An attractive synthetic approach to methyl formate from methanol *via* methyl nitrite

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Received 27 August 2001; accepted 14 February 2002

Catalytic synthesis of methyl formate has been investigated by a novel route starting from methyl nitrite in vapor phase. The acidic sites of the catalysts play a crucial role for the catalytic activity and the selectivity of formation of methyl formate. The H-Y zeolite catalyst gave higher yield and selectivity of the target product. This study provides a new approach for the synthesis of methyl formate from methanol *via* methyl nitrite.

KEY WORDS: methyl formate; methyl nitrite; oxidation; dehydrogenation.

1. Introduction

Methyl formate (MF) is an important intermediate in organic synthesis [1]. In recent years, it was found that MF was an effective gasoline additive instead of MTBE [2]. Various synthesis methods have been developed. For example, methyl formate is easily produced on a large scale *via* base-catalyzed methanol carbonylation, dehydrogenation of methanol over metal catalysts, and oxidative dehydrogenation of methanol with bimetallic combination [2,3]. In particular, carbonylation of methanol in liquid phase was widely used [4–7]. However, there exist some disadvantages associated with low yield and product separation problems, etc. Therefore, the development of a heterogeneous process seems more attractive to us. In this paper, a novel catalytic synthesis of methyl formate with high yield and high selectivity in vapor phase is reported. This method may be termed a "two-step oxidation of methanol", which has not been reported so far. The principle of the reactions can be expressed as

$$4CH_3ONO \rightarrow HCOOCH_3 + 2CH_3OH + 4NO. \quad (1)$$

The by-products methanol and nitric oxide can be reused for the synthesis of methyl nitrite as given in equation (2), whereas the methyl nitrite is the starting material in equation (1).

$$4CH_3OH + O_2 + 4NO \rightarrow 4CH_3ONO + 2H_2O. \quad (2)$$

Combining the above two equations, the overall reaction can be expressed as

$$2CH_3OH + O_2 \rightarrow HCOOCH_3 + 2H_2O. \quad (3)$$

Methyl nitrite (MN) is readily prepared (equation (2)) under mild conditions (*e.g.* at room temperature without any catalysts). Its optimum reaction conditions have been discussed in the literature [8,9]. In this study our investigation focuses on reaction (1).

2. Experimental

2.1. Materials

The catalysts used for this study were H-Y zeolite, Na-Y zeolite, 4 Å molecular sieve, γ-Al_2O_3 and silica (KSG type). All are commercially available. Na-Y zeolites (Si/Al = 5.1) were purchased from Wenzhou Catalyst Company, H-Y zeolite (Si/Al = 5.1) was obtained by thermal treatment of NH_4-Y zeolite (from Wenzhou Catalyst Company) at 500 °C for 4 h, and 4 Å molecular sieve, γ-Al_2O_3 and KSG silica were supplied by Shanghai Hengye Molecular Sieve Company. They were all calcined at 500 °C for 4 h before use.

Methyl nitrite was prepared by slow addition of aqueous 6 M H_2SO_4 to a mixture of methanol, H_2O and nitrite sodium in a three-neck flask. The gaseous products were passed through potassium carbonate and a 5 Å molecular sieve column for purification, then diluted with high-purity nitrogen before being carefully measured. The detailed procedure is described in reference [9].

2.2. Catalytic performance

The measurements of catalytic activity were carried out in a continuous-flow reaction system with a fixed-bed reactor (8 mm inner diameter). The catalyst loading was maintained at 5.0 g. The reactant gases were added by passing a mixture of methyl nitrite (30% in volume)

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1011-372X/02/0600-0171/0

Table 1
Catalytic performances of methyl formate formation on different catalysts

Catalyst	H-Y	Na-Y	γ-Al_2O_3	4 Å	KSG silica
Conversion (%) of MN	83.3	81.4	70.6	63.9	56.7
STY (g/g cat h^{-1})	467.3	448.6	342.7	261.7	218.1
Sel. (%) of MF[a]	90.1	88.5	78.2	65.8	61.6

Note: Reaction conditions: 140 °C, 0.1 MPa, WHSV = 1200 h^{-1}.
[a] The selectivity of MF excludes the formation of methanol.

and nitrogen (70% in volume) through the glass tubular reactor. The products were condensed by an ice bath and analyzed by a gas chromatograph (HP-1102) equipped with a flame ionization detector and identified by GC-MS (HP-5973).

2.3. Measurements of catalyst acidity

Pyridine temperature-programmed desorption (Py-TPD) measurements in the range 100 °C to 800 °C were performed in a conventional flow apparatus. A heat rate of 11.7 °C/min and a He carrier flow rate of 25 STP ml/min were applied. After the pretreatment (800 °C, 2 h in He), the samples (~100 mg) were cooled down to 100 °C and saturated with pyridine. Then, samples were purged in the He flow until a constant baseline level was obtained. The desorption process was monitored by a temperature-programmed controller (Al-708), and a thermal conductivity detector was used for recording TPD patterns.

