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An investigation of the preparation of TiO_2-based catalysts using methods of thermal analysis

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Abstract

Thermal analysis and X-ray diffraction techniques were used to investigate the preparation of TiO_2-based catalysts. It was found that anatase can transform to rutile, a highly stable modification, at high temperature (> 1000 K), but with anatase alone the transformation is slow and not completed at 1273 K. An La promoter has little effect on the transformation. However, an Li promoter dramatically accelerates the transformation and decreases the transformation temperature to 853 K. The effect of an Li promoter on the transformation is possibly due to the substitution of Li^+ ions for lattice Ti^{4+} ions. The catalytic activity was measured at 1073 K in a fixed-bed reactor and the results showed that rutile has a preference over anatase for the coupling of CH_4. The addition of an Li promoter greatly improves the selectivity of C2 hydrocarbons which suggests a new form of active center on the surface of TiO_2.

INTRODUCTION

Partial oxidation coupling of methane (POCM) to C_2H_4 is an important and challenging process in the natural gas industry. From a practical point of view, natural gas, predominantly as CH_4, is found in abundant reserves and could function as an attractive alternative source of hydrocarbons, especially when the world faces predicted shortages in the supply of conventional oil. Furthermore, the expected product C_2H_4 is a key raw material for many chemical productions and increasing supplies are in great demand. But in another way, from the scientific point of view, CH_4 is chemically a highly stable molecule. Any methods to activate the C–H in CH_4 may easily lead to deep oxidation, thus forming CO_2. Great efforts have to be made to find a catalyst with good selectivity to C2 hydrocarbons, especially to C_2H_4 with good conversion of CH_4 for this reaction, as well as to investigate the scientific nature of the catalyst and the reaction itself [1–3]. TiO_2 is a

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well-known photocatalytic oxidation catalyst with good selective oxidation capability; it may also be useful in the POCM after modification. Some authors [4–8] have reported the catalytical properties of both TiO_2 alone and of promoted samples. It was found that TiO_2 alone, either anatase or rutile, is a poor catalyst for POCM but that an Li promoter can improve its activity significantly. To achieve a good understanding of the catalytic theory and practice, the function of an Li promoter in TiO_2 or other oxides [1–3] deserves investigation.

TiO_2 occurs in three crystal modifications: rutile, anatase and brookite. Brookite is an unstable modification. The most common modifications are rutile and anatase. Anatase can transform to rutile at high temperature and this transformation will affect the catalytic properties of TiO_2. TiO_2 supports from two different sources, one rutile and the other a mixture of rutile and anatase but rich in anatase, were promoted with Li^+ ions and La^{3+} ions and the catalytic reactivity measured [4]. In this paper, methods of thermal analysis and X-ray diffraction were used to study the process of catalyst formation, with special emphasis on the phase transformation of anatase to rutile and the effect of the transformation on the catalytic reactivity. An improvement in catalyst preparation is suggested on the basis of the results of this investigation.

EXPERIMENTAL

The two TiO_2 supports used in this study were both 40–60 mesh size from the Chemical Company of Tianjin; one was AR grade (purity $> 99.99\%$) with a BET specific surface area of $51.1\ m^2\ g^{-1}$, and the other was CR grade (purity $> 99\%$) with a BET specific surface area of $74.3\ m^2\ g^{-1}$. The first ($TiO_2(R)$) was determined as rutile and the second ($TiO_2(A)$) as a mixture of rutile and anatase but rich in anatase. $Li_2SO_4 \cdot H_2O$ and $La(NO_3)_3 \cdot nH_2O$, both AR grade from the Chemical Company of Shanghai, were used as the Li^+ and La^{3+} ion sources, respectively, without further treatment.

The following procedures were used to prepare and analyze all samples. Both TiO_2 supports were analyzed using X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetric analysis (TGA) techniques before use. Then both were calcined at 1123 K for 3.5 h and analyzed using XRD to observe the changes after calcination; Li- and La-promoted TiO_2 were prepared by adding an Li or La salt solution in certain proportions to both calcined TiO_2 supports, respectively, stirring for 2 h, leaving to stand for 24 h and evaporating the solvent at 473 K. A part of each sample was used to perform the DTA and TGA. The remaining part was calcined at 1123 K for 3.5 h with an air flow of $100\ ml\ min^{-1}$, then analyzed by XRD and its catalytic reactivity determined.

