CHEMICAL KINETICS =

Dehydrogenation of Propane in the Presence of CO_2 on Supported Monometallic MO_y/SiO_2 and CrO_xMO_y/SiO_2 (M = Fe, Co, and Ni) Bimetallic Catalysts

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Abstract—An analysis is performed of the physicochemical properties of M/SiO_2 (M = Fe, Co, and Ni) oxide monometallic and CrM/SiO₂ (M = Fe, Co, and Ni) bimetallic catalysts supported on amorphous silica. The catalysts are characterized via TGA, XRD, UV–Vis diffuse reflectance spectroscopy, and SEM. Adding 1 wt % of a second transition metal (Fe, Ni, and Co) to the 3% CrO_x/SiO₂ chromium oxide catalyst substantially raises the conversion of propane to 64% with a drop in the selectivity towards propylene and formation of methane as a main by-product in the case of nickel. Introducing iron and cobalt raises the selectivity towards propylene to 72% with a drop in the conversion of propane.

Keywords: bimetallic catalysts, metal oxides, silica gel, oxidative propane dehydrogenation, propylene, carbon dioxide, carbon dioxide utilization, diffuse reflectance UV spectroscopy, scanning electron microscopy, XRD

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INTRODUCTION

The dehydrogenation of propane is a highly endothermic and energy-intensive process, due to the high temperature of the reaction. As a result, catalysts of dehydrogenation deactivate rapidly because of carbon deposited on their surfaces [1]. Catalysts for propane dehydrogenation reaction include noble metals (Pt, Rh, and Ru) that are more resistant to carbon deposition, but their limited availability and high cost make it difficult to use them in the dehydrogenation of propane. The oxidative dehydrogenation of propane in the presence of CO_2 is another way of obtaining propylene. Adding CO_2 increases the yield of propylene in two independent ways. First, CO_2 can participate as an oxidant in the redox cycle

$$C_3H_8 + MeO_x \rightarrow C_3H_6 + MeO_{x-1} + H_2O, \quad (1)$$

$$CO_2 + MeO_{x-1} \rightarrow CO + MeO_x.$$
 (2)

Such a redox cycle was proposed for catalysts based on chromium [2-4], manganese [5, 6], vanadium [7, 8], and iron oxides [9]. Second, CO₂ can help remove the hydrogen produced after the dehydrogenation of propane, which can increase the yield of propylene:

$$C_3H_8 \to C_3H_6 + H_2, \tag{3}$$

$$CO_2 + H_2 \rightarrow CO + H_2O. \tag{4}$$

Reducing the partial pressure of hydrogen shifts the equilibrium toward the formation of propylene [10–13]. This stimulating effect of carbon dioxide has been postulated not only for the dehydrogenation of propane but for other hydrocarbons as well: ethane [14, 15], butane [16, 17], and ethylbenzene [18]. Carbon dioxide can participate in the oxidative dehydrogenation of propane, another way of producing propylene, and in the carbon dioxide gasification of coke, which lengthens the life of a catalyst:

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O, \tag{5}$$

$$CO_2 + C \rightarrow 2CO.$$
 (6)

 CO_2 transforms into CO in reactions of propane dehydrogenation (2), (4)–(6), making it more valuable as a reagent for the chemical industry [19–21].

The main disadvantage of using CO_2 as an oxidizing agent in propane dehydrogenation is that it is inert. This can be avoided by using metal oxide catalysts. Supported chromium oxides are currently the ones most effective for the reaction of propane dehydrogenation in the presence of CO_2 [22–24].

A support can have a substantial effect on a catalyst's activity in the dehydrogenation of propane in the presence of CO_2 . In [25], CO_2 had an adverse effect on activity of the Al₂O₃ and ZrO₂ catalysts; at the same time, it had a stimulating effect on catalysts supported on SiO₂. CrO_x/SiO_2 catalysts in particular display the highest activity and selectivity in propane dehydrogenation in the presence of CO₂. The efficiency of supported chromium oxide catalytic systems depends strongly on the physical properties of the support and the amount of chromium in the system. In [26], a relationship was revealed between the catalytic activity of chromium catalysts and a support of the same chemical nature but with different physical characteristics. The authors showed that 3 wt % CrO_{y}/SiO_{2} catalyst (Acros) displays the highest catalytic activity. The aim of this work is to prepare bimetallic catalysts based on this chromium oxide catalyst with the addition of iron, cobalt, or nickel oxides; and to comparatively study their physicochemical and catalytic properties.

