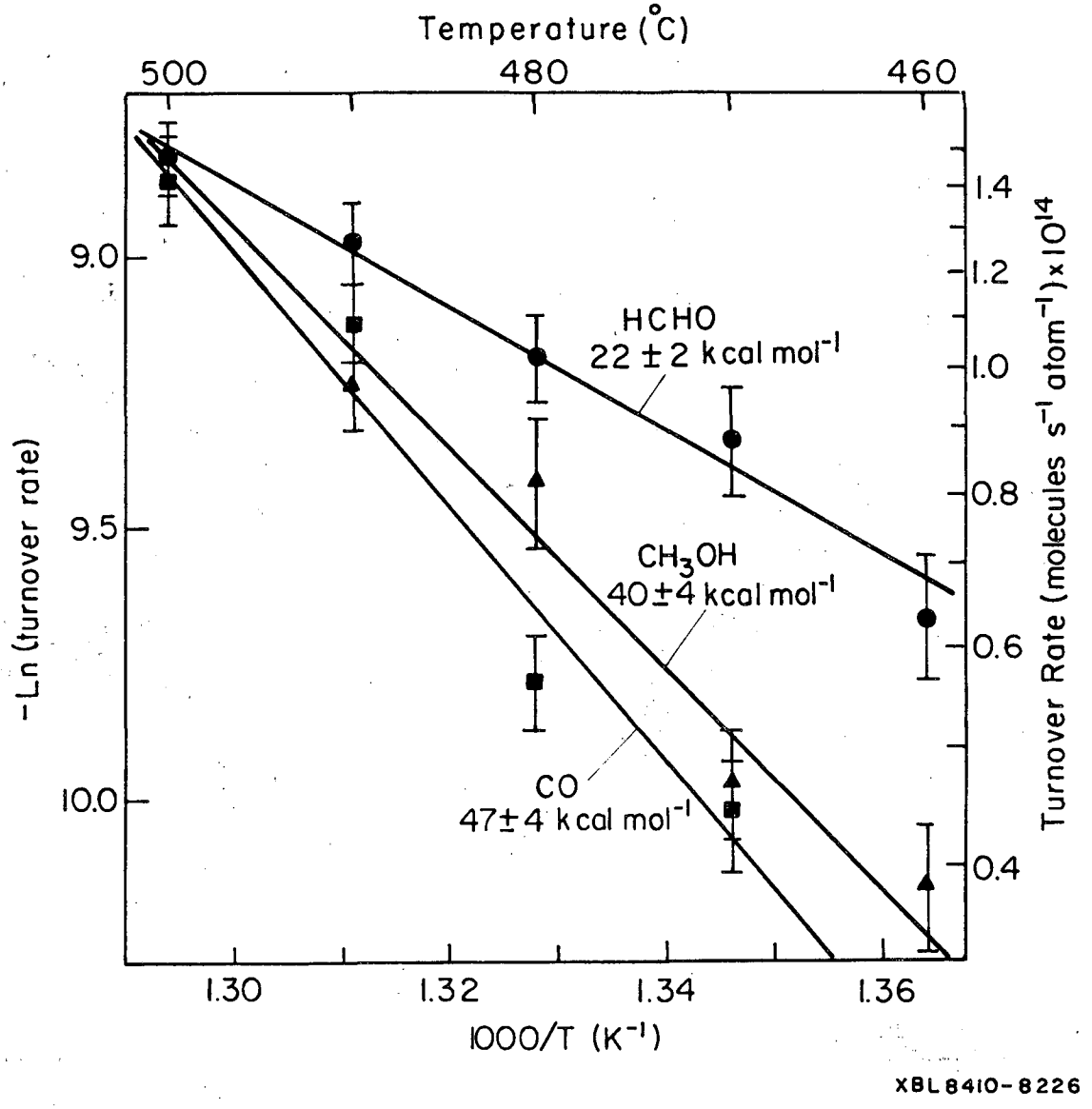
Temperature (°C)
500
480
460
9.0
9.5
10.0
-Ln (turnover rate)
1.4
1.2
1.0
0.8
0.6
0.4
Turnover Rate (molecules s⁻¹ atom⁻¹) x 10¹⁴
HCHO
22 ± 2 kcal mol⁻¹
CH₃OH
40±4 kcal mol⁻¹
CO
47±4 kcal mol⁻¹
1.30
1.32
1.34
1.36
1000/T (K⁻¹)
XBL8410-8226

