# A comparative study of the complete oxidation of dimethyl ether on supported group VIII metals

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In the study of the interaction of dimethyl ether with alumina-supported platinum metals by means of infrared spectroscopy, methoxy species bonded to the alumina and CO adsorbed on the metals have been detected. The complete oxidation of dimethyl ether in a flow system sets in above 400 K and proceeded to 100% conversion at $\sim$ 673 K. No or only very slight deactivation was observed in 5 h. The specific activity order of the catalysts is: Ru > Pt > Ir > Pd > Rh.

**Keywords:** oxidation of dimethyl ether, decomposition of dimethyl ether, infrared spectra of adsorbed dimethyl ether, supported platinum catalysts, deactivation of catalysts, formation of adsorbed CO, dimethyl ether as an alternative fuel, environmental catalysis

## 1. Introduction

A great effort is being made to find an alternative fuel, the use of which results in lower emissions. Recently, it has been reported that dimethyl ether (DME) that contains small amounts of methanol and water, can be used in conventional systems with excellent performance [1,2]. It burns completely smokeless with lower $NO_x$ emissions, and easily meets the stringent 1998 California emission standards. Less reduction was measured for the hydrocarbons and CO emission: depending on the extent of its dilution with water and methanol, hydrocarbon and CO emission may increase [1]. As we experience the introduction of more and more rigorous laws for automobile emissions, exhaust catalysts may remain in use even in the application of DME as a fuel. In the light of this consideration we examine the catalytic oxidation of DME on supported platinum metals; some of them are used in automobile exhaust catalysis.

## 2. Experimental

The catalysts were prepared by impregnating the alumina support with solutions of metal compounds to yield a nominal 1 wt% metal. The following salts of Pt metals were used: $H_2PtCl_6{\cdot}6H_2O$, $PdCl_2$, $RhCl_3{\cdot}3H_2O$, $H_2IrCl_6{\cdot}6H_2O$ and $RuCl_3{\cdot}3H_2O$. The impregnated powders were dried at 383 K. The fragments of catalyst pellets were oxidized at 773 K for 30 min and reduced at 773 K in the catalytic reactor for 1 h. DME was a product of Aldrich. The gases used were initially of commercial purity. The Ar (99.995) was deoxygenated with an oxytrap. The other impurities were adsorbed by a 5A molecular sieve at the temperature of liquid nitrogen.

Catalytic measurements were carried out in a fixed-bed continuous-flow reactor made of quartz (17 mm i.d.). The amount of catalyst pellets used was 0.3 g. Analyses of the exit gases were performed with a Hewlett-Packard 5890 gas chromatograph using a Porapak QS column. The system was operated at a total pressure of 1 atm. The carrier gas was argon. In the study of the decomposition of DME it contained 10.0 vol% DME. In the oxidation of DME the carrier gas contained 1 vol% DME and 5 vol% $O_2$. In both cases the flow rate was 20 ml/min, which corresponds to 4000 $h^{-1}$ (GHSV).

Infrared spectroscopic studies were made in a vacuum IR cell using self-supporting wafers of catalyst powders (30 × 30 mm, $\sim 20\ mg/cm^2$) which underwent the same pretreatments as before catalytic measurements. The IR cell used made it possible to register the spectra between 100 and 300 K. Spectra were recorded with a Biorad (Digilab. Div.) Fourier transform IR spectrometer (FTS 155).

The dispersity of the supported metals was determined by hydrogen adsorption at 300 K. Data are listed in table 1.

