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Promoting effects of thoria and molybdena on cobalt catalysts in the hydrogenation of CO

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Thoria- or molybdena-promoted Co/silica (alumina) catalysts were prepared by co-impregnation. The catalysts were characterized with temperature programmed reduction and temperature programmed surface reaction techniques and hydrogenation of carbon monoxide. Thoria enhanced not only the activity but also the selectivity of olefins and long-chain hydrocarbons. Molybdena effectively promoted only the activity, but did not alter the product distribution pattern. Thoria and molybdena exhibited a tendency to spread onto and to interact intimately with alumina; the promoting effects on alumina were much less pronounced than on silica.

Keywords: Promoter; thoria; molybdena; cobalt; carbon monoxide; hydrogenation

1. Introduction

In hydrogenation of carbon monoxide, promoters are generally used to enhance the productivity or selectivity with respect to olefins, long-chain hydrocarbons or oxygenated compounds. There has been much interest in effects of added alkali and transition-metal oxides on the catalytic properties of group VIII metals. The addition of potassium to iron increases the selectivity of olefins and long-chain hydrocarbons [1]. Lithium increases the activity and selectivity of methanol for Pd/CeO_2 catalysts [2]. An improved total activity and selectivity of long-chain hydrocarbons is observed with added vanadium, niobium, molybdenum or tungsten oxides to Ru/Al_2O_3 and Rh/SiO_2 catalysts [3–5]. Addition of titanium, lanthanum or cerium improves the activity of methanation for nickel–alumina catalysts [6]. Molybdenum enhances the activity and chromium increases the selectivity of long-chain hydrocarbons [7] for the Ni/SiO_2 catalyst. Thoria effectively promotes the total activity and selectivity of gasoline-range hydrocarbons for nickel [8] and iron [9] catalysts.

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Cobalt is an active metal for hydrogenation of CO. Some promoters are used; alkali [10], alkaline earth [11], copper [12], rhenium or strontium [13] improves the selectivity of C_2-oxygenates. Lanthanum [14] or thorium [15] enhances the activity and selectivity of olefins and long-chain hydrocarbons.

Testing the cobalt boride catalysts, we found that the added thorium or molybdenum effectively promoted the selective hydrogenation of a carbonyl group that was conjugated to the olefinic group in cinnamaldehyde [16]. In order to obtain a simple rule to design catalysts for hydrogenation reactions, we sought to examine the characteristics of promoter effects on carbon monoxide and organic compounds with the carbonyl group. Here we report the promoting effects of thorium and molybdenum on general cobalt catalysts supported on SiO_2 and Al_2O_3 for the hydrogenation of CO (the simplest carbonyl compound).

This paper presents the catalytic results of hydrogenation of CO when a supported cobalt catalyst was promoted with thorium or molybdenum oxide. The results of characterization obtained with temperature programmed reduction (TPR) and temperature programmed surface reaction (TPSR) techniques are discussed in relation to the catalytic performance. The promoters were introduced in appropriate amounts by co-impregnation. The reduction process was followed by TPR. The surface reaction behavior was characterized by TPSR. The initial activity and selectivity were determined using on-line gas chromatographic analysis.

2. Experimental

Catalyst preparation. The promoted cobalt catalysts were prepared by the co-impregnation method with cobalt nitrate, $CO(NO_3)_2 \cdot 6H_2O$ and thorium nitrate, $Th(NO_3)_4 \cdot 5H_2O$ (or ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) dissolved in water, dried in air at 100°C for 6 h and calcined in air at 400°C for 3 h.

Temperature programmed reduction. TPR of the catalysts calcined at 400°C was carried out in a conventional apparatus consisting of a U-shaped quartz reactor attached to a thermal-conductivity detector. The catalyst (40–60 mg) was first pretreated at 500°C for 2 h under a stream of nitrogen, followed by cooling to room temperature. Then the catalyst was reduced up to 800°C at a rate of 10°C/min in a stream of 10% H_2/Ar (20 ml/min). The water produced was trapped with zeolite (3A) and hydrogen consumption was monitored with a thermal-conductivity detector.

