Novel Activity of TiO_2 for Catalytic Conversion of CO and H_2O to Alcohols in the Presence of K_2CO_3

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In the presence of K_2CO_3, TiO_2 shows good catalytic activity and stability for the alcohols synthesis from CO and H_2O. CO conversion of 7.6% and the STY of MeOH (about 24 mg g^{-1} h^{-1}) and EtOH (about 8 mg g^{-1} h^{-1}) are obtained under reaction conditions of $T = 573$ K, $P = 0.5$ MPa, CO flow rate of 30 ml min^{-1} and $CO/H_2O = 3/2$ during the period of 12 h to 44 h time-on-stream.

Methanol is one of the important feedstocks in chemical industries. For the last two decades most of the research work has concentrated on the production of alcohols from CO and H_2 and a large number of findings have been reported in the literature.[1–4] In those processes a large amount of H_2 ($H_2/CO = 2$) is required.

An alternative process is that CO reacts with H_2O to produce alcohols. It is of particular advantage that no hydrogen is required and CO can be provided as a by-product from the steel industry, the partial oxidation of coal and typical coal gasification processes. In 1984, Klinger et al.[5] first reported the reaction:

$$3CO+2H_2O = CH_3OH + 2CO_2 \tag{1}$$

They supposed that lead oxide combined with an alkali metal formate catalyzed the reaction. However, the catalyst deactivated slowly with reaction progressing because of the reduction of PbO in the presence of CO. How to keep the catalyst active center not to be reduced in the presence of CO is the key point for the reaction. In our experiment, it is found that TiO_2 possesses such feature in the presence of CO for the reaction and it shows good catalytic performance. Here, we report the interesting results.

TiO_2 was prepared by decomposition of titanium hydroxide. The details of this process were as follows: $TiCl_4$ was dissolved in distilled water, and an aqueous ammonia was added until the PH value attained 4. The resultant precipitate was washed until no Cl^- ions were detected. Subsequently it was treated with *n*-butanol azeotropic distillation method to obtain a gel powder, which was further calcined at 773 K in air for 4 h. HCOOK, K_2CO_3, ZnO, Al_2O_3 and PbO were purchased from Beijing Chemical Reagent Plant of China, MgO and ZrO_2 were obtained by decomposition of magnesium carbonate and zirconium hydroxide respectively, in an N_2 stream at 723 K for 2 h.

The reaction of CO and H_2O was carried out in a 60 ml stainless steel reactor. The gas reactants (carbon monoxide mixed with N_2) were saturated with water by bubbling the gas into a reservoir, which was kept at a suitable temperature to obtain the desired water concentration in the reactant flow. The flow rate of CO was 30 ml min^{-1}. A mixture of 3.0 g alkali carbonate (K_2CO_3, Na_2CO_3 or Li_2CO_3) and 2.0 g of catalyst was suspended in 30 ml of solvent. Catalytic decomposition of HCOOK was carried out in the same reactor when the N_2 was supplied instead of CO under the same conditions. An internal standard method was employed to calculate the conversion of CO. Then the feed and effluent gases were analyzed with a thermal conductivity detector using carbon molecular sieve column. The liquid products were collected in a trap cooled by a mixture of ice and water before they were analyzed with a gas chromatograph (Shimadzu GC-8A) equipped with a flame ionization detector using Porapak Q column.

Klinger et al.[5] reported that the reaction mechanism was as follows:

$$CO_3{}^{2-}+2CO+H_2O \rightarrow 2HCO_2{}^{-}+CO_2 \tag{2}$$

$$4HCO_2{}^{-} \xrightarrow{\text{catalyst}} CH_3OH+CO+2CO_3{}^{2-} \tag{3}$$

$HCO_2{}^-$ is an important intermediate. In our experiment, it was found that only under catalyst TiO_2 and alkali carbonate, could alcohols be detected. In other words, without the catalyst or $CO_3{}^{2-}$ no product could be detected. These phenomena clearly suggest that, for CO reacting with H_2O and $CO_3{}^{2-}$ to produce alcohols, first, the intermediate $HCO_2{}^-$ should be formed under proper conditions, at the same time, the catalyst employed should catalyze the intermediate $HCO_2{}^-$ to produce alcohols. K_2CO_3, Na_2CO_3 and Li_2CO_3 all may be converted to the intermediate HCO^{2-} under suitable reaction conditions as eq. 2. As shown in Table 1, for the same catalyst TiO_2, the reaction performance of alkali carbonate increases with their increasing solubility ($K_2CO_3 > Na_2CO_3 > Li_2CO_3$).

