Supporting Information

Kinetic and DRIFTS Studies of IrRu/Al_2O_3 Catalysts for Lean NO_x Reduction by CO at Low Temperature

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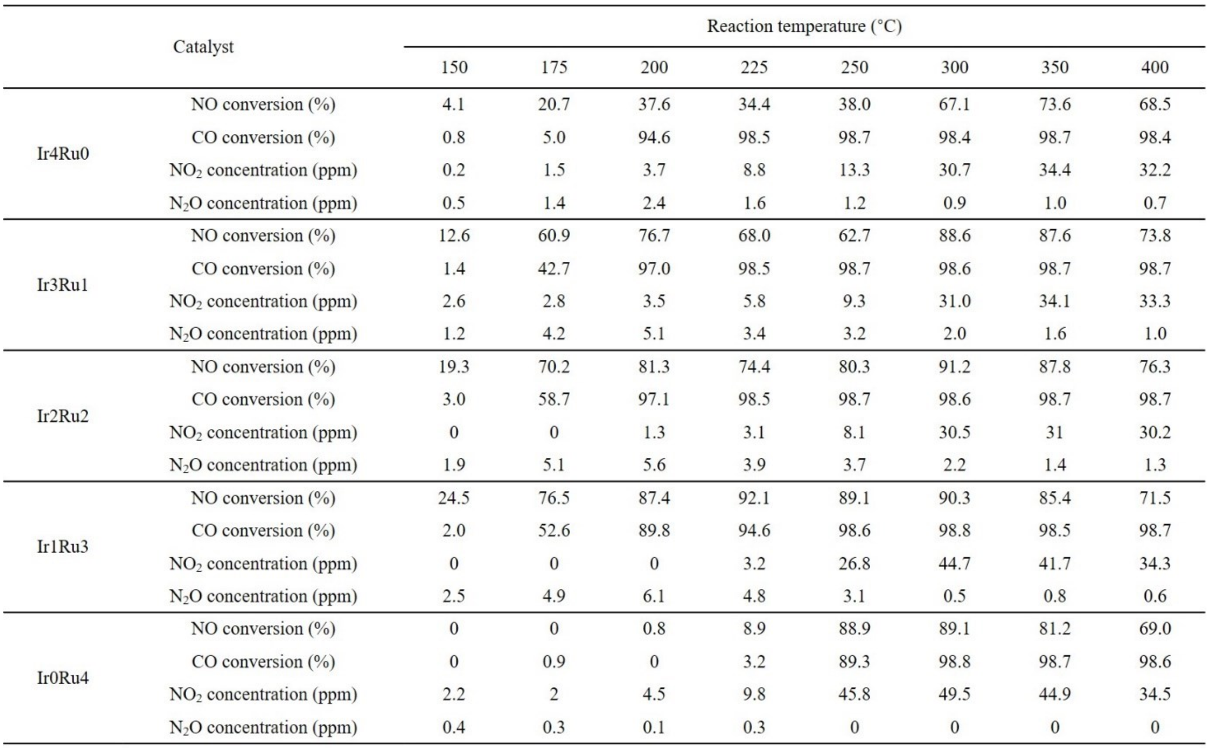
Table S1 Detailed values for NO conversion, CO conversion, NO_2 concentration, and N_2O concentration over the catalyst series, with regard to reaction temperatures.