Fig. 2

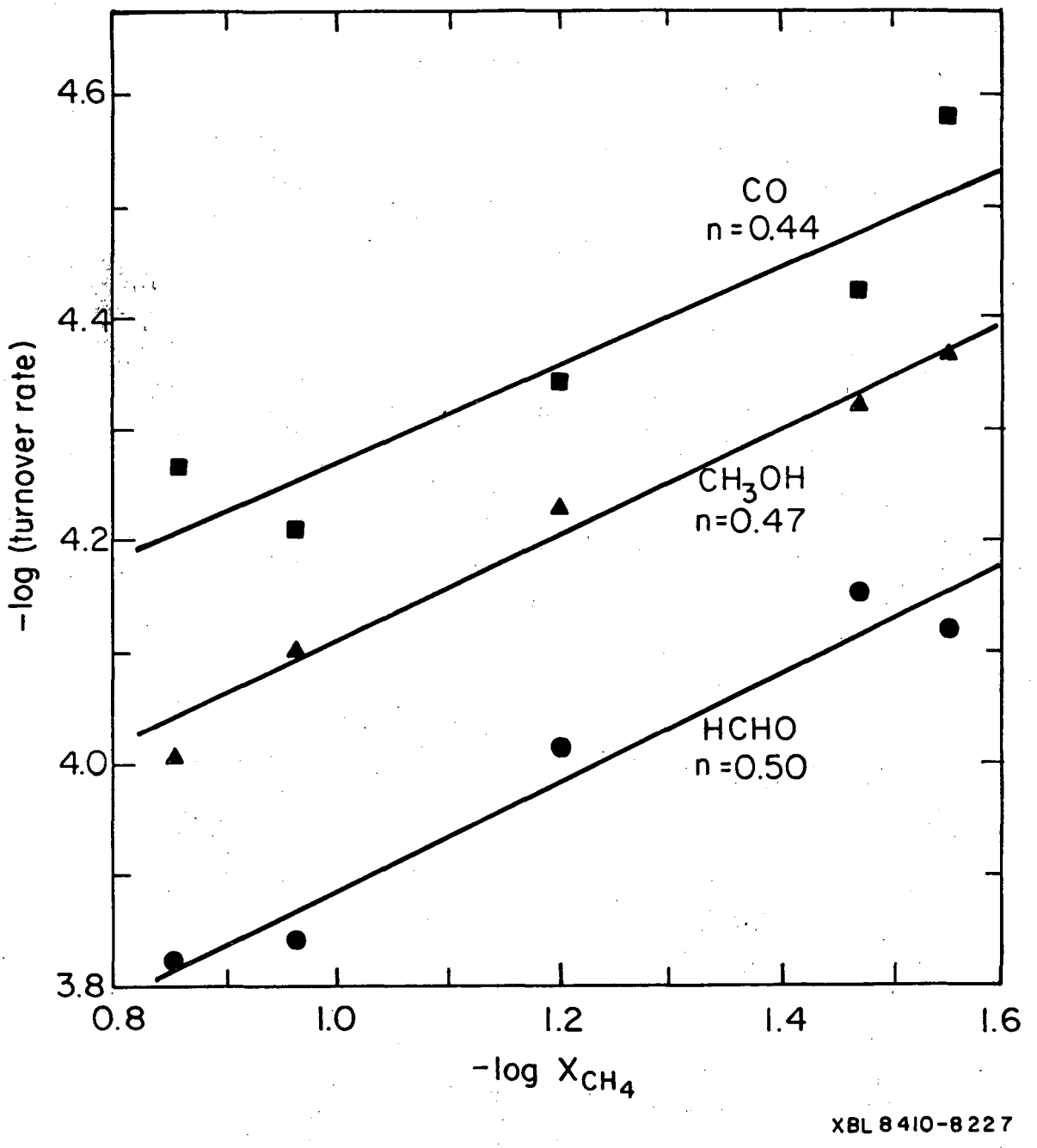
4.6
4.4
4.2
4.0
3.8
0.8
1.0
1.2
1.4
1.6
-log (turnover rate)
-log $X_{CH_4}$
CO
n = 0.44
$CH_3OH$
n=0.47
HCHO
n =0.50
XBL 8410-8227

