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Rearrangement and Disproportionation of Toluene over La$_{1-x}$Sr$_x$NiO$_3$ Catalysts

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The gas-phase oxidation of toluene over La$_{1-x}$Sr$_x$$BO_3$ (B = Mn, Fe, Co, Ni) catalysts was studied with the aid of a GC/MS. Unlike the products resulting from the use of Mn-, Fe-, and Co-series or LaNiO$_3$ catalysts, when La$_{1-x}$Sr$_x$NiO$_3$ ($x > 0$) was employed, bicyclo-[2.2.1.]-hept-2,5-diene and 2-propenylidene cyclobutene were formed by the rearrangement of toluene, while *o*-xylene, *m*-xylene, *p*-xylene, and ethyl benzene were produced by the disproportionation of toluene. It is believed that the rearrangement and disproportionation of toluene on the perovskite catalysts are due to the NiO- and La$_2$NiO$_4$-phases. The amount of NiO- and La$_2$NiO$_4$-phases in the La$_{1-x}$Sr$_x$NiO$_3$ ($x > 0$) catalysts was found to increase with x, and hence affected toluene oxidation activity as well. The disproportionation products were formed when either NiO, the mixture of NiO (50%) and LaNiO$_3$ or the mixture of La$_2$NiO$_4$ · NiO (50%) and LaNiO$_3$ as the catalysts were used. It is shown that the disproportionation of toluene is due to the NiO- and La$_2$NiO$_4$-phases. A change in the carrier gas from nitrogen to helium showed that nitrogen gas can react with the adsorbed oxygen and the lattice oxygen on the catalyst surface, leading to a decrease in the oxidation and disproportionation reaction rates of toluene. Substituting benzene for toluene revealed that the rearrangement of toluene starts at the methyl group. The mechanisms for the rearrangement and disproportionation of toluene were based on the GC/MS analysis for the products.

INTRODUCTION

The performance and behavior of Mn-, Fe-, Co-, and Ni-series catalysts in regards to the oxidation of toluene were examined in our preceding study (*1*). Since, when La$_{1-x}$Sr$_x$NiO$_3$ ($x > 0$) catalysts were used, in contrast with the Mn-, Fe-, and Co-series catalysts, novel rearrangement and disproportionation products were formed, further study of the formation mechanisms of these products is required.

An examination of the X-ray diffraction patterns of La$_{1-x}$Sr$_x$NiO$_3$ ($0.3 \leq x \leq 0.7$) revealed the existance NiO- and La$_2$NiO$_4$-phases in addition to the LaNiO$_3$ perovskite structure, while SrNiO$_3$ had NiO- and SrO$_2$-phase structures (Fig. 1). The catalytic activity and oxidation rate of toluene seem to be affected by the NiO- and La$_2$NiO$_4$-phase structures of La$_{1-x}$Sr$_x$NiO$_3$ ($x > 0$) catalysts, increasing with increasing x.

The surface of perovskite-type oxides is highly heterogeneous (*2, 3*). When the NiO- and La$_2$NiO$_4$-phases dominates in the Ni-series catalysts, the La$_{1-x}$Sr$_x$NiO$_3$ ($x > 0$) nickel atom, whose strong metal–support interaction is similar to that of Ni/TiO catalyst (*4, 5*), can recover its metal character through the chemisorption of hydrogen. Such transition metals (Ni, Pd, and Pt) of group VIII$_3$ possess strong hydrogen chemisorptic activity (*6*) and catalytic activity for disproportionation reaction (*7–10*).