Catalyst		Reaction temperature (°C)							
		150	175	200	225	250	300	350	400
Ir4Ru0	NO conversion (%)	4.1	20.7	37.6	34.4	38.0	67.1	73.6	68.5
	CO conversion (%)	0.8	5.0	94.6	98.5	98.7	98.4	98.7	98.4
	NO_2 concentration (ppm)	0.2	1.5	3.7	8.8	13.3	30.7	34.4	32.2
	N_2O concentration (ppm)	0.5	1.4	2.4	1.6	1.2	0.9	1.0	0.7
Ir3Ru1	NO conversion (%)	12.6	60.9	76.7	68.0	62.7	88.6	87.6	73.8
	CO conversion (%)	1.4	42.7	97.0	98.5	98.7	98.6	98.7	98.7
	NO_2 concentration (ppm)	2.6	2.8	3.5	5.8	9.3	31.0	34.1	33.3
	N_2O concentration (ppm)	1.2	4.2	5.1	3.4	3.2	2.0	1.6	1.0
Ir2Ru2	NO conversion (%)	19.3	70.2	81.3	74.4	80.3	91.2	87.8	76.3
	CO conversion (%)	3.0	58.7	97.1	98.5	98.7	98.6	98.7	98.7
	NO_2 concentration (ppm)	0	0	1.3	3.1	8.1	30.5	31	30.2
	N_2O concentration (ppm)	1.9	5.1	5.6	3.9	3.7	2.2	1.4	1.3
Ir1Ru3	NO conversion (%)	24.5	76.5	87.4	92.1	89.1	90.3	85.4	71.5
	CO conversion (%)	2.0	52.6	89.8	94.6	98.6	98.8	98.5	98.7
	NO_2 concentration (ppm)	0	0	0	3.2	26.8	44.7	41.7	34.3
	N_2O concentration (ppm)	2.5	4.9	6.1	4.8	3.1	0.5	0.8	0.6
Ir0Ru4	NO conversion (%)	0	0	0.8	8.9	88.9	89.1	81.2	69.0
	CO conversion (%)	0	0.9	0	3.2	89.3	98.8	98.7	98.6
	NO_2 concentration (ppm)	2.2	2	4.5	9.8	45.8	49.5	44.9	34.5
	N_2O concentration (ppm)	0.4	0.3	0.1	0.3	0	0	0	0

