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The Effects of Neutron Irradiation on Methanol Oxidation Catalysts

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The oxidation of methanol to formaldehyde was studied over a temperature range of 209° to 270°C in a differential flow gas-phase reactor using catalysts that had been irradiated with neutron doses up to 10^{20} neutrons/cm^2. Attempts were made to correlate the altered catalytic activity to defects produced by radiation damage and to a quantity of foreign atoms introduced throughout the catalyst by nuclear transmutations. The catalysts investigated were pure vanadium pentoxide, vanadium pentoxide mixed with 1% chromium oxide, and a mixed tungsten oxide–molybdenum oxide. The gaseous reactant stream consisted of 20% oxygen, 0.75% to 6% methanol, and the remainder, nitrogen.

The doped vanadium pentoxide (1% chromium) catalyst was found to be 30% to 50% more active than pure vanadium pentoxide with or without irradiation. The tungsten-molybdenum mixed oxide catalyst was 25% more active for methanol oxidation after irradiation and was 6% to 10% more active even after high-temperature annealing. By calculation from nuclear constants it was determined that 0–0.03% chromium and 0–0.06% rhenium were introduced by nuclear transmutation in the vanadium oxide and tungsten-molybdenum oxide catalysts, respectively. No significant differences in reaction mechanism or energy of activation were observed between the unirradiated and irradiated catalysts.

INTRODUCTION

The effects of various types of irradiation on solids have been studied extensively during the last 15 years and changes in electrical resistivity (*1*), optical properties (*2*), bulk growth (*2, 3*), and thermal and mechanical properties have been attributed to irradiation damage.

The effects of irradiation on solid catalysts have also been investigated: gamma radiation has been used extensively (*4–10*) owing to the ready availability of intense sources and because, unlike particle irradiation, it does not produce radioactive catalyst that could constitute a potential health hazard; neutrons have also been used to irradiate catalysts (*11–17*). Neutrons have two advantages for catalyst modification over gamma rays: impurity atoms formed by neutron-induced nuclear transmutations can be introduced uniformly throughout solid catalyst, and defect structures can be readily produced, both of which phenomena can markedly affect the catalytic activity. Previous studies revealed that the nature and extent of irradiation effects are unique to a particular catalyst, its previous history, and the type of catalytic reaction.

Electronic theories of catalysis (*18, 19*) postulate that irradiated solid catalysts should exhibit different catalytic activity because the products of irradiation include trapped electrons, positive holes, displaced atoms, and possibly, transmuted atoms—all of which affect the electron structure of the solid, hence its ability to interchange electrons with adsorbed molecules. Likewise, both Bragg (*14*) and Donato (*16, 17*) suggested that, in addition to the catalytic effects caused by crystal changes, trapped charges and lattice changes formed by particle irradiation, foreign atoms introduced by thermal-neutron-induced transmutations could affect catalytic activity. Such impurities could feasibly be produced in concentrations up to 0.1% and catalysts with similar small quantities of impurities added by other means were found (*20*) to have changed in their catalytic properties as a result of the impurity addition. In order to study this effect it was considered desirable to choose a semiconductor oxide catalyst that had a large thermal neutron absorption cross section constant and, one that would not be so radioactive after irradiation as to constitute a handling problem and a potential health hazard. Therefore the oxidation reaction of methanol to formaldehyde was chosen, based on previous work (*21*, *22*, *23*), and the two catalysts vanadium pentoxide and tungsten-molybdenum oxides were selected from the wide variety of methanol oxidation catalysts because of the favorable nuclear properties of vanadium and tungsten.