EXPERIMENTAL

Preparation of the Catalysts

Monometallic catalysts were prepared via incipient wetness impregnation from aqueous solutions of chromium, iron, cobalt or nickel nitrates. Bimetallic catalysts were obtained via incipient wetness impregnation from aqueous solutions of a mixture of chromium and iron nitrates and cobalt or nickel nitrates. Granular silica gel SiO_2 (Acros) was used as a support to prepare the catalyst samples. Ground silica gel (fraction 0.25-0.5 mm) was dried for 6 h in air at 120°C. The active component was applied by impregnating silica gel with an aqueous solution of a nitrate of the corresponding metal, or of a mixture of chromium nitrate and nitrate of a corresponding metal. $Cr(NO_3)_3 \cdot 9H_2O$ (Acros), $Fe(NO_3)_3 \cdot 9H_2O$ (Acros), $Co(NO_3)_2 \cdot 6H_2O$ (Acros), and Ni(NO₃)₂ \cdot 6H₂O (Fisher Chemical) were used. Each sample was then dried completely at 100°C and calcined for 4 h in air at 500 °C. The resulting monometallic catalysts contain 0.5, 1, and 3 wt % of the metal (chromium, iron, cobalt or nickel), while bimetallic ones contain 3 wt % chromium and 0.5, 1, and 3 wt % of the second metal (iron, cobalt, or nickel).

Procedures

The textural properties of a support were studied using nitrogen adsorption isotherms measured at 77 K on an ASAP 2020 Plus unit (Micromeritics). The specific surface area was calculated according to BET, and the pore size distribution was found from the desorption branch of isotherm via Barrett–Joyner–Halenda (BJH) analysis. The micropores in the samples were monitored using a *t*-plot.

Thermal analysis was performed with a combination of thermogravimetry, differential thermogravimetry, and differential thermal analysis (TG-DTG-DTA) on a Derivatograph-C unit (MOM). Each sample was placed into an alundum crucible and heated linearly from 20 to 600°C in air at a rate of 10 K/min. α -Al₂O₃ was as a standard; the weight of the samples was 100 mg.

X-ray diffraction patterns of the samples were obtained on a DRON-2 diffractometer (Cu K_{α} radiation). The samples were scanned in 2 θ range 20°-70° at a rate of 1 deg/min.

Diffuse reflectance UV–Vis spectra were obtained on a Shimadzu UV-3600 Plus spectrophotometer equipped with an ISR-603 integration sphere. The spectra were recorded at 200–800 nm and room temperature, and $BaSO_4$ was used as the standard and diluent. The weight of the catalysts was 0.1 g and of $BaSO_4$ was 0.5 mg. The UVProbe software was used to process the spectra.

The morphology, particle size, and elemental composition on the catalyst surface were studied via scanning electron microscopy (SEM) on a LEO EVO 50 XVP electron microscope (Carl Zeiss, Germany) equipped with an INCA Energy 350 energy dispersive spectrometer (Oxford Instruments, Great Britain).

Catalytic Tests

The dehydrogenation of propane into propylene was conducted using CO_2 at atmospheric pressure in a flow catalytic setup with a steel reactor with an inner diameter of 4 mm. $C_3H_8 + CO_2$ gas mixture was supplied into the reactor in a volume ratio of 1 : 2. The total flow of the gas mixture was 30 mL/min. The weight of the catalyst was 1 g. The volumetric gas flow rate was 2000 h⁻¹. The reaction products were analyzed in real time on a Chromatec-Crystal 5000 gas chromatograph equipped with a thermal conductivity detector and a 3 m × 2 mm Hayesep Q column (80/100 mesh).