Temperature programmed surface reaction. For TPSR of CO, the catalyst sample (30–50 mg) was prereduced under hydrogen as described above for TPD. The reduced catalyst was cooled in hydrogen to room temperature, and then exposed to carbon monoxide for 30 min. After purging with hydrogen for 1 h, the catalyst was subjected to a linearly increased temperature (10°C/min) to 500°C under a stream of hydrogen (10 ml/min). Some carbon monoxide desorbed directly and most reacted with hydrogen to form methane which desorbed and was continuously monitored by a flame-ionization detector.

Hydrogenation of CO. Hydrogenation of CO was performed in a U-shaped pyrex reactor at 100 kPa, 200–250°C and $H_2/CO = 3$. The catalyst was prereduced as described above, reaction was conducted at a large space velocity (3000–6000 h^{-1}) and small conversion ($<10\%$) to minimize the influences of heat and mass transfer. The steady outlet stream was analyzed by gas chromatograph through a column (Porapak Q, 3 mm × 180 cm) attached to a flame ionization detector.

3. Results and discussion

3.1. TEMPERATURE PROGRAMMED REDUCTION

3.1.1. Thorium oxide (thoria) promotion

The TPR profiles of the thoria-promoted Co/support catalysts are presented in figs. 1 and 2. The profile of 10% Co/SiO_2 catalyst in fig. 1 shows that the major consumption of hydrogen occurred at 300 and 360°C. The thoria-promoted Co/SiO_2

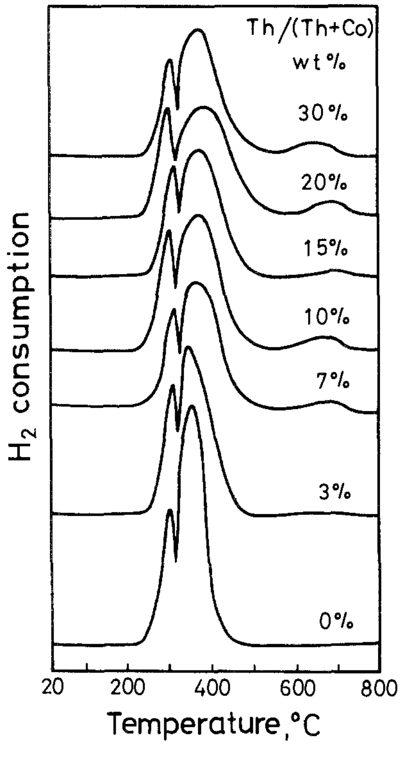

Fig. 1. TPR profiles of thoria-promoted Co/SiO_2 catalysts.

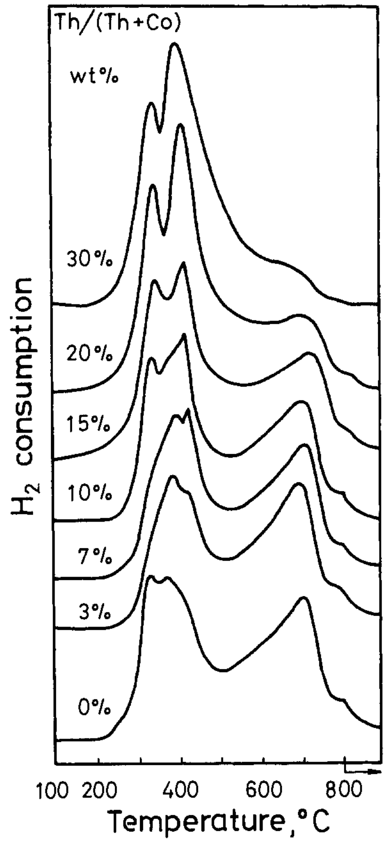

Fig. 2. TPR profiles of thoria-promoted Co/Al_2O_3 catalysts.

catalysts exhibited similar profiles. Thoria was not reduced under these programmed conditions; hence the consumption of hydrogen was due to the reduction of cobalt oxide, Co_3O_4. The ratio of the hydrogen consumption at lower temperature to that at higher temperature was 1/3. That ratio was consistent with the reduction of cobalt oxide in two stages [17,18]; $Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$, $3CoO + 3H_2 \rightarrow 3Co + 3H_2O$. The second peak shifted to higher temperature with the added thoria. This fact indicated that thoria tended to stabilize the cobalt oxide CoO.