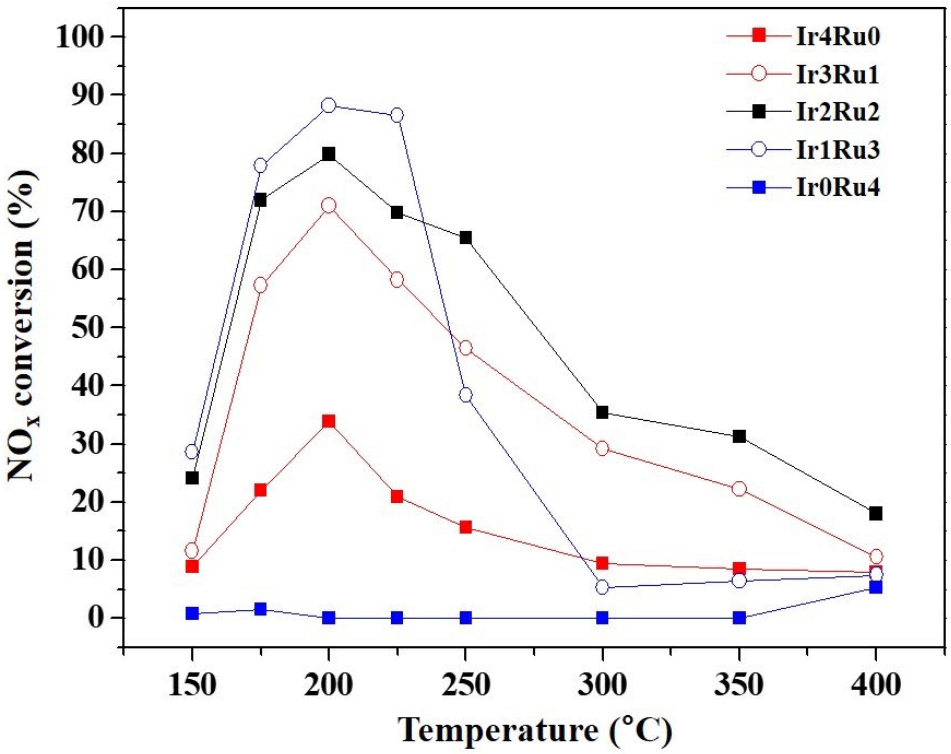


Figure S1. NO$_x$ conversion of the catalysts with regard to reaction temperatures. The catalysts were pretreated by flowing 10 % H_2/N_2, at 450 °C for 1 hour. Inlet feed was comprised of NO (50 ppm), CO (7000 ppm), and O_2 (5 %) balanced with N_2. Contact time was set to 120,000 ml/h·g-catalyst. NO$_x$ conversions were calculated by the following equation.

$$\text{NO}_x \text{ conversion (\%)} = ([\text{NO}_x]_{in}-[\text{NO}_x]_{out})/[\text{NO}_x]_{in} \times 100$$

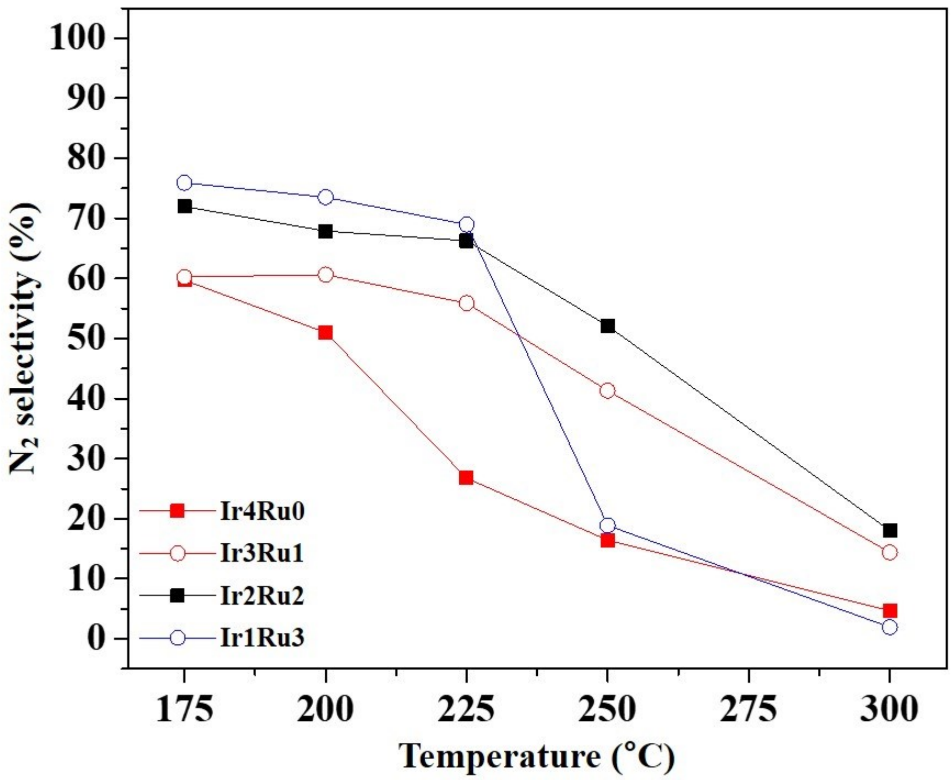


Fig. S2. N_2 selectivity of the catalyst series. Ir0Ru4 sample is excluded from calculation due to its inert activity in NO reduction. Selectivity values over 175-300 °C is shown only, as selectivity values calculated in regions where diminished catalytic activity is exhibited may compromise the reliability of the calculated results. N_2 selectivity calculation was made by the following equation, assuming only N_2, NO_2, and N_2O is formed as a result of NO conversion (NH_3 formation was not detected).

$$N_2 \text{ selectivity } (\%) = [N_2]_{out}/([N_2]_{out}+[NO_2]_{out}+[N_2O]_{out}) \times 100$$