RESULTS AND DISCUSSION

Physicochemical Properties of Supports and Catalysts

The textural characteristics of our SiO_2 support and $3Cr/SiO_2$ supported catalyst were determined. Figure 1a shows the nitrogen adsorption-desorption isotherms for the support and the catalyst.

Silica support has a type I isotherm according to the IUPAC classification, confirming its microporous structure. Figure 1b shows the pore size distribution



Fig. 1. (a) Nitrogen adsorption-desorption isotherms of silica support and 3Cr/SiO₂ catalyst and (b) pore size distribution.

calculated from the adsorption branch of isotherms according to BJH. The pore distribution in SiO₂ is 0.9–5 nm, confirming its microporous structure. The specific surface area of the silica gel was 747 m²/g, and it fell to 570 m²/g when the active component (3 wt % Cr) was supported. We may assume that chromium oxide particles were deposited on the surface of the support, and the resulting clusters and crystallites of Cr₂O₃ partially blocked access to micropores [27].

DTA-TG was used to study the heating of a silica gel sample impregnated with a solution of $Cr(NO_3)_3$, Fe(NO₃)₃, Co(NO₃)₂, and Ni(NO₃)₂ and dried for 2 h in air at 100°C (Fig. 2).

The first maximum on the DTG curve from 50 to 200°C corresponds to the desorption and evaporation of water for all samples, which lowered the weight of the sample. This process also shows an endo-effect on the DTA curve. The subsequent drop in weight was due to the decomposition of nitrates to form metal oxides on the surface of the support. The total weight loss from 50 to 400°C was 8-15.6%. It should be noted that there was no weight loss at temperatures above 400°C, indicating that this temperature was sufficient for the complete decomposition of nitrates.

The crystal structure of the prepared catalyst samples was studied via XRD and UV–Vis diffuse reflectance spectroscopy. The $3Fe3Cr/SiO_2$, $3Co3Cr/SiO_2$, and $3Ni3Cr/SiO_2$ samples were studied via XRD. The diffraction patterns do not contain the peaks attributed to chromium, iron, cobalt, and nickel oxides. Similar data were obtained for chromium [26], with peaks attributed to Cr_2O_3 for the 5% Cr/SiO_2 (Degussa) sample. Those of much lower intensity were attributed to Cr_2O_3 for the 5% Cr/SiO_2 (KSKG) sample, while no such peaks were observed for the 5% Cr/SiO_2 sample (Acros). We may assume that no

peaks were observed for the samples with particles of supported metal oxides, which were smaller than the region of coherent scattering (less than 3-5 nm).

Figure 3 shows the UV–Vis spectra of $3M/SiO_2$ (M = Cr, Fe, Co, and Ni) monometallic and $3Cr(0.5, 1, 3)M/SiO_2$ (M = Fe, Co, and Ni) bimetallic catalysts measured before catalytic tests.

For purposes of comparison, all figures show the spectrum of the $3Cr/SiO_2$ catalyst, which contains two intense absorption bands at 260 and 360 nm and a weaker one at 455 nm. The bands at 260 and 360 nm are attributed to Cr(VI) in tetrahedral coordination, while the one at around 455 nm corresponds to the octahedral coordination of Cr(III) in Cr₂O₃ or CrO_x clusters [22, 28–30]. The spectra have no band at 600 nm, which is also attributed to the octahedral coordination of Cr(III). The above indicates that chromium in the 3Cr/SiO₂ sample was mainly in the tetrahedral coordination of Cr(VI).

There is an intense absorption band at ~250 nm in the spectrum of 3Fe/SiO_2 (Fig. 3a), indicating that charge was transferred with lower energy $d\pi - p\pi$ from the ligand to the Fe(III) ion in the tetrahedral coordination (FeO₄). A weak shoulder is also observed at 380 nm, due to the absorption of Fe in the Fe_xO_y oligomeric cluster [31]. The peaks attributed to chromium in the tetrahedral coordination of Cr(VI) and iron(III) in tetrahedral coordination (FeO₄) overlap in the spectra of $x\text{Fe}_3\text{Cr/SiO}_2$ bimetallic samples (x =0.5, 1, and 3%). The peak attributable to iron(III) falls gradually upon an increase in the amount of iron.