The TPR profiles of thoria-promoted Co/Al_2O_3 catalysts exhibited peaks in two groups – one from 300 to 400°C, the other at about 700°C (fig. 2). The consumption between 300 and 400°C is ascribed to reduction of Co_3O_4 and CoO. The two stages of reduction of cobalt oxide on alumina were less clear than on silica. The consumption of hydrogen near 700°C was assigned to the reduction of surface phase of Co^{2+} [18] that might occupy the sites of imperfect spinel structure of alumina on the surface. The consumption of hydrogen from 300 to 400°C increased with the added thoria, but that near 700°C decreased. This behaviour indicated that thoria interacted more strongly with alumina than cobalt oxide and even spread onto the support beneath cobalt oxide. Thus thoria shielded and weakened the interaction between cobalt oxide and the support.

3.1.2. Molybdenum oxide (molybdena) promotion

The TPR profiles of the molybdena-promoted Co/SiO_2 catalysts are presented in fig. 3. The first peak at 300°C was unaltered, but the second peak shifted to higher temperature and became broader. This behaviour indicated that the doped molybdena intimately contacted with cobalt oxide CoO and stabilized it. The consumption of the second peak increased with added molybdena, because of the reduction of cobalt oxide and molybdena. When the added amount exceeded 15%, the profile due to reduction of molybdena protruded.

As shown in the profiles of the molybdena-promoted Co/Al_2O_3 catalysts (fig. 4), the consumption of hydrogen from 300 to 400°C increased with the amount of molybdena doped and that near 700°C decreased significantly. Compared with the profiles of the thoria-promoted catalysts (fig. 2), molybdena seemed to interact more strongly with, and exhibited a greater tendency to spread onto alumina than thoria. Thus molybdena more effectively weakened the interaction between alumina and cobalt oxide. These results are consistent with the phenomena of monolayer adsorption of MoO_3 on alumina proposed by Xie [19].

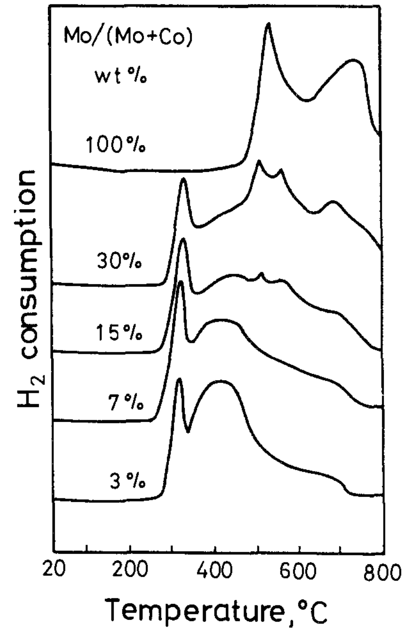

Fig. 3. TPR profiles of molybdena-promoted Co/SiO_2 catalysts. (The Mo loading of MoO_3/SiO_2 is 10 wt%.)