EXPERIMENTAL

Apparatus and Procedure

The apparatus used for the catalytic oxidation of methanol in the gas phase is shown schematically in Fig. 1. Oxygen and nitrogen were admitted from high-pressure cylinders into the apparatus. The gases were passed through a purification train of Ascarite and calcium chloride to remove any carbon dioxide and water impurities. The gases were then premixed in desired ratios and a suitable portion bubbled through a methanol carburetor immersed in a constant-temperature bath. The effluent stream was passed through a sodium sulfite trap which retained formaldehyde. Formaldehyde production was determined

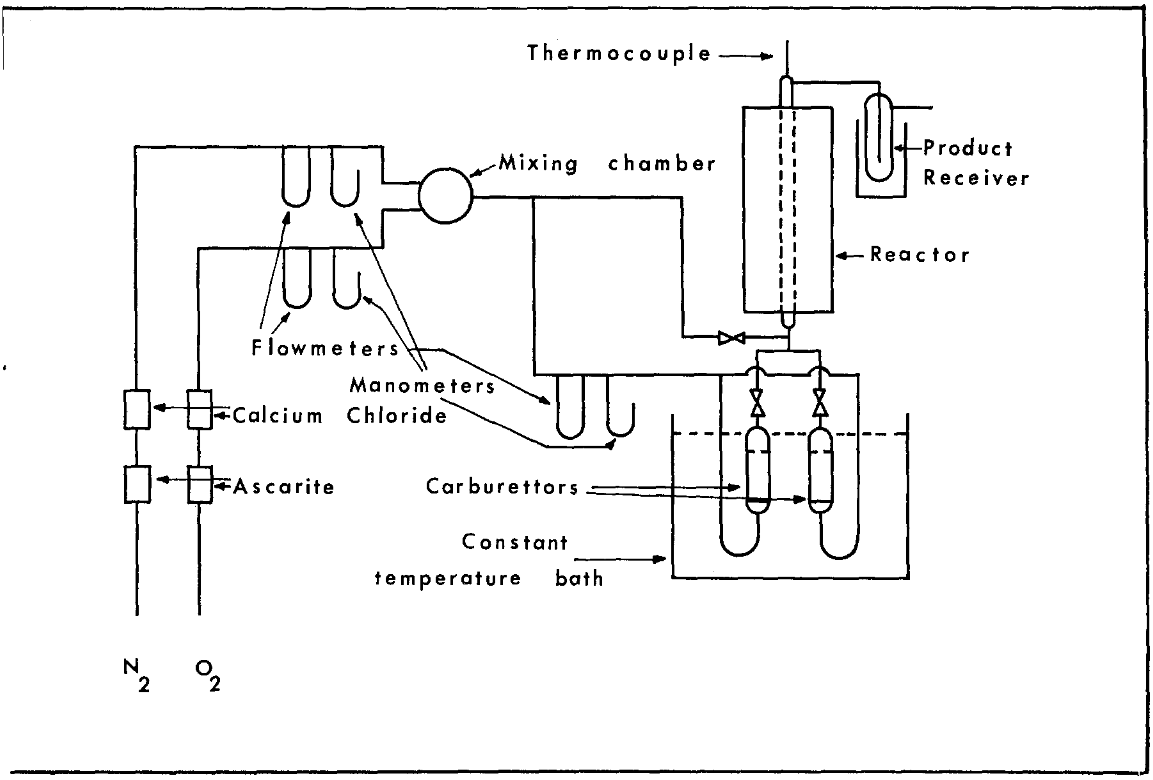

FIG. 1. Schematic diagram of the catalytic oxidation apparatus.

quantitatively by standard titration methods (*24*).

The reactor was constructed from a 1-inch diameter silica tube of 33 inches length with a constriction near the middle to hold a catalyst basket. Two tubular furnaces were fixed around the silica tube to preheat and heat the gas mixture to the required temperature. A chromel/alumel thermocouple was placed in the catalyst bed at a central location. Electrically heated nickel wire was wound around the glass tubes leading to and from the reactor to prevent any methanol or product condensation.

A gas mixture was passed through the catalytic reactor for 20 to 30 min using a secondary carburetor until constant temperature was obtained. Then the reactants and products were diverted to a weighed carburetor and fresh product trap, respectively, and the reaction allowed to proceed for periods from 20 min to 2 hr. The gaseous mixture flowed through the reactor at 0.5 liter/min STP and approximately 1 g of catalyst was used.