This paper represents the second in a series of comparative studies on La$_{1-x}$Sr$_x$$BO_3$ catalysts, and investigates the novel behavior of La$_{1-x}$Sr$_x$NiO$_3$ ($x > 0$) catalysts on the oxidation of toluene. The total concentration of intermediate and converted products at various reaction temperatures were first measured and plotted in order to gain an understanding of their effect on the oxi-

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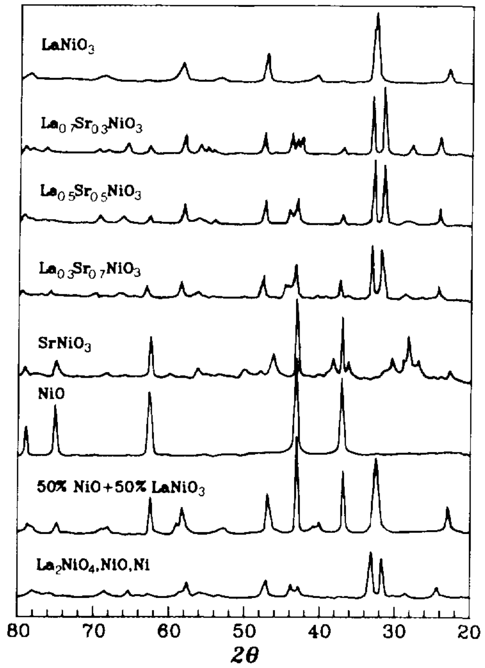

FIG. 1. X-ray diffraction patterns (Cu*Kα* radiation) of the catalysts prepared.

dation reaction. The reactor's exit gas mixtures, at certain reaction temperatures, were analyzed by a GC/MS in order to determine the intermediate products. The oxidation of benzene was also investigated in hopes that it might help in elucidating the mechanism involved in the oxidation of toluene. The effect of nitrogen on the reaction was also studied by changing the carrier gas from nitrogen to helium.

EXPERIMENTAL METHODS

Catalyst preparation. In this study, the perovskite-type catalysts were prepared by the alkaline coprecipitation method using K_2CO_3 solution (0.181 *M*) as the precipitant. The precipitates were filtered, dried (at 120°C), and then calcined in air for 6 *hr* at the maximum calcination temperatures determined from TGA thermograms (*1*). The NiO catalyst was prepared by calcination of nickel nitrate ($Ni(NO_3)_2 \cdot 4H_2O$) at 1000°C in air for 6 *hr*. The $La_2NiO_4 \cdot NiO$ catalyst was prepared by reduction of $LaNiO_3$ with H_2 for 1 *hr* at 250°C and sintering in He for 3 *hr* at 800°C (*11*).

Powder X-ray diffraction (XRD) patterns (Fig. 1) of the catalysts prepared were obtained from an X-ray diffractometer (Rigaku D/MAX III. V XRD) using Cu*Kα* radiation.

Apparatus and procedure. Catalytic activity data were obtained using a conventional fixed-bed flow reactor at atmospheric pressure. A stainless steel tube (S.S. 316) with an inner diameter of 0.5 *in* was chosen as the reactor.

Prior to each experimental run, the catalysts (35–60 mesh, 0.4 *g* diluted with 1.6 *g* of quartz powder) were pretreated with a mixed gas (O_2 33.3%, N_2 or He balance) stream for 1 *hr* at 400°C. A gaseous mixture of toluene or benzene (0.42%), O_2 (33.3%), and N_2 or He (balance) at a flow rate of 120 ml/min was fed into the reactor through a preheater set at 120°C. The gas leaving the reactor was channeled into a condenser where the water vapor was removed, and the remaining components were analyzed by a G.C.-FID.

Analysis. Products were analyzed by a gas chromatograph (Shimadzu GC 9A-FID) using a 3-*m* Silicone OV-17 column (50% phenyl and methyl) kept at 120°C. A 50-*m* capillary column (SGE 50QC2/BP20-0.25 Polar, kept at 40°C) was also used in the analysts of ethyl benzene and xylene isomers by a GC-FID. A high-resolution gas chromatograph mass spectrometer (VGA VG70-250S) completed with a data processing system (VC11-250J) and a 50-*m* capillary column (SGE 50QC2/BP20-0.25 Polar) was employed for further analysis of the compounds exiting the GC. The capillary column was initially heated from 55 to 135°C at a rate of 4°C/min, and subsequently maintained at 135°C. A heated chemiluminescence nitrogen oxides (NO_x) analysis system (Analysis Automation Limited model 443) was used to measure nitric oxide (NO) which was formed in the oxidation of nitrogen.