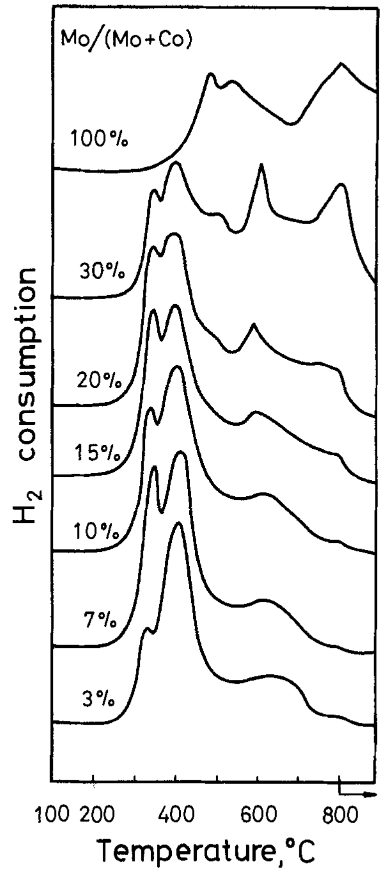

Fig. 4. TPR profiles of molybdena-promoted Co/Al_2O_3 catalysts. (The Mo loading of MoO_3/Al_2O_3 is 10 wt%.)

3.2. TEMPERATURE PROGRAMMED SURFACE REACTION OF CO

3.2.1. Thoria promotion

The hydrogenation of adsorbed CO on the promoted Co/support catalysts was investigated as a function of the added promoter. As most adsorbed CO reacted to form methane during heating in a stream of hydrogen [20], the desorption profiles monitored by FID are nearly profiles of methane.

The TPSR profiles of the thoria-promoted catalysts are shown in figs. 5 and 6. With silica used as support, most methane was formed in a single peak (fig. 5). The temperature of the maximum decreased from 163 to 135°C and the amount of methane increased as the amount of added thoria increased from 0 to 20%. In contrast the peak shifted to higher temperature and less methane was formed for the doped catalyst with 30% of thoria. The main mechanism of the programmed sur-

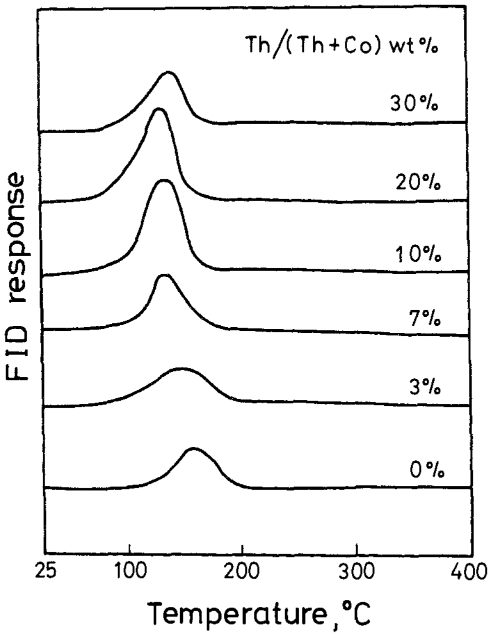

Fig. 5. TPSR profiles of thoria-promoted Co/SiO_2 catalysts.

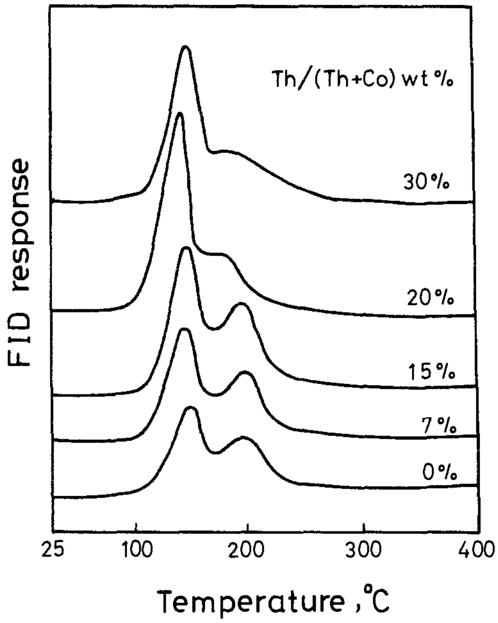

Fig. 6. TPSR profiles of thoria-promoted Co/Al_2O_3 catalysts.

face reaction of CO is dissociation of CO and hydrogenation of surface carbon. Thoria might enhance the dissociation of carbon monoxide and facilitate the formation of methane. When the added amount exceeded 20%, some thoria segregated and shielded the sites of cobalt.