DTA–TGA measurements were performed on a Du Pont 1090B thermoanalyzer and thermogravimetric analyzer from 298 to 1273 K using a heating rate of 10 K min^{-1} and an air flow of 100 ml min^{-1} under dynamic non-isothermal conditions. XRD measurements were performed on a Hitachi D/max-YA instrument with Cu Kα radiation. Diffraction patterns were compared with those obtained from the ASTM powder diffraction files.

The catalytic reactivity was investigated in a quartz micro-flow-reactor with a fixed bed at 1073 K. The catalyst charge was 0.5 g. The reactant was a mixture of CH_4(> 99.99%), O_2(> 99.5%) and N_2(> 99.5%) under 1 atm pressure. The products were analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector. The conversion of CH_4 and the selectivity to C_2H_4 and C_2H_6 were calculated using the carbon-balance method

$$\text{Conversion of } CH_4\ (\%) = \frac{\text{Carbon in all products}}{\text{Total carbon flow through reactor}} \times 100$$

$$\text{Selectivity } (\%) = \frac{\text{Carbon in a certain product}}{\text{Carbon in all products}} \times 100$$

In turn, the yield of a certain product is defined as the percentage of the amount of carbon in the product in the total flow through the reactor. It can be expressed as

$$\text{Yield } (\%) = \text{Conversion of } CH_4 \times \text{Selectivity}$$

RESULTS AND DISCUSSION

TiO_2

TiO_2(R) and TiO_2(A) were analyzed before and after calcination using XRD, as shown in Fig. 1A–D. TiO_2(R), before and after calcination, indicates rutile. TiO_2(A), before and after calcination, is a mixture of anatase and rutile, but after calcination it contains more rutile and less anatase than before calcination. This indicates that rutile is a stable crystal modification and that anatase may transform to rutile; but the transformation is not complete even after the sample has been calcined at 1123 K for 3.5 h.

Figures 2 and 3 show the DTA–TGA curves for TiO_2(R) and TiO_2(A) from 298 to 1273 K. TiO_2(R) shows no considerable changes in the DTA–TGA curves except for a drift in the baseline, which is due to the change in heat capacity of the sample with increasing temperature. This confirms that rutile is a highly stable crystal modification TiO_2(A) exhibits an endothermic feature which appears in the DTA curve after 873 K and up to 1273 K, but with no considerable weight loss in the TGA curve except below 373 K,

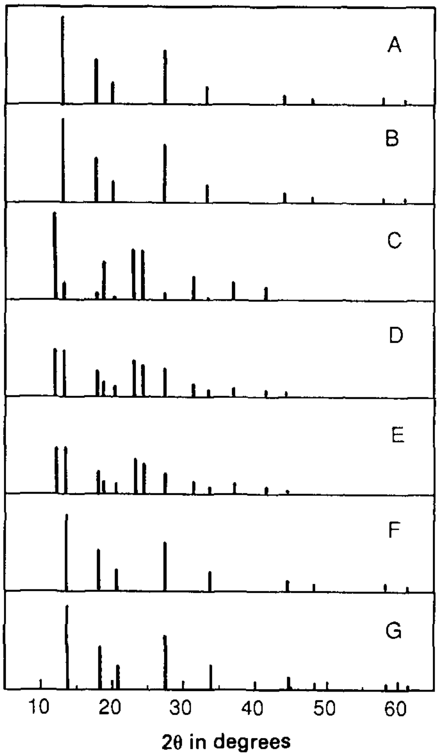

Fig. 1. The XRD patterns: A, TiO_2(R) before calcination; B, TiO_2(R) after calcination; C, TiO_2(A) before calcination; D, TiO_2(A) after calcination; E, La/TiO_2(A) after calcination; F, Li/TiO_2(A) after calcination; and G, La/Li/TiO_2(A) after calcination.

which is due to dehydration. The transformation of anatase to rutile appears to be responsible for the curve from 873 to 1273 K. However, it is difficult to recognize the beginning of the transformation because of the slow changes in the curve which suggests that the speed of the phase transformation from anatase to rutile is not as fast as that of an ordinary phase transformation in which phase changes usually take place at a fixed temperature. The change results from the difference in heat capacity and its temperature coefficients between anatase and rutile, and in the differing relative amounts of the two crystal modifications. The curve becomes steep at about 1000 K which may imply an acceleration of the transformation. However, the transformation is not complete at 1273 K which agrees with the results from XRD analysis.