RESULTS AND DISCUSSION

Conversion Curves of Toluene Oxidation

The oxidation of toluene, catalyzed by the Ni-series compounds, as a function of temperature is shown in Fig. 2a. Note that these conversion curves are not smooth and that they differ from those obtained previously (*1*) for the Mn-, Fe-, and Co-series catalysts.

The "fluctuation" in data at low temperatures suggests that certain reactions are temperature dependent. Based on this consideration, the total concentrations of the intermediate products (which were later confirmed as being formed from the disproportionation of toluene), are plotted against reaction temperature, as shown in Fig. 2b. Note that for those catalysts containing Sr, three or four peaks appear in each of the curves, whereas no peaks appear in that of $LaNiO_3$. In order to determine the identity of these intermediate products, the exit gas mixtures were further analyzed by a GC/Ms. Characteristics of the $La_{1-x}Sr_xNiO_3$ catalysts are shown in Table 1.

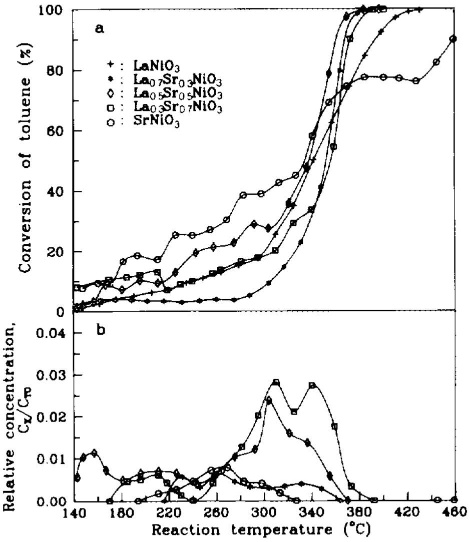

FIG. 2. The conversion and the relative total concentration of disproportionation products (C_D/C_{TO}, where C_D is total concentration of the disproportionation products; C_{TO} is the concentration of toluene feed) as a function of reaction temperature during the toluene oxidation with N_2 as the carrier gas over $La_{1-x}Sr_xNiO_3$ catalysts.

Analysis of Intermediate Products by GC/MS

The exit gas mixtures from the oxidation of toluene (of 226, 302, and 340°C) using $La_{0.3}Sr_{0.7}NiO_3$ as the catalyst were separately collected and analyzed by a GC/MS. In each of the three total ion chromatograms obtained, there are three strong peaks (retention times are around 10 *min*) and one weak peak (retention time is 25.6 *min*). These strong peaks, using a data

TABLE 1

Characteristics of the $La_{1-x}Sr_xNiO_3$ Catalysts

Description	x				
	0	0.3	0.5	0.7	1
Maximum calcination temp. (°C)	850	1020	1020	1020	1050
Structure	P[a]	P + NiO	P + NiO	P + NiO	NiO + SrO_2
BET surface area (m^2/g)	3.042	3.097	2.475	2.693	2.633
Total pore volume (cc/g)	0.0101	0.0114	0.0057	0.0110	0.0108
Average pore diameter (Å)	132.305	147.194	91.822	163.575	163.400
Surface atomic percent	(%)[b]				
La	49.06	31.08	29.94	18.99	—
Sr	—	21.26	26.58	28.18	51.29
Ni	16.67	16.56	14.62	20.55	14.21
O	32.27	31.10	28.86	32.28	34.50

[a] Perovskite structure.

[b] Surface atomic percent were measured by AES.

search (processing system: VC17-250J), were qualitatively identified as 2-propenylidene cyclobutene, bicyclo-[2.2.1]-hept-2,5-diene, and toluene for the first, second, and third peaks, respectively. Since the first two products have the same molecular formula as the last, it is conceivable that they are formed by a rearrangement of toluene. Ethyl benzene, *ortho-*, *meta-*, and *para-*xylene are four possible candidates for the weak peak, as they all arise from the disproportionation of toluene. Table 2 shows the yields of products from the disproportionation of toluene over $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts. Because no rearrangement or disproportionation was detected when operating temperatures exceeded 385°C, these products are the probably intermediate products of toluene oxidation since: (1) the purity of all the compounds was very high (typically more than 860 parts per thousand), in comparison to the reference spectra; (2) both yield and molecular weight of these compounds matched the overall stoichiometry; and (3) the presence of all these compounds can reasonably be explained by side reactions.