The TPSR profile of 10% Co/Al_2O_3 in fig. 6 shows that methane is formed in two peaks – one at 153°C and the other at 200°C. Under the programmed condition, some adsorbed CO and H on cobalt spilled over to alumina and associated to form a methoxy complex (CH_3O) [20,21]. The methoxy complex dissociated at a higher temperature, and CO from it diffused back and reacted with hydrogen to form methane on cobalt. The first peak was the methane formed from the CO adsorbed on cobalt, and the second one was the methane formed from the methoxy complex adsorbed on alumina [20,21]. The temperature of the first maximum decreased from 150 to 138°C as the amount of added thoria increased from 0 to 20%. Thoria might promote dissociation of CO adsorbed on cobalt, and resulted in the shifting of the first peak to a lower temperature. The second peak did not alter obviously; thoria seemed not to promote the dissociation of the methoxy complex. The amount of methane formed from the methoxy complex at the second peak decreased markedly. As the added amount exceeded 15%, thoria effectively shielded the surface of support so as to impede the spillover of CO and H from cobalt.

3.2.2. *Molybdena promotion*

The TPSR profiles of the molybdena-promoted cobalt/support catalysts are shown in figs. 7 and 8. With silica used as support, methane was formed in a single peak; the maximum shifted from 163 to 146°C and the amount of methane increased as the amount of added molybdena increased from 0 to 10%. The shifting of the maximum is attributed to the promoting effect of molybdena on CO dissociation. When alumina was used as support, the first maximum shifted to a lower temperature and the methane formed increased with the added molybdena. Molybdena was more effective at inhibiting the formation of methane from methoxy complex than thoria (fig. 6). This result also indicates that molybdena exhibited a greater tendency to spread onto alumina and impeded the spillover of CO and H from cobalt.

3.3. HYDROGENATION OF CO

In tables 1–4 we present results of hydrogenation of CO at 210°C, $H_2/CO = 3$ and 100 kPa over the thoria- and molybdena-promoted catalysts. Hydrogenation of CO on the thoria-promoted Co/SiO_2 catalysts (table 1) shows that the activity was enhanced up to four times as large as that of the unpromoted one. Thoria not only promoted the activity but also altered the selectivity pattern. Thoria significantly enhanced the formation of olefins and long-chain hydrocarbons. Furthermore added thoria resulted in increased activation energy.

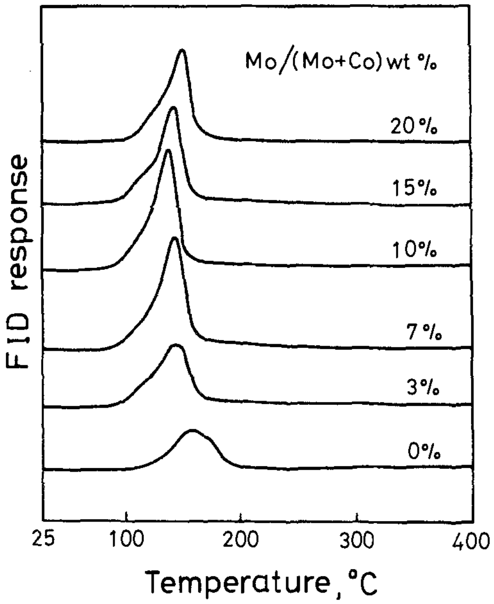

Fig. 7. TPSR profiles of molybdena-promoted Co/SiO_2 catalysts.