A perfect rutile crystal of TiO_2 is tetragonal with two TiO_2 in one primitive cell; anatase is also tetragonal but with four TiO_2 in one primitive cell [9]. Rutile is a stable crystal modification; anatase is a metastable crystal modification. Anatase can transform to rutile at high temperature but whether the transformation can be completed is highly dependent on the conditions.

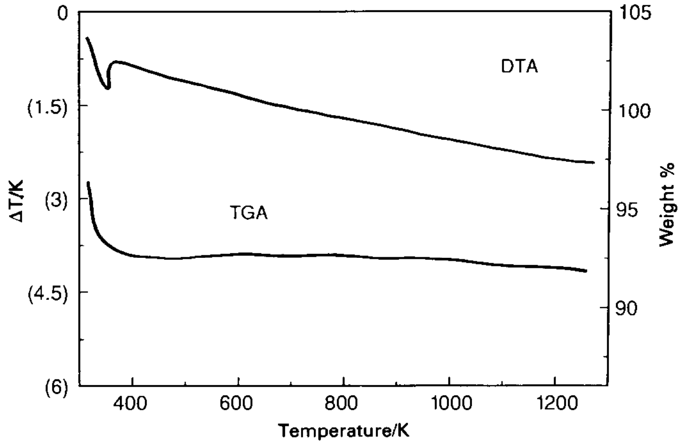

Fig. 2. DTA–TGA curves of $TiO_2(R)$.

Mo [9] indicated that the transformation started at 883 K, accelerated after 1003 K and completed at 1188 K. But Kobata et al. [10] reported that some anatase can be detected even after being calcined at 1273 K. They proposed that the transformation of anatase to rutile initiated from the surface then developed to the bulk. Therefore, many conditions, for example, the particle size, the contaminant, the surface structure and the temperature, may affect the transformation. Under our experimental conditions, the anatase in the sample $TiO_2(A)$ cannot completely transform to rutile.

As rutile is a highly stable crystal modification, Li and La promoters do not change its stability. In the following sections, discussion concerning changes in the sample, especially the phase transformation, is restricted to $TiO_2(A)$ and its promoted samples alone.

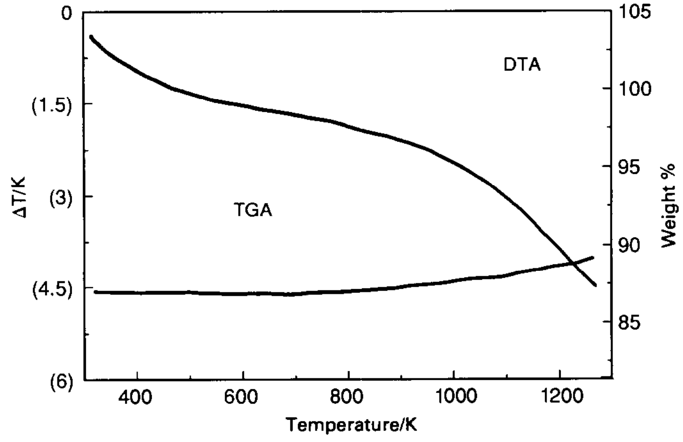

Fig. 3. DTA–TGA curves of $TiO_2(A)$.

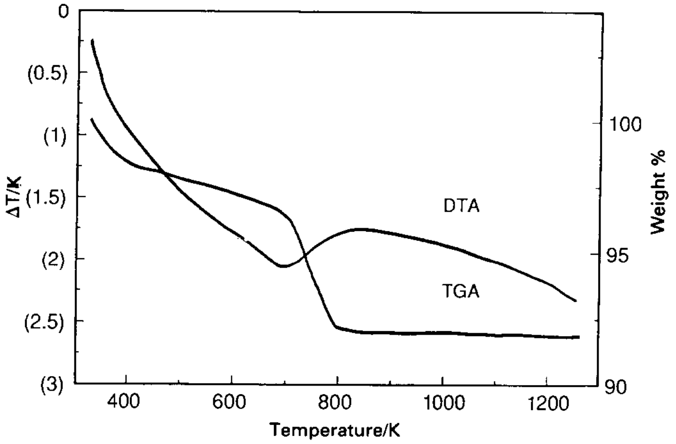

Fig. 4. DTA-TGA curves of La/TiO_2(A).

