

Effect of acid–base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts on the direct synthesis of dimethyl carbonate from methanol and carbon dioxide: A TPD study of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts

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Abstract

$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts were prepared by a sol–gel method, and were applied to the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. The acid and base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts were measured by NH_3 -TPD and CO_2 -TPD experiments, respectively, to correlate the catalytic activities with the acid and base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. In the direct synthesis of dimethyl carbonate from methanol and carbon dioxide, the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ was superior to the corresponding $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. The catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ showed a volcano-shaped curve with respect to cerium content. The catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ increased with increasing acidity (acid amount) and with increasing basicity (base amount) of the catalyst. Among the catalysts tested, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ with the largest acidity and basicity showed the best catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide.

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1. Introduction

Dimethyl carbonate (DMC) has been used as a green and alternative chemical for corrosive and toxic reagents such as dimethyl sulfate and phosgene in methylation and carbonylation processes [1,2]. Several commercialized processes have been developed for the production of DMC, including the methanolysis of phosgene [3], the oxidative carbonylation of methanol catalyzed by cuprous chloride [4], and a direct synthesis catalyzed by palladium and an alkyl nitrate promoter [5]. However, these conventional processes involve the use of toxic, flammable, and corrosive gases, such as phosgene, hydrogen chloride, and carbon monoxide [6]. Therefore, direct synthesis of DMC from methanol and carbon dioxide has attracted considerable attention in an environmental point of view [7–18]. A wide range of

catalysts, such as organometallic compounds [7,8], metal tetraalkoxides [9], potassium carbonate [10], $\text{Ni}(\text{CH}_3\text{COO})_2$ [11], zirconia [12,13], CeO_2 - ZrO_2 [14,15], $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$ [16], H_3PO_4 - V_2O_5 [17], and Cu-Ni/VSO [18] have been employed for the direct synthesis of DMC from methanol and carbon dioxide.

It is known that both acid and base sites on the catalyst surface play an important role in the direct synthesis of DMC from methanol and carbon dioxide [12]. It was reported that Brønsted acid sites in $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$ favorably devoted to the methanol activation and to the enhancement of the catalytic activity of ZrO_2 in the direct synthesis of DMC [16]. The effect of Brønsted acidity in the CO_2 methanol reforming reaction over the liquid phase $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst has also been addressed recently [19]. However, not much investigation has been made on the acid–base properties of the catalysts employed for the direct synthesis of DMC from methanol and carbon dioxide. Therefore, a systematic approach to elucidating the effect of acid–base properties on the catalytic

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activity in the direct synthesis of DMC would be of interest.

In this work, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts were prepared by a sol-gel method with an aim of providing both acid and base sites, and were applied to the direct synthesis of DMC from methanol and carbon dioxide in a batch reactor. $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts were also prepared by a sol-gel method for the purpose of comparison. The acid and base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ were measured by NH_3 -TPD and CO_2 -TPD experiments, respectively. The catalytic activities were then correlated with the acid and base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts.

2. Experimental

$\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ ($x=0, 0.1, 0.2, 0.4, 0.6, 0.8,$ and 1.0) catalysts were prepared by a sol-gel method using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ as the cerium and titanium precursors. $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ was added to a solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol. Ammonium hydroxide (29 wt% NH_3) was then added to the solution containing the cerium and titanium precursors. The mixed solution was stirred for 1 h at room temperature. The precipitate was filtered and dried in an air stream at 80°C for 24 h. The resulting solid was calcined at 300°C for 4 h to yield the $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$.

$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ ($x=0, 0.1, 0.2, 0.4, 0.6, 0.8,$ and 1.0) catalysts were also prepared by a sol-gel method. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ dissolved in ethanol was added to a solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol. $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ and ammonium hydroxide were then added to the solution containing $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and cerium precursor. The mixed solution was stirred for 1 h at room temperature. The precipitate was filtered and dried in an air stream at 80°C for 24 h. The resulting solid was calcined at 300°C for 4 h to yield the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. The loading of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ was fixed at 15 wt% in all cases.

The direct synthesis of DMC from methanol and carbon dioxide was carried out in a 100 ml stainless steel autoclave. 6.4 g of methanol and 0.5 g of catalyst were charged into the autoclave, and the reactor was then purged with carbon dioxide. After pressurizing the autoclave to 5 MPa with carbon dioxide, the reactor was heated to the reaction temperature with constant stirring. The catalytic reaction was carried out at 170°C for 12 h. The reaction products were periodically sampled and analyzed with a gas chromatography (HP 5890 II).