Preliminary work indicated that high methanol concentrations, i.e., greater than 37%, in the reactant stream were not suitable since, with the various catalysts used, the reactor temperature increased by as much as 180°C, making accurate temperature measurements or control impossible; also the catalysts turned black and became inactive very quickly. Therefore, the methanol concentration was reduced and kept below 6% to avoid the explosive region of between 6% and 37% methanol in air.

Experiments were conducted with different catalysts over a range of temperatures from 209° to 270°C and at different reactant stream compositions to determine relative catalytic activities and to examine the mechanism of the reaction briefly. Periodic checks of catalyst stability showed no appreciable changes over 2-week intervals. Periodic gas chromatographic tests were performed on the effluent stream for carbon monoxide, carbon dioxide, and hydrogen and none of these gases were detected as products. The absence of formic acid in the product stream was also ascertained. Blank experiments indicated that neither the catalyst mesh basket nor the silica-tube reactor were catalytically active.

Materials

The vanadium pentoxide was Fisher "Certified Reagent." The catalyst was prepared by slurrying the powder with water, pressing the slurry into pellets, drying the pellets for 15 hr at 115°C, and crushing the pellets into particles of a size from +20 to −8 mesh. Vanadium pentoxide catalyst with 1% chromium oxide added was prepared as described above but with an appropriate amount of chromium oxide added to the slurry.

Tungsten-molybdenum mixed oxide catalyst was prepared as described by Arnold (*25*). On baking, the porous mass turned from a yellow color to dark green. Particles of mesh size −4 to +10 were treated with air for 28 hr at 450°C. After this oxidation treatment the catalyst turned a light green color. Ammonium paramolybdate and paratungstate were obtained from Anachemia Chemicals, Ltd.

The methanol was "Spectranalyzed" Fisher certified reagent and the oxygen and nitrogen were obtained in pressure cylinders from the British Oxygen Company.

Neutron Irradiation of Catalysts

A few grams of dry catalyst were packaged in aluminum containers with watertight lids for reactor neutron irradiation. The containers were placed inside NRX or NRU irradiation capsules and were irradiated in the McMaster University swimming pool reactor (thermal neutron flux: 10^{13} neutrons/cm^{2}sec) or in the Chalk River NRU reactor (flux: 2.7×10^{14} neutrons/cm^{2}sec). The estimated integrated thermal neutron doses received by the catalysts are given in Table 1. Copper monitors placed in one sample showed the neutron flux to be essentially uniform throughout the bulk of the sample.

The catalytic activity of the irradiated catalysts was tested to detect differences in oxidation rate by comparison with unirradiated catalyst as soon as the radio-

TABLE 1

CATALYST HISTORY

Catalyst[a]	Irrad. time (hr)	Neutron flux (thermal) (neutrons/cm² sec)	Integrated neutron dose (neutrons/cm²)	% Impurity introduced
$W_{1,2}$ (unirrad.)	0	—	—	—
W_{1A} (unirrad. & annealed)	0	—	—	—
W_3 (irrad.)	125[b]	2.7×10^{14}	1.2×10^{20}	0.06% Re
W_{3A} (irrad. & annealed)	125[b]	2.7×10^{14}	1.2×10^{20}	0.06% Re
W_4 (irrad.)	192	1.0×10^{13}	7.2×10^{18}	0.0035% Re
W_{4A} (irrad. & annealed)	192	1.0×10^{13}	7.2×10^{18}	0.0035% Re
V_1 (unirrad.)	0	—	—	—
V_2 (irrad.)	1	5.2×10^{12}	1.9×10^{16}	4.8×10^{-6}% Cr
V_3 (irrad.)	159	5.2×10^{12}	3.0×10^{18}	7.7×10^{-4}% Cr
V_4 (irrad.)	317	5.2×10^{12}	5.9×10^{18}	1.5×10^{-3}% Cr
V_5 (irrad.)	125[b]	2.7×10^{14}	1.2×10^{20}	0.031% Cr
V_c (unirrad. & 1% Cr added)	0	—	—	1.0% Cr

[a] V refers to vanadium pentoxide catalyst.
W refers to tungsten-molybdenum mixed oxide catalyst.

