The effects of yttrium on the hydrogenation performance and surface properties of a ruthenium-supported catalyst

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Abstract: The effects of yttrium on the hydrogenation performance and surface properties of a Ru/sepiolite catalyst were studied. With CO_2 methanation and CS_2 poisoning as the testing reactons, TPR, TPD, XRD and CO chemisorption as the characterizations, the results showed that the presence of yttrium can increase the hydrogenation activity and anti-poisoning capacity of the Ru/sepiolite catalyst, which is due to a change of surface properties of the Ru/sepiolite. In the process of the catalytic reaction, the adjusting behavior of yttrium for the Ru/sepiolite catalyst aids in increasing the catalytic activity and anti-poisoning capacity of the catalyst.

Keywords: yttrium, ruthenium catalyst, sepiolite, hydrogenation.

INTRODUCTION

Over last few years, rare earths (RE) have attracted great attention because of their importance in a wide range of applications. As excellent promoters, RE have shown their usability for hydrogenation,[1] petroleum reforming,[2] purification of exhaust gas [3] and water gas shift,[4] *etc*. processes. However, due to the complexity of the RE-promoting mechanism, there are some on-going debates. Some researchers have claimed that the main role of RE in catalytic reactions is *via* an electronic effect, while some others have shown that a steric effect of the RE can sometimes dominate the catalytic process. Actually, the range of the investigations is still quite limited; the research has concentrated on either lanthanum or cerium.[5,6] Compared to these two RE, the research concerning other RE, such as yttrium *etc.*, is almost completely deficient, though their promotion behavior is also excellent.

In present study, the role of yttrium on the catalytic process was investigated. With CO_2 methanation and CS_2 poisoning as the testing reactions, TPR, TPD, XRD and CO chemisorption as the characterizations, the specific effect of yttrium on the hydrogenation performance and surface properties of a Ru/sepiolite catalyst

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was shown. One of main purposes was to obtain some information, especially intrinsic information, on the role of RE in the catalytic process.

EXPERIMENTAL

Catalysts preparation

Using 'incipient wetness' impregnation, Ru-supported catalysts were prepared. Sepiolite (Leping, China), which does not activate carbon dioxide hydrogenation, was impregnated first with a $RuCl_3$ solution, followed by 2 h drying (383 K) and 3 h calcination (653 K). For the preparation of the Ru-Y/sepiolite catalyst, as for the Ru/sepiolite, Sepiolite was put first into an $Y(NO_3)_3$ solution, followed by impregnation with a $RuCl_3$ solution. In both catalysts, the loading of ruthenium was 1.0 wt. % (based on the support), and yttrium, 1.0 wt. %.

Catalytic activity measurement

The methanation of carbon dioxide was performed in a continuous micro-reactor. The catalyst sample (200 mg) was reduced in situ first in H_2 (60 ml/min) at 653 K for 3 h, followed by the introduction of $CO_2 - CH_4$ mixed gas (volume ratio 1:4) into the reactor under the operation conditions of 2.0×10^5 Pa operation pressure and 12000 h^{-1} of GHSV. The final products were analyzed by on-line gas chromatography using a TCD detector and a TDX-01 column.

Carbon monoxide chemisorption

CO chemisorption is an efficient means for the determination of the metal surface area of a catalyst. Following a literature procedure,[7] saturation adsorption of carbon monoxide was performed, and the active surface area of the catalyst was calculated by:

$$A_{Ru} = \frac{V_0 N A_m}{22.4W \times 10^8}$$

where V_0 is the total amount of CO absorbed under standard conditions, A_m, the effective cross section of a CO molecule (13×10^{-16} cm^2), and N, the Avogadro constant (6.023×10^{23}).