## 3. Results and discussion

### 3.1. Interaction of DME with the catalysts

The interaction of DME with alumina and alumina-

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Table 1
Kinetic data for the decomposition and oxidation of DME

| Catalyst | $D^{a}$ (%) | $N_{\mathrm{DME}}{}^{b} \times 10^{-4}$ (s$^{-1}$) | | |
|---|---|---|---|---|
| | | decomposition | | oxidation |
| | | initial | steady state | |
| 1% Rh/$Al_2O_3$ | 46.2 | 81.31 | 3.90 | 135.80 |
| 1% Pd/$Al_2O_3$ | 23.2 | 186.85 | 181.23 | 194.18 |
| 1% Ru/$Al_2O_3$ | 5.5 | 60.66 | 8.59 | 778.17 |
| 1% Pt/$Al_2O_3$ | 41.3 | 131.72 | 118.48 | 347.93 |
| 1% Ir/$Al_2O_3$ | 75.5 | 8.92 | 0.67 | 204.76 |

[a] $D$ = dispersity of the metal determined by hydrogen adsorption.
[b] Turnover frequency at 523 K.

supported platinum metals was first investigated by means of FTIR spectroscopy. Previous IR studies showed that dimethyl ether molecules adsorb on alumina surfaces at 150 K, via hydrogen bonding of the oxygen atom of the ether to isolated surface hydroxyl groups [3,4]. Heating the adsorbed layer above 250 K revealed the formation of surface methoxy species [3]. IR spectra obtained on our alumina sample at different temperatures are consistent with this picture. Marked spectral changes indicating the formation of a new surface species with different C–H vibrational modes were experienced above 200–230 K. The formation of methoxy species is suggested by the appearance of absorption bands at around 2960, 2848, 1470, 1440, 1158 and 1059 cm$^{-1}$.

Similar measurements have been performed on alumina-supported platinum metals. It appears that the transformation of DME into methoxy species on alumina has not been altered significantly by the presence of 1% metal, which is not surprising taking into account the large surface area of the alumina. New features, not observed for alumina support, are the appearance of weak bands in the CO stretching region at and above 300 K. The position of the CO bands varied from sample to sample. The highest intensity was measured for the Pt sample and the lowest one for Ru catalyst (fig. 1a). A general observation is that the intensity of the CO bands