[b] Estimated fast neutron flux: 6.5×10^{13} neutrons/cm² sec.

active handling hazard was below the prescribed safe limits. This meant that the vanadium catalysts were studied within 1 week after irradiation and the mixed oxide catalysts were studied about 3 weeks after irradiation (and storage at room temperature). The catalysts were annealed after initial measurements of catalytic activity by heating them in a furnace for 3 to 5 hr at 800°F.

RESULTS AND DISCUSSION

A differential type of catalytic reactor was used as it minimized large changes in temperature, composition, and gas stream velocity along the catalyst bed, all of which could cause difficulty in accurate kinetic measurements. Mean oxidation rates as determined from cumulative product yields over a measured time interval could be used without appreciable error as the methanol conversion was generally well below 15% (*26*).

Repeated measurements showed that there were no aging effects or deterioration in the activity of either catalyst even after they were used up to 40 hr in the reactor. Figure 2 shows that the vanadium pentoxide was two to three times more active catalytically per unit weight than tungsten-molybdenum mixed oxide, but was 30% less active than vanadium doped mechanically with 1% chromium oxide. After irradiation of the pure vanadium pentoxide catalyst no significant differences were found in catalytic activity nor in the activation energy for the methanol oxidation reaction which was 18.5 ± 1.5 kcal/mole as determined from the slope of the line of Fig. 2. Further, no change was evident in the exponents of the concentration terms in the rate equation for the process

$$\text{Rate of oxidation, } r = k/w[\text{MeOH}]^{0.35}\,[O_2]^{0.13}$$

as can be seen in Fig. 3. These results indicate that there were no detectable irradiation effects on the catalytic activity of the vanadium pentoxide catalyst. Any lattice defects produced on neutron bombardment probably annealed rapidly at the reaction temperature and, the introduction of up to 0.031% chromium in the catalyst by neutron transmutation would appear too small to have any appreciable effect, from these tests.

The nonintegral exponents of oxygen and methanol in the rate equation, which were found in these experiments to have the values 0.13 and 0.35, respectively, indicate a complicated methanol oxidation mechanism in the catalytic reaction with the oxygen concentration exerting little influ-