3. Results and discussion

Preliminary experiments with the reactor filled with quartz chips only showed that no reaction occurred at 100–200 °C, indicating that thermal decomposition of methyl nitrite could be neglected at this temperature region. The reaction performances of methyl formate synthesis over five different catalysts were compared. The results are listed in table 1, where it can be seen that H-Y zeolite appears to give superior catalytic activity compared with other catalysts. The catalytic activity decreased in the order H-Y > Na-Y > γ-Al_2O_3 > 4 Å > KSG silica. The results indicate that the decomposition of methyl nitrite is remarkably enhanced when the acidity of catalysts increases. Methyl nitrite is unique because it has a very weak CH_3O–NO bond (42 kcal/mol) which dominates its chemistry both in solution and vapor phase [10]. The presence of acidic sites accelerates the decomposition rate of methyl nitrite. As a result, the formation rate of methyl formate increases dramatically compared with those catalysts with low acidity.

The Py-TPD patterns of studied catalysts were compared in figure 1, as well as their desorption maximum temperatures. It can be seen that the five catalysts showed different desorption behaviors. The H-Y zeolite and γ-Al_2O_3 exhibited relatively high strong acidic sites ($T_d = 775.4\,^\circ C$ and 744.5 °C, respectively), while the Na-Y zeolite showed large and wide desorption peaks in the region of 220–500 °C, corresponding to weak acidic sites. It was also observed that there were almost no strong acidic sites over the Na-Y zeolite, 4 Å molecular sieve and KSG silica. Associating the TPD patterns with the corresponding catalytic activity of the catalysts, it seemed that the acidic strength of the catalysts exhibited no obvious influence on the catalytic activity of the reaction. The Na-Y zeolite, which showed a different TPD pattern compared with those of the H-Y zeolite and γ-Al_2O_3, also gave fairly high reactivity. On the other hand, the catalysts which showed relatively high desorption amounts of pyridine (*e.g.* H-Y zeolite, Na-Y zeolite and γ-Al_2O_3) gave high catalytic activities. Therefore, the results revealed that the reaction was probably catalyzed by both weak and strong acidic sites. These catalytic activities depended on the acidic amount of the catalysts. The relative ratio of total amount of acidic sites of five catalysts was 8.80 (H-Y zeolite), 7.85 (Na-Y zeolite), 7.83 (γ-Al_2O_3), 1.00 (4 Å molecular sieve) and 2.74 (KSG silica), according to the TPD patterns. The results were consistent with the catalytic activities of those catalysts.

Although a high yield of methyl formate was obtained on the H-Y catalyst, some by-products, predominantly in the form of dimethyl methane, were also detected. The results showed that H-Y and Na-Y zeolites exhibit much higher selectivity compared with the other three catalysts given in table 1. It is worthwhile to note that the stability of the catalysts is quite good in our experimental duration (for about 24 h) under steady-state operation conditions. However, the yield of MF dramatically decreases if the reaction temperature exceeds 200 °C.

The effect of temperatures on the performance of methyl formate formation on the H-Y zeolite catalyst was also examined, as shown in table 2. The conversion of methyl nitrite increased steadily with elevated reaction temperatures from 80 °C to 180 °C. The highest space–time yield (STY) of methyl formate reached 486.0 g/g cat h^{-1} at 159 °C. The apparent activation energy was also estimated to be 20.14 kJ/mol, based on the Arrhenius plot.