Characterization

Temperature-programmed desorption (TPD). Under H_2 gas, catalyst (400 mg) was heated from ambient temperature to 693 K at a rate of 10 K/min and this temperature was maintained for 1 h. When the system had cooled down to room temperature, N_2 gas (40 ml/min) was used to remove the H_2 in the gas-phase. Subsequently, the desorption of the absorbed H_2 was performed at a heating rate of 10 K/min the desorption being monitored by on-line chromatography.

Temperature-programmed reduction (TPR). The catalyst sample (400 mg) was first heated to 653 K in N_2 (40 ml/min) to remove possible impurities contained in the sample. After cooling to room temperature under N_2, a gas mixture consisting of H_2 (10 % by volume) – N_2 (90 % by volume) was introduced into the system. At a heating rate of 10 K/min. the change of the hydrogenation concentration in the mixture gas was recorded.

Catalyst poisoning

With the hydrogenation of benzene containing CS_2 ($V_{Ben} / V_{CS_2} = 100/1$) as the test reaction, the poisoning of the catalyst was determined. The catalyst (200 mg) was reduced in situ first in H_2 (80 ml/min) at 673 K for 2 h, followed by iterative injection of 1 μL of the benzene–CS_2 mixture. The change of the catalyst activity was determined by on-line gas chromatography. The anti-poisoning capacity of catalyst was calculated as follows:[8,9]

$$SR = \frac{2C \sum V}{W_{cat}}$$

where SR is the sulfur-resistance of the catalyst, C, the concentration of CS_2, ΣV, the total injection volume, and W_{cat}, the mass of catalyst used. The active sites (Na) and Ru dispersity ($D\%$) of the catalyst were calculated as follows:[8,9]

$$Na = \frac{4C \times \sum V}{3W} \times 10^{19};$$

$$D\% = \frac{Na}{N_{Ru}} \times 100\%$$

Where N_{Ru} is the total number of Ru contained in 1 g of catalyst.

RESULTS AND DISCUSSION

Effect of yttrium on the hydrogenation activity of ruthenium catalysts

The effect of yttrium on the activity of the Ru catalyst for carbon dioxide hydrogenation is shown in Table I. In comparison to Ru/sepiolite, the Ru-Y/sepiolite catalyst presents higher CO_2 conversion under comparable condition. This indicates that yttrium can play an important role by aiding the increase of the catalytic activity of Ru/sepiolite. It is well known that the catalytic activity of a catalyst, to a great extent, can be related to its surface properties. As is apparent from Table I, the presence of yttrium in the Ru/sepiolite catalyst obviously increases the number of active sites in this catalyst and improves the dispersion of ruthenium over the support. Thus, logically, the increase in CO_2 conversion due to the presence of yttrium can be related to the change of surface properties of this catalyst.

TABLE I. Effect of yttrium on the activity and surface properties of a Ru/sepiolite catalyst

Catalyst	Conversion of carbon dioxide				Active surface area/m^2 g^{-1}	Ru dispersion/%	Number of active sites
	633 K	653 K	673 K	693 K			
Ru/sepiolite	8.1	10.5	12.2	16.4	2.23	42.0	2.50×10^{19}
Ru-Y/sepiolite	21.7	25.1	28.1	32.4	3.07	63.2	3.76×10^{19}