TABLE 2

Percentages of Products from Toluene Disproportionation over $La_{1-x}Sr_xNiO_3$ ($x > 0$)

Product (mol %)	Temperature (°C)		
	220	280	340
$La_{0.7}Sr_{0.3}NiO_3$			
Ethylbenzene	36.36	32.02	30.51
p-Xylene	25.20	22.26	18.53
m-Xylene	22.34	28.43	33.52
o-Xylene	16.10	17.29	17.44
$La_{0.5}Sr_{0.5}NiO_3$			
Ethylbenzene	25.46	19.53	17.85
p-Xylene	23.53	25.18	25.93
m-Xylene	30.96	31.20	31.25
o-Xylene	21.05	24.09	24.97
$La_{0.3}Sr_{0.7}NiO_3$			
Ethylbenzene	32.08	25.79	17.09
p-Xylene	21.20	22.80	27.34
m-Xylene	29.54	27.01	33.21
o-Xylene	17.18	24.40	22.36
$SrNiO_3$			
Ethylbenzene	31.11	22.66	22.24
p-Xylene	22.17	26.33	24.51
m-Xylene	26.52	32.82	28.87
o-Xylene	20.20	19.19	24.38

Due to the fact that no intermediate products were detected when $LaNiO_3$ was employed as the catalyst (see Fig. 2), substitution of La by Sr most likely engendered the rearrangement and disproportionation of toluene on the catalyst surface.

The Role of NiO- and La_2NiO_4-Phases

In the previous study (*1*), the NiO- and La_2NiO_4-phases structure of $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts were found to increase with increasing x. The amounts of rearrangement and disproportionation products changed with both the content of NiO- and La_2NiO_4-phases and reaction temperature. As an analysis of the GC/MS results confirmed that oxidation of toluene did not lead to rearrangement and disproportionation when either Mn-, Fe-, and Co-series or $LaNiO_3$ catalysts were used, it is therefore believed that the NiO- and La_2NiO_4-phases are responsible for this behaviour.

Figure 3 shows the conversion of toluene and the total concentration of the disproportionation products when various nickel-containing catalysts were used for the oxidation of toluene. It can be seen that the disproportionation products were formed (see Fig. 3b and Table 3) when either NiO, $La_2NiO_4 \cdot NiO$, the mixture of NiO (50%) and $LaNiO_3$, and the mixture of $La_2NiO_4 \cdot NiO$ (50%) and $LaNiO_3$ were used as the catalysts. It is hence shown that the NiO- and La_2NiO_4-phases are responsible for the disproportionation of toluene.

Due to the fact that no rearrangement products were detected and the amount of the disproportionation products were lower (see Figs. 2 and 3) when either NiO, $La_2NiO_4 \cdot NiO$, the mixture of NiO and $LaNiO_3$, and the mixture of $La_2NiO_4 \cdot NiO$ and $LaNiO_3$ were employed as the catalyst, it might be concluded that the rearrangement of toluene occurs only when the cata-

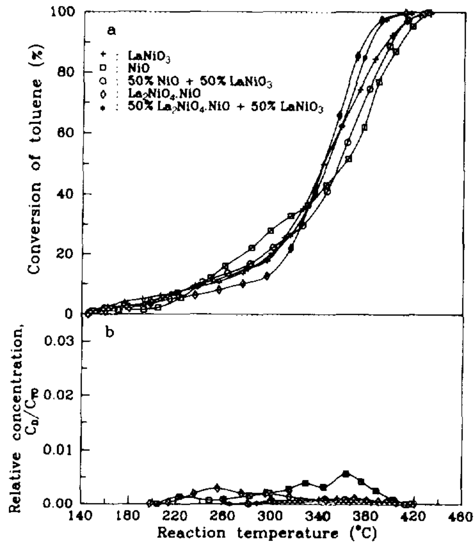

FIG. 3. Comparison of the conversion and the relative concentration of disproportionation products over some nickel-containing catalysts (refer to Fig. 2 for the nomenclature).