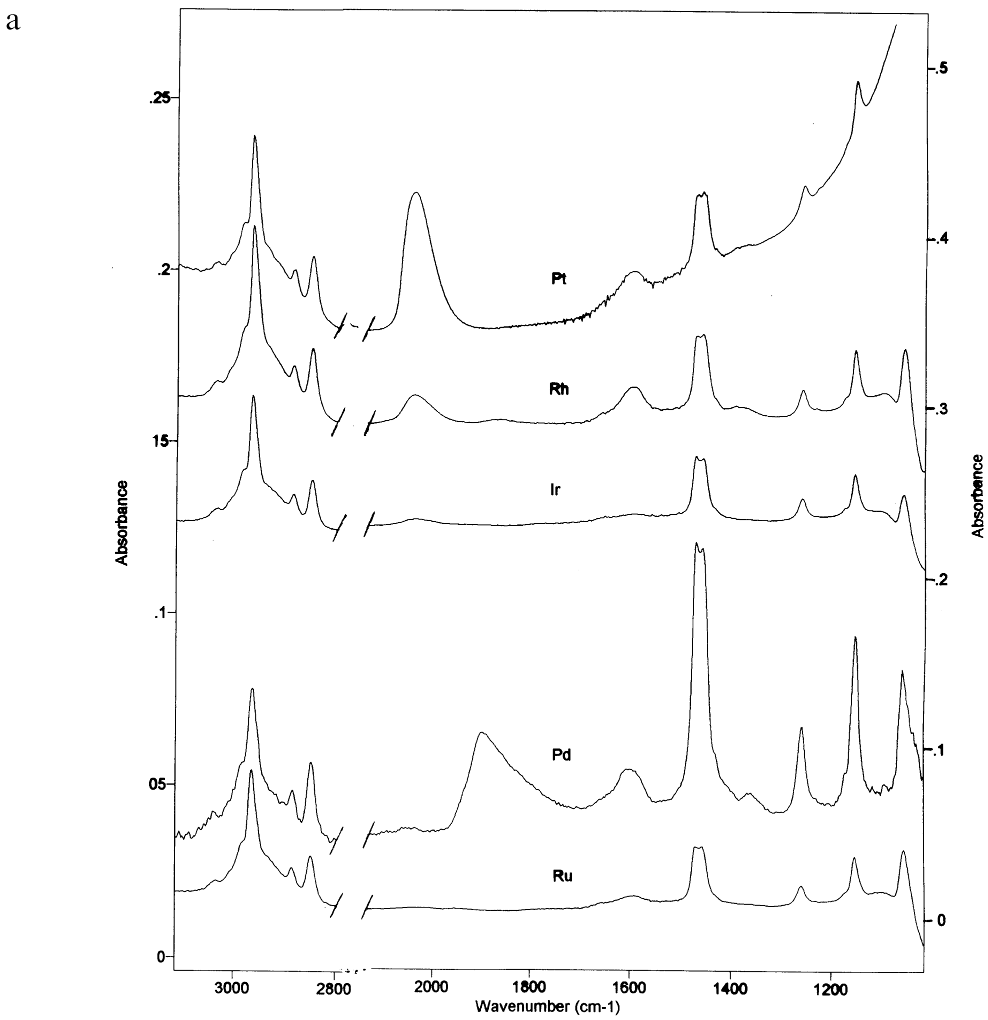

Fig. 1. (a) Infrared spectra of DME adsorbed on alumina-supported platinum metals and heated to 400 K. (b) Infrared spectra of adsorbed DME on Pt/$Al_2O_3$ after heating to different temperatures under continuous evacuation. All the spectra were recorded at 300 K.