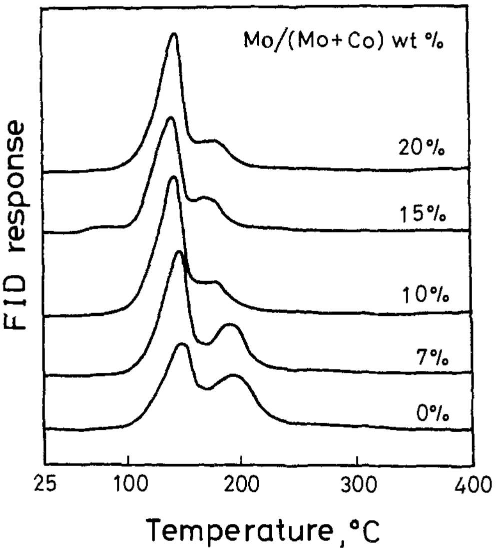

Fig. 8. TPSR profiles of molybdena-promoted Co/Al_2O_3 catalysts.

Table 1
The hydrogenation results at 210°C over the thoria-promoted 10% Co/SiO_2 catalysts

Th/(Th + Co) (wt%)	Reactivity (μmol/(g s))	Selectivity (carbon%)					Olefin/paraffin C_2–C_4	E_a (kJ/mol)
		C_1	C_2	C_3	C_4	C_{5+}		
0	0.66	41.8	8.8	15.7	14.2	19.5	0.25	77.8
3	1.33	34.8	7.0	14.4	15.0	28.9	0.54	87.3
7	1.86	36.6	6.2	13.8	15.6	27.9	0.61	96.6
10	2.20	34.3	6.3	14.2	15.0	30.4	0.60	99.7
15	2.56	30.7	5.6	13.4	15.4	35.0	0.58	81.6
20	2.85	26.5	4.6	12.3	15.2	41.5	0.70	98.1
30	1.36	36.5	5.9	13.2	14.6	29.7	0.46	77.1

The results for the molybdena-promoted Co/SiO_2 catalysts (table 2) show that the activity was also enhanced up to 2.7 times as large as that of the unpromoted one, whereas the addition of molybdena appeared not to affect the selectivity pattern and activation energy. The enhancement of activity by thoria and molybdena was consistent with the shifting of peak maxima to lower temperature in the TPSR profiles. The activity increased and the temperature of peak maximum decreased with the added amount of promoter. However, thoria and molybdena shielded the active sites, and hampered the activity as the added amount exceeded 20% for thoria and 7% for molybdena.

Thoria and molybdena in calcined catalysts existed as ThO_2 and MoO_3. Thoria is not reduced under the prereduction condition. Most molybdena is reduced to Mo on silica, and partially reduced to MoO_2 on alumina before reaction [22].

Sachtler [23], Rieck [24,25], and Chen [26] proposed a side-bond model based on the activation of carbon monoxide by the interaction of promoter ion with the oxygen dipole in CO. The thorium ion Th^{4+} and partially reduced molybdenum ion Mo^{x+} had an affinity for the oxygen atom, so the ions Th^{4+} or Mo^{x+} on the surface of the interface of metal particles provided the sites at which carbon monoxide bonded with its carbon atom to a metal atom and with its oxygen atom to a promo-

Table 2
The hydrogenation results at 210°C over the molybdena-promoted 10% Co/SiO_2 catalysts

Mo/(Mo + Co) (wt%)	Reactivity (μmol/(g s))	Selectivity (carbon%)					Olefin/paraffin C_2–C_4	E_a (kJ/mol)
		C_1	C_2	C_3	C_4	C_{5+}		
0	0.66	41.8	8.8	15.7	14.2	19.5	0.25	77.8
3	1.27	45.4	7.5	14.1	14.3	18.7	0.36	79.6
7	1.79	48.3	8.6	14.5	13.3	15.2	0.33	80.8
10	1.00	35.6	7.2	14.9	16.2	26.2	0.35	87.6
15	1.10	37.6	7.5	15.3	15.9	23.6	0.35	89.2
20	0.76	41.5	6.7	13.9	14.2	23.7	0.32	79.2

Table 3
The hydrogenation results at 210°C over the thoria-promoted 10% Co/Al_2O_3 catalysts