lyst has both the perovskite structure and the NiO-phase or La_2NiO_4-phase. The calcination at very high temperature for mechanical mixing method can subsequently be applied to provide the desired homogeneity and crystalline structure formation by thermal diffusion and solid-state reaction.

Kudievskii *et al.* (*7*) recently studied the disproportionation of carbon monoxide over a nickel catalyst and found that its catalytic decomposition is temperature sensitive, increasing with the hydrogen content in the carbon monoxide gas mixture increases. Matolin and Gillet (*8*) also reported on the disproportionation of carbon monoxide, although in this case it was over supported palladium particles. Mironov *et al.* (*9*), on the other hand, employed palladium particles in a catalytic disproportionation reaction between tetramethylsilane and germanium tetrachloride in the gas phase, while Elsheikh (*10*) reported the formation of both 1-chloro-1-fluoroethene and 1,1-difluoroethene by gas-phase disproportionation of 1-chloro-1,1-difluoroethane over a NiF_2-containing catalyst. These studies illustrate the fact that both Ni- and Pd-containing catalysts demonstrate peculiar behavior, tending to produce interesting products.

TABLE 3

Percentages of Products from Toluene Disproportionation over NiO and $La_2NiO_4 \cdot NiO$

Product (mol %)	Temperature (°C)		
	220	280	340
NiO			
Ethylbenzene	29.90	26.33	19.52
p-Xylene	25.67	24.87	26.40
m-Xylene	25.62	28.51	32.09
o-Xylene	18.81	21.29	21.99
$La_2NiO_4 \cdot NiO$			
Ethylbenzene	26.29	23.01	18.84
p-Xylene	25.92	23.39	20.62
m-Xylene	31.59	36.54	40.03
o-Xylene	16.20	17.06	20.23

Through the chemisorption of hydrogen, the surface nickel atom in the NiO- and/or La_2NiO_4-phases of $La_{1-x}Sr_xNiO_3$ ($x > 0$) recovers both its group $VIII_3$ transition metals character, and thereby the force which drives the catalytic disproportionation reaction. This phenomenon is comparable to that of strong metal support interaction (SMSI).

Effect of Nitrogen Gas on the Catalytic Reactions

The conversion and the relative total concentration of products in the oxidation and disproportionation of toluene catalyzed by the Ni-series catalysts with helium as the carrier gas are shown in Fig. 4. As in the case of nitrogen, the conversion curves for $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts are also not smooth. Note that those catalysts containing Sr exhibit three common peaks in each of their disproportionation product curves. The peak areas and heights increase with both increasing x and temperature, reaching a maximum value at $x = 0.7$. The activity sequence of those Ni-series catalysts tested is: $La_{0.5}Sr_{0.5}NiO_3 > LaNiO_3 > La_{0.7}Sr_{0.3}NiO_3 > La_{0.3}Sr_{0.7}NiO_3 > SrNiO_3$.

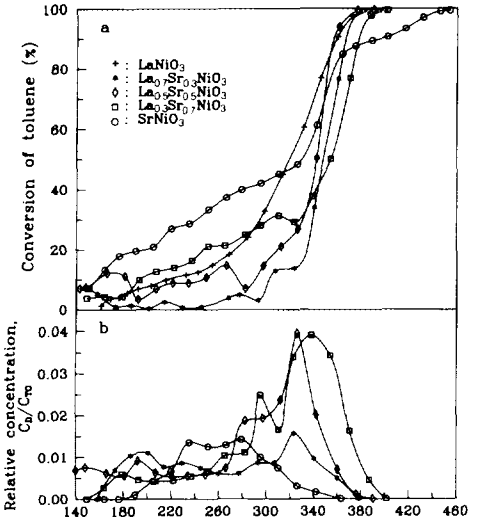

FIG. 4. The conversion and the relative total concentration of disproportionation products (C_p/C_{T0}, where C_p is total concentration of the disproportionation products; C_{T0} is the concentration of toluene feed) as a function of reaction temperature during the toluene oxidation with He as the carrier gas over $La_{1-x}Sr_xNiO_3$ catalysts.