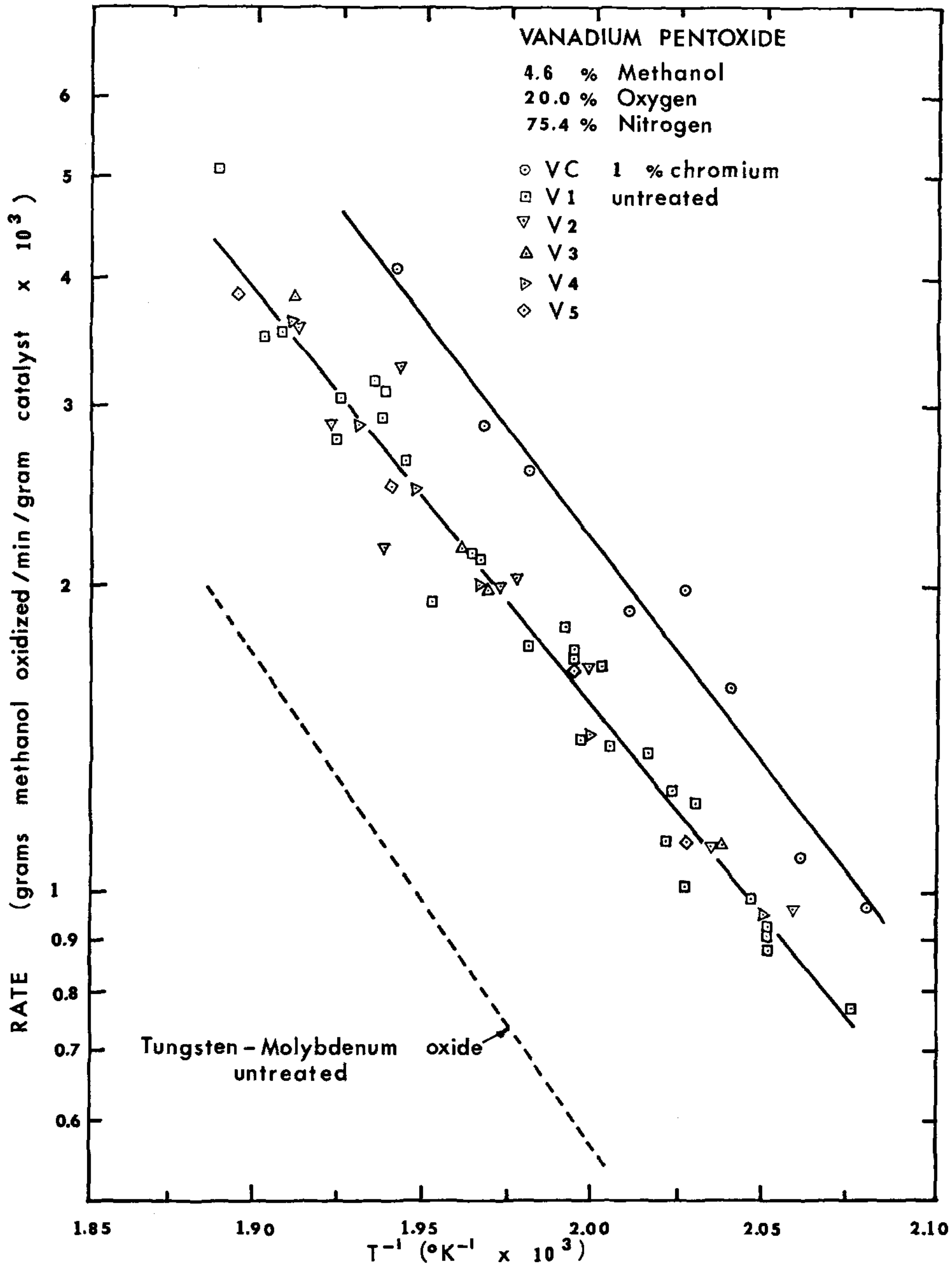

FIG. 2. Arrhenius plots for the oxidation of methanol over vanadium pentoxide catalysts from 209 to 270°C. ⊙ VC; ⊡ V1; ▽ V2; △ V3; ▷ V4; ◇ V5.

ence on the rate. The mechanism itself was not further investigated in this study of possible catalyst modification.

The tungsten-molybdenum mixed oxide catalyst was not as active as the vanadium pentoxide catalysts and the activation energy was found to be slightly higher, viz. 22.0 ± 0.7 kcal/mole. Varying doses of neutron irradiation caused no change in the activation energy as shown by the constancy of the slopes of Fig. 4, nor in the mechanism, as shown by the invariability of the rate