La/TiO_2

DTA-TGA curves for La/TiO_2(A) are shown in Fig. 4. The TGA curve shows a step-down curve with increasing temperature. The shape of the curve is similar to that for $La(NO_3)_3 \cdot nH_2O$ but with fewer variations because the amount of $La(NO_3)_3$ is small in La/TiO_2(A). The weight loss before 373 K is caused by dehydration from $La(NO_3)_3 \cdot nH_2O$. The weight loss from 683 to 783 K possibly coincides with the decomposition of $La(NO_3)_3$ to $LaONO_3 \cdot La_2O_3$ and further to La_2O_3

$$3La(NO_3)_3 \rightarrow LaONO_3 \cdot La_2O_3 + 4N_2O_5 \qquad (1)$$

$$2LaONO_3 \cdot La_2O_3 \rightarrow 3La_2O_3 + N_2O_5 \qquad (2)$$

La_2O_3 is stable up to 1273 K. The DTA curve shows two broad endothermic curves, one with a minimum at 693 K, another from after 1013 K with baseline drift but no minimum up to 1273 K. The first coincides with the decomposition of $La(NO_3)_3$ to $LaONO_3 \cdot La_2O_3$ as indicated in the TGA curve. The second appears to be responsible for the transformation of anatase to rutile. But the transformation remains incomplete at 1273 K, as observed in TiO_2(A) alone. The second peak (the minimum is not observed) is not large which suggests that an La promoter has a limited effect on the phase transformation.

After calcination at 1123 K, La/TiO_2(A) was analyzed using XRD as shown in Fig. 1E. La/TiO_2(A) shows both anatase and rutile in the sample, with some changes in the amounts compared with TiO_2(A) alone before calcination but with minor differences as compared with TiO_2(A) alone after calcination. This indicates that an La promoter has little effect on the transformation of anatase to rutile. Trace amounts of $La_2O_3 \cdot 2TiO_2$ and $La_{0.66}TiO_{2.993}$ crystals appear in the XRD pattern which result from the

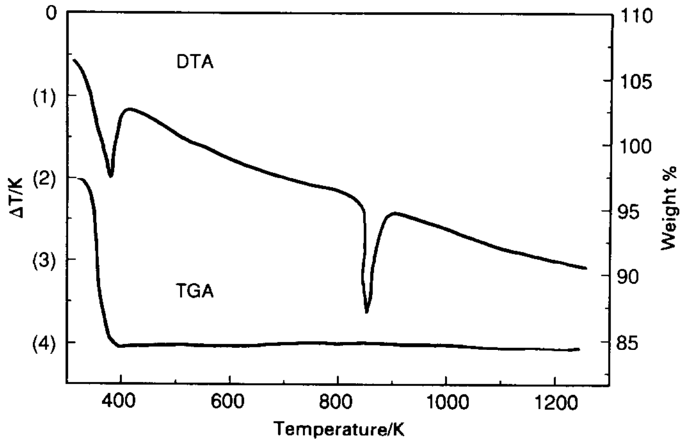

Fig. 5. DTA-TGA curves of Li/TiO_2(A).

interaction between $La(NO_3)_3$ and TiO_2. $La_2O_3 \cdot 2TiO_2$ and $La_{0.66}TiO_{2.993}$ have been reported [11] to exist mostly on the surface of the particles and could inhibit the further tarnsformation of anatase to rutile; this may be the reason why an La promoter has little effect on the transformation of anatase to rutile. The formation and the stability of $La_2O_3 \cdot 2TiO_2$ and $La_{0.60}TiO_{2.993}$ may mean that an La promoter could be used as a structure promoter in TiO_2 catalysts and greatly increase the life time of a catalyst at high temperature [4].