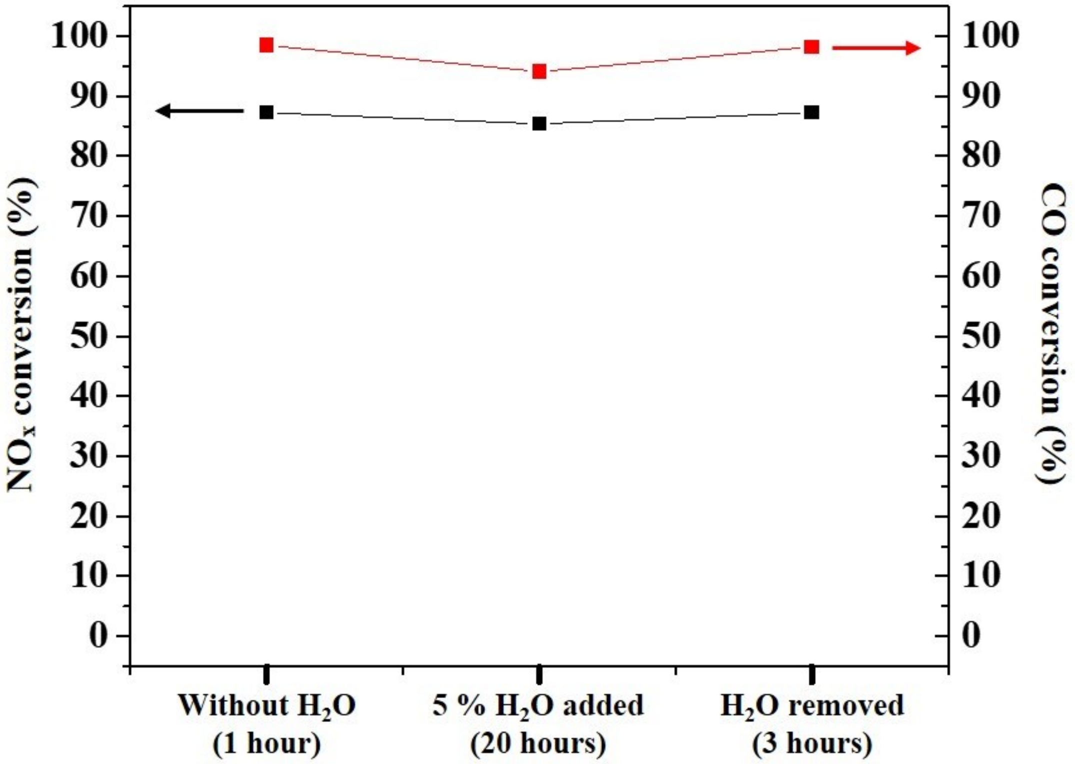


Fig. S3. Effect of adding H_2O within the inlet feed on NO_x and CO conversions of $IrRu/Al_2O_3$ (Ir1Ru3) catalyst, where the catalytic activities were measured at 200 °C. After 1 hour of operation under dry conditions (50 ppm NO, 7000 ppm CO and 5 % O_2 balanced with N_2), 5 % of H_2O was added into the feed stream, and maintained for 20 hours, followed by another 3 hours after the removal of H_2O. Pretreatment conditions and contact time were maintained the same with those of standard reaction tests.