Figure 3b shows the spectrum of the 3Co/SiO_2 sample. The two broad bands at ~455 and 713 nm indicate there were clusters of Co_3O_4 [32–34]. The peaks attributed to chromium in the octahedral coordination



Fig. 2. Derivatograms of freshly prepared samples dried at 100°C: (a) 3% Cr/SiO₂, (b) 3% Fe/SiO₂, (c) 3% Co/SiO₂, and (d) 3% Ni/SiO₂.

of Cr(III) and cobalt in the Co_3O_4 clusters overlap in the spectra of the xCo_3Cr/SiO_2 bimetallic samples (x = 0.5, 1, and 3%).

Figure 3c shows the spectrum of the 3Ni/SiO₂ sample. There is a broad UV band at 200-350 nm, due to charge transfer $O^{2-} \rightarrow Ni^{2+}$ in the NiO octahedral coordination [35, 36]. The band at 450 nm indicates that nickel silicate was formed and/or that there was a chemical bond between nickel ions and the silica gel [37]. The band in this region depends on the coordination, the aggregation of Ni²⁺, and the degree of dispersion [38], an indirect indication that there was stronger metal-support interaction between smaller Ni particles and silica gel. The peaks attributed to chromium in the tetrahedral coordination of Cr(VI) and nickel(II) in the octahedral coordination of NiO overlap in the spectra of $xNi3Cr/SiO_2$ bimetallic samples (Ni = 0.5, 1, and 3%). The peak of nickel(II) in the spectrum was much more intense upon an increase in an amount of nickel.

Samples $3Cr/SiO_2$, $1Fe_3Cr/SiO_2$, $1Ni_3Cr/SiO_2$, and $1Co_3Cr/SiO_2$ were studied via SEM (Fig. 4).

The micrographs of the samples did not show any particles of chromium oxide or the oxide of a second metal, which could indicate that the metal oxide particles were smaller than the resolution of the microscope; i.e., the size of particles of chromium and cobalt oxides was less than 10 nm. As an example, Fig. 4a presents a micrograph of the surface of the 1Fe₃Cr/SiO₂ sample, which shows the mapping of the elements chromium (Fig. 4b) and iron (Fig. 4c). Figures 4b, 4c clearly show that the particles of chromium and iron were in a microdispersed state and quite uniformly distributed on the surface of the support. Similar micrographs were also obtained for the 3Cr/SiO₂, 1Ni₃Cr/SiO₂, and 1Co₃Cr/SiO₂ samples, indicating that chromium and the second metal were also uniformly distributed on the surface of the support. Elemental analysis of the sample's surface was performed via energy dispersive microanalysis (EDM). Figure 4d shows the characteristic X-ray spectrum and the elemental analysis data for the 1Fe3Cr/SiO₂ sample. The spectra contain peaks corresponding to the lines of chromium and iron, indicating there were nanoparticles of metal oxides on the surface of the support and no impurities in the samples. It should be noted that



Fig. 3. UV–Vis diffuse reflectance spectra of: (a) (0.5-3%)Fe3Cr/SiO₂, (b) (0.5-3%)Co3Cr/SiO₂, and (c) (0.5-3%)Ni3Cr/SiO₂.

according to the data from energy dispersive microanalysis, the nominal and actual amounts of chromium and iron in the samples were similar.

Oxidative Dehydrogenation of Propane on Monometallic and Bimetallic Catalysts in the Presence of CO₂

The dehydrogenation of propane in the presence of CO_2 proceeds according to the reaction

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O.$$

Some by-products (methane, ethane, and ethylene) form in addition to propylene.

The monometallic catalysts in which the amounts of the active component were 0.5, 1, and 3 wt % were studied at the first stage. Table 1 shows the results from catalytic tests.