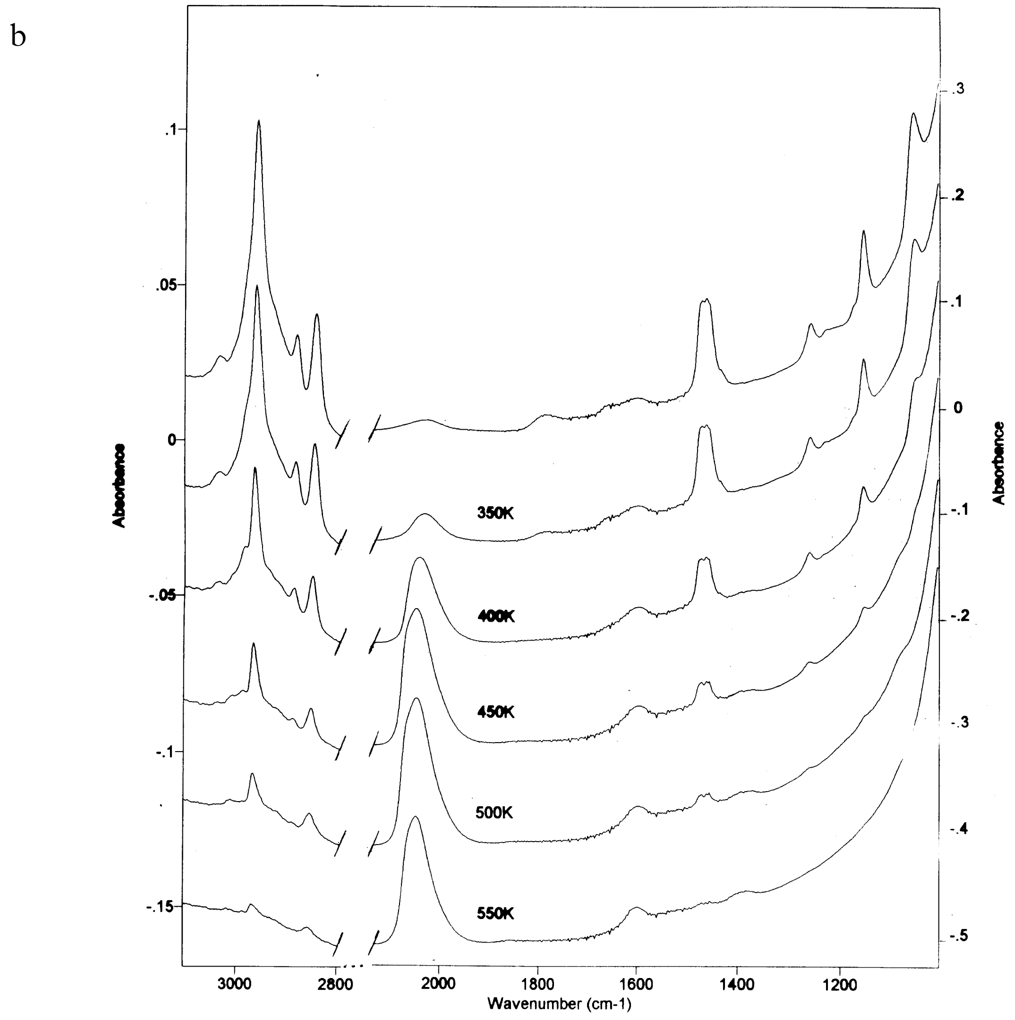

Fig. 1. (Continued.)

exhibited a maximum around 500 K. The effect of annealing on the IR spectra of the adsorbed layer for Pt/$Al_2O_3$ is presented in fig. 1b.

The development of weak, but stable adsorption bands at 1595 and 1365 $cm^{-1}$ above 350–400 K suggests the formation of formate species. These bands are attributed to the asymmetric and symmetric O–C–O stretching vibrations of formate ions. On the basis of our previous results obtained in $H_2$, CO and $CO_2$ mixture [5] and the low stability of formate on platinum metals [6], it seems very likely that formate is located on the alumina support and produced by the reaction among the products, $H_2$, CO and OH,

$$OH(a) + CO(a) \rightleftharpoons HCOO(a)$$

The interaction of DME with the catalysts was also followed in a flow system by the determination of the products of the reaction. A measurable decomposition occurred at 523 K. The catalytic influence of platinum metals exhibited a great variety. The highest and constant activities were exhibited by alumina-supported Pd and Pt (fig. 2). In all other cases, the extent of the decomposition markedly decayed to a low value (1–3%) after 30–50 min. The main products of the decomposition were $H_2$, CO and $CH_4$. In very small amounts, methanol, ethane and propane were also formed. From the variation of the concentration of DME in the carrier gas we obtained that the decomposition of DME follows first-order kinetics.

On the basis of IR spectroscopic results the decomposition of DME can be described by the migration of methoxy species from the alumina onto metals where it decomposes to CO and H,

$$CH_3O{-}M \rightleftharpoons M + CO + 1.5H_2$$

The decomposition of DME, however, can occur directly on the metal crystallites. Recent results obtained on Rh(111) in UHV showed that above 300 K DME interacts strongly with Rh metal producing initially $CH_3O$ and $CH_3$ surface species, which decompose to CO and $H_2$ [7]. We found that DME decomposed on Rh/$SiO_2$, too (with somewhat lower rate than on Rh/$Al_2O_3$ although there is no IR spectroscopic evidence for the formation of adsorbed DME or methoxy species on