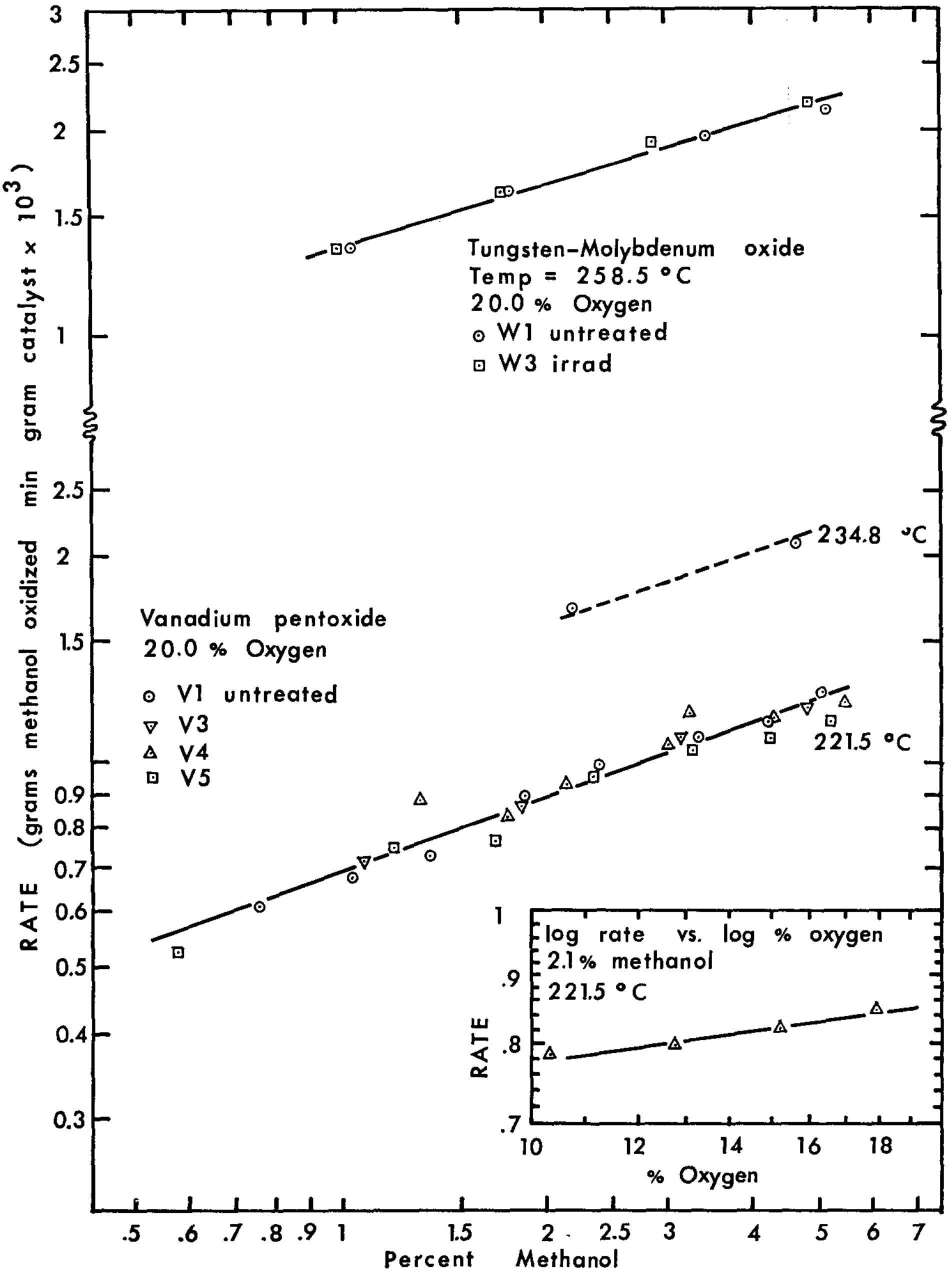

FIG. 3. Variation of methanol oxidation rates with methanol and oxygen concentrations for vanadium pentoxide and tungsten-molybdenum oxide catalysts. Upper plot: 258.5 C, 20.0% oxygen, ⊙ W1; □ W3. Lower plots: broken curve: 234.8 C; ⊙ V1. Solid curves 221.5 C, ⊙ V1; ▽ V3; △ V4; □ V5.

dependence on oxygen and methanol in Fig. 3. The same exponent of methanol concentration was found for the mixed oxide catalysts. The oxidation rate of the irradiated catalyst was increased by 25% over the unirradiated (Fig. 4) but this gradually annealed over a period of 20 days of intermittent use and storage at room