La_2O_3 is not detected in the XRD pattern because of its present in low amounts. For the same reason, the formation of $La_2O_3 \cdot 2TiO_2$ and $La_{0.66}TiO_{2.993}$ cannot be recognized in the DTA-TGA curves, they can, however, be recognized in the XRD pattern, possibly due to their connection to TiO_x. Therefore a combination of DTA, TGA and XRD may reveal more information about the process of catalyst formation. Both the DTA and XRD results for La/TiO_2(A) indicate that the transformation of anatase to rutile is not completed up to 1273 K.

Li/TiO₂

The DTA-TGA curves of Li/TiO_2(A) are shown in Fig. 5. The DTA curve shows two distinct endothermic peaks at 383 and 853 K. At 383 K, the TGA curve exhibits a big mass loss and the ratio of the mass loss suggests that it is the dehydration of $Li_2SO_4 \cdot H_2O$. At 853 K, the DTA curve shows a distinct endothermic peak but the TGA curve shows no considerable mass loss. This endothermic peak is caused by the transformation of anatase to rutile. This was demonstrated using a sample at this temperature for an XRD analysis. It was found that all the anatase had transformed to rutile after 853 K. Because the endothermic peak is sharp and at a much lower tmeperature, it is clear that the transformation of anatase to rutile for Li/TiO_2(A) is faster than that for TiO_2(A) alone, which has a broad curve and a high transformation temperature as shown in Fig. 3. This implies that an Li promoter considerably changes the characteristics of TiO_2(A).

After calcination at 1123 K, Li/TiO_2(A) was analyzed using XRD as shown in Fig. 1F. The pattern shows rutile with traces of Li_2TiO_3 and $Li_2SO_4 \cdot H_2O$. No anatase or other Li–Ti compounds were detectable. The acceleration of an Li promoter on the transformation of anatase to rutile appears significant, which may suggest that there has been a change in the electronic configuration.

Electronic paramagnetic resonance (EPR) is a powerful tool with which to study the change in electronic configuration. Dynamic EPR was performed at low temperature (from 295 to 110 K) to study TiO_2, Li/TiO_2 and La/TiO_2 after they were calcined at 1123 K [12]. TiO_2 shows F-electrons (localized free electrons) and Ti^{3+} ion signals, but Li/TiO_2 exhibits a great loss of surface F-electrons compared with TiO_2 alone. As the substitution of low valence ions for lattice high valence ions in an n-type semiconductor may result in the loss of free electrons, the discovery of the F-electron loss in Li/TiO_2 may be due to the substitution of Li^+ ions for lattice Ti^{4+} ions in the n-type semiconductor TiO_2. La/TiO_2 shows a different behavior to Li/TiO_2, but is similar to TiO_2 alone. The reason is that the La^{3+} ions are too large to substitute for Ti^{4+} ions. The radii of Li^+ ions and Ti^{4+} ions are almost the same (67 pm; 1 pm $= 10^{-12}$ m) [13]; the radius of La^{3+} ions (107 pm) is much larger than that of Ti^{4+} ions. The substitution of Li^+ ions for lattice Ti^{4+} ions is easier than that of La^{3+} ions. Therefore Li/TiO_2 shows a very different behavior to that of La/TiO_2 because of changes in electronic configuration after the lattice substitution. This difference would certainly result in the different catalytic behavior of the two samples, as shown below in the discussion of catalytic reactivity. The transformation acceleration and the lower transformation temperature of anatase to rutile at 853 K possibly result from the lattice substitution.

La/Li/TiO_2

The DTA–TGA curves of Li/La/TiO_2 are shown in Fig. 6. There are endothermic peaks at 313, 380, 683 and 853 K in the DTA curve, accompanied by mass losses at 313, 380 and 683 K, as shown in the TGA curve. As previously discussed, the endothermic peaks and mass loss curves at 313 and 380 K are due to dehydration and the lattice dehydration from $Li_2SO_4 . H_2O$ and $La(NO_3)_3 \cdot nH_2O$. The peak at 683 K is caused by the different stages of the decomposition of $La(NO_3)_3$ as shown in eqns. (1) and (2). The endothermic peak at 853 K, though showing no considerable mass loss, similar to that of Li/TiO_2(A), coincides with the transformation of anatase to rutile.