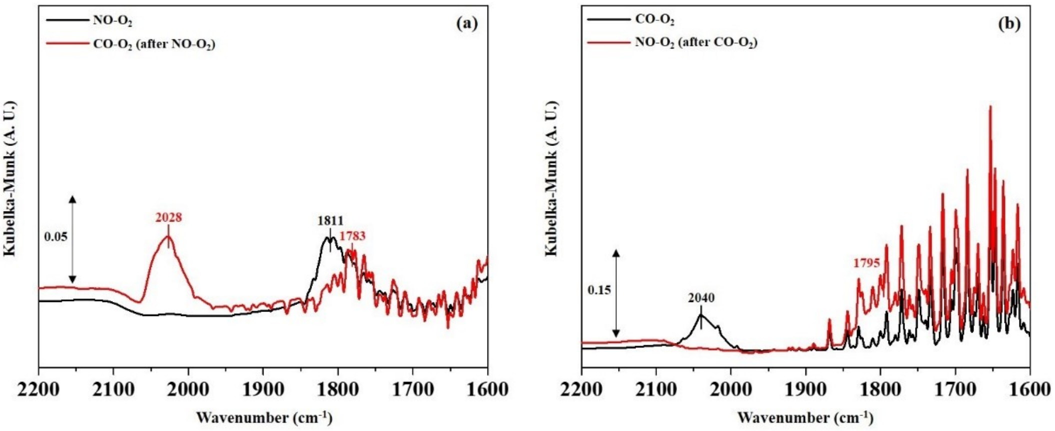


Fig. S4. DRIFTS spectra of Ir/Al_2O_3 (Ir4Ru0) catalyst during the sequential adsorption of (a) 200 ppm NO and 5 % O_2 balanced with N_2 for 1 hour followed by 7000 ppm CO and 5 % O_2 balanced with N_2 for 1 hour, and (b) 7000 ppm CO and 5 % O_2 balanced with N_2 for 1 hour followed by 200 ppm NO and 5 % O_2 balanced with N_2 for 1 hour. During the analysis, the total flow rate and the adsorption temperature were kept to 50 ml/min and 150 °C, respectively. Each CO adsorption step was followed by 10 minutes of N_2 purging, to alleviate the interference of gas-phase CO bands.

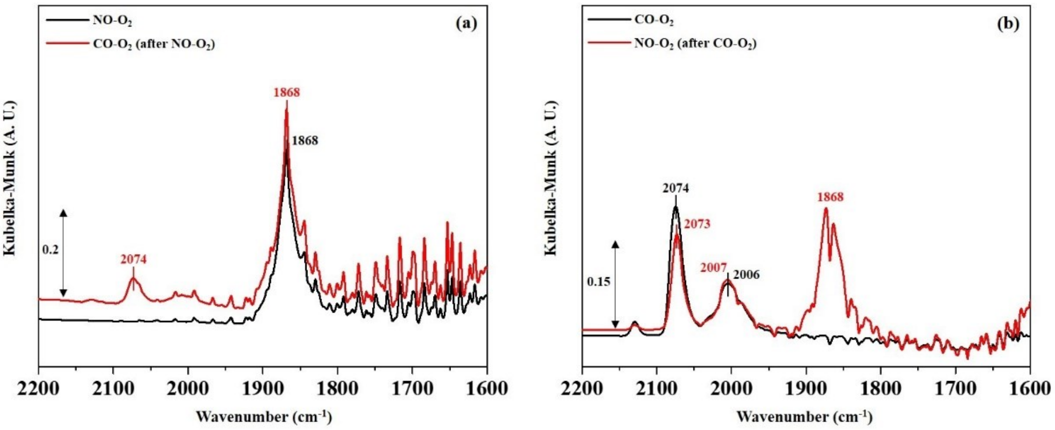


Fig. S5. DRIFTS spectra of Ru/Al_2O_3 (Ir0Ru4) catalyst during the sequential adsorption of (a) 200 ppm NO and 5 % O_2 balanced with N_2 for 1 hour followed by 7000 ppm CO and 5 % O_2 balanced with N_2 for 1 hour, and (b) 7000 ppm CO and 5 % O_2 balanced with N_2 for 1 hour followed by 200 ppm NO and 5 % O_2 balanced with N_2 for 1 hour. During the analysis, the total flow rate and the adsorption temperature were kept to 50 ml/min and 150 °C, respectively. Each CO adsorption step was followed by 10 minutes of N_2 purging, to alleviate the interference of gas-phase CO bands.

