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Oxidation of Ketones over Metal Oxide Catalysts. II. Biacetyl Synthesis over Co_3O_4-Lanthanoid Oxide Catalysts

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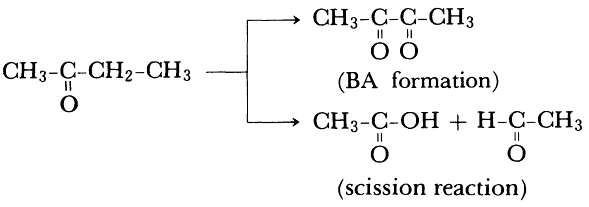
The effects of the addition (10 atomic%) of lanthanoid oxides into Co_3O_4 on the oxidation of methyl ethyl ketone (MEK) were studied. The addition of La_2O_3 brought about marked enhancement of the rate of biacetyl (BA) formation. MEK conversion increased by a factor of 2.8 and the BA selectivity was improved at 450—500K owing to the suppression of deep oxidation. The addition of CeO_2 much improved the MEK conversion but BA selectivity decreased to less than 50% and the scission reaction leading to acetaldehyde and acetic acid was enhanced. The addition of Pr_6O_{11} improved MEK conversion but the addition of Nd_2O_3, Gd_2O_3, or Er_2O_3 showed little effect on MEK conversion. The reduction of both scission reaction and deep oxidation and the compensative increase in BA selectivities were observed. An approximately linear relationship was found between the specific rate of BA formation of the catalysts and logarithmic solubitity product constants of hydroxides of tervalent lanthanoid elements added, suggesting that the basicity of the catalysts is one of major factors for BA formation. The maximum efficiency (23.4%) of BA formation was attained at a La content of ca. 10 at.%.

In the previous papers,[1,2] we have been studied the gas phase oxidation of methyl ethyl ketone over the various metal oxides. In part I of this series,[2] the following findings were reported. Two types of competitive partial oxidation, i.e., biacetyl formation and oxidative scission reaction leading to acetaldehyde and acetic acid took place on every oxide studied at 400—500K.



The former reaction was accelerated on the basic or amphoteric oxides such as Co_3O_4, NiO, ZnO, and CuO, while the latter reaction became predominant on the acidic oxides such as MoO_3, V_2O_5, WO_3, and Cr_2O_3. The addition of Li_2O or Na_2O into Co_3O_4, the most effective biacetyl former of the single component oxides, improved BA selectivity by depressing the scission reaction and deep oxidation. The addition of K_2O or Rb_2O brought about negative effects on BA formation, however, it was somewhat effective to depress the scission reaction and successive complete oxidation at higher temperatures. These results suggest that basic oxides added diminish acidic sites of the catalysts on which scission reaction proceeds.

Lanthanoid oxides are known to belong to a group of basic oxides. Basisity of La_2O_3, Pr_2O_3, and Gd_2O_3 are comparable to that of CaO.[3] So that provided that the oxides of lanthanoid elements are added into Co_3O_4, the lanthanoid oxides added can be expected to induce the desirable effects for BA formation.

In the present paper, we describe the effects of lanthanoid oxide addition into Co_3O_4 on the methyl ethyl ketone oxidation.

Experimental

Catalysts. Binary oxide catalytsts used in this work were prepared by the following procedure. Aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and either of lanthanoid nitrates, phosphoric acid, telluric acid, or selenous acid were mixed and evaporated to dryness on a hot plate with stirring. The powder obtained was submitted to calcination at 673 K for 3 h followed by pressing at 500 $kg\,cm^{-2}$. 24—32 mesh granules of the oxides were finally calcined at 823 K for 4 h in the air.

Apparatus and Method. Experimental procedures and analyses of reactants and products were the same as described in the previous paper.[2]

The oxidation reaction was carried out in a conventional flow type reaction system using a 17-mm-i.d. Pyrex glass tubular reactor with a fixed catalyst bed inside. An aqueous solution of MEK was introduced by means of a microliquid feeder to a glass wool bed which was located at the entrance of the reactor and heated at 473 K, where the solution was evaporated and mixed with oxygen and nitrogen. Before every experimental run, prereaction was carried out for 10 h at the temperature where MEK conversion reached about 10% for the stabilization of activity of catalyst.