To further investigate the probable reason for yttrium affecting the catalytic performance, XRD analysis was conducted. As shown in Fig. 1 and Table II, in comparison to that of the Ru/sepiolite, the XRD profile of the Ru-Y/sepiolite catalyst shows not only diffraction peaks of Ru_2O_3 and $Ba_4Ru_4O_3$, but also diffraction peaks of other species, such as RuO_2 and $CaYAlO_4$, *etc*. The presence of $Ba_4Ru_4O_3$ may be the result of the interaction between ruthenium and the support sepiolite. Also it can be seen that the magnitude of the $Ba_4Ru_4O_3$ peak in the diffractogram of Ru-Y/sepolite is actually weaker than that in the diffractogram of the Ru/sepiolite catalyst. This indicates that the existence of yttrium on the surface of the support decreases the interaction between the active metal ruthenium and the support, thereby presenting a convenient way of increasing the catalytic activity.
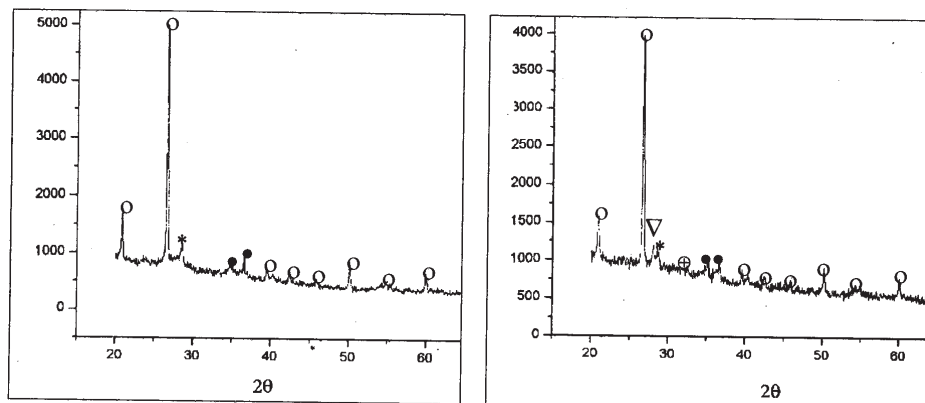
Fig. 1. XRD profiles of Ru/sepiolite (left) and Ru-Y/sepiolite (right) catalysts: ($\bigcirc$) Sepiolite; (✱) $Ba_4Ru_4O_3$; ($\triangledown$) RuO_2; (●) Ru_2O_3; (⊗) $CaYAlO_4$.

TABLE II. The intensity of diffraction peaks of Ru/sepiolite and Ru-Y/sepiolite

Catalyst	Relative intensity ratio to the main peak of sepiolite (I/I_0)			
	Ru_2O_3	RuO_2	$Ba_4Ru_4O_3$	$CaYAlO_4$
Ru/sepiolite	0.15	0	0.21	0
Ru-Y/sepiolite	0.19	0.22	0.19	0.18

Effect of yttrium on the selectivity of methanation

It is well known that CO_2 hydrogenation can produce two main products, that is methane and carbon monoxide. The effect of yttrium on the yields of both products is shown in Fig. 2. At 673K, the ratio of the yields of CH_4 to CO with the Ru/sepiolite catalyst was 0.75, whereas the ratio increased to 1.54 with the Ru-Y/sepiolite catalyst. The presence of yttrium in Ru/sepiolite obviously results in the preferential increase in the yield of methane, compared to the increase in the yield of CO. As has already been shown,[10] CO_2 hydrogenation actually involves many dynamic steps, from the original formation of the intermediate, formyl, to the final production of the hydrogenation products. The final ratio of methane to CO in the products depends intrinsically on the hydrogenation level; a higher level of hydrogenation favors the formation of methane. Conversely, a lower degree of hydrogenation results in the production of more CO. Thus, the observation that the yield of methane increases due to the presence of yttrium indicates that yttrium plays a role in promoting the further hydrogenation of CO_2. Obviously, this can be related to the effect of yttrium on the surface of the ruthenium catalyst. The transition of CO_2 to methane or CO is a reduction reaction, requiring the input of electrons from outside. As mentioned before, REs can often act as good promoters in catalysis due to their unique f-electron structure. During the catalytic reaction, this unique, electron rich structure can aid in transferring electrons to the reaction, thereby improving the possibility of further reaction. Therefore, the increase in methane yield due to the presence of yttrium can be associated with the electron structure of the RE.
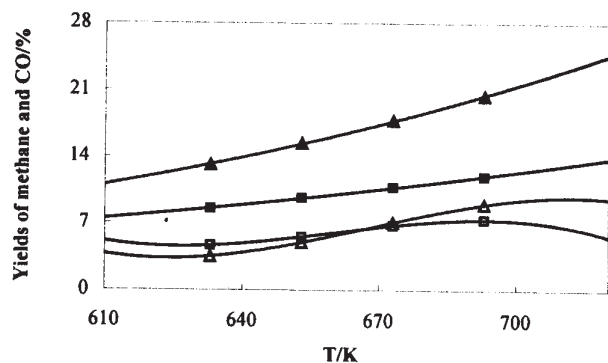
Fig. 2. Effect of yttrium on the yields of methane and CO during CO_2 hydrogenation; ($\triangle$) methanol yield for Ru/sepiolite; ($\square$) CO yield for Ru/sepiolite; ($\blacksquare$) methanol yield for Ru-Y/sepiolite; ($\blacktriangle$) CO yield for Ru-Y/sepiolite.