Fig. 3

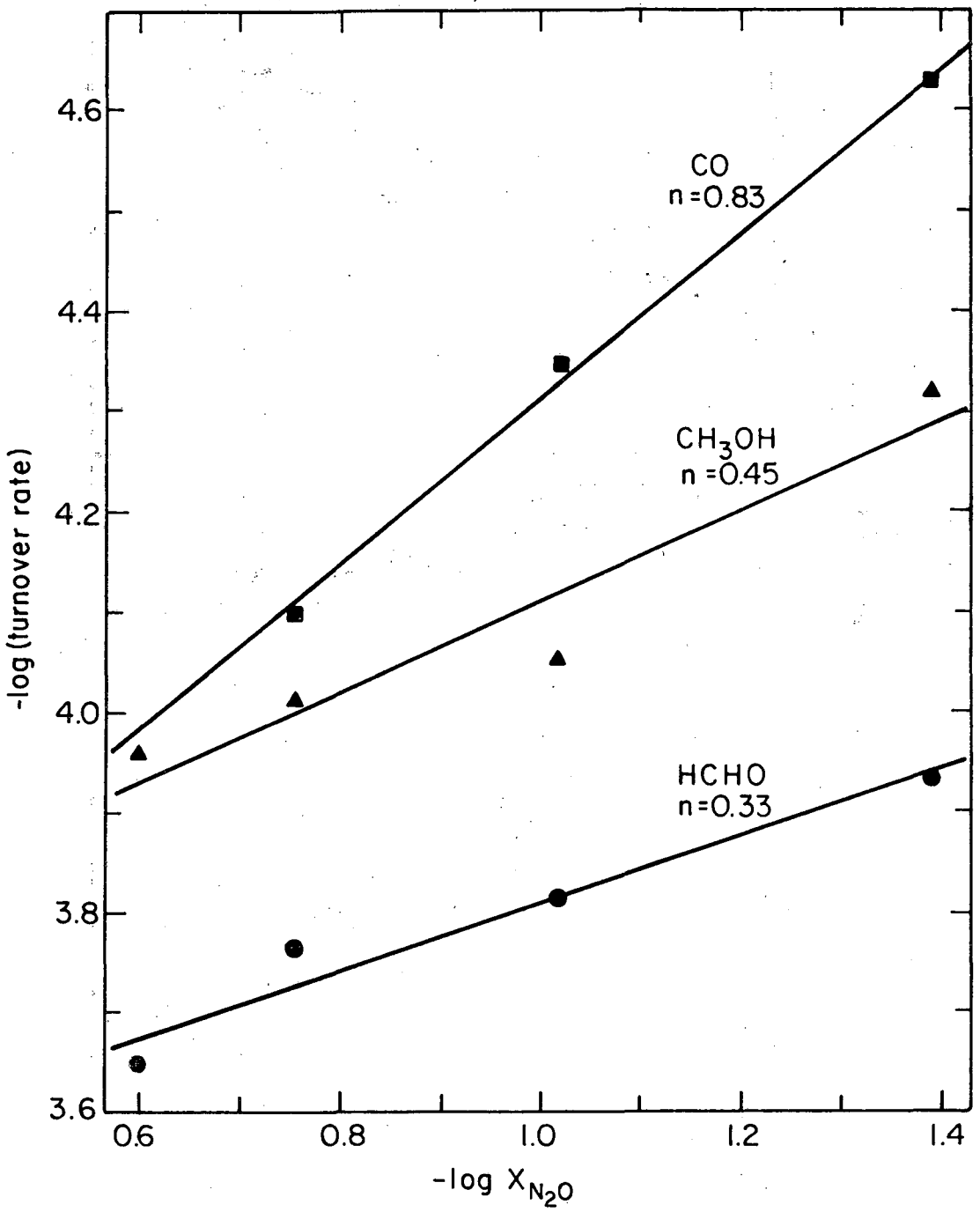
4.6
4.4
4.2
4.0
3.8
3.6
-log (turnover rate)
CO
n=0.83
CH3OH
n=0.45
HCHO
n=0.33
0.6
0.8
1.0
1.2
1.4
-log XN2O
XBL 8410-8228