The effluent gas was led into a cold trap kept at ca. 290 K, to condense the products having high boiling points along with water vapor. Both trapped products and the gas that passed through the trap were analyzed by gas chromatography. The column packings used were PEG No. 1000 (3 m, 313 K) for aldehydes, ketones, and alcohols, silica gel (1.5 m, r.t.) for carbon dioxide, molecular sieves 5A (1.5 m, r.t.) for oxygen, nitrogen, and carbon monoxide, and DOS (dioctyl sebacate, 2 m, 363 K) for carboxylic acids. The selectivity of a product A is defined as

$$\frac{\text{Moles of MEK converted to A}}{\text{Total moles of MEK consumed}} \times 100\ (\%).$$

Table 1. Oxidation of MEK over Co_3O_4 Catalysts Promoted by Lanthanide Oxide

Catalyst[a]	Temperature	Conversion	Selectivity[b]/%					Specific surface area
	K	%	$(CH_3CO)_2$	CH_3CHO	CH_3COOH	CH_3COCH_3	$CO+CO_2$	$m^2 g^{-1}$
(a) Co_3O_4-La_2O_3	423	5.2	75.5	5.2	15.4	1.1	1.9	12.9
	454	16.9	65.0	6.8	19.8	1.7	5.9	
	472	28.4	62.6	8.1	16.8	2.3	9.5	
	493	43.0	54.5	9.9	19.0	3.2	12.2	
	524	68.5	6.6	1.7	0.4	3.8	74.2	
(b) Co_3O_4-CeO_2	425	10.0	44.7	4.3	45.8	0.9	3.6	20.3
	450	29.6	45.7	4.7	40.6	1.7	6.1	
	473	51.2	33.6	5.0	43.1	3.0	13.4	
	499	50.1	15.6	7.7	32.0	8.3	34.0	
(c) Co_3O_4-Pr_6O_{11}	444	11.2	66.4	4.8	15.1	2.4	10.8	17.8
	473	25.2	55.3	6.3	13.4	5.2	19.2	
	492	41.9	43.7	8.3	9.6	9.9	27.8	
	507	48.7	14.7	4.1	1.0	7.4	66.0	
(d) Co_3O_4-Nd_2O_3	422	2.4	77.5	5.3	6.9	3.2	4.1	12.3
	453	6.2	72.6	5.4	9.3	3.2	8.0	
	495	18.1	58.2	6.7	5.8	10.2	18.1	
	533	35.4	28.5	9.2	4.4	17.3	39.6	
(e) Co_3O_4-Gd_2O_3	428	2.7	71.2	6.3	16.1	4.4	—	8.4
	473	9.3	64.4	7.0	12.8	5.4	9.4	
	503	21.2	44.0	8.0	8.1	10.1	28.9	
	524	38.2	23.5	7.9	4.5	15.3	47.9	
(f) Co_3O_4-Er_2O_3	426	3.7	68.7	5.9	11.8	5.4	5.3	12.9
	471	12.4	53.5	6.7	20.2	5.4	13.7	
	496	21.1	40.0	8.6	11.3	9.4	29.5	
	518	32.8	20.0	10.3	4.6	19.3	42.8	
(g) Co_3O_4-Yb_2O_3	453	5.75	36.5	19.8	36.0	0.8	4.8	11.0
	473	9.33	42.6	18.2	30.2	1.1	6.1	
	492	21.2	39.6	18.8	31.9	1.4	7.2	
	518	38.2	34.6	19.8	34.9	1.2	8.6	

a) Ten atomic% Lanthanoid oxide. b) Normalized to MEK; W/F=2.00 s g-cat. cm^{-3}; feed gas composition: 1.5 mol% MEK, 8.5 mol% O_2, 30.0 mol% H_2O, 60.0 mol% N_2.

Results and Discussion

The Oxidation of MEK over Binary Oxides of Cobalt- Lanthanoid Elements. Modification of Co_3O_4 by the addition of lanthanoid oxides was examined to develop more effective catalysts for BA synthesis. The results of the MEK oxidation are shown in Fig. 1 and Table 1. The results of Co_3O_4 containing no lanthanoid oxide are also shown in Fig. 2 for comparison although the reaction conditions are somewhat different.

The addition of lanthanoid oxides into Co_3O_4 more or less affected the activities of the catalysts and the product distributions, however, gave rise to the formation of no new compound other than formed in the oxidation over Co_3O_4.