TPD and TPR

The H_2-TPD and TPR curves of the Ru/sepiolite and Ru-Y/sepiolite catalysts are shown in Figs. 3 and 4, respectively. As can be seen, both profiles of the Ru-Y/sepiolite show obvious differences from those of Ru/sepiolite. The original three TPD peaks and the one TPR peak change into four and two corresponding peaks, respectively. Obviously, the presence of yttrium also affects the adsorption and reduction of the Ru/sepiolite catalyst, in addition to the effects decribed above. It can be assumed that the appearance of a new peak in both profiles may result from the interaction between yttrium and ruthenium. It can also be seen that the positions of the corresponding peaks in the TPD profile are at somewhat lower temperatures for Ru-Y/sepiolite than for Ru/sepiolite. It is well known that the position of a TPD peak corresponds to the adsorption strength. The higher the temperature is, the stronger the adsorption would be, and vice versa.[11] Therefore, the observed decrease of the H_2 desorption temperature due to the presence of yttrium indicates that yttrium weakens the adsorption bond. During a catalytic reaction, the decrease in the strength of the adsorption bond is beneficial for the migration of the absorbed/activated specimens,[12] hence the catalytic process is promoted.

Poisoning of catalysts

Sulfur poisoning is one of the most important factors in decreasing the catalytic activity of a catalyst. In the course of a catalytic reaction, the catalyst can be poisoned even if the reactive system contains only a small amount of sulfur. The effect of yttrium on the poisoning of the Ru/sepiolite catalyst is presented in Fig. 5, from which it can be seen that larger amount of CS_2 were required to completely deactivate the Ru-Y/sepiolite than was the case with the Ru/sepiolite catalyst. This indicates that the presence of yttrium in the Ru/sepiolite catalyst increased the tolerance of the catalyst to poisoning. It is known[13] that the mechanism of CS_2 poisoning lies in the fact that the C–S bond is much weaker than the C–C bond and, hence, it can dissociate and form H_2S or sulfides in the presence of hydrogen. During the catalytic reaction, the released H_2S or sulfides can easily combine with the
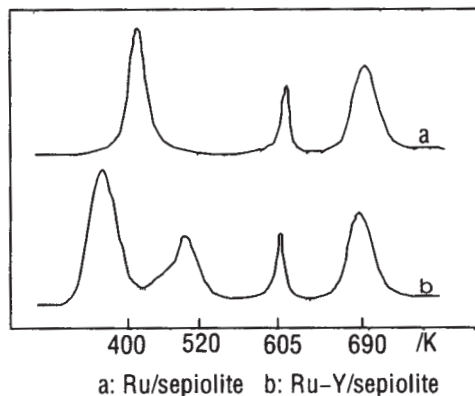
a: Ru/sepiolite   b: Ru–Y/sepiolite

Fig. 3. TPD curves of the Ru catalysts.