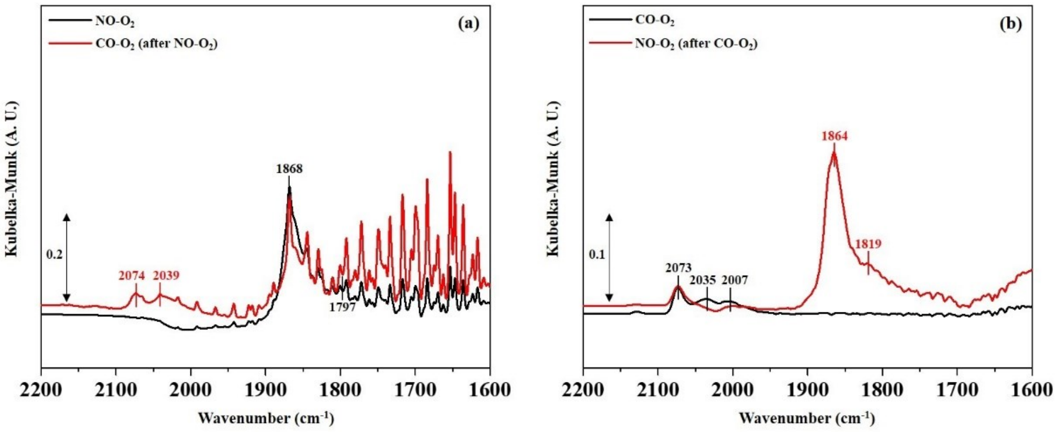


Fig. S6. DRIFTS spectra of IrRu/Al_2O_3 (Ir1Ru3) catalyst during the sequential adsorption of (a) 200 ppm NO and 5 % O_2 balanced with N_2 for 1 hour followed by 7000 ppm CO and 5 % O_2 balanced with N_2 for 1 hour, and (b) 7000 ppm CO and 5 % O_2 balanced with N_2 for 1 hour followed by 200 ppm NO and 5 % O_2 balanced with N_2 for 1 hour. During the analysis, the total flow rate and the adsorption temperature were kept to 50 ml/min and 150 °C, respectively. Each CO adsorption step was followed by 10 minutes of N_2 purging, to alleviate the interference of gas-phase CO bands.

Eley-Rideal mechanism assumption for surface O removal (CO oxidation)

After the dissociation of NO on the catalyst surface, when it is assumed that the surface O species is removed by CO through an Eley-Rideal mechanism, the overall scheme can be represented by the following equations (S1), (S2) and (S3).

$$NO(g) + * \rightarrow NO^* \tag{S1}$$

$$NO^* + * \rightarrow N^* + O^* \tag{S2}$$

$$CO(g) + O^* \rightarrow CO_2\uparrow \tag{S3}$$

Considering equation (S3) as the rate limiting step, the rate law and the surface coverage for O species (θ_O) can be respectively written as equations (S4) and (S5), where k, S_0, and K_i respectively represents the rate constant, total number of active sites, and k_{ads}/k_{des} for species i. It is assumed that the dissociation of the adsorbed NO species into N and O is facile.

$$r = kS_0\theta_O P_{CO} \tag{S4}$$

$$\theta_O = \frac{(K_{NO}P_{NO})^{1/2}}{1 + 2(K_{NO}P_{NO})^{1/2}} \tag{S5}$$

Substituting equation (S5) into equation (S4) yields equation (S6). From the analysis, Eley-Rideal mechanism of surface O removal by CO would result in positive reaction orders for both NO (between 0 and 0.5) and CO (first order of 1), which is inconsistent with the current kinetic results (Table 1).

$$r = kS_0 \frac{(K_{NO}P_{NO})^{1/2}}{1 + 2(K_{NO}P_{NO})^{1/2}} P_{CO} = k'P_{NO}^{x} P_{Co}^{1} \quad (0 < x < 1/2) \tag{S6}$$