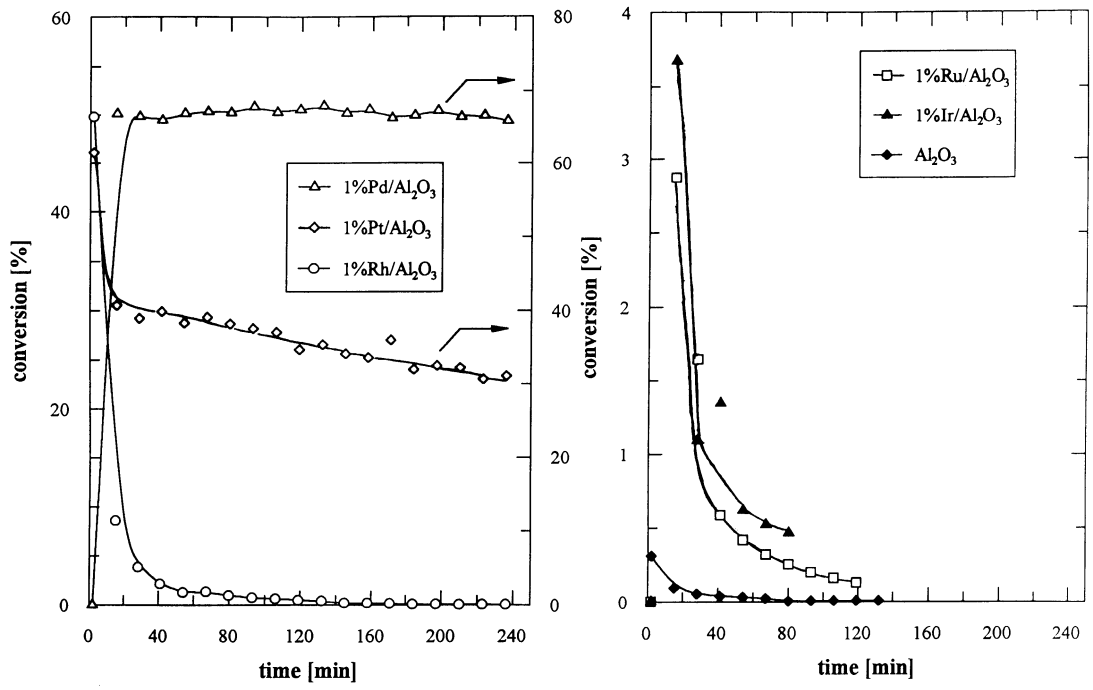

Fig. 2. Thermal decomposition of DME on alumina-supported platinum metals at 523 K in a flow system.

silica surface. All these features suggest that the major route of the decomposition of DME on supported metals is its adsorption and decomposition on the metal surface itself.

In the analysis of the catalyst surface after the decomposition of DME at 523 K for 2 h, we found carbon deposition on the catalysts. Its amount was determined by TPR measurements from the amount of $CH_4$ formed in the hydrogenation of carbon after desorbing CO and undecomposed. The reactivity of carbon towards hydrogen agreed well with that produced by the decomposition of methane on the same catalysts [8]. The largest amount was obtained for Ru and Rh and much less amount for Pt and Pd catalysts. This corresponds to the ease and the difficulty of the dissociation of CO on these metals. On the basis of these results we may conclude that the dramatic decay in the activity of the Ru, Rh and Ir compared to Pd and Pt is due to the carbon deposition on the catalyst surface.

### *3.2. Oxidation of DME*

In the first series of measurements the oxidation of DME was studied by gradually heating the catalyst bed in the presence of the reacting gas mixture from 300 K. The heating rate was 2 K/min. The conversion–temperature curves are presented in fig. 3. According to the analysis, the total oxidation of DME can be described by the equation

$$CH_3{-}O{-}CH_3 + 3O_2 \rightleftharpoons 2CO_2 + 3H_2O$$

These products were mainly formed at the lowest temperature of oxidation. The reaction started at the lowest temperature, slightly above 473 K on $Pt/Al_2O_3$ and on $Ir/Al_2O_3$. At 573 K the conversion of DME approached the value of 98–99%. At this temperature, besides the main products of the oxidation, small amounts of $H_2$, $CH_4$, $C_2H_6$, $C_3H_8$ and $CH_3OH$ were detected. 100% conversion was attained at $\sim$ 673 K. At and above 723 K, these hydrocarbon compounds were no longer detectable. A very small amount of $H_2$ (0.25–0.6% of the hydrogen content of DME) however, was still produced. $Rh/Al_2O_3$ and $Ru/Al_2O_3$ were slightly less active catalysts, but they exhibited the same features (fig. 3). Although the initial activity of $Ru/Al_2O_3$ was high, 100% conversion was not attained even at 773 K (fig. 3). The effect of pure alumina support was also determined: the oxidation started slightly above 573 K and completed only at around 873 K. In the empty reactor the reaction began above 873 K. The activity order of the catalysts at 523 K, related to the number of surface metal atoms, is as follows: Ru $>$ Pt $>$ Ir $>$ Pd $>$ Rh. Data are presented in table 1.