Th/(Th + Co) (wt%)	Reactivity (μmol/(g s))	Selectivity (carbon%)					Olefin/paraffin	E_a (kJ/mol)
		C_1	C_2	C_3	C_4	C_{5+}	C_2–C_4	
0	0.68	30.5	5.2	12.1	15.4	36.7	0.34	84.9
3	0.73	28.5	4.8	12.0	14.7	40.1	0.39	83.4
7	0.87	27.7	5.5	14.1	15.6	37.2	0.34	96.0
10	1.04	23.5	4.2	12.5	15.7	44.1	0.97	97.8
15	1.23	22.2	3.8	12.0	10.6	51.4	1.19	100.4
20	1.84	17.6	3.5	11.4	14.4	53.0	1.05	102.1
30	0.96	19.4	3.4	10.8	13.2	53.2	1.80	112.2

ter ion. This arrangement resulted in a weakening of the C–O bond, and so enhanced dissociation and reaction of CO. Furthermore the enhancement dissociation of CO resulted in enrichment of intermediates of carbene on the surface, which favored the formation of olefins and long-chain hydrocarbons. Molybdena not only promoted the dissociation of CO, but also might facilitate the consecutive hydrogenation of intermediates of carbene. Hence molybdena effectively promoted the activity, but appeared not to alter the product distribution.

The addition of thoria to 10% Co/Al_2O_3 catalyst also significantly promoted the activity up to 2.7 times as large as that of the unpromoted one, and shifted the product distribution to olefins and long-chain hydrocarbons (table 3). This promoting effect on alumina was less significant than that on silica. The addition of molybdena to 10% Co/Al_2O_3 catalyst only slightly promoted the activity (table 4). That effect is attributed to the intimate interaction between molybdena and alumina as aforementioned in TPR and TPSR analyses. The strong interaction between promoter and support weakened the effect of promoter on cobalt.

Our studies on the selective hydrogenation of α, β-unsaturated aldehyde over cobalt boride catalysts showed that thoria and molybdena effectively promote the

Table 4
The hydrogenation results at 210°C over the molybdena-promoted 10% Co/Al_2O_3 catalysts

Mo/(Mo + Co) (wt%)	Reactivity (μmol/(g s))	Selectivity (carbon%)					Olefin/paraffin	E_a (kJ/mol)
		C_1	C_2	C_3	C_4	C_{5+}	C_2–C_4	
0	0.68	30.5	5.2	12.1	15.4	36.7	0.34	84.9
3	0.67	36.2	6.0	12.5	14.8	30.5	0.26	76.5
7	0.68	37.0	6.2	13.1	15.4	28.2	0.24	82.8
10	0.73	35.8	6.1	12.8	15.4	28.0	0.23	80.0
15	0.90	32.2	5.8	13.4	16.7	31.7	0.38	81.8
20	0.87	35.8	6.5	13.7	15.3	28.7	0.23	74.6
30	0.91	36.9	6.2	13.1	15.0	28.7	0.21	78.4

formation of unsaturated alcohol. Molybdena effectively promotes the hydrogenation of carbonyl and olefinic groups in unsaturated aldehydes, whereas thoria promotes the hydrogenation of only the carbonyl group [16]. Obviously thoria and molybdena exhibited similar promoting effects on the hydrogenation of CO and carbonyl compounds, they might play a similar promoting role by their affinity to the negative oxygen dipole of the carbonyl group. Therefore, a transition-metal oxide that is a good promoter in hydrogenation of CO may be a potential promoter of the hydrogenation of carbonyl compounds.

4. Conclusion

Thoria effectively enhanced the activity and selectivity of olefins and long-chain hydrocarbons. Molybdena promoted only the activity, but did not alter the product distribution pattern. These promoting effects are explained by the weakening of the C–O bond by the side-bond interaction of promoter ion with the oxygen dipole of CO. Thoria and molybdena exhibit a tendency to spread onto, and to interact intimately with alumina; in this way the promoting effects on alumina were much less pronounced than that on silica.

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