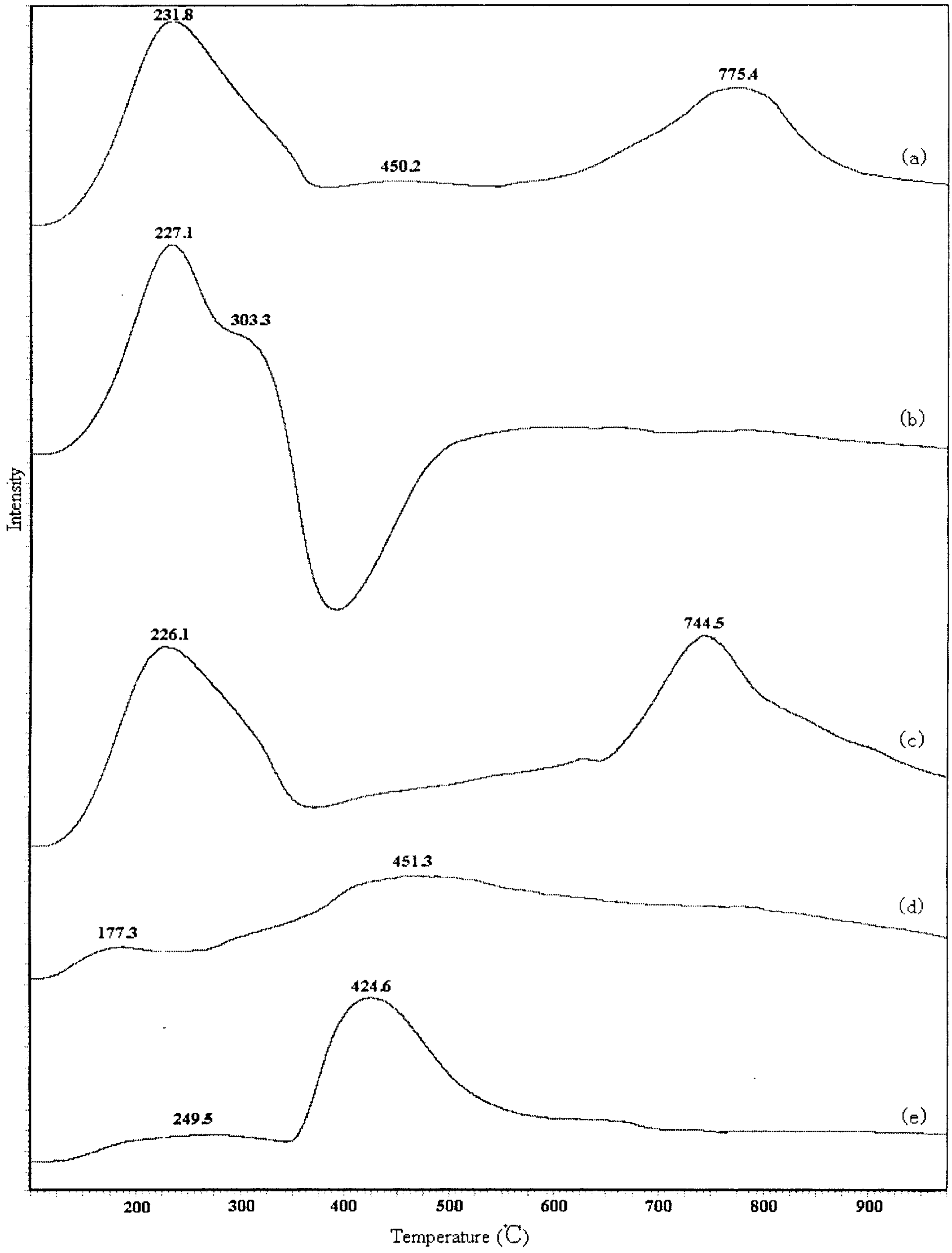


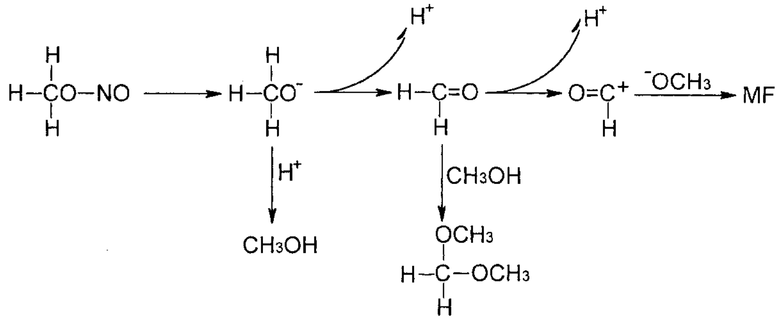
Figure 1. Py-TPD spectra of (a) H-Y zeolite, (b) Na-Y zeolite, (c) γ-Al_2O_3, (d) 4 Å molecular sieve and (e) KSG silica.

Table 2
The effect of temperature on the yield of methyl formate over H-Y zeolite catalyst

Temperature (°C)	79	100	122	140	159	180
Conversion (%) of MN	50.3	70.5	74.2	83.3	84.5	86.2
STY (g/g cat h^{-1})	267.9	405.0	423.7	467.3	486.0	467.3
Sel. (%) of MF[a]	85.6	92.4	91.5	90.1	92.5	87.8

Note: Reaction conditions: 0.1 MPa, WHSV = 1200 h^{-1}.

[a] The selectivity of MF excludes the formation of methanol.



Scheme 1.

The results obtained in this report are fairly significant compared with other gas-phase reactions for synthesis of methyl formate. More importantly, this study provides an entirely new strategy for methyl formate synthesis. Despite the toxic and explosive nature of methyl nitrite, this new method at least possesses the following advantages: (1) the reaction condition was fairly mild, (2) the yield and selectivity of methyl formate was quite high and (3) the catalyst contained no precious metals such as Rh or Pd. Although detailed reaction mechanisms are still being investigated, we suggest that the plausible mechanism undergoes the sequential dehydrogenation of methyl nitrite over acidic sites. A possible mechanism is proposed here as shown in scheme 1.

4. Conclusions

The catalytic synthesis of methyl formate *via* a novel route starting from methyl nitrite in vapor phase is reported for the first time. The results revealed that both the weak and strong acidic sites of the catalysts play a crucial role in the catalytic performance. The zeolites H-Y and Na-Y exhibit higher selectivity and yield of methyl formate. This new method exhibited the following advantages: the reaction condition was fairly mild, the yield and selectivity of methyl formate was quite high, and the catalyst contained no precious metals, such as Rh or Pd. However, further study is needed both for elucidating the detailed mechanism and developing an industrial process.

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