The oxidation of DME was also followed under isotherm conditions in time of stream at 523 K. After a short activating period, the catalysts exhibited a constant activity for the measured time period (4 h). Besides the total oxidation, $H_2$, $C_2H_6$, $CH_4$ and $C_3H_6$ were produced in trace amounts.

The effect of the concentration of reactants on the rate of oxidation of DME was examined on $Pt/Al_2O_3$. We found that an increase in the concentration of both

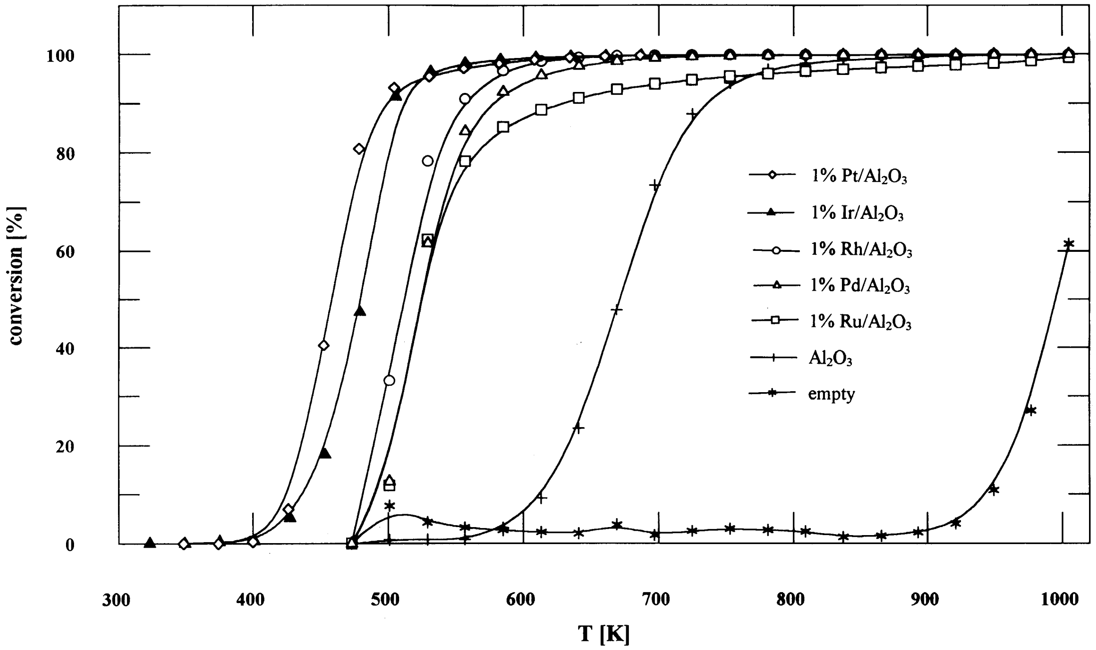

Fig. 3. The oxidation of DME on alumina-supported platinum metals in a flow system as a function of temperature.

compounds increased the rate of oxidation. The kinetic order with respect to $O_2$ was found to be 0.34. The order with respect to DME is about 0.27.

Although the present data are not sufficient to establish the detailed mechanism of the oxidation reaction, on the basis of the results obtained on Rh(111) surface [7], we believe that the oxidation of DME proceeds via the formation and decomposition of methoxy species and the oxidation of its decomposition products, CO and H.

Studies are in progress concerning the effects of support materials on the oxidation process.

## 4. Conclusions

(i) The decomposition of DME on alumina-supported platinum metals occurs at measurable rates at 523 K to yield $H_2$, CO, $CH_4$. Highest and constant activity was exhibited by Pt and Pd.

(ii) The complete oxidation of DME on the same catalysts takes place above 400 K. Rutenium and platinum were found to be the most effective catalysts.

(iii) It is assumed that the oxidation of DME proceeds through the formation and oxidation of methoxy species.

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