The acid properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ were measured by NH_3 -TPD experiments. Each catalyst (0.5 g on the basis of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$) was charged into the quartz reactor of the conventional TPD apparatus. The catalyst was pretreated at 200°C for 4 h under a flow of helium (20 ml/min) to remove any physisorbed organic molecules. Twenty milliliters of NH_3 was then pulsed into the reactor every minute at room temperature under a flow of helium (5 ml/min), until the acid sites were saturated with NH_3 . The physisorbed NH_3 was removed by evacuating the catalyst sample at 50°C for 1 h. The furnace temperature was increased from room temperature to 500°C at a rate of $5^\circ\text{C}/\text{min}$ under a flow of helium (10 ml/min). The desorbed

NH_3 was detected using a GC-MSD (Agilent, 5975MSD-6890N GC). The base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ were measured by CO_2 -TPD experiments. The experimental procedures for CO_2 -TPD were identical to those for NH_3 -TPD, except that CO_2 instead of NH_3 was used to probe the base properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$.

3. Results and discussion

Fig. 1 shows the catalytic activities of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ in the direct synthesis of DMC from methanol and carbon dioxide at 170°C after a 12-h reaction. In the catalytic reaction, $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ were highly selective for the formation of DMC without any by-products. The amount of DMC produced was increased with increasing reaction time, but no significant increase was observed after 10 h. As shown in Fig. 1, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ showed a better catalytic performance than the corresponding $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. It is known that the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst retains mainly Brönsted acid sites [20]. This indicates that the Brönsted acid sites of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ played an important role in enhancing the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$, as previously reported for $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$ [16]. It is believed that the enhanced catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ was due to the bifunctional catalysis by acid sites (mainly provided by $\text{H}_3\text{PW}_{12}\text{O}_{40}$) and base sites (mainly provided by $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$) [12,16]. Another important point is that the catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ showed a volcano-shaped curve with respect to cerium content. Among the catalysts tested, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ showed the best catalytic performance.

In order to verify the effect of acid properties on the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$, NH_3 -TPD experiments were conducted over the catalysts. Fig. 2 shows the NH_3 -TPD profiles of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$. Although the NH_3 -TPD peak of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$

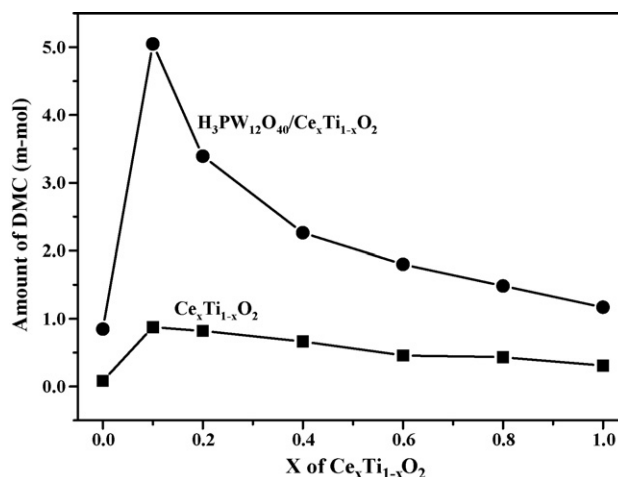


Fig. 1. Catalytic activities of $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ in the direct synthesis of DMC from methanol and carbon dioxide at 170°C after a 12-h reaction.

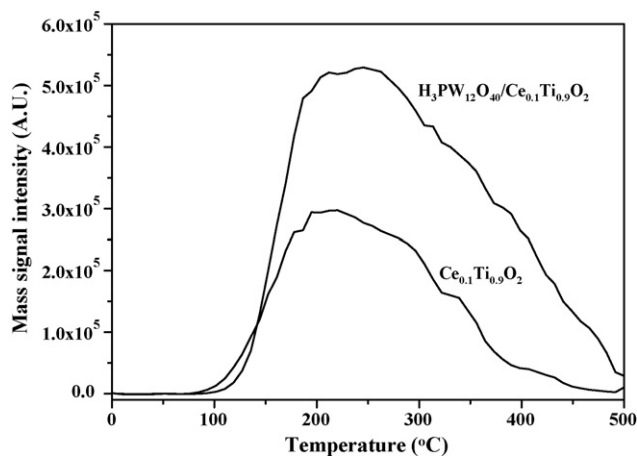


Fig. 2. NH_3 -TPD profiles of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$.

appeared at a lower temperature than that normally observed in the $\text{H}_3\text{PW}_{12}\text{O}_{40}$, it is not unusual considering that a TPD peak can shift to either high temperature or low temperature depending on the experimental conditions, such as heating rate and carrier flow rate. Both catalysts showed a broad NH_3 -TPD peak. However, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ exhibited a larger acidity (acid amount, peak area) than $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$. The acidity of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ is due to the presence of Lewis acid sites. Therefore, it is believed that the acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ is due to the Lewis acid sites of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and to the Brönsted acid sites of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The difference in acidity between $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ corresponds to the Brönsted acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$. This indicates that the enhanced acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ was due to the Brönsted acid sites provided by $\text{H}_3\text{PW}_{12}\text{O}_{40}$. On the other hand, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ showed a higher acid strength (peak temperature) than $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$.

We attempted to correlate the catalytic activity with the acid properties (acidity and acid strength) of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. No clear correlation between catalytic activity and acid strength (peak temperature of NH_3 -TPD profile) of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ was observed. However, a good correlation between catalytic activity and acidity (acid amount) was found. Fig. 3 shows the correlation between catalytic activity and relative acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. The relative acidity was defined as the ratio of the acidity of a $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ with respect to that of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$. The correlation clearly shows that the catalytic activity is closely related to the acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. The catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ was increased with increasing acidity of the catalyst. Among the catalysts tested, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ with the largest acidity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. According to the mechanism of DMC formation, methanol is activated to methyl species on the acid sites, which is known to be the rate-determining step [13,21,22]. Thus, the acidity plays an important role in

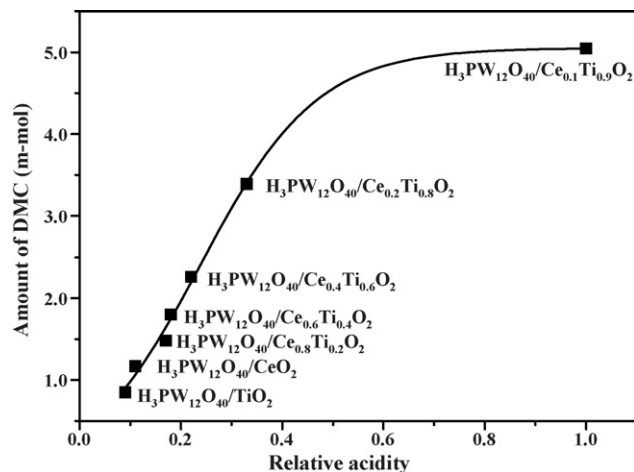


Fig. 3. A correlation between catalytic activity and relative acidity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$.

determining the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$, and a large amount of acid sites is favorable for the facile activation of methanol to methyl species in the direct synthesis of DMC from methanol and carbon dioxide.

To investigate the effect of base properties on the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$, CO_2 -TPD experiments were carried out over the catalysts. Fig. 4 shows the CO_2 -TPD profiles of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$. Both catalysts showed two CO_2 -TPD peaks (peaks I and II). The basicity (base amount, peak area) of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ was slightly smaller than that of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ (the ratio of peak area of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ with respect to that of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ was 0.9). This indicates that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ partially blocked the base sites of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ in the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ catalyst. The difference in base strength (peak temperature of CO_2 -TPD profile) between $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ can be attributed to the interaction between $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ in the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$. The experimental results showed that all the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts showed two CO_2 -TPD peaks. It can be inferred that the base properties of

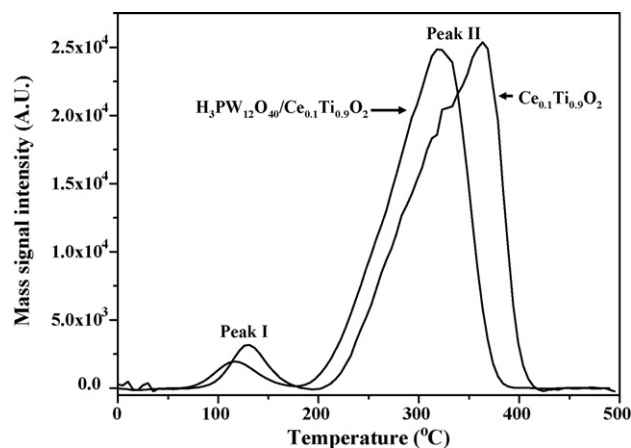


Fig. 4. CO_2 -TPD profiles of $\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$.

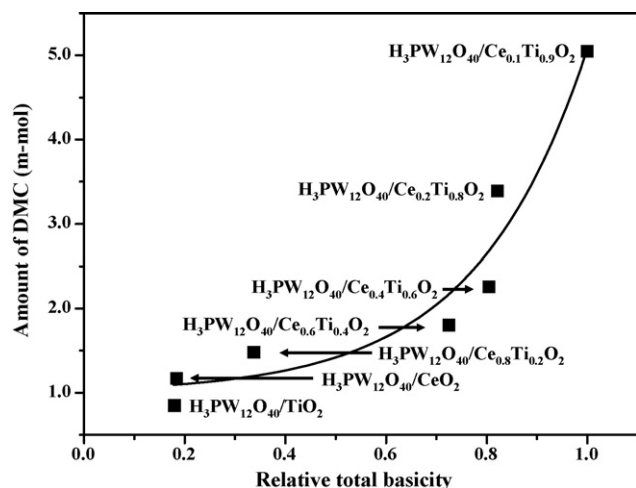


Fig. 5. A correlation between catalytic activity and relative total basicity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂.

H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ would be mainly influenced by the composition of Ce_xTi_{1-x}O₂.

Attempts were made to correlate the catalytic activity with the base properties (basicity and base strength) of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂. No clear correlation between catalytic activity and base strength (peak temperature of either weak base site or strong base site in the CO₂-TPD profile) was observed. However, a reliable correlation between catalytic activity and basicity (base amount) was observed. The catalytic activity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ was increased with increasing basicity of weak base site (peak I) and with increasing basicity of strong base site (peak II). In other words, the catalytic activity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ was increased with increasing total basicity of the catalyst. Fig. 5 shows the correlation between catalytic activity and relative total basicity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂. The relative total basicity was defined as the ratio of the total basicity of a H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ with respect to that of H₃PW₁₂O₄₀/Ce_{0.1}Ti_{0.9}O₂. The correlation shows that the catalytic activity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ was increased with increasing total basicity of the catalyst. Among the catalysts tested, H₃PW₁₂O₄₀/Ce_{0.1}Ti_{0.9}O₂ with the largest total basicity showed the best catalytic performance in the direct synthesis of DMC. The first reaction step in the direct synthesis of DMC from methanol and carbon dioxide is the activation of methanol to methoxy species on the base sites, and a methoxy carbonate anion is then formed by the reaction of methoxy species with carbon dioxide on the base sites [16]. Thus, the total basicity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ also appears to play an important role in determining the catalytic performance of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂, and a large amount of base sites is favorable for the formation of methoxy species and their subsequent reaction with carbon dioxide. An interesting point is that the order of relative acidity (Fig. 3) showed the same trend with that of relative total basicity (Fig. 5). Experimental findings also revealed that both large acidity and large basicity were favorable in the direct synthesis of DMC. It is believed that H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ formed a different composite structure

depending on the composition of Ce_xTi_{1-x}O₂, which is responsible for different catalytic performance, relative acidity, and relative total basicity.

4. Conclusions

Ce_xTi_{1-x}O₂ and H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ catalyst were prepared by a sol-gel method, and were applied to the direct synthesis of DMC from methanol and carbon dioxide. The acid and base properties of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ catalysts were measured by NH₃-TPD and CO₂-TPD experiments, respectively, in an attempt to correlate the catalytic activities with the acid and base properties of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂. In the direct synthesis of DMC from methanol and carbon dioxide, H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ showed a better catalytic performance than the corresponding Ce_xTi_{1-x}O₂ due to the Brønsted acid sites provided by H₃PW₁₂O₄₀. The catalytic performance of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ showed a volcano-shaped curve with respect to cerium content, and H₃PW₁₂O₄₀/Ce_{0.1}Ti_{0.9}O₂ showed the best catalytic performance. It was found that the catalytic activity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ increased with increasing acidity of the catalyst. The large amount of acid sites facilitated the activation of methanol to methyl species in the direct synthesis of DMC. The findings also showed that the catalytic activity of H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ increased with increasing total basicity of the catalyst. The large amount of base sites was required for the facile formation of methoxy species and their subsequent reaction with carbon dioxide. In conclusion, H₃PW₁₂O₄₀/Ce_{0.1}Ti_{0.9}O₂ with the largest acidity and basicity showed the best catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide.

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