Note that this sequence is different from that shown in Figs. 2a and 2b.

Changing the carrier gas from nitrogen to helium in the Ni-series catalyzed oxidation of toluene resulted in (1) enhanced activity for both $LaNiO_3$ and $SrNiO_3$ and (2) higher concentrations of disproportionation products at lower temperatures.

Figure 5 compares yield of nitric oxide on $La_{0.3}Sr_{0.7}NiO_3$ catalyst and with or without oxygen gas. No nitric oxide was detected in blank experiment (curve 3). It can be seen that nitric oxide was formed not only by the reaction between nitrogen and oxygen gases over the catalyst (curve 1), but also by the reaction between nitrogen and the chemsorbed and/or lattice oxygens (curve 2) when $La_{0.3}Sr_{0.7}NiO_3$ catalyst was used. When nitrogen was used as the carrier gas, reaction between nitrogen and the absorbed oxygen on the catalyst surface resulted in the decrease in the reaction rate of toluene oxidation and disproportionation.

The gas samples collected at the exit of the reactor were also analyzed by a GC/MS. Since the retention times of the four peaks of the total ion chromatograms are identical to those obtained from experiments with nitrogen as the carrier gas, it is conceivable that the same rearrangement and disproportionation products were formed.

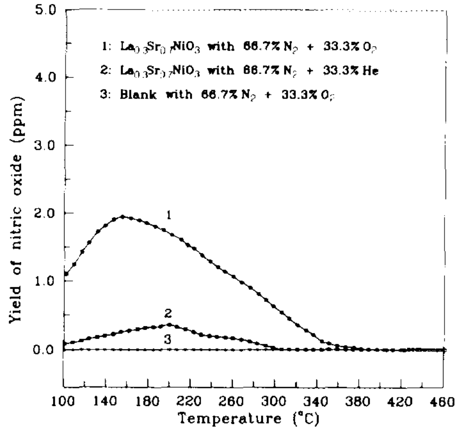

FIG. 5. Yield of nitric oxide on $La_{0.3}Sr_{0.7}NiO_3$ catalyst (and blank) with and without O_2. The heating rate was 2°C/min and the flow rate was 120 ml/min.

Oxidation of Benzene

The results of benzene oxidation catalyzed by the Ni-series catalysts are shown in Fig. 6. Note that the complete absence of those rearrangement and disproportiona-

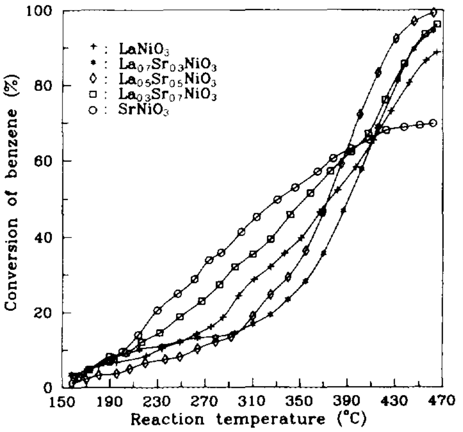

FIG. 6. The conversion as a function of reaction temperature during the benzene oxidation on $La_{1-x}Sr_xNiO_3$ catalysts.

tion products of toluene, and that the conversion curves are entirely smooth. In the case of benzene, the lack of rearrangement products implies that a branched point (methyl group) on the aromatic ring is essential for the commencement of rearrangement reactions.