The addition of La_2O_3 into Co_3O_4 brought about the increase of MEK conversion by a factor of 2.5—2.8 (Table 1(a)). It can be seen from the comparison of Fig. 1 with Fig. 2 that the addition of La_2O_3 into Co_3O_4 gave no significant influence on the selectivity of scission reaction but depressed the deep oxidation over the whole temperature range examined, especially at below 500 K. Consequently the selectivity of BA was improved at 450—500 K. In the previous paper we noted the maximum efficiency of 13% in BA formation over Co_3O_4-Li_2O (Co/Li=93/7) catalyst.[2] The much higher BA yield (17.7 and 23.4% at 472 and 493 K, respectively) was attained over Co_3O_4-La_2O_3 (Co/La=90/10) catalyst.

The activity of Co_3O_4-CeO_2 was 4—5 times as high as that of Co_3O_4 (Table 1(b)). Almost equimolar BA and acetic acid were formed at 425—450K as the major products and the selectivities of both products decreased monotonously with increasing the reaction temperature. Acetaldehyde and acetone were also formed, the selectivity of the both products remained less than 10% at all temperatures examined.

Co_3O_4-Pr_6O_{11} also showed higher activity for MEK oxidation (Table 1(c)). The selectivity of acetic acid

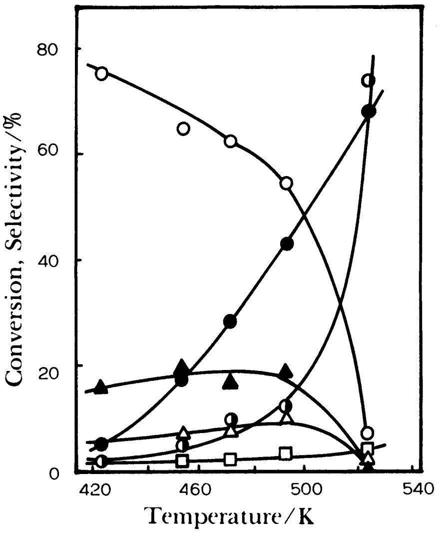


Fig. 1. The oxidation of MEK over Co_3O_4-La_2O_3 catalyst. Catalyst: 10 at.% La_2O_3, 2.48 g. W/F=2.00 (s.g-cat.cm^{-3}). Feed gas composition is the same as in Table 1. Symbols: ●, MEK conversion; ○, BA; △, acetaldehyde; ▲, acetic acid; ◑, carbon oxides; □, acetone.

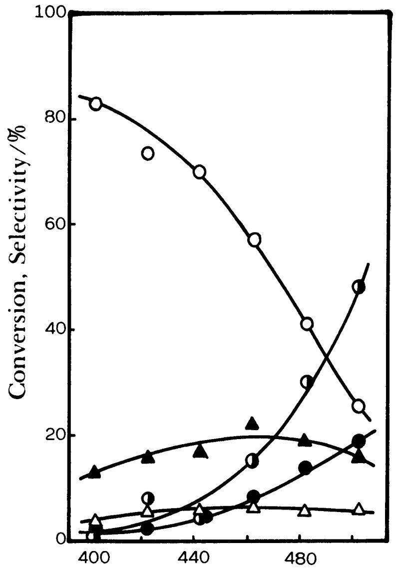


Fig. 2. The oxidation of MEK over Co_3O_4 catalyst. W/F=2.65 (s.g-cat.cm^{-3}). Feed gas composition: 1.62 mol% MEK, 32.8 mol% each of N_2, O_2, and H_2O. Symbols are the same as in Fig. 1.

was reduced at >460 K and the selectivity of deep oxidation was also suppressed at 470—490 K and compensatory increase in BA selectivity was observed at 460—490 K.

The activities of the catalysts containing Nd_2O_3, Gd_2O_3, and Er_2O_3 were comparable to that of Co_3O_4. Comparing the results of Table 1(d)—(f) with Fig. 2, it emerges that the addition of these oxides brought about the inhibition of scission reaction and deep oxidation at relatively high reaction temperatures. Therefore, BA selectivities were improved compensatively at above 440 K.