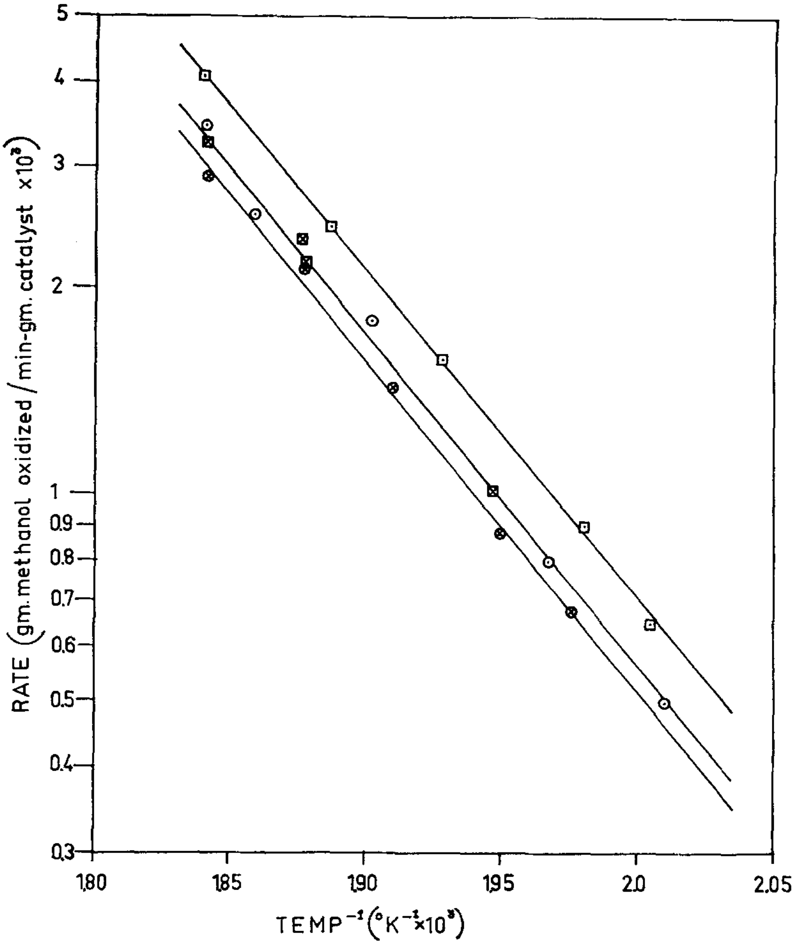

FIG. 4. Arrhenius plots for oxidation of methanol over tungsten-molybdenum oxide catalysts from 209 to 270°C. ⊙ W1; ⊗ W1A; ⊡ W3; ⊠ W3A.

temperature. A comparison of irradiated, high-temperature-annealed and unirradiated-annealed catalysts showed a statistically significant increase of about 10%, at the 99% confidence level, for the irradiated-annealed catalyst which had received an integrated neutron dose of 1.2×10^{20} neutrons/cm^2 (Fig. 4). There was also an increase of about 6%, significant at the 97.5% confidence level, after a catalyst had received an integrated neutron dose of 7.2×10^{18} and then had been annealed.

These results for the unirradiated-annealed and irradiated-annealed mixed oxide catalysts suggest that the enhancement in catalytic activity was partly due to defects created by neutron (and reactor gamma) irradiation which annealed slowly, and partly due to the 0.06% rhenium impurity introduced into the catalyst as a result of neutron transmutation of tungsten atoms, which effect is irreversible even on high-temperature annealing.

Visually it was observed that the color of the irradiated mixed oxide catalyst which had changed to dark blue, from light green in the unirradiated condition, annealed slowly to its original color over 20 days standing. On the other hand, the color of the irradiated vanadium catalyst which had become a dark brown, annealed very quickly to its original yellow-orange color after being placed in the heated catalytic reactor. Some attempts were made to examine X-ray diffraction patterns of the irradiated catalysts. Residual radioactivity in the catalysts caused some photographic fogging in the X-ray camera, but in the poor patterns obtained, no appreciable differences could be detected in the irradiated specimens.

A comparison of the findings for the two different catalysts reveals that the inherently more active vanadium pentoxide catalyst was not modified through neutron bombardment while the catalytic activity of the inherently less active mixed oxide catalyst was increased. This finding is in agreement with previous studies on irradiation of catalysts with other forms of irradiation (*27, 5, 10*) in which it was found that, for a given reaction, less-active catalysts were modified more than catalysts of greater inherent activity.

SUMMARY

No change in mechanism or in activation energy for the catalytic oxidation of methanol resulted after the catalysts received appreciable doses of neutron irradiation. It was estimated that 0.03% and 0.06% chromium and rhenium were formed in vanadium pentoxide and tungsten-molybdenum mixed oxide catalysts in this irradiation treatment, but a vanadium catalyst doped mechanically with 1% chromium showed a 30% increase in catalytic activity whereas no change could be found in the irradiated vanadium catalyst. The mixed oxide catalyst showed an increased activity of 25%, with about 60% of this increase due to radiation damage effects and 40% of the increase due to nuclear transmutations leading to the introduction of foreign atoms uniformly throughout the catalyst. The former effect annealed slowly at the reaction temperature and completely after 3 hr annealing at 800° while the latter increase was irreversible.