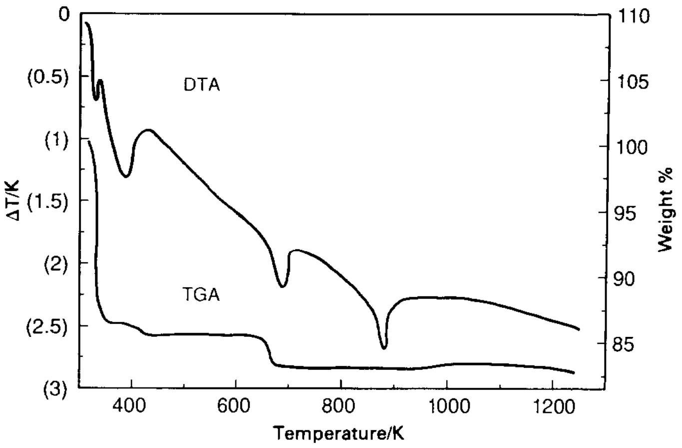

Fig. 6. DTA-TGA curves of La/Li/TiO_2(A).

After calcination at 1123 K, La/Li/TiO_2 was analyzed by XRD, as shown in Fig. 1G. La/Li/TiO_2 shows rutile and traces of Li_2TiO_3, $La_2O_3 \cdot 2TiO_2$ and $La_{0.66} \cdot TiO_{2.993}$ in the XRD pattern. No anatase or other La-Li-Ti compounds are detected. This implies that Li^+ ions can accelerate the transformation of anatase to rutile despite the presence of La^{3+} ions in the La-Li-TiO_2 system.

Catalytic activity

The catalytic reactivity of TiO_2-based catalysts for the POCM are listed in Table 1. The products were mainly C_2H_4, C_2H_6, CO_2 and H_2O. CO and hydrocarbons larger than C_3H_8 were not detected under our test conditions.

TABLE 1

Catalytic properties of TiO_2-based catalysts for partial oxidation coupling of methane (%)

Catalyst	Conv. CH_4	S_{C2}	Y_{C2}	$S_{C_2H_4}$	$Y_{C_2H_4}$
TiO_2(A)	8.0	0.0	0.0	0.0	0.0
TiO_2(R)	6.3	13.8	0.88	7.5	0.45
La/TiO_2(A)	13.8	0.3	0.05	0.1	0.01
La/TiO_2(R)	14.9	20.1	2.8	12.7	1.8
Li/TiO_2(A)	10.9	83.7	9.1	61.6	6.7
Li/TiO_2(R)	13.5	75.3	10.2	58.4	7.9
Li/La/TiO_2(A)	15.0	76.7	11.5	59.0	8.8
Li/La/TiO_2(R)	12.2	81.6	10.0	62.2	7.6

Key: S, selectivity. Y, yield; C2 is $C_2H_4 + C_2H_6$. Li, 10 wt.%; La, 4 wt.%. Temperature, 1073 K. $CH_4:O_2:N_2$ is 3:1:1. GHSV = 1700 h^{-1}. Catalyst charge, 0.5 g.

Catalysts without an Li promoter were used to compare the coupling activity between anatase and rutile. As can be seen from the table, TiO_2(A) and La/TiO_2(A) are inactive or show low activity for coupling; TiO_2(R) and La/TiO_2(R) show a significant improvement. The preference of the rutile precursor for coupling over the anatase precursor is obvious. This phenomenon was also observed on Mn-promoted TiO_2 [4]. The conversion of CH_4 and the selectivity to C2 hydrocarbons for Mn/TiO_2(R) were 17.7% and 23.0%, respectively, while those for Mn/TiO_2(A) were 16.6% and 8.9%, respectively. It appears that La and Mn promoters can improve the coupling activities of TiO_2 to a small extent for both the selectivities and the conversion, and that the rutile precursor shows a small effect on the conversion of CH_4 but a considerable effect on the selectivities to C2 hydrocarbons as compared with the anatase precursor.

Therefore it is important when choosing a catalyst with good selectivity to C2 hydrocarbons to eliminate the anatase during the preparation. An Li promoter shows a good ability to accelerate the transformation of anatase to rutile as discussed in the previous sections. It could be a potential promoter for POCM catalysts. In fact, an Li promoter shows a dramatic improvement in the selectivity to C2 hydrocarbons, as shown in Table 1. The selectivities to C2 hydrocarbons improved from about 20% for TiO_2(R) or La/TiO_2(R) to above 75% for Li/TiO_2 or Li/La/TiO_2. Li/TiO_2(A) or Li/TiO_2(R) and La/Li/TiO_2(A) or La/Li/TiO_2(R) show similar catalytic reactivity because the transformation of anatase to rutile leads to a similar structure after calcination.