Fig. 4

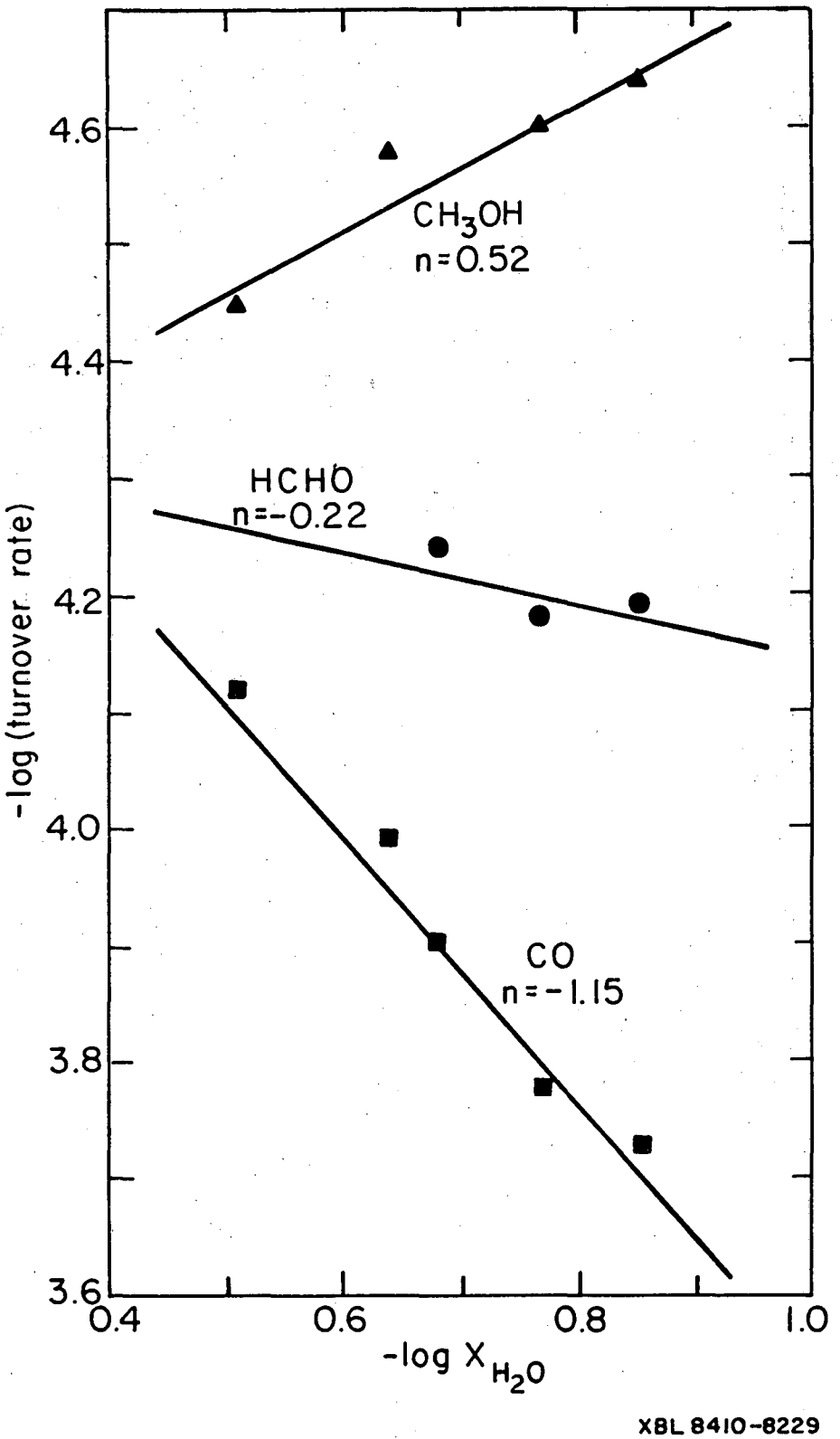
4.6
4.4
4.2
4.0
3.8
3.6
0.4
0.6
0.8
1.0
-log (turnover rate)
-log $X_{H_2O}$
$CH_3OH$
n=0.52
HCHO
n=-0.22
CO
n=-1.15
XBL 8410-8229