Benzene is a much more stable structure than toluene, and hence requires much more rigorous oxidation conditions. Note, however, that benzene can be completely oxidized by some Ni-series catalysts (at about 460°C; see Fig. 6). This behaviour may be attributable to the fact that hydrogen is more easily adsorbed on nickel containing catalysts (*12–17*), the transfer causing the destruction of benzene ring.

Reaction Mechanism of Toluene Oxidation

Based on the results at hand, when toluene comes in contact with $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts at high enough temperatures, two possibilities exist for the chemisorption of hydrogen (from toluene) on the catalyst surface: (1) adsorption of a hydrogen from the methyl group and/or (2) adsorption of the hydrogen in the *para* position. The former results in an electron-deficient methyl group which then rearranges through one of two migratory paths: (1) the C_{methyl} bonds with C_2, leading to the opening of the aromatic ring and subsequent formation of 2-propenylidene cyclobutene and (2) the C_{methyl} bonds with C_4, leading to formation of bicylo-[2.2.1]-hept-2,5-diene. The rearrangement mechanisms are shown in Fig. 7.

Bicylo-[2.2.1]-hept-2,5-diene is the key monomer in the synthesis of unique polycyclic strained hydrocarbons (*18*). A review of the literature revealed that the diene is mainly synthesised by reacting cyclopentadiene or dicyclopentadiene with acetylene in a Diels–Alder type reaction (*19–28*) at temperatures and pressures between 150–400°C and 1–20 atm, respectively. However, in the present study, bicylo-[2.2.1]-hept-2,5-diene is produced by the rearrangement of toluene at atmospheric pressure and temperatures below 300°C.

On the other hand, when hydrogen in the para position is chemisorbed onto the catalyst surface, the methyl group transfers an electron to the benzene ring, becoming activated in the process. The activated methyl group is now able to bond with a toluene molecule in one of two ways: (1) with the side chain, forming ethyl benzene, and/or (2) with the aromatic ring, forming either *o*-xylene, *m*-xylene, or *p*-xylene. An analysis of the GC/MS results for the oxidation of

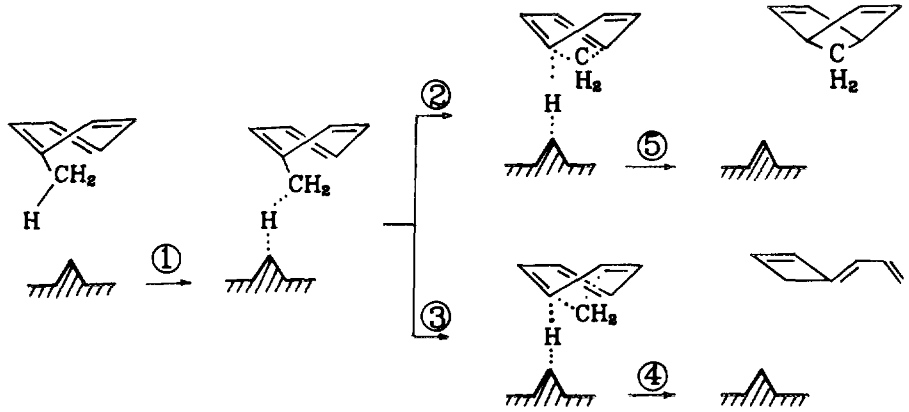

FIG. 7. Mechanism for the rearrangement reaction of toluene on $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts. ① Adsorption of toluene, ② surface rearrangement reaction of C_{methyl}–C_4 bonding, ③ surface rearrangement reaction of C_{methyl}–C_2 bonding, ④ desorption of 2-propenylidene cyclobutene, and ⑤ desorption of bicyclo-[2.2.1]-hept-2,5-diene.

toluene with Ni-series catalysts, revealed the presence of a very small peak attributable to benzene (retention time 4.9 min). It is interesting to note that the concentration of benzene increasing with the reaction temperature, although it never did achieve the level of other intermediate products. It is possible that toluene adsorbed on a catalyst surface loses an activated methyl group, becoming desorbed as benzene which can then be adsorbed on catalyst surface once again, and further oxidized. These disproportionation mechanisms are shown in Fig. 8.