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REFERENCES

1. FAN, H. Y., *Solid State Physics* **1,** 317 (1955).

2. WITTELS, M., AND SHERRILL, F. A., *Phys. Rev.* **93,** 1117 (1954).

3. MURRAY, G. T., AND TAYLOR, W. E., *Acta Metallurgica* **2,** 52 (1954).

4. TAYLOR, E. H., AND WETHINGTON, J. A., *J. Am. Chem. Soc.* **76,** 971 (1954).

5. KOHN, H. W., AND TAYLOR, E. H., *J. Am. Chem. Soc.* **79,** 252 (1957).

6. KOHN, H. W., AND TAYLOR, E. H., *J. Phys., Chem.* **63,** 500 (1959).

7. KOHN, H. W., AND TAYLOR, E. H., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2,** 1461 (1961) (Paper 71).

8. BARRY, T. I., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2,** 15 (1961) (Paper 70).

9. KOHN, H. W., *J. Catalysis* **2,** 208 (1963).

10. TURKEVICH, J., IKAWA, T., NOZAKI, F., AND STAMIRES, D., *Conf. Proc. Industrial Uses of Large Radiation Sources* **1,** 41 (I.A.E.A., Vienna, 1963).

11. LUCCHESI, P. J., BAEDER, D. L., LONGWELL, J. P., AND SCHROEDER, M. C., *J. Chem. Phys.* **31,** 558 (1959).

12. WEISZ, P. B., AND SWEGLER, E. E., *J. Chem. Phys.* **23,** 1567 (1955).

13. MIKOVSKI, R. J., AND WEISZ, P. B., *J. Catalysis* **1,** 345 (1962).

14. BRAGG, R. H., MORRITZ, F., HOLTZMAN, K., FENG, P. Y., AND PIZZAROLLO, F., *WADC Tech. Rept.* **59-286** (1959).

15. SHANKAR, J., SRIVASTAVA, S. B., AND RAO, M. H., *Proc. Symp. Chem. Effects Nuclear Transformations* **2,** 325 (I.A.E.A., Vienna, 1962).

16. DONATO, M., *J. Phys. Chem.* **67,** 773 (1963).

17. DONATO, M., Mines Branch Research Report R 105 (Aug. 1962), Dept. of Mines and Technical Surveys, Canada.

18. TURKEVICH, J., *Proc. 2nd Intern. Conf. Peaceful Uses At. Energy, Geneva* **29,** 375 (1958).

19. TAYLOR, E. H., *Nucleonics* **20,** 53 (1962).

20. OTWINOWSKA, H., TRESZCZANOWICZ, E., AND CIBOROWSKI, S., *Actes Congr. Intern. Catalyze 2ᵉ, Paris, 1960,* p. 1733 (1961) (Paper 85).

21. DOUGLAS, D., M.A.Sc thesis, Dept. Chem. Eng., U. of Toronto, 1959.

22. CANNERI, G., AND COZZI, D., *Chim. Ind.*

(*Milan*) **21,** 653 (1939) [*Chem. Abstr.* **34,** 3237 (1940)].

23. Franciscod, J., *Rev. Gen. Mat. Plastiques* **15,** 302 (1939) [*Chem. Abstr.* **34,** 5413 (1940)].

24. Walker, J. F., "Formaldehyde," 3rd ed., p. 486. Rheinhold, 1964.

25. Arnold, H. R., U.S. Patent 2439880 [*Chem. Abstr.* **42,** 4724 (1948)].

26. Davidson, B., and Thodos, G., *A.I.Ch.E. J.* **10,** 568 (1964).

27. Teller, A. S., Poska, F. L., and Davies, H. A., *Intern. J. Appl. Radiation Isotopes* **11, 123** (1962).