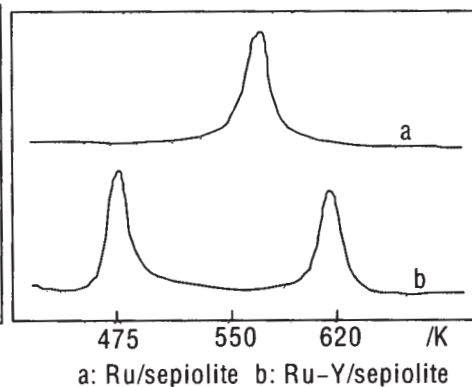a: Ru/sepiolite   b: Ru–Y/sepiolite

Fig. 4. TPR curves of the Ru catalysts.

active metal, *i.e.,* ruthenium, and form non-active Ru–S bond, thereby the catalyst is deactivated. The increased tolerance of the Ru/sepiolite catalyst in the presence of yttrium can be related to: 1) an accumulation of negative charges on the surface of ruthenium due to the presence of Y^{3+} increases the difficulty of absorbing nucleophilic S^{2-} ions; 2) the reactive Y^{3+} probably combines with the S^{2-} first; 3) Y^{3+} plays a minor role in the catalyst system, and therefore retards the poisoning.[14]
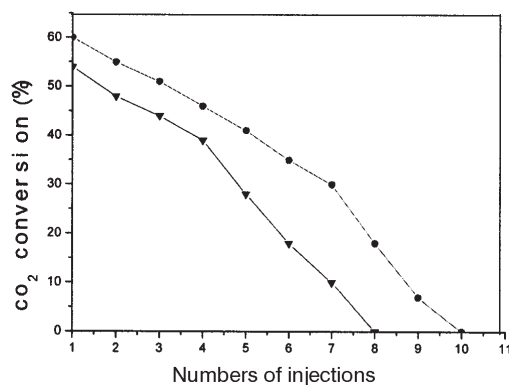

Fig. 5. Poisoning curves of the Ru catalysts: (▼) Ru/sepiolite; (●) Ru-Y/sepiolite.

It can also be seen from Fig. 5, that the poisoning curves of both the Ru/sepiolite and Ru-Y/sepiolite catalysts consist of two lines of differing slopes. This indicates that the process of poisoning the catalysts proceeds at two different rates, or in other words, there are probably two different active centers in the catalyst[15] (entitled α- and β-centers). During the poisoning, the α-centers are poisoned first, followed by the β-centers, with the poisoning of the α-centers proceeding at a slower rate than the poisoning of the β-center. This indicates that compared to the β-centers, the α-centers are stronger poisoning sites for sulfur, but, however, they contribute less to the catalytic activity for hydrogenation.

CONCLUSION

This study showed that the catalytic activity of a Ru/sepiolite catalyst can be efficiently improved by the addition of an appropriate amount of yttrium. The addition of yttrium can also affect the selectivity for the formation of methane during CO_2 hydrogenation. The results also revealed that yttrium changes the surface properties of the Ru/sepiolite catalyst. Thus, the addition of yttrium increases the active surface area and the dispersion of ruthenium, and decreases the interaction between ruthenium and the support. In addition, the research indicates that yttrium can also affect the adsorption and reduction properties of a Ru/sepiolite catalyst.

И З В О Д

УТИЦАЈ ИТРИЈУМА НА СПОСОБНОСТ ХИДРОГЕНОВАЊА И ПОВРШИНСКЕ ОСОБИНЕ РУТЕНИЈУМА НА НОСАЧУ КАО КАТАЛИЗАТОРУ

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Проучавани су утицаји итријума на способност хидрогеновања и површинске особине Ru/сепиолит катализатора. Посматране су реакције метанације CO_2 и тровања катализатора са CS_2 користећи TPR, TPD, XRD и CO хемисорпцију. Резултати су показали да присуство итријума повећава активност за хидрогеновање и отпорност на тровање Ru/сепиолит катализатора, а што је последица промене површинских особина Ru/сепиолит катализатора.

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