The addition of Yb_2O_3 gave negative effects on BA formation as shown in Table 1 (g). In this catalyst, since scission reaction was much promoted the BA selectivity remained low value even at low conversion level although the deep oxidation was much suppressed over the whole temperature range examined. A very small amount of acetone was formed over the Co_3O_4 catalyst whereas the Co_3O_4 catalysts containing lanthanoid oxides gave no neglectable extent of acetone and the catalysts containing Nd, Gd, and Er were somewhat peculiar in its ability to form acetone.

It is well-known that the decomposition of metal acetate gives acetone. Alternatively, lanthanoid oxides have been reported to be effective catalysts for vapor phase synthesis of ketones from C_2-C_4 alcohols and carboxylic acids.[4-7] According to mechanistic investigations for 1-butanol, at first 1-butanol was dehydrogenated to corresponding aldehyde which was rapidly succeively converted to aldol and then final ketone.[4,8] In latter case, feed gas contained no molecular oxygen. In the previous work,[2] a large amount of acetone formation (20—55% selectivity) from MEK was observed on the Co_3O_4 catalysts supported on MgO and CaO and it was presumed that acetone plausibly originates from acetate ions adsorbed on the basic supports. Although acetaldehyde was actually formed during the oxidation over every lanthanoid oxide containing catalyst, its selectivities were less than those of acetic acid. It appears that there is no correlation between the selectivities of acetaldehyde and those of acetone.

In addition, in this study feed gas contained 8.5 mol% O_2 which was larger than the stoichiometric concentration of complete oxidation of MEK. It is

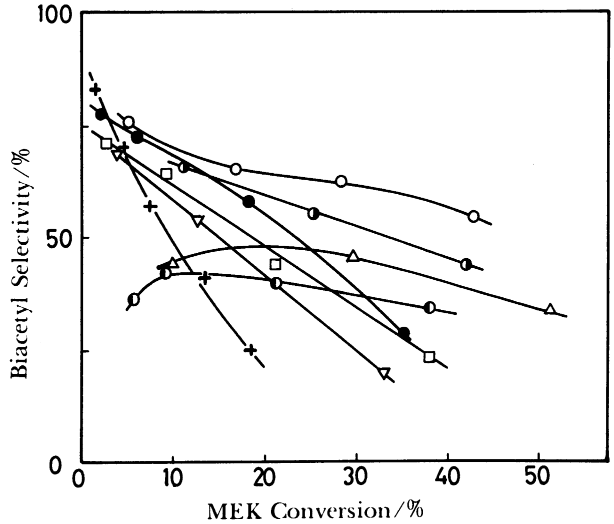


Fig. 3. Improvement in BA selectivity of Co_3O_4 catalyst by the addtion of lanthanoid oxide.
○: La_2O_3, ●: Nd_2O_3, ◑: Pr_6O_{11}, ◐: Yb_2O_3, △: CeO_2, ▽: Er_2O_3, □: Gd_2O_3, +: none (Co_3O_4 only).

confirmed by IR that only the bands arising from surface acetate and carbonate appeared when acetaldehyde was introduced on a wafer of Co_3O_4 at 373 K. So that it is believed that acetone was formed through the carboxylate intermediate on the surface. The activity-selectivity profiles of the catalysts are shown in Fig. 3. In case of Co_3O_4, BA selectivity decreased steeply with increase in conversion. This figure explicitly shows the improvement in the BA selectivity at higher MEK conversion by the addition of lanthanoid oxides especially by the addition of La_2O_3. Specific surface area of the Co_3O_4 catalyst was determined to be 8.4 m^2g^{-1} by BET method and those of the catalysts containing lanthanoid oxides are listed in Table 1. The values were distributed 8.4—20.3 m^2g^{-1} and the active catalysts in general had relatively large specific surface area, however, there is no simple correlation between the catalytic activities per unit weight and the specific surface areas of the catalysts. Specific activities of the catalysts for the MEK consumption (rate per unit surface area at 443—483 K) decreased in the order of

$$Ce > La > Pr > none > Gd > Er > Nd, Yb.$$

While the specific activities of BA formation decreased in the order of

$$La > Ce, Pr, Gd > none > Nd, Er, Yb.$$

It can be roughly said from these orders that the addition of lighter lanthanoid oxides into Co_3O_4 are favorable to BA formation.