The *x*Fe/SiO₂ samples (x = 0.5, 1, and 3%) exhibited the least activity. The conversion of propane was only 3–7%. Ethylene and ethane were the main reaction products. The *x*Ni/SiO₂ samples (x = 0.5, 1, and 3%) displayed high activity. At a conversion of ~26%,

the sole product was methane, which is in good agreement with the published data [39]. The $1Co/SiO_2$ catalyst displayed good catalytic activity, with propylene selectivity reaching 41% at a propane conversion of 18%.

The 3Cr (0.5, 1, and 3%)M/SiO₂ (M = Fe, Co, and Ni) bimetallic catalysts were studied at the next stage. The catalytic tests (Table 2) showed that the catalytic activity was greatest when chromium oxide catalysts were modified with 1 wt % of the second metal (Fig. 5). A subsequent increase in the amount of the modifying metal reduced the activity of the catalyst. The 1Ni3Cr/SiO₂ sample displayed the highest degree of propane conversion (64%) of all the mono- and bimetallic catalysts.

However, some cracking side reactions proceeded more actively when nickel was added, so the selectivity toward propylene fell relative to the initial $3Cr/SiO_2$ catalyst and the selectivity toward methane grew considerably.



Fig. 4. (a) Micrograph, (b) mapping for chromium, (c) mapping for iron, and (d) EDM data for 1Fe3Cr/SiO₂ sample.



Fig. 5. Temperature dependences of: (a) propane conversion and (b) propylene selectivity on $1Fe_3Cr/SiO_2$, $1Co_3Cr/SiO_2$, and $1Ni_3Cr/SiO_2$ catalysts.

Adding iron and cobalt reduces the conversion of propane, but it contributes to a slight increase in propylene selectivity. The $1Fe3Cr/SiO_2$ and $1Co3Cr/SiO_2$ catalysts displayed the highest selectivity toward propylene: 71 and 72%, respectively.

CONCLUSIONS

In summary, we may conclude that the addition of a second transition metal (Fe, Co, and Ni) to the chromium oxide catalyst 3Cr/SiO₂ (1 wt %) leads to a slight increase in propylene selectivity with a decrease

Sample	$C(C_3H_8)$	$S(C_3H_6)$	$S(C_2H_6)$	$S(C_2H_4)$	$S(CH_4)$	$Y(C_3H_6)$
3Cr/SiO ₂	48	68	7	2	23	33
0.5Fe/SiO ₂	3	0	11	77	12	0
1Fe/SiO ₂	6	0	43	43	14	0
3Fe/SiO ₂	7	0	6	59	35	0
0.5Fe3Cr/SiO ₂	14	70	7	3	20	18
1Fe3Cr/SiO ₂	26	71	6	3	20	11
3Fe3Cr/SiO ₂	19	68	6	5	21	13
0.5Co/SiO ₂	6	0	14	52	34	0
1Co/SiO ₂	18	41	2	16	41	7
3Co/SiO ₂	20	0	1	3	96	0
0.5Co3Cr/SiO ₂	17	65	10	8	17	11
1Co3Cr/SiO ₂	28	72	7	3	18	20
3Co3Cr/SiO ₂	5	0	15	8	77	0
0.5Ni/SiO ₂	26	0	0.5	0.5	99	0
1Ni/SiO ₂	26	0	1	0.5	98.5	0
3Ni/SiO ₂	29	0	1	0.5	98.5	0
0.5Ni3Cr/SiO ₂	45	31	6	2	61	14
1Ni3Cr/SiO ₂	64	28	7	2	63	18
3Ni3Cr/SiO ₂	24	28	3	2	67	7

Table 1. Conversion of propane (*C*), selectivity of products (*S*), and yield of propylene (*Y*) for catalysts in the reaction of propane dehydrogenation in the presence of CO_2 ($T = 650^{\circ}C$, $\omega = 2000 \text{ h}^{-1}$, and $C_3H_8 : CO_2 = 1 : 2$)

in propane conversion in the case of iron and cobalt. This leads to a significant increase in propane conversion from 48 to 64% with a decrease in propylene selectivity to form methane in the case of nickel.

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