Fig. 5

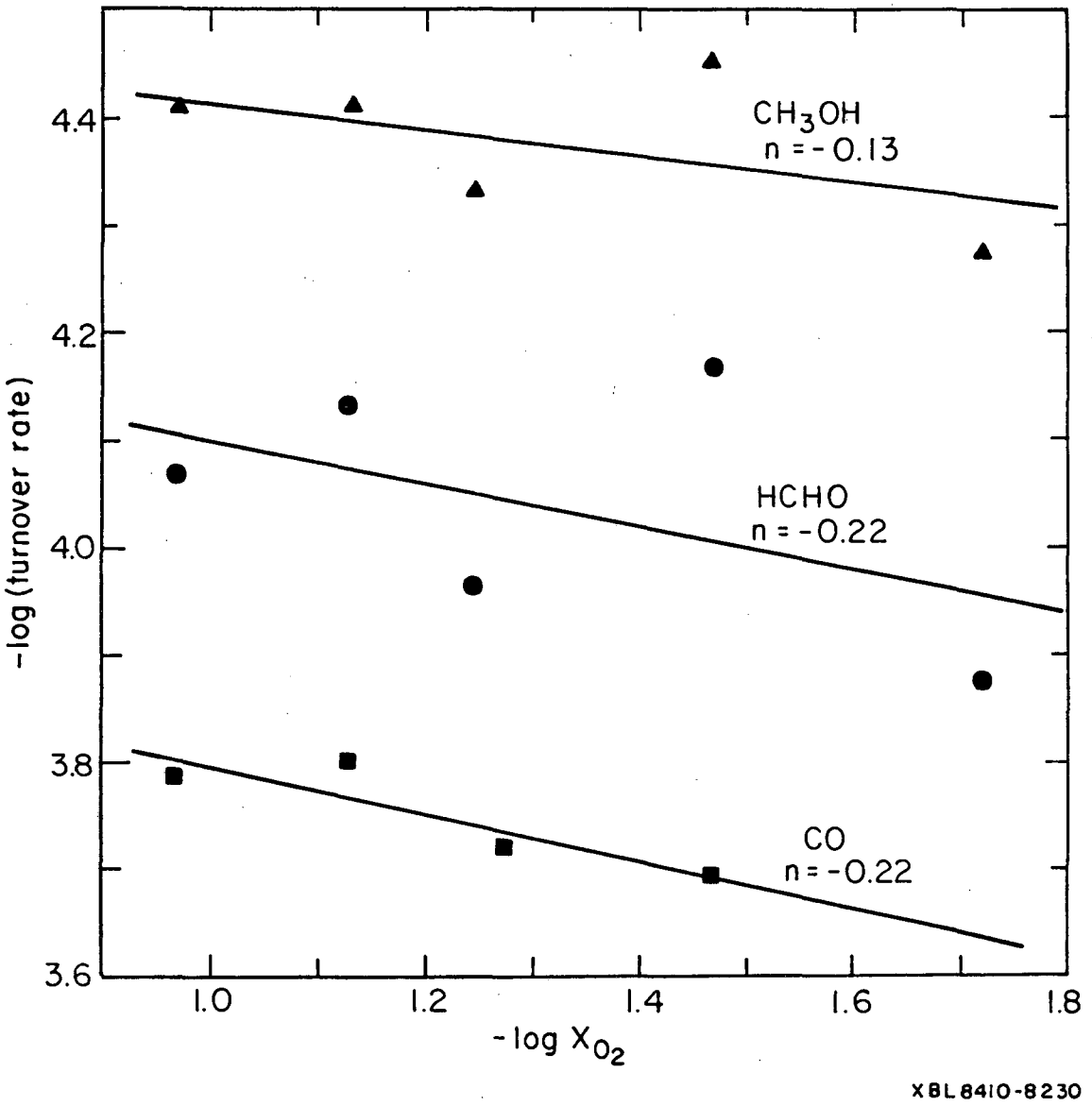
4.4
4.2
4.0
3.8
3.6
-log (turnover rate)
CH3OH
n = -0.13
HCHO
n = -0.22
CO
n = -0.22
1.0
1.2
1.4
1.6
1.8
- log X02
XBL8410-8230

Fig. 6

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