The specific rates of BA formation of the catalysts were plotted in Fig. 4 against logarithmic solubility product constants (log K) of hydroxides of tervalent lanthanoid elements[9] as a measure of basicity of the catalysts. The figure shows an approximately linear relationship, suggesting that the basicity of the catalysts in one of the major factors for BA formation.

The Effects of Composition in Co_3O_4-La_2O_3 System. In foregoing section, it has become apparent that the Co_3O_4-La_2O_3 catalyst exceeds the Co_3O_4-Li_2O catalyst in the activity of BA formation. So that the effects of La content of the catalysts on the activity and BA selectivity were examined. At first, the oxidation of MEK was examined over La_2O_3 catalyst (9.0 m^2g^{-1}) under the same reaction conditions as those in Table 1. Oxidation took place with measurable rate at above 500 K, MEK conversion, however, reached only 1.5% even at 558 K. BA selectivity was less than 15% and acetaldehyde, acetone and methyl vinyl ketone were formed as major products. The MEK oxidation was examined over four Co_3O_4-La_2O_3 catalysts with different compositions at 423—493 K. No new kind of products appeared in the reactions over these catalysts.

Figure 5 shows specific surface areas and specific rates of BA formation of the catalysts. The catalysts showed almost similar surface areas except the catalyst of 10% La content (5.8 m^2g^{-1}). While BA formation rates have taken sharp peaks at 10% La content in the different reaction temperatures. Since it has been well known the compounds $LnCoO_3$ (Ln: lanthanoid elements) with perovskite structure[10,11] in Co_3O_4-Ln_2O_3 systems, the catalyst powder with 10% La content was examined by X-ray diffractmeter. However only the diffractions characteristic of Co_3O_4 crystallites of spinel structure were observed. The absence of the perovskite type compounds may be due to the relatively low calcination temperature in the catalyst preparation process. The thickness of La_2O_3 layer is calculated to be about 4.9 nm from its density (6.51 $g\,cm^{-3}$) assuming that the whole amount of La_2O_3 covered the surface of Co_3O_4 in the Co_3O_4-La_2O_3 (Co/La=9/1) catalyst. This thickness is sufficient to be detected by XRD. Absence of diffraction arising from La_2O_3 in the XRD measurement suggests that the catalyst composed of no simple mixture of the component oxides.

In summary, it has become apparent that the addition of ca. 10 atomic% of La oxide into Co_3O_4 is much preferable to BA formation.

Effect of the Addition of Acidic Oxides. So far, it

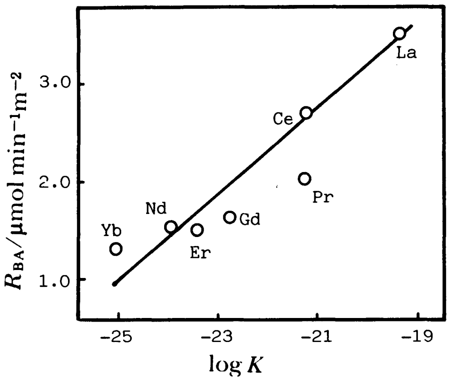


Fig. 4. The effect of acid-base properties of lanthanoid oxides promotors on the activity of BA formation. R_{BA}: Specific rate of BA formation. K: See text.

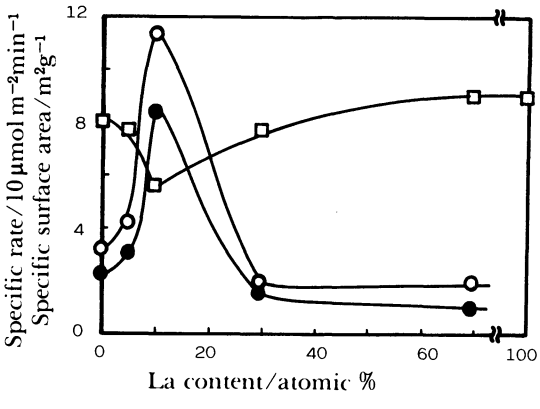


Fig. 5. The effects of La content on the specific surface area and specific rate of BA formation. □: Specific surface area, ●: specific rate at 453 K, ○: specific rate at 473 K.

Table 2. Oxidation of MEK

Catalyst[a)]	Temperature	Conv.	Selectivity[b)]/%				
	K	%	$(CH_3CO)_2$	CH_3CHO	CH_3COOH	MVK	$CO+CO_2$
Co_3O_4-P_2O_5	403	11.4	1.3	46.3	22.6	8.2	21.2
	443	21.9	6.7	42.5	22.4	Tr.	26.9
	463	25.8	16.6	35.1	20.1	Tr.	26.9
Co_3O_4-TeO_2	373	3.4	5.2	28.3	60.1	3.3	—
	403	14.1	2.0	39.5	36.4	0.1	18.2
	463	28.4	17.3	33.8	19.9	0.5	27.7
Co_3O_4-SeO_2	403	9.6	29.9	29.2	9.1	17.3	13.6
	423	16.1	39.7	35.7	9.1	0.6	14.1
	463	29.4	39.9	33.7	8.0	0.4	16.4
Co_3O_4-SeO_2-Li_2O	423	2.4	41.0	40.7	6.3	—	11.5
	443	3.9	39.3	37.5	7.1	—	15.4
	463	5.0	52.9	24.1	8.1	—	13.9

a) Ten atomic% P_2O_5, TeO_2, SeO_2, Li_2O. b) Normalized to MEK; $W/F=4.27$ s g-cat. cm^{-3}; feed gas composition: 1.16 mol% MEK, 32.9 mol% each of N_2, O_2, and H_2O.

has been examined the effects of basic additives on MEK oxidation. The effects of some acidic additives were studied in this section.

The addition of P_2O_5 brought about exceeding acceleration of scission reaction as it is expected (Table 2). The selectivity of scission reaction went up over 55% and BA selectivity remained very low value at the all temperatures examined. MEK conversion of the catalyst was presumed to be higher than that of the Co_3O_4-La_2O_3 catalyst even if the difference of W/F is taking into account.

Scission reaction was also enhanced over Co_3O_4-TeO_2 catalyst and the product distribution was closely similar to that of Co_3O_4-P_2O_5.

In case of Co_3O_4-SeO_2 catalyst, activity of the catalyst was somewhat lower than the P_2O_5 or TeO_2 containing catalyst and both BA formation and acetaldehyde formation proceeded with comparable rates and substantially the selectivities did not vary at between 423—463K.

According to Sanderson,[3)] SeO_2 do not act as a base since the partial negative charge of the oxide ions in SeO_2 is very low (0.07), on one hand, TeO_2 possessing relatively high partial charge (0.13) is rather amphoteric. So that Co_3O_4-TeO_2 catalyst is expected to be more efficient in BA formation than Co_3O_4-SeO_2 catalyst. The specific activity of Co_3O_4-SeO_2 catalyst, however, was far beyond that of Co_3O_4-TeO_2 catalyst both for MEK conversion and for BA formation. Selective inhibition of scission reaction was attempted by the addition of Li_2O into the Co_3O_4-SeO_2 catalyst (Table 2). MEK conversion was significantly reduced by the addition of Li_2O, and the oxidative dehydrogenation to methyl vinyl ketone was completely inhibited. Although the scission reaction was somewhat depressed at higher reaction temperatures, the improvement in BA selectivity was rather small.

When scission reaction takes place, a part of acetaldehyde molecules formed can be successively oxidized to acetic acid and a part of acetic acid molecules formed can likewise be oxidized to carbon oxides. Then the selectivity of acetaldehyde (normalized to reactant) never surpasses the sum of the selectivities of acetic acid and carbon oxides. In practice, that is the case in all catalysts except for the catalysts containing SeO_2. In case of Co_3O_4-SeO_2 catalyst the selectivity of acetaldehyde was greater than that of acetic acid but also corresponding to the sum of selectivities of acetic acid and carbon oxides. This may suggests that there is another path of acetaldehyde formation expressed by

$$MEK + 1/2\ O_2 = 2\ CH_3CHO.$$

The reason of the complicated behavior of Co_3O_4-SeO_2 catalyst in MEK oxidation is obscure at the present stage. Measurement of the concentrations of surface acidic and basic sites, observation of surface structure, and detailed study on the reaction mechanism will be required for understanding the result of Co_3O_4-SeO_2.

It can be said from the results in this section that the addition of acidic oxides into Co_3O_4 generally enhance the activity of the Co_3O_4 catalyst for scission reaction.

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