Table 1. Relationship between solubility and reaction performance of alkali carbonate over TiO_2

		Li_2CO_3	Na_2CO_3	K_2CO_3
Solubility (wt%)[7]		1.52	6.54	51.35
Conversion of CO (%)		3.2	4.1	8.9
	CO_2	52.1	63.5	111.9
Product distribution	HCHO	tr.	0.88	3.12
(mg g-cat^{-1} h^{-1})	MeOH	2.51	4.49	23.95
	EtOH	0.06	1.53	8.29

Reaction conditions: 573 K; CO flow rate of 30 ml min^{-1}; $CO/H_2O = 3/2$; Solvent-tetraethylenepentamine.

TiO_2, PbO, Al_2O_3 and other oxides were employed to catalyze decomposition of intermediate HCOOK to alcohols. The results are summarized in Table 2. Al_2O_3 is known to have both acidic and basic properties, but does not show any catalytic activity. ZnO, MgO, and ZrO_2 yield more hydrogen and CO with trace amount of alcohols product, suggesting they make the deep reaction which is shown in eq. 4. As reported in many literatures, ZnO and CuO[6] are good catalysts for CO reforming reaction.

Table 2. Catalytic decomposition of HCOOK over various oxides

Catalyst	Products (mmol g^{-1})					
	MeOH	HCHO	EtOH	H_2	CO	CO_2
TiO_2	0.99	0.13	0.28	1.34	1.12	0.87
PbO	1.19	0.15	0.11	1.08	1.25	1.33
SnO_2	0.39	0.03	—	0.09	1.12	0.33
ZrO_2	0.08	0.01	—	1.90	1.39	1.18
MgO	0.03	0.02	—	2.02	3.11	1.17
Al_2O_3	0.01	—	—	0.51	0.14	0.27
ZnO	0.04	—	—	1.24	1.88	0.68

Reaction conditions: 573 K; 15 g HCOOK and 4 g catalyst; dilute gas N_2; TOS = 5 h.

TiO_2 shows good catalytic activity (1.27 mmol/g), similar with that of PbO (1.30 mmol/g).

$$2HCO_2^- \rightarrow H_2 + CO + 2CO_3^{2-} \qquad (4)$$

Subsequently, the catalytic conversion of CO, H_2O and K_2CO_3 to alcohols was examined over TiO_2 in various solvents, such as triethylamine, liquid paraffin and liquid polyamines. Investigation of the effects of the solvents shows that tetraethylenepentamine is an effective solvent. Therefore, another determinant factor affecting the catalytic activity is possibly the alkalescence of the solvent.

As shown in Figure 1, under reaction conditions of $T = 573$ K, $P = 0.5$ MPa, CO flow rate of 30 ml min^{-1} and $CO/H_2O = 3/2$, the stabilities of the PbO and TiO_2 catalysts for the CO reacting with H_2O and K_2CO_3 to produce alcohols are compared. At the first 12 h of time-on-stream (TOS), the two catalysts show similar catalytic activity. The STY of MeOH and EtOH increase from about 20 to about 35 mg g^{-1} h^{-1}, then reach a plateau. From 24 h to 44 h of time-on-stream, CO conversions of the two samples show no significant change besides the value of PbO is somewhat higher than that of TiO_2. It should be emphasized that TiO_2 preserves the stable catalytic activity (STY of MeOH and EtOH are kept about 24 and 8 mg g^{-1} h^{-1}, respectively), while the yield of MeOH over PbO decreases obviously from 24 mg g^{-1} h^{-1} (24 h) to only 10 mg g^{-1} h^{-1} (44 h), accompanied with the increase product of CO_2. It implies that the reaction active center may be TiO_2 or PbO for the two catalysts employed. In the presence of CO, TiO_2 remains to be oxidic state while PbO is readily to be reduced to metallic state.[5]

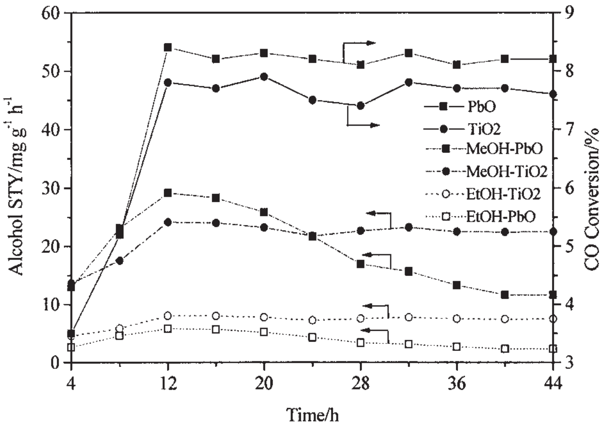

Figure 1. Changes in average production of alcohols as a function of time over TiO_2 and PbO. Reaction conditions: 573 K; 0.5 MPa; CO flow rate of 30 ml min^{-1}; CO/H_2O = 3/2; Solvent: tetraethylenepentamine.

An attempt to conducting further study about the mechanism for the reaction over TiO_2 catalyst is in progress in our laboratory, and the result will be reported later.

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