Recently, the disproportionation of toluene in xylene production over HZSM-5, zeolite H-beta, or metal-loaded H-mordenite catalysts has been well documented by many authors (*29–33*). These papers suggest that the catalytic disproportionation of toluene is initiated when a H^+ ion bonds to a toluene molecule. However, since there is no source of H^+ ions when $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts are employed, the disproportionation reaction mechanism for toluene in this study must differ from that obtained by other catalysts.

An examination of the total ion chromatograms reveals that the rearrangement products of toluene increases with the reaction temperature, enhancing the relative ion currents (quantities) of 2-propenylidene cyclobutene and bicyclo-[2.2.1]-hept-2,5-diene. Note that the quantity of 2-propenylidene cyclobutene is larger than that of toluene when temperatures exceed 300°C. Also note that the yields of "intermediate" products due to the disproportionation of toluene are much smaller than those due to rearrangement. Since the methyl group has three relatively easily extractable hydrogen atoms situated external to the aromatic ring, rearrangement proceeds much more readily. Thus, the close proximity of C_2 and C_6 to the C_{methyl} results in a greater yield of 2-propenylidene cyclobutene (formed by C_{methyl} bonding to either C_2 or C_6), than that of bicyclo-[2.2.1]-hept-2,5-diene (formed by C_{methyl} bonding to C_4). In addition, 2-propenylidene cyclobutene possesses the added stability of a conjugated triene (diene chain and cyclobutene ring).

CONCLUSION

Due to the NiO- and La_2NiO_4-phase structures of the catalysts, instead of the expected oxidation of toluene, rearrangement and disproportionation reactions predominate when $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts are used. These catalysts' SMSI (which is similar to that of Ni/TiO catalysts), demonstrates strong hydrogen chemisorptic activity. It is the characteristic that is responsible for the above mentioned side reactions.

The relative amounts of rearrangement products (2-propenylidene cyclobutene and bicyclo-[2.2.1]-hept-2,5-diene) increases with the reaction temperature, becoming larger than that of toluene when tempera-

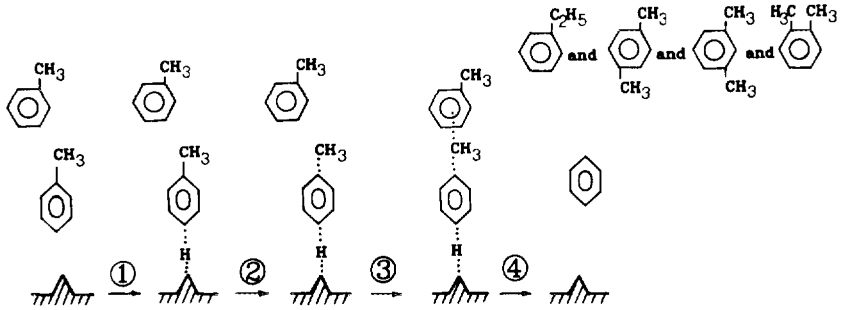

FIG. 8. Mechanism for the disproportionation reaction of toluene on $La_{1-x}Sr_xNiO_3$ ($x > 0$) catalysts. ①Adsorption of toluene, ②surface reaction, ③reaction between an adsorbed toluene and a toluene in the gas phase, and ④ desorption of products.

tures exceed 300°C. Due to the three relatively easily extractable hydrogens of the methyl group located external to the aromatic ring, rearrangement product yields are larger than those of disproportionation reactions.

Benzene is among the products formed by the disproportionation of toluene. Since its hydrogen atoms can be adsorbed onto $La_{1-x}Sr_xNiO_3$ ($0.3 \leq x \leq 0.7$) catalysts, the aromatic ring can be completely oxidized at about 460°C. Note, however, that its concentration never approaches that of the other products.

Nitrogen gas can react with the adsorbed oxygen and lattice oxygen on the Ni-series catalyst surfaces, decreasing the reaction rates of both oxidation and disproportionation of toluene. The substitution of benzene for toluene revealed that the rearrangement of toluene begins at the methyl group.

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