The dramatic improvement in the selectivities for an Li-promoted TiO_2 could not be explained entirely by the effect of transformation of anatase to rutile. The improvement is thought to be caused by some new catalytically active centers related to the Li^+ ions in the catalysts. Lunsford [14] suggested an Li^+-ion-related center $[Li^+O^-]$ as a catalytically active center on Li/MgO. But O^- centers are not stable on Li/TiO_2 according to the results of oxygen chemisorption, investigated using the dynamic EPR technique [12]. It was found that the capability of O_2 adsorption and O_2^- formation decrease after the substitution of Li^+ ions for lattice Ti^{4+} ions. The amount of surface O_2 and O_2^- is not responsible for the active reactivity in the POCM because the least active TiO_2 had the most O_2 and O_2^-, and the most active Li/TiO_2 had the least O_2 and O_2^-. It is suggested that the lattice oxygen O^{2-} close to the low-coordinated Ti^{4+}, formed through the substitution of Li^+ ions for lattice Ti^{4+} ions, may be the active center. In the presence of an Li promoter, the following process was observed at low temperature [12]

$$O_2^- + Ti^{4+} \rightarrow O_2^- \cdot Ti^{4+} \rightarrow [O_2 \cdot Ti^{3+}] \qquad (3)$$

On admission of O_2, low coordinated Ti^{4+} reacts with O_2^- to form a coordination compound $[O_2 \cdot Ti^{3+}]$ where Ti^{4+} and Ti^{3+} are low coordinated and there are spaces for O_2 or O_2^- to coordinate with them. This means that low coordinated Ti^{4+} or Ti^{3+} can trap O_2^- or O_2, and the trap in turn lowers the oxidative ability of O_2^- or O_2. Because TiO_2 with the largest amount of O_2^- or O_2 shows the largest deep oxidation selectivity when comparing the catalytic reactivity of TiO_2, La/TiO_2 and Li/TiO_2, O_2^- or O_2 is assumed to be responsible for deep oxidation on TiO_2 catalysts. As an Li promoter greatly decreases the amount of surface O_2^- or O_2 and traps some O_2^- or O_2, an Li-promoted TiO_2 would show less deep oxidative selectivity. The lowering of deep oxidation selectivity means an increase in C2 hydrocarbons selectivity. It is suggested that these are the reasons why an Li promoter increases the C2 hydrocarbon selectivity dramatically. Therefore the use of an Li promoter in the preparation of TiO_2 catalysts is important to achieve a good catalyst with high selectivity to C2 hydrocarbons.

CONCLUSIONS

In this study, TiO_2-based catalysts were prepared from two TiO_2 precursors, rutile and a mixture of anatase and rutile but rich in anatase, with La and Li promoters. Thermal analysis and X-ray diffraction techniques were used to investigate the process of catalyst preparation and their results were compared with the results from the dynamic EPR study. Catalytic activities were compared among these catalysts and the effect of promoters on the catalytic activities was discussed. From this investigation, the following conclusions may be drawn.

(i) Under our experiment conditions, the anatase in the sample of TiO_2(A) could not completely transform to rutile, even after being calcined at 1273 K for 3.5 h.

(ii) An La promoter has little effect on the transformation.

(iii) An Li promoter accelerates the transformation and decreases the transformation temperature from about 1000 to 853 K. The effect of an Li promoter is thought to be due to the substitution of Li^+ ions for lattice Ti^{4+} ions, as shown in the results of the EPR investigation.

(iv) Rutile as a precursor shows a preference to coupling activity over anatase. An La promoter improves the activity slightly.

(v) An Li promoter dramatically improves the selectivity to C2 hydrocarbons. It is suggested that some new forms of active centers are produced due to the substitution of Li^+ ions for lattice Ti^{4+}.

(vi) Using an Li promoter on TiO_2 catalysts is important for achieving a good catalyst with high selectivity to C